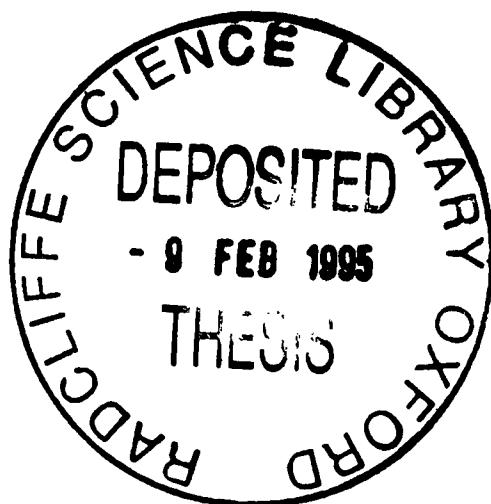


An experimental study of some two-dimensional antiferromagnets

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Abstract

This thesis discusses the investigation of the two-dimensional $S = \frac{1}{2}$ Heisenberg antiferromagnet copper formate tetrahydrate (CFTH) and the layered triangular lattice material NaTiO_2 which was thought to be a candidate for the possession of a non-classical antiferromagnetic ground state due to the frustration inherent in a triangular antiferromagnet.

Single crystals of CFTH are investigated using elastic, quasielastic and inelastic neutron scattering, electron spin resonance (ESR) spectroscopy and DC magnetometry. Using the appropriate theory, these measurements are used to determine values for the terms in the Hamiltonian which describes the interactions between the Cu^{2+} ions in this material. The Hamiltonian is compared with that of La_2CuO_4 , and the two are determined to be quite similar. There does not appear to be any evidence for a non-classical ground state in either material. This was proposed to exist in La_2CuO_4 to account for the superconductivity of doped samples.

The difficulties in preparing pure NaTiO_2 have been surmounted, and a technique is described for preparing powder samples with very reproducible structural and magnetic properties. The structural properties have been investigated using X-ray and neutron diffraction, the latter at temperatures between 100 K and room temperature. The magnetic properties have been probed using DC magnetometry and ESR spectroscopy. The sample dependence of the structural and magnetic properties of samples prepared in slightly different ways is discussed. The temperature dependence of the magnetic susceptibility and of the structural parameters is explained by comparison with other oxides and chlorides of trivalent Ti and V, many of which show similar behaviour. The magnetic and structural changes which occur between 200 and 250 K are assigned to changes in the Ti-Ti bonding within the layers, which leads to a transition between two metallic states with subtle differences in their band structures.

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List of Abbreviations

2D	Two-dimensional
3D	Three-dimensional
ξ	Magnetic correlation length
κ	Inverse magnetic correlation length
ρ_s	Spin-wave stiffness constant $\simeq 0.15J$
χ	Magnetic susceptibility
AECL	Atomic Energy of Canada Limited
AFC	Automatic frequency control
AU	Arbitrary Units
CFTD	Copper (II) deuteroformate tetradeuterate
CFTH	Copper (II) formate tetrahydrate
CHN	Chakravarty, Halperin and Nelson
DM	Dzyaloshinsky-Moriya antisymmetric exchange interaction
EA	Neutron energy transfer in the spin-wave experiment
E_i	Incident (initial) neutron energy
E_f	Scattered (final) neutron energy
ESR	Electron Spin Resonance
FCC	Face centred cubic
GSAS	General Structure Analysis System
$\mathcal{H}$	Hamiltonian
HAF	Heisenberg antiferromagnet
HFR	High Flux Reactor
ICL	Inorganic Chemistry Laboratory
ILL	Institut Laue-Langevin, Grenoble, France
IPA	Isopropyl alcohol
J	Nearest-neighbour in-plane exchange coupling constant
J'	Nearest-neighbour between-plane exchange coupling constant
J_2	Next-nearest-neighbour in-plane exchange coupling constant
J_D	In-plane antisymmetric exchange constant
k_B	Boltzmann's constant ($1.381 \times 10^{-23} \text{ JK}^{-1}$)
$\vec{k}_f$	Wavevector of scattered neutron
$\vec{k}_i$	Wavevector of incident neutron
KT	Kosterlitz-Thouless
LRO	Long range order
μ_0	Vacuum permeability ($4\pi \times 10^{-7} \text{ TmA}^{-1}$)
μ_B	Bohr Magnetron ($9.27408 \times 10^{-24} \text{ JT}^{-1}$)
μSR	Muon spin relaxation
MF	Molecular (or Mean) Field
NMR	Nuclear Magnetic Resonance
nn	Nearest neighbour
nnn	Next nearest neighbour
OUCS	Oxford University Computing Service
QES	Quasielastic Scattering
p_b	Bond percolation limit
p_s	Site percolation limit
PG	Pyrolytic graphite
PSD	Position Sensitive Detector (for X-ray Diffractometer)
$\vec{Q}$	Neutron scattering vector

$\vec{q}$	Displacement vector from the magnetic Brillouin zone centre
QNL σ M	Quantum non-linear sigma model
RAL	Rutherford Appleton Laboratory
RG	Renormalisation Group
r.l.u.	Reciprocal lattice unit
$\vec{S}_i$	Spin vector of atom i
SC	Seehra and Castner
SG	Spin Glass
SQUID	Superconducting QUantum Interference Device
T_c	Superconducting transition temperature
T_N	Néel temperature of an antiferromagnet
TALHAF	Triangular lattice Heisenberg antiferromagnet
TAS	Triple axis neutron spectrometer
VSM	Vibrating sample magnetometer

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Chapter 1

Introduction

The layout of this thesis is as follows: the current chapter gives a brief introduction to the compounds studied and to related materials. The following chapters deal with the results of experiments carried out on the materials of interest. Experimental techniques are dealt with as an integral part of each chapter and each is described at the point at which it is first used. Similarly, theories of magnetism are included together with the experimental results. References are included in a single bibliography at the end of the thesis.

1.1 Collective magnets

Magnetism in solids arises from the presence of either nuclear or electronic magnetic moments. The electronic magnetism of interest to most chemists and physicists arises from the magnetic moments of unpaired valence electrons. In species such as many organic free-radicals, the moment on a molecule may be regarded as independent from the others to first order, and the magnetic behaviour is easily interpreted using the Curie Law. In the cases considered in this thesis, the magnetism is cooperative; the magnetic moments of transition metal ions can interact with one another via a number of mechanisms which are discussed later in this section. These interactions greatly complicate the magnetic behaviour giving rise, on lowering the temperature or applying a magnetic field, to phenomena such as phase transitions to an ordered

state. The classical view of the ordered state is of one in which the orientation of all moments in the solid may be inferred from the orientation of any single one. The behaviour of cooperative systems in the region close to a phase transition — which is called the critical region — is of major interest to physicists and of some interest to chemists; it is described in detail by Stanley [1] and Kadanoff [2], and there is a brief discussion of the general phenomena later in this section.

The electronic magnetism of insulating solids, in which the moments are localised on metal ions, has generated great interest over the previous few decades. A number of factors influence the behaviour of such systems and they will be considered in detail later in this section. In general, one investigates a particular system in the hope that it will shed some light on a particular physical problem by realising experimentally a theoretical model. This has particularly been the case over the last few years with one- and two-dimensional systems in relation, for example, to the Haldane problem [3] and high-temperature superconductivity [4].

1.1.1 Magnetic Exchange

Magnetic cations in an insulating solid separated by a distance r may interact via a number of mechanisms [5]. The dipolar interaction of strength D is a through-space interaction with a long range, falling off in strength as r^{-3} . Its magnitude is not usually sufficient to cause the ordering of electronic moments even at very low temperatures, because $k_B T \gg D$ at reasonably accessible experimental temperatures, leading to thermal disruption of dipolar ordering of the moments. However, the dipolar interaction may be a source of anisotropy which dictates the spin direction in the ordered state, and is also the usual force behind the ordering of nuclear moments. The superexchange interaction of strength J is a through-bond interaction with a short range, empirically observed to fall off as approximately $J \propto r^{-12}$. This interaction is usually only significant between nearest neighbour magnetic ions which are not widely separated.

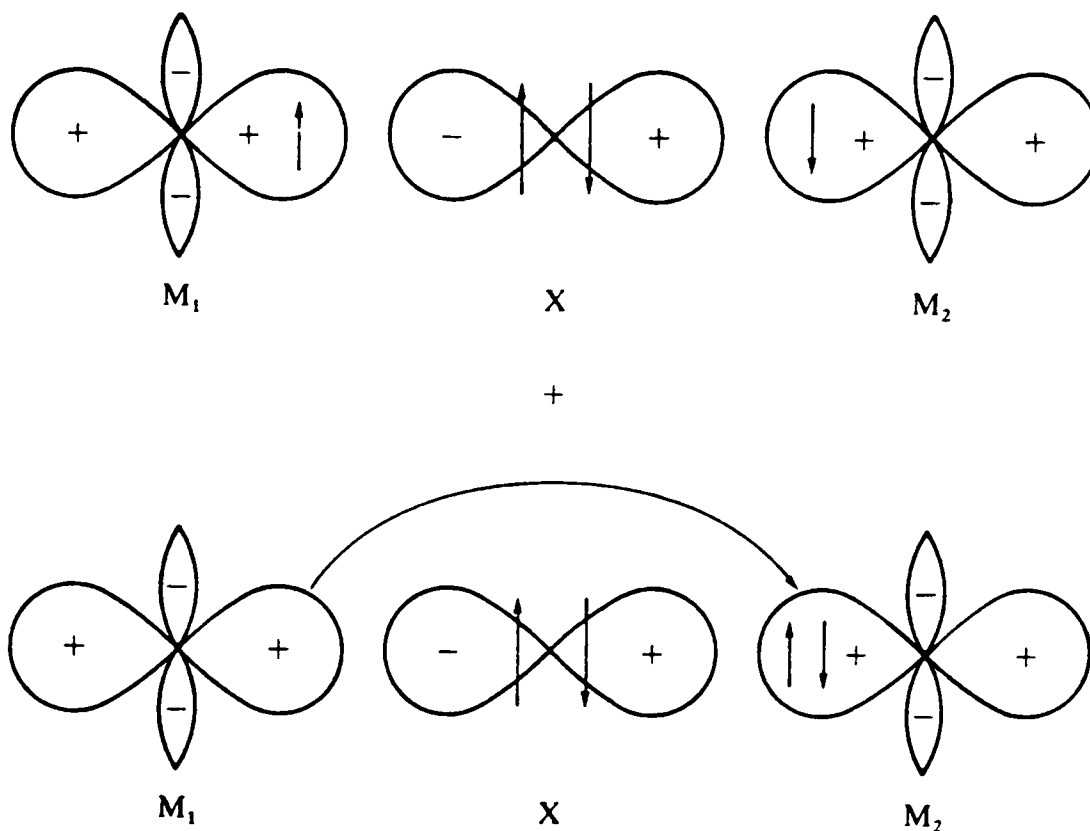
The superexchange interaction may be composed of direct exchange terms which

only involve the electrons on the metal ions, and indirect exchange terms which involve other electrons present in the material. The large exchange interactions present in insulators cannot always be attributed to direct exchange because the cations are widely separated by anions. The indirect superexchange which operates in these materials has a number of components [5]:

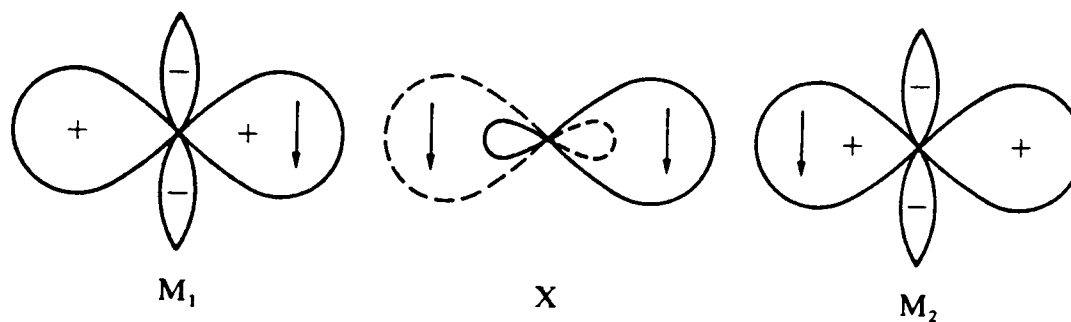
- Direct potential exchange involving orthogonal orbitals on the magnetic ions. This interaction is ferromagnetic in nature.
- Kinetic exchange arising from the virtual transfer of electrons between singly-occupied orbitals of the ions in conjunction with correlation effects. This may be described as second order coupling and it is always antiferromagnetic.
- Indirect exchange through spin polarisation of intervening groups. This may be ferromagnetic or antiferromagnetic.
- Correlation superexchange in which two anion electrons make virtual transitions to the neighbouring paramagnetic ions. This is antiferromagnetic. Alternatively, anion electrons can make virtual transitions to excited states of the metal ion. This is antiferromagnetic if the excited state is non-degenerate and ferromagnetic if it is a degenerate state.

One assumes that the material is an insulator and that the participant valence orbitals are thus quite localised and are singly occupied in the magnetic ions while being filled in the anions. In addition some empty valence orbitals exist, into which electrons may be formally excited. The exchange interaction is summarised diagrammatically in Figure 1.1.

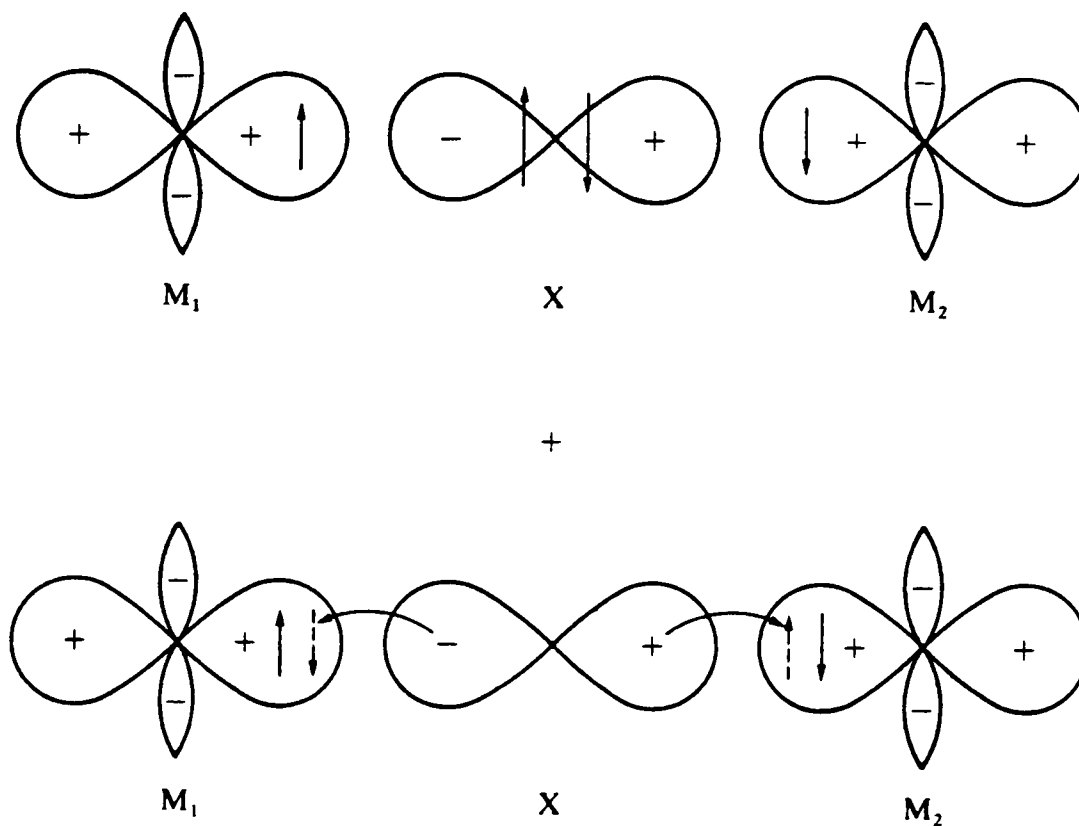
The strength and sign of the overall exchange, which is quantified by the exchange constant, J , depends on the magnitude and sign of each of the components considered above. J , is a tensor expressing the interaction energy between the spins on pairs of coupled ions and may be experimentally determined. J may be expressed in the



Kinetic exchange involving one-electron transfer.



Exchange in which the ligand electrons are polarised.



Correlation superexchange which involves the transfer of two anion electrons to the neighbouring metal ions.

Figure 1.1: Diagram showing the orbital overlap leading to superexchange between two metal ions separated by an intervening anionic group

following form

$$J = \begin{pmatrix} J^{xx} & J^{xy} & J^{xz} \\ -J^{xy} & J^{yy} & J^{yz} \\ -J^{xz} & -J^{yz} & J^{zz} \end{pmatrix} \quad (1.1)$$

in which x , y and z represent an orthonormal coordinate system. The terms on the leading diagonal represent the symmetric (scalar) exchange, and the off-diagonal terms represent antisymmetric exchange [6, 7] and anisotropic exchange. The off-diagonal terms may be zero if there is no spin-orbit coupling [7]. The symmetry relation between two ions which interact via the superexchange interaction also determines which off-diagonal terms are zero [6, 7]. If the off-diagonal terms are zero, the exchange is simply scalar in nature and the overall exchange constant, J , which is quoted is expressed by

$$J = \frac{J^{xx} + J^{yy} + J^{zz}}{3}. \quad (1.2)$$

Usually the superexchange interaction couples the ions antiferromagnetically and the symmetric, scalar part of J is negative, though under certain circumstances the coupling may be ferromagnetic (J is positive). Rules developed by Goodenough [8] and by Kanamori [9] from ideas of Anderson [10] and Kramers [11], attempt to predict the sign of the superexchange under different circumstances. However, they are only approximate and if there are opposing effects in competition, the wrong answer may be obtained. The interaction between nearest-neighbour (nn) cations is usually the dominant one, although next nearest neighbour (nnn) exchange may be comparable in strength to the nn exchange if the distances are similar or if the nn overlap is poor. This can result in competitive magnetism described as frustration.

1.1.2 Factors affecting the properties of collective systems

The classical view of a ferromagnet is of a material which, in its ordered ground state, has each magnetic moment aligned parallel to all its nearest neighbours. In an antiferromagnet, each moment is aligned antiparallel to its nearest neighbours. We shall see that this so-called Néel state is too simple a picture for many antiferromagnets.

A more rigorous view of a collective magnetic system is one in which the ground state is a mixture of all the possible states which can be derived from the classical ground state by interchange of any two spins [12, 13]. Each possible state is weighted according to its energy. For a *ferromagnet*, the true ground state is equivalent to the classical ground state. However for an *antiferromagnet*, interchange of a pair of spins gives rise to a state which is not the Néel state, but which makes some contribution to the quantum mechanical ground state. In fact the Néel state is not even an eigenstate of the system. The exchange energy is proportional to the square of the size of the spin, and if S is large (eg $S=\frac{5}{2}$), most states can be neglected as being too high in energy and so the Néel state is a reasonable approximation to the ground state. For a low moment system ($S=\frac{1}{2}$), many states have a weight comparable to that of the Néel state and so the true ground state must be expressed in quantum mechanical terms. This view was originally expressed by Anderson [14] who proposed that low moment systems would provide the best candidates for this form of non-classical ground state. This constraint limits the number of materials suitable for study.

As well as the sign of the magnetic exchange, there are a number of other factors which will influence the properties of a collective magnetic system:

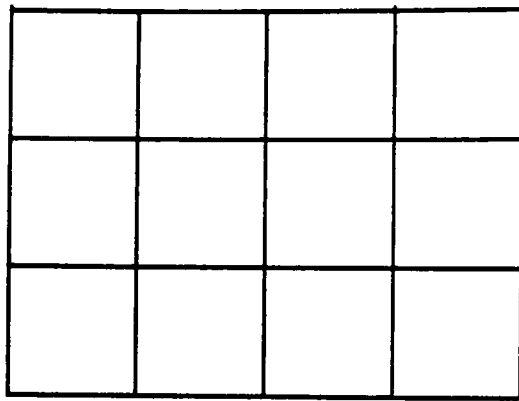
- The size of the spin, S , on the ions (as discussed above) which depends on number of unpaired electrons on the ion and the ground term of the ion. This affects the exchange *energy* which is roughly equal to $zJS(S+1)$, where z is the number of nearest neighbour moments exchanging with the ion.
- The dimensionality of the spin — Ising, XY or Heisenberg. In an Ising system, the magnetic moment of the ion is constrained to occupy one dimension (ie ‘up’ or ‘down’). In an XY system, the moment occupies a plane and in a Heisenberg system the moment is isotropic. In practice no system is truly isotropic, hence a nominally Heisenberg system will display some Ising or XY character usually as a result of a single ion anisotropy which becomes significant at low temperatures. Co^{2+} systems usually have Ising symmetry, while Mn^{2+} systems are usually approximately Heisenberg.

- The lattice dimensionality: the magnetic ions may occupy a chain, a plane or a 3D space due to the features of the structure of the solid which cause the exchange to be strong in some directions but not in others.
- The lattice geometry. In a planar system, the magnetic ions may occupy a square array, a triangular one or some other array such as a Kagomé network. A variety of lattice geometries are also possible in three dimensions. Some such lattices are shown in Figure 1.2.

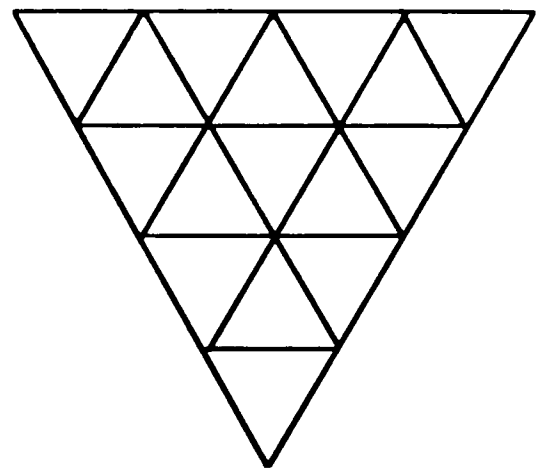
The properties of collective magnets of interest to chemists and physicists include the manner in which the system approaches a phase transition — ie. its *critical* properties [1, 15], its response to dilution of the magnetic lattice and its ground state properties. The critical behaviour of many systems, which are not necessarily all magnetic, may be mapped on to one another via universal behaviour of their critical properties. This concept of Universality [2] is a very powerful one which pervades physics. The way in which a parameter, such as the magnetisation of one sublattice of an antiferromagnet, changes as one approaches a transition (Section 2.4.1) is characterised by a critical exponent, for example

$$M \propto \left(\frac{T_N - T}{T_N} \right)^\beta \quad (1.3)$$

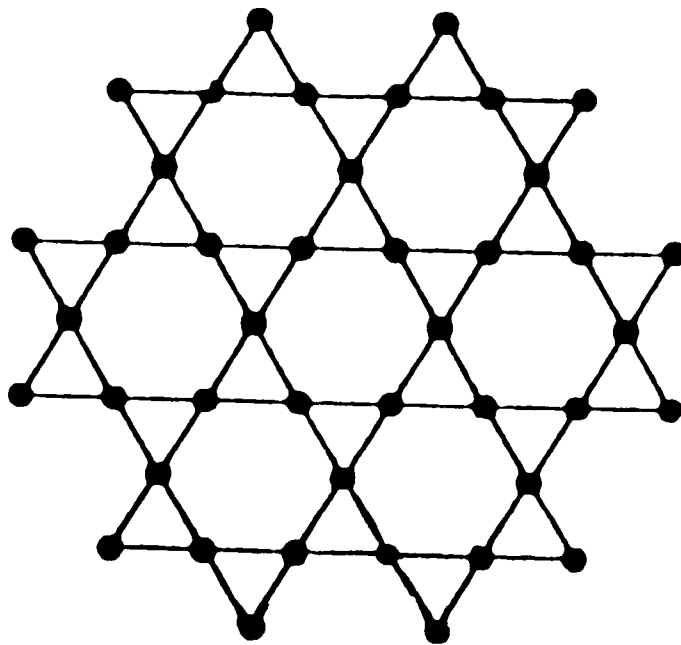
where M is the magnetisation of one sublattice of an antiferromagnet, T is the temperature, T_N is the transition temperature, and β is the critical exponent for the magnetisation. Other critical exponents may be defined for the behaviour of the heat capacity and the length scale of ordering in the critical region. Systems belonging to the same Universality class share the same critical exponents. The values of the critical exponent β for those systems which can be solved exactly are summarised in Table 1.1. The value of $\frac{1}{2}$ which is predicted by Molecular (or Mean) Field (MF) theory is an overestimate since this theory does not take account of short-range order in collective systems. The deviations from the simple predictions of MF theory become larger as the lattice and spin dimensionalities are reduced. MF theory is expected to be correct for a lattice dimensionality of 4 which is unattainable.



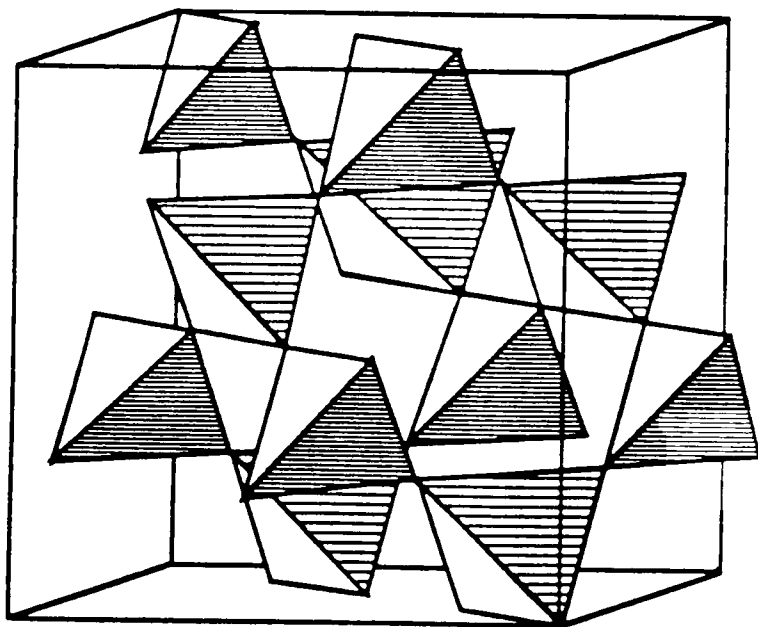
Square lattice



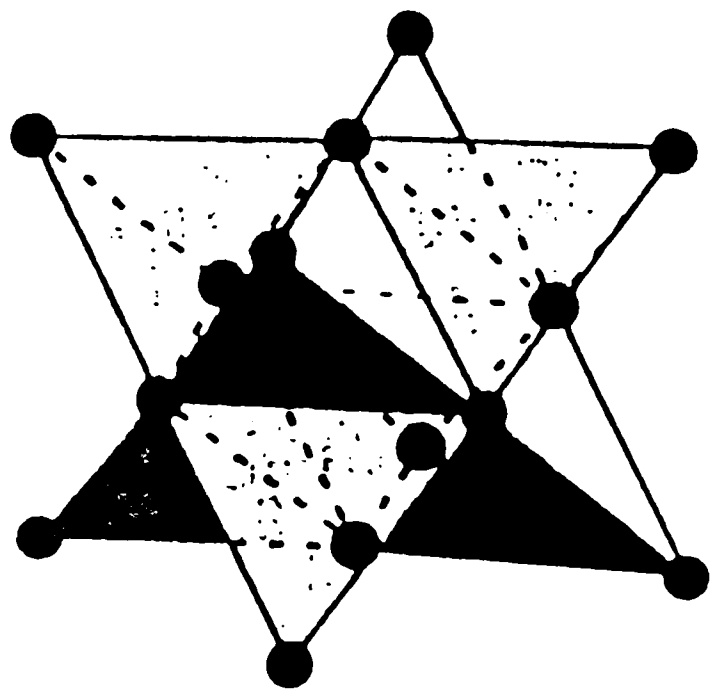
Triangular lattice



Kagome lattice



Pyrochlore lattice



FCC lattice

Figure 1.2: Diagram of various lattice types. The Kagomé lattice may be thought of as linked Stars of David, or alternatively as a triangular lattice of side a from which a triangular superlattice of side $2a$ has been removed. The pyrochlore lattice may be thought of as corner linked tetrahedra, or alternatively as four interlinked Kagomé nets. The FCC lattice is made up of four interlinked triangular nets.

Lattice dimensionality	Spin dimensionality	β
MF		$\frac{1}{2}$
3	1	0.31
3	2	0.33
3	3	0.35
2	1	$\frac{1}{8}$

Table 1.1: A list of the critical exponents for different systems. The MF result is expected to be correct for a lattice dimensionality of 4.

A discussion of Universality is given by Kadanoff [2], who developed it. In general, for a magnetic system, a change in the lattice or spin dimensionality changes the Universality class to which the magnet belongs, and this can have a profound effect on its experimental properties. For example, regardless of the spin dimensionality, a 3D system exhibits long range order (LRO) below a critical temperature, $T_c > 0$. However a truly 1D system never undergoes LRO since there is a favourably high entropy associated with the introduction of a disruption. 2D systems show intermediate behaviour and whether ordering occurs or not depends on the spin dimensionality. This is one of the reasons why they are so interesting.

1.1.3 Two dimensional systems

The motivation for the work discussed in this thesis was to study the collective magnetic properties of insulating two-dimensional (2D) systems. These possess a structure in which neighbouring first row transition metal ions arranged in a planar array are coupled together by the superexchange interaction mediated by intervening ions. There is magnetic exchange between ions both within planes and between planes. The magnetic properties of 2D materials are reviewed by de Jongh [16].

For a system to be truly 2D in the critical behaviour of its magnetic properties, the inter-planar exchange constant, J' , should be zero. The behaviour is effectively 2D when the length-scale over which the magnetic moments are correlated, the correlation length, ξ/a , is less than $\sqrt{(J/J')}$. ξ is measured in Å and a is the separation in Å between nearest-neighbour ions in the plane. In practice this means that in order to

observe 2D behaviour, the intra-planar exchange constant, J , should exceed J' by at least a factor of 100. Typically, values of J/J' of between 10^3 and 10^5 may be realised because the planes of coupled ions are magnetically isolated from one another by slabs of non-magnetic material. This is the case in La_2CuO_4 , K_2NiF_4 , K_2MnF_4 and in copper formate tetrahydrate which is considered in Chapters 2 and 3.

The critical magnetic properties of the ideal 2D Ising model can be solved exactly, and the solution due to Onsager [17] calculates the 2D ordering temperature, T_C , for a 2D Ising ferromagnet in terms of the inter and intra-planar exchange constants: $\sinh(2J/k_B T_C) \cdot \sinh(2J'/k_B T_C) = 1$. The Ising model is conceptually and experimentally the easiest to realise since most ions display some anisotropy and in many cases this is of the easy-axis type. Many experiments have been performed on 1D, 2D and 3D Ising systems, eg. the 2D system K_2NiF_4 [18, 19].

It was shown by Mermin and Wagner [20] that 2D ordering in XY and Heisenberg magnets was ruled out above $T=0$; However, the XY model was shown to mimic LRO by undergoing a Berezinskii-Kosterlitz-Thouless (KT) transition [21, 22, 23] which is a transition to a state with an infinite correlation length but no spontaneous order; below the KT transition, spin vortices are closely bound together in pairs and at the transition these unbind and there is a sudden change in the response to an external magnetic field. It has recently been shown by Bramwell and Holdsworth [24, 25, 26] that although the Mermin-Wagner theorem is true in the thermodynamic limit, that this limit cannot be reached experimentally until the sample has an almost infinite size. In their words [25]: “The sample would need to be bigger than the state of Texas for the Mermin-Wagner theorem to be relevant”. This is because spin-spin correlations decay so slowly with distance [26], that any realisable XY system has a measurable magnetisation at a non-zero temperature.

Since the critical behaviour of neither the 2D-XY nor the 2D-Heisenberg model can be solved exactly, all the information about such systems must be obtained experimentally. The properties of the 2D Heisenberg system are very poorly documented partly due to the lack of suitable experimental systems. We set out to investigate the low temperature properties of 2D approximately Heisenberg antiferromagnetic sys-

tems with low values of the spin ($S=1/2$). Low moment antiferromagnets are most likely to display non-classical behaviour, because with a smaller exchange energy, excited states will be mixed into their ground states to a larger degree than in other cases.

The Hamiltonian for a generic 2D system which just has exchange between nearest neighbours is

$$\mathcal{H} = J \sum_{\langle ij \rangle} (aS_i^x \cdot S_j^x + bS_i^y \cdot S_j^y + cS_i^z \cdot S_j^z) \quad (1.4)$$

where S_i^x and S_j^x represent the x components of the spin vectors on nearest neighbour ions and J is the exchange coupling constant between them. In the Ising case, $(S^z)^2 = S(S+1)$, for XY, $(S^x)^2 + (S^y)^2 = S(S+1)$ and for Heisenberg, $(S^x)^2 + (S^y)^2 + (S^z)^2 = S(S+1)$. For the Heisenberg model $a=b=c$, so one may write:

$$\mathcal{H} = J \sum_{ij} \vec{S}_i \cdot \vec{S}_j. \quad (1.5)$$

There are smaller terms for inter-planar exchange, J' , next-nearest-neighbour exchange, J_2 and possibly antisymmetric exchange, J_D which arises from non-zero off-diagonal terms in the J -tensor (Equation 1.1). In an *ideal* 2D system these are all zero and one should choose an experimental system in which they may be neglected to first order. There may also be a single-ion anisotropy term, D , which causes the behaviour to be Ising or XY-like at low temperatures. So a more general Hamiltonian, which includes these terms is:

$$\mathcal{H} = J \sum_{ij} \vec{S}_i \cdot \vec{S}_j + J_D \sum_{ij} \vec{S}_i \times \vec{S}_j + J' \sum_{ik} \vec{S}_i \cdot \vec{S}_k + J_2 \sum_{il} \vec{S}_i \cdot \vec{S}_l + D \sum_i \vec{S}_i \quad (1.6)$$

where i and j are nearest-neighbours in the plane, i and l are next-nearest-neighbours in the plane and i and k are nearest neighbours in neighbouring planes.

1.2 Square antiferromagnets with $S = \frac{1}{2}$

The interest in the 2D Heisenberg model was rekindled by the discovery in 1986 by Bednorz and Müller [27] that the compound $\text{Ba}_x\text{La}_{5-x}\text{Cu}_5\text{O}_{5(3-y)}$ ($x=1.0$ or 0.75 , $y > 0$) was a superconductor at 30 K, and the discovery since then of related materials

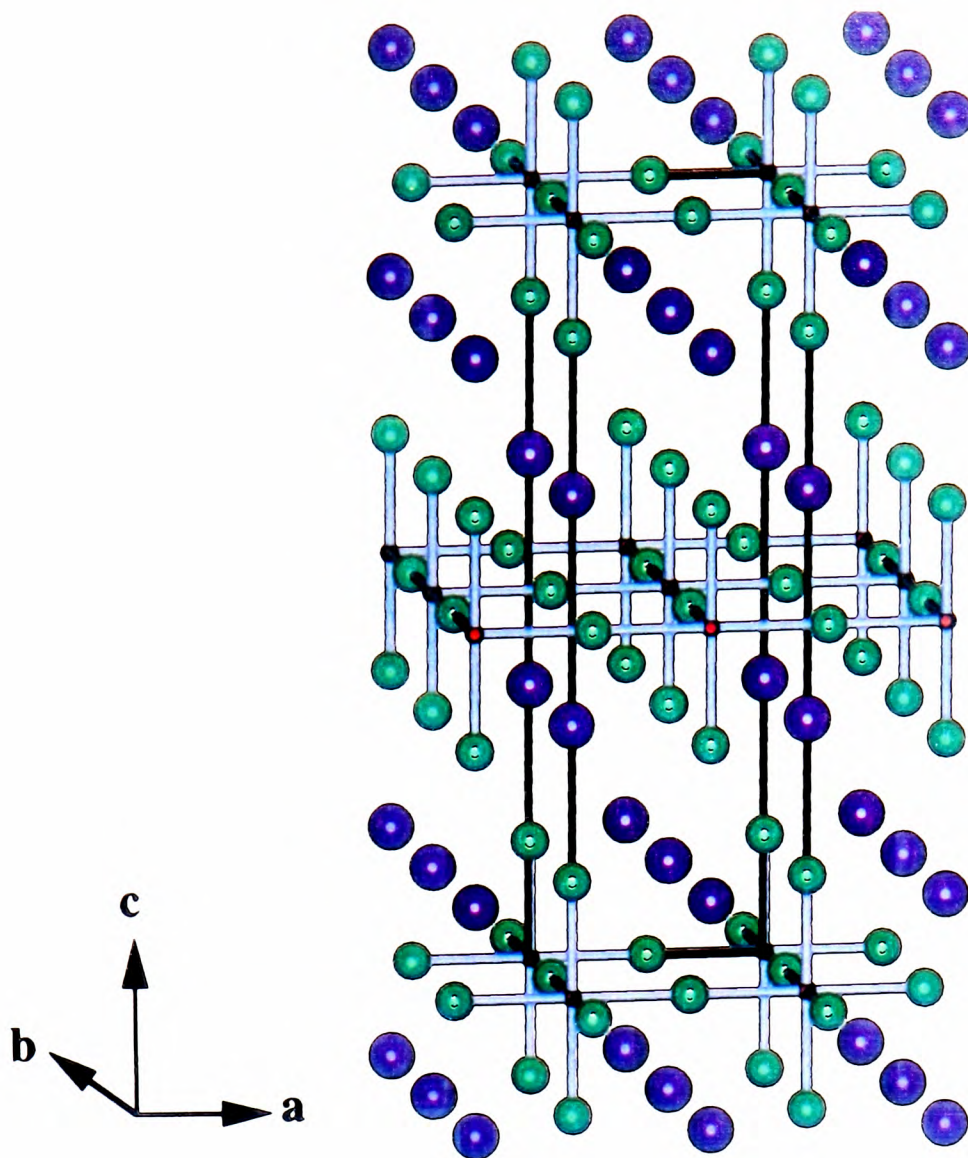


Figure 1.3: The structure of K_2NiF_4 . Ni are orange, K are purple and F are green. This is similar to the structure of La_2CuO_4 although the latter has an orthorhombic distortion and the a and c axes defining the basal plane are not identical in length.

such as $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ [28] which superconducts at 90 K and the current world record holder, $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+y}$ ($y > 0$) which superconducts at 134 K at ambient pressure and at 164 K under high pressure [29, 30]. The simplest of these superconductors to envisage is based on La_2CuO_4 . This has a structure very similar to that of the layered perovskite K_2NiF_4 which has layers of NiF_2 separated by blocks of $(\text{KF})_2$ as shown in Figure 1.3. In La_2CuO_4 the Cu^{2+} ions occupy an almost square array and they have $S=1/2$. The moment has Heisenberg symmetry since the spin anisotropy arising from the Jahn-Teller distortion is small compared with the exchange energy. La_2CuO_4 is thus an example of a 2D Heisenberg antiferromagnet. When 7% or so of the La^{3+} ions are replaced by Sr^{2+} , the compound superconducts.

Before the discovery of the layered cuprate superconductors, the general belief was that the 2D Heisenberg model could be understood using classical arguments [12]. However, the belief was revised after the appearance of superconductivity in layered cuprates and neutron scattering studies on La_2CuO_4 . A summary of the relation of high- T_c superconductors to the square Heisenberg model with $S=\frac{1}{2}$ is

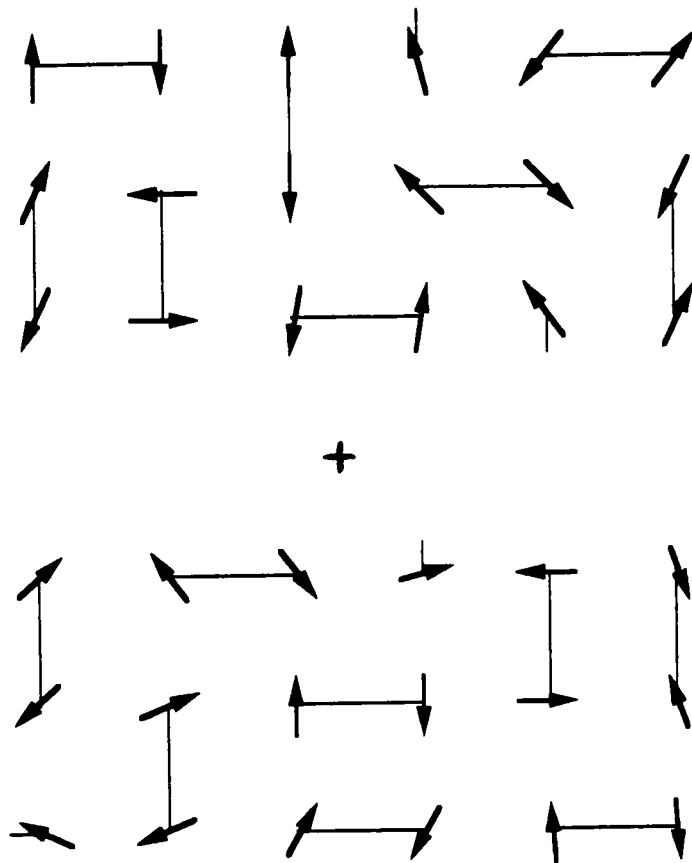


Figure 1.4: A representation of the RVB state. It is composed of a linear combination of all possible pairings of nearest neighbour spins

given by Manousakis [31]. Anderson [14] together with Fazekas [32] had proposed the existence of a non-Néel state for an antiferromagnet which they described as a Resonating Valence Bond (RVB) state. The RVB state is a fluctuating ground state consisting of antiferromagnetically coupled pairs of spins, the actual ground state being a linear combination of all the possible pairings of nearest-neighbour spins. The term was coined by Anderson by analogy with Pauling's model of resonance in covalent bonding. The state has also been described as a Quantum Spin Fluid [33, 34]. Figure 1.4 is a crude representation of the idea behind the RVB state.

At the time it was first developed, it was not clear what the exact nature of the RVB state was, or what kind of ordering it possessed. It is still unclear what the experimental properties of such a magnet are, although Anderson's predictions include the possession of a large heat capacity and a low magnetic susceptibility.

Calculations of the energy of this non-magnetic state by Anderson [14] showed that the energy of the RVB state for a Triangular Lattice Heisenberg Antiferromagnet (TALHAF) with $S=\frac{1}{2}$ was 15% lower than that of the classical Néel state. Fazekas and Anderson [32] showed that the RVB state competes well with the Néel state at a range of anisotropies ranging from Ising to Heisenberg. Anderson further predicted that the

square lattice will be undoubtedly RVB in the presence of *nnn* frustration. Soon after the discovery of superconductivity in the layered cuprates, Anderson expressed the belief [35, 36] that the existence of the state in these materials could provide spin-singlet pairs which could allow the formation of charged superconducting Cooper pairs when the material was doped with charge carriers.

Soon after Anderson's prediction [35], Shirane *et al.* [33, 34] carried out elastic and inelastic neutron scattering studies on single crystals of La_2CuO_4 . These first neutron scattering experiments on this material were similar to those described in Section 2.4 and the results will be contrasted at the appropriate point. The observations were that above a transition to 3D LRO driven by the interlayer coupling, the 2D correlation length was large (about 200 Å at 300 K), but there was no static character observed in the magnetic fluctuations which one would normally expect for a large correlation length. The workers suggested that their result was evidence for what they called a Quantum Spin Fluid (QSF) state which is equivalent to the RVB state. La_2CuO_4 has a very large exchange constant because the energies of the Cu 3*d* and O 2*p* orbitals are very close in energy and this leads to excellent in-plane orbital overlap. This leads to a very large energy scale for magnetic fluctuations, and it now seems that it was this that made the material appear to be a QSF. The 2DHAF appeared worthy of study and in need of a model material which was easier to study than La_2CuO_4 which, at the time, was hard to grow as homogeneous single crystals. The system has been realised by copper (II) formate tetrahydrate and this has been extensively studied by both magnetic neutron scattering, by Electron Spin Resonance (ESR) spectroscopy and by DC SQUID magnetometry. The investigation of this compound is described in Chapters 2 and 3. The principal terms in its magnetic Hamiltonian are compared with those in La_2CuO_4 .

Recently, a third model material, $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ [37] has been investigated using neutron scattering experiments very similar to those described in Section 2.4 and its behaviour has been found to be similar to that of copper formate tetrahydrate, La_2CuO_4 , Monte-Carlo simulation and the best theoretical model yet developed for the 2DHAF [38].

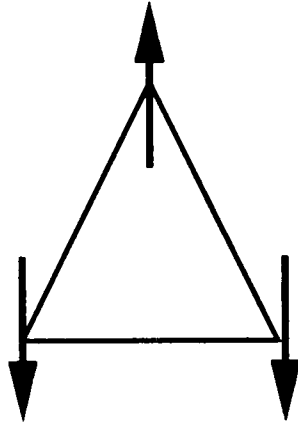


Figure 1.5: The frustration in a triangular Ising antiferromagnet

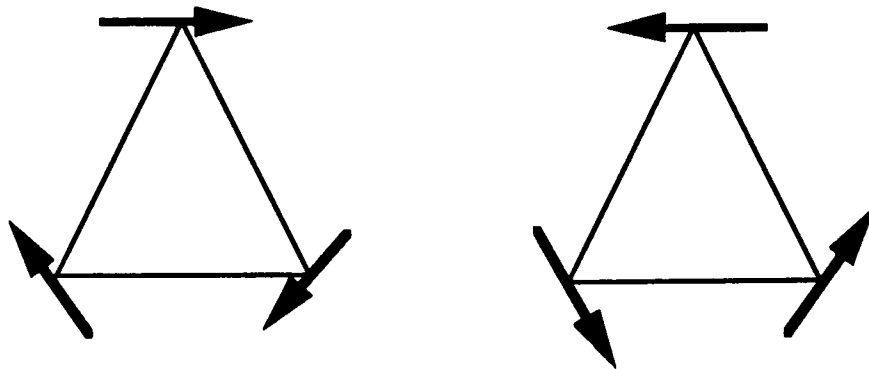


Figure 1.6: The frustrated triangular Heisenberg antiferromagnet adopts a 120° structure which displays chirality as shown.

1.3 Frustrated magnets

Another feature of certain magnetic systems is frustration. Consider a triangular array of moments coupled by an antiferromagnetic nearest-neighbour coupling constant, J . If the moments have Ising symmetry, it is not possible for the three moments on a triangular plaquette to all be arranged in a mutually antiferromagnetic fashion; the second moment can be aligned antiparallel to the first, but the third must be *parallel* to one of the first two as shown in Figure 1.5. The frustration per bond may be partially lifted as the anisotropy of the moments decreases and they become Heisenberg. In the XY and Heisenberg cases, the Néel state is the so-called 120° structure of Figure 1.6.

The 120° state is still frustrated since at no time can the three moments of a plaquette be antiferromagnetically aligned. It is also chiral [39, 40] since there are two enantiomeric ways in which the moments can be arranged at 120° to one another. It is a geometrical requirement that frustrated lattices with only nearest neighbour

exchange must be based on 3-fold symmetry since one requires an uneven number of bonds in a closed loop and 5-fold and 7-fold plaquettes do not tessellate a plane. The triangular case is considered in Chapter 4. The Kagomé lattice [41] shown in Figure 1.2 is also highly frustrated if nn interactions only are considered. There are frequently further neighbour interactions competing with the nn interaction which increase the frustration. The garnet $\text{SrCr}_9\text{Ga}_3\text{O}_{19}$ is the best material yet studied in detail although its Kagomé planes are not fully occupied. This incomplete occupancy together with high frustration causes the material to exhibit spin-glass (SG) like behaviour in its magnetisation as a result of the ‘blocking’ of antiferromagnetic regions. The local fluctuations in the SG state measured by neutron scattering [42] resemble those of an ordered antiferromagnet. The materials $\text{Na}_2\text{M}_3\text{Cl}_8$ where M is either Fe or Mn also possess a Kagomé lattice, but their magnetic properties have yet to be determined in detail [43]. It is hoped that these materials will shed further light on the Kagomé problem which has recently generated much theoretical interest [44].

In 3D, even greater frustration is possible. The pyrochlore lattice based on 4 interleaved Kagomé planes, and shown in Figure 1.2, has been extensively studied [45] and such materials tend to show spin-glass like behaviour. The half-occupied fcc lattice considered in Chapter 4 is also a frustrated system.

Frustration may occur in the square lattice if there are nnn interactions which disrupt the non-frustrated Néel state. Usually the nnn interactions are much weaker than the nn interactions and may be ignored. However Figure 1.7 shows that if the nnn interaction is also antiferromagnetic and comparable in strength to the nn interaction, frustration will result.

These frustrated systems are also candidates for having non-Néel ground states. However, when Anderson proposed this [14], he did acknowledge that the experimental realisation of the RVB state may not be easy due to the general lack of nnn interactions of sufficient size in the square lattice and due to the fact that triangular lattices are often slightly distorted with, for example, the possibility that the frustration may be relieved by further structural distortion to produce a quasi-one-dimensional material.

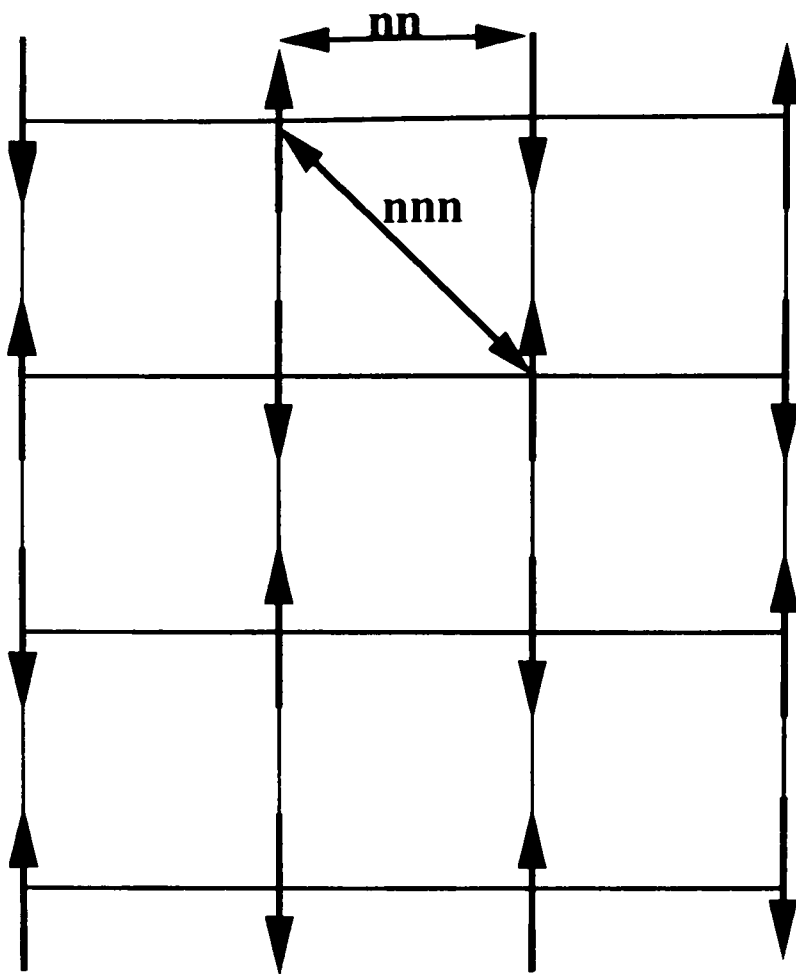


Figure 1.7: the frustration in the square antiferromagnet caused by a nnn antiferromagnetic interaction of comparable strength to the nn interaction

Recently, theoretical treatments [46] have indicated that the ground state energy of ordered square and triangular arrays of $S=\frac{1}{2}$ spins obtained by variational calculations is lower than that of Anderson's RVB prediction and the similar Gutzwiller wavefunction [47, 48]. These conclusions have largely been borne out by experiments on the model square 2DHAFs in which no unusual features are apparent. However, while the square lattice antiferromagnet has become less controversial, there is still no consensus on the properties of its triangular counterpart. The current favourite theory is that it is Néel ordered [49] but has a greatly reduced moment per ion due to quantum fluctuations. However, there is a need to investigate this by experiment.

The most promising material put forward as a candidate for the TALHAF with a RVB ground state is NaTiO_2 . There do not appear to be any other potential model materials known at present. The investigation of NaTiO_2 is described in Chapter 4. Although we have developed a means of preparing clean powder specimens, The investigation and interpretation of the results has been hampered by the difficulty in preparing the material in the form of a single crystal. We have carried out a detailed structural and magnetic analysis of stoichiometric NaTiO_2 and partially oxidised material obtained by reducing the Na-content.

The behaviour of our samples of NaTiO_2 is contrasted with that of other workers, most of whom seem to have been measuring Na-deficient material. Similarities with

other binary and ternary transition metal oxides and chlorides from the beginning of the first transition series have been noted and used to shed light on the magnetic and structural behaviour of NaTiO_2 . We have discovered that the investigation of this material cannot be used to confirm or deny the existence of the RVB state in a triangular lattice antiferromagnet.

The behaviour of LiTiO_2 , which is not a 2D material, has been investigated in order to compare it with NaTiO_2 . This work is also discussed in Chapter 4.

Chapter 2

Measurement of magnetic ordering and characterisation of spin-waves in deuterated copper formate tetrahydrate (CFTH) using neutron scattering

2.1 Comparison of CFTH with La_2CuO_4

The object of carrying out a series of experiments on $\text{Cu}(\text{HCO}_2)_2 \cdot 4\text{H}_2\text{O}$ (CFTH) was to determine how good a model material it is for the 2D Heisenberg antiferromagnet. The first, and most thoroughly studied example of this class of magnet is La_2CuO_4 , which becomes superconducting at around 30 K when some of the La is replaced by Sr. This model gained importance with the possibility that it had unusual behaviour which would help to account for the origin of the superconductivity. Anderson [35] proposed that the existence of his RVB state in these magnets would offer an explanation for the superconductivity. In this section, the similarities and differences between CFTH and La_2CuO_4 are briefly examined. The results of experiments on CFTH are described in the later sections of this chapter and in Chapter 3. The properties of the two materials are reviewed during the discussion. Comparisons are also made with $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ which has recently [37] emerged as a third model for this magnetic class.

2.1.1 Structure

At room temperature, CFTH has the monoclinic space group $P2_1/a$ and the lattice constants are: $a=8.15$, $b=8.18$, $c=6.35\text{\AA}$ and $\beta=101.1^\circ$. There are two formula units per unit cell [50, 51]. The structure contains layers of $\text{Cu}(\text{HCO}_2)_2$ in the ab plane separated by water molecules. The Cu^{2+} ions are coordinated by four different HCO_2^- groups in a square planar array and two H_2O molecules, one above and one below the ab plane. The environment of the Cu^{2+} ions is Jahn-Teller distorted as expected for a d^9 system with an E_g ground state; the bond lengths between Cu^{2+} ions and the formate group oxygen atoms are 1.96 and 1.99 $\text{\AA}$, while those between Cu^{2+} ions and the oxygen atoms of water molecules are 2.35 $\text{\AA}$.

There is a paraelectric-antiferroelectric phase transition at 236.1K in CFTH [50, 51] and at 246.1K in the fully deuterated analogue, CFTD [52, 53]. The transition is a result of dipolar ordering [54] of the H_2O molecules between the planes. Shifts of the hydrogen atoms of the H_2O molecules, which are disordered above the transition but ordered below it [52, 53, 55], causes a loss of the centre of symmetry in the unit cell and doubling of the c axis [56, 57]. Below the phase transition, the space group is $P2_1/n$ [52, 53, 55]. There is very little change in the environment of the Cu^{2+} ions [53, 58]. The structure below the antiferroelectric phase transition is shown in Figure 2.1.

The structure of CFTH should be compared with that of La_2CuO_4 which is shown in Figure 2.2. Above about 500 K this has the tetragonal K_2NiF_4 structure with space group $\text{I}4/\text{mmm}$, but then undergoes a distortion to an orthorhombic unit cell with space group Cmca and dimensions $a=5.354\text{\AA}$, $b=13.153\text{\AA}$ and $c=5.401\text{\AA}$ at room temperature. The symmetry is lowered considerably from that in the high-temperature phase by a tilting of the CuO_6 octahedra by 4° out of the ac plane. Both structures have 2D character, because the almost square planes of copper ions are separated by layers of H_2O molecules in CFTH and by layers of La_2O_2 in La_2CuO_4 . Note that the ab plane contains the magnetic ions in CFTH, and is equivalent to the ac plane in La_2CuO_4 .

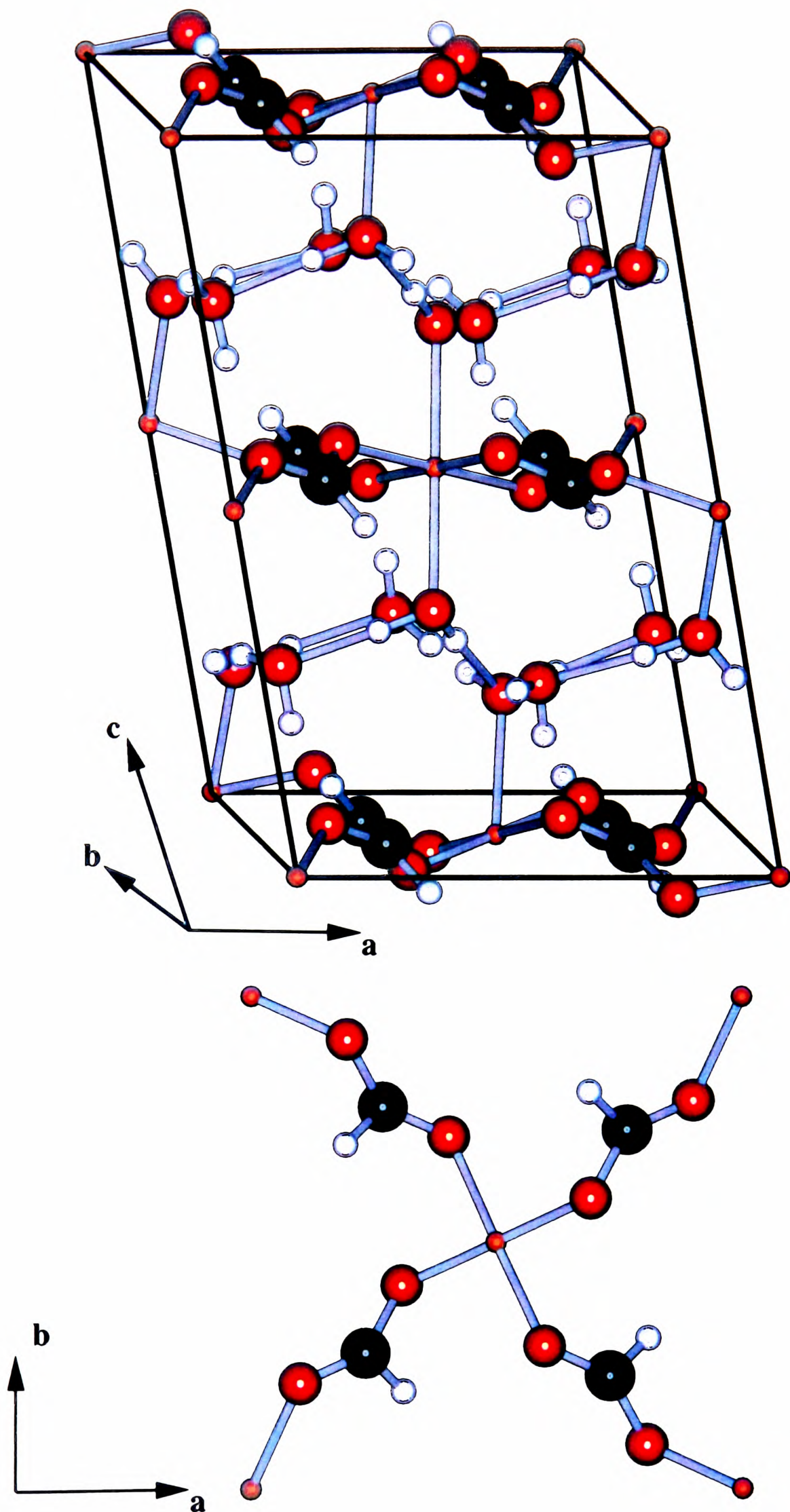


Figure 2.1: Crystal structure of CFTH below the antiferroelectric phase transition: Upper: The unit cell showing planes of copper formate separated by water molecules. Lower: A square plane of copper formate. Cu ions are orange, O are red, C are black and H(D) are white. In the upper diagram the hydrogen bonds between water molecules are shown as well as the covalent bonds between atoms.

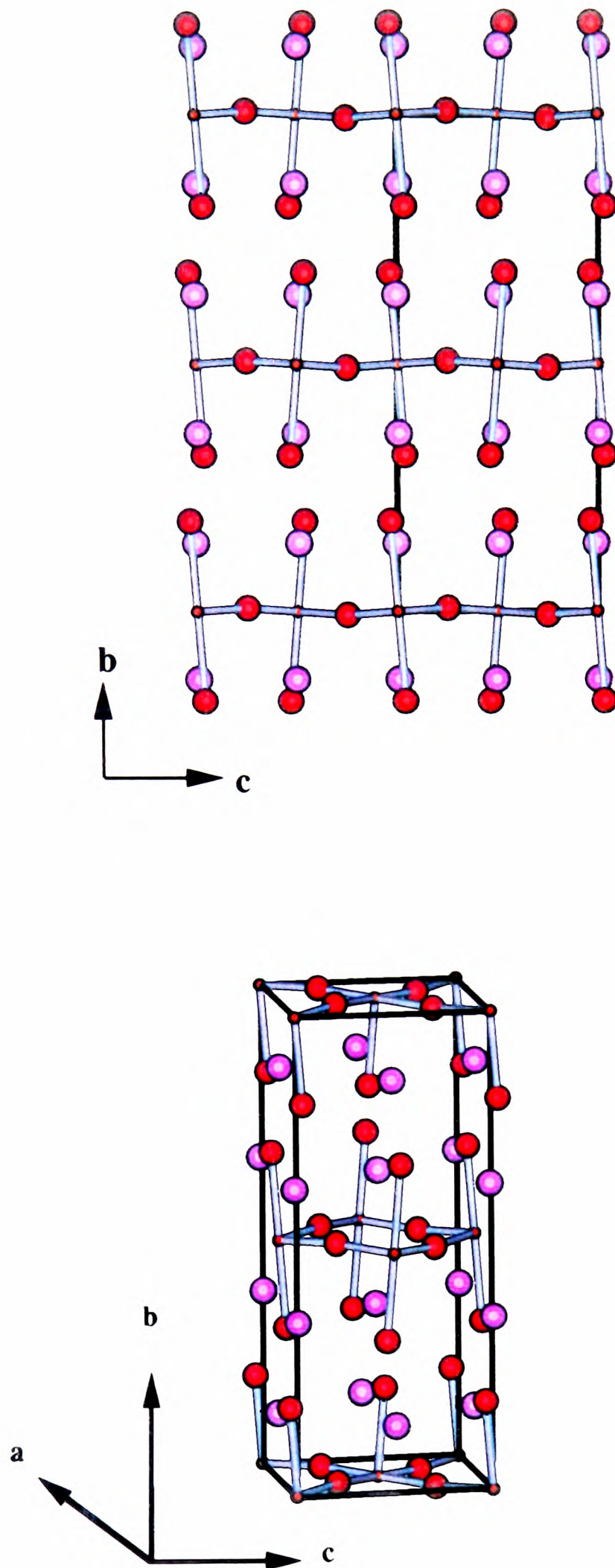


Figure 2.2: The crystal structure of La_2CuO_4 . The upper diagram is a view along the a axis showing the tilting of the CuO_6 octahedra. The lower diagram is a perspective representation of the unit cell. Copper ions are orange, oxygen ions are red and lanthanum ions are pink.

Neither compound is of very high symmetry, and this produces small terms in the magnetic Hamiltonian in addition to the nearest neighbour symmetric exchange.

2.1.2 Magnetic behaviour

At about 16K, CFTH undergoes a transition from a paramagnetic state to an antiferromagnetic state. The presence of antiferromagnetic interactions between Cu^{2+} ions mediated by formate groups was first suggested by Martin and Waterman [59]. Magnetic susceptibility measurements carried out by Kobayashi and Haseda [60] and by Flippen and Friedberg [61] show Curie-Weiss behaviour from room temperature down to about 80K. The Weiss constant is about -175K. There is a broad susceptibility maximum at around 60K when the sample is measured along an axis in the ab plane. There are much sharper maxima in the b and c directions at around 16K. The temperature dependent moment, large negative Weiss constant and susceptibility maxima, together with a low room temperature moment of 1.46 Bohr Magnetons (μ_B) per ion [59], suggest that there are 2D antiferromagnetic interactions in this compound. Seehra [62] demonstrated quantitatively that the broad susceptibility maximum is due to short range ordering of the spins within the planes. He also demonstrated that the observed paramagnetic susceptibility coincides very well with the predictions of the Rushbrooke-Wood high temperature series expansion for a 2D-HAF with $S=\frac{1}{2}$. Van der Leeden *et al.* [63] carried out proton NMR at 4.2K on $\text{Cu}(\text{HCO}_2)_2 \cdot 4\text{D}_2\text{O}$. Their resonance pattern was characteristic of an antiferromagnet. The nearest-neighbour in-plane exchange for CFTH was determined to be about 6 meV (70 K) [62].

The magnetic susceptibility of La_2CuO_4 [64] is qualitatively very similar to that of CFTH, although the value of T_N is about 200 K, and the value of J is about 100 meV (1200 K) [65].

As discussed in Chapter 1, the magnetic Hamiltonian for an ideal 2D antiferromagnetic system with isotropic spins contains only a term for nearest-neighbour symmetric superexchange

$$\mathcal{H} = -J \sum_{ij} \vec{S}_i \cdot \vec{S}_j. \quad (2.1)$$

The fact that neither such a Heisenberg system nor an XY system can undergo long-range ordering in 2-dimensions in the thermodynamic limit was discussed in Chapter 1. Thermal fluctuations lead to short-range spin correlations in such materials. In *real* 1D and 2D magnets, there are always finite interchain or interplane interactions which lead to 3D LRO at low temperatures. Interplane interactions in CFTH are responsible for this ordering at 16 K. From an experimental determination of the magnetic correlation length which is discussed later in this chapter, J/J' is calculated to be approximately 3×10^4 which is very similar to the value of about 4×10^4 in La_2CuO_4 [64], and indicates that CFTH is a good approximation to a 2D magnet. The transition at 16 K is not associated with any structural change. The magnetic unit cell was shown by Burger *et al.* [66] to be the same as the nuclear unit cell at low temperatures, ie. double the room temperature cell. The same authors also showed that the magnetic structure could be described as a four-sublattice array which is shown in Figure 2.3 where it is compared with the magnetic structure of La_2CuO_4 . In CFTH, there is a weak canting of the moments out of the ab plane. In zero-field, the canting in different planes cancels out, and there is no net moment in zero-field. However, when a field is applied along either the b or c directions, a net magnetisation is produced [66].

There is a similar canting in La_2CuO_4 which Thio *et al.* [64] have determined to be about 0.2° in the b direction. This arises from an antisymmetric exchange term in the Hamiltonian which is allowed by symmetry [6, 7] due to tilting of the CuO_6 octahedra. Thio *et al.* calculate that the antisymmetric exchange term in the Hamiltonian is second in magnitude only to the symmetric nearest-neighbour exchange. There is evidence for a similar interaction in CFTH [67] which we have measured in the experiments discussed in this chapter and in Chapter 3.

As will be discussed in greater detail in this chapter and the next, it seems that CFTH and La_2CuO_4 have very similar magnetic Hamiltonians arising from similarities in their structures. In addition to the symmetric exchange term, there is an antisymmetric exchange term arising from non-zero off-diagonal elements in the tensor representing the total in-plane exchange, and there is a still smaller term for the

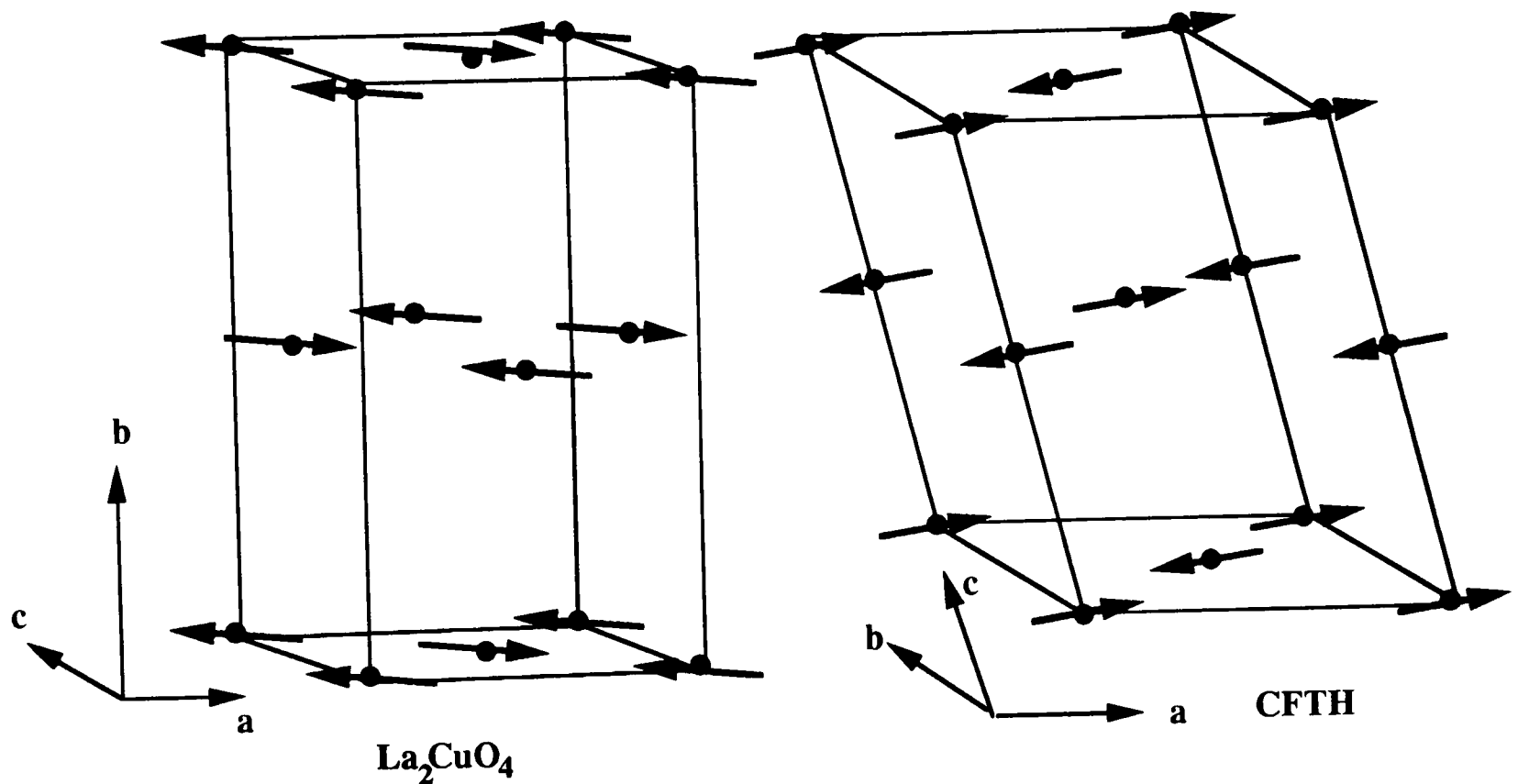


Figure 2.3: The magnetic structures of CFTH and La_2CuO_4 .

inter-planar exchange with exchange constant J' :

$$\mathcal{H} = -J \sum_{ij} \vec{S}_i \cdot \vec{S}_j + J_D \sum_{ij} \vec{S}_i \times \vec{S}_j + J' \sum_{ik} \vec{S}_i \cdot \vec{S}_k \quad (2.2)$$

where spins i and j are nearest neighbours in the plane and i and k are nearest neighbours in neighbouring planes.

The great advantage of studying CFTH over La_2CuO_4 is that all the terms are smaller due to the greater separation between the magnetic ions. This makes many of the standard experiments more straightforward and less open to misinterpretation.

2.2 Preparation of CFTH

Single crystals of CFTH were prepared by dissolving basic copper (II) carbonate in a solution of 10% formic acid in water and evaporating the solution in a vacuum desiccator containing a large quantity of silica gel. Filtration was used to remove dust particles and minimise the number of possible nucleation sites in order to maximise the chances of growing a small number of large crystals. The desiccator was placed in a reasonably isothermal ($\Delta T < \pm 2 \text{ K}$) and vibration-free environment to increase

the crystal quality.

The deuterated material, CFTD, for use in neutron scattering was produced by a similar route, except that anhydrous copper (II) sulphate was used as the starting material. This was dissolved in D₂O and added with stirring to a solution of anhydrous sodium carbonate dissolved in D₂O. All the manipulations using D₂O were performed in a nitrogen-filled glove-box to minimise exchange of deuterium with hydrogen from the atmosphere. The resulting blue-green precipitate was dried in a vacuum dessicator and the result was green deuterated basic copper (II) carbonate. This was dissolved in a 10% solution in D₂O of fully deuterated formic acid (formic acid-*d*₂) obtained from MSD Isotopes (Now trading as CDN Isotopes) and with 99% of the hydrogen atoms substituted by deuterium.

It was possible to grow large crystals of between 0.5 and 2 cm³ by this route. This is an ideal size for inelastic neutron scattering work in which the scattering intensity is low.

2.3 Neutron Scattering

2.3.1 Introduction

Neutrons suitable for solid state research are produced either from a low power 10-100 MW uranium fuelled nuclear reactor such as those at the Institut Laue-Langevin, Grenoble, Brookhaven National Laboratory, Long Island, Risø National Laboratory, Denmark, and Chalk River Laboratories, Ontario or from a spallation source in which high energy protons are accelerated at a heavy metal (typically U or Ta) target such as those at ISIS, UK and LANSCE, New Mexico. The neutrons produced from a nuclear reactor have energies of between about 5 and 50 meV.

$$1 \text{ meV} = 11.605 \text{ K} = 4.136 \text{ THz} = 81.805/\lambda^2 \text{ (}\lambda \text{ in } \text{\AA}\text{)} \quad (2.3)$$

Hence, according to Equation 2.3 they have wavelengths of between about 1.5 and 4 Å. This makes the neutron an ideal probe of atomic-scale properties. Neutrons with different ranges of energy are obtained from the reactor by scattering them from a

material called the moderator. Thermal neutrons with wavelengths of about 1 Å are produced when a H₂O or D₂O moderator is at 300 K. Cold neutrons with wavelengths of about 4 Å are produced when a liquid H₂ moderator at around 25 K is used. The neutrons produced by a reactor have a Maxwellian distribution of energies with the peak at $k_B T_M$, where T_M is the temperature of the moderator. Different energy neutrons are used for different tasks. The neutrons produced by spallation occur as high intensity pulses with a broad range of energies and energy selection is performed.

Neutrons cannot interact with nuclei via the electromagnetic force because they are uncharged. The gravitational attraction between a neutron and a nucleus is negligible. Neutron scattering from nuclei can only arise when the neutron interacts with a nucleus via the strong nuclear force. This force is only effective over a very short range and, as the nucleus is so small, the interaction is improbable, so neutrons have a mean free path in solids of about 1 cm; hence radiation shielding using lead, cadmium or plastic impregnated with B₄C, all of which absorb neutrons, is very important.

The neutron has a magnetic dipole moment given by

$$\mu_n = -\gamma\mu_N\sigma \quad (2.4)$$

where $\gamma=1.913$ is the gyromagnetic ratio of the neutron, μ_N is the nuclear magneton ($5.05082 \times 10^{-27} \text{ JT}^{-1}$) and σ is a Pauli spin operator for a particle with $S=\frac{1}{2}$. Magnetic scattering can occur due to the interaction of this magnetic moment with local magnetic fields arising from the spin and orbital angular momenta of unpaired valence electrons in the solid. The interaction is intrinsically weaker than the interaction with nuclei but has a similar probability as it is mediated by the electromagnetic force and extends over a much longer distance. The mean free path for magnetic scattering events is also about 1 cm.

Form factors

The intensity of a particular type of scattering falls off with increasing scattering vector according to a form factor which is defined as the fourier transform of the density of whatever the neutron scatters from. The physical reason for this fall-off

is that when the scattering takes place from a volume comparable in size to the wavelength of the radiation being scattered, not all the scatterers scatter in phase. There is partial cancellation of scattering intensity due to destructive interference, and this is greater at large scattering vectors.

The nucleus is very much smaller than the wavelength of a thermal neutron, and the fall-off of neutron scattering intensity with angle due to this effect is negligible, ie. the form factor for nuclear scattering is almost invariant with scattering vector.

X-rays are scattered from the electron density of atoms which is concentrated around the electronic core. The core has a similar size to the wavelength of an X-ray, and so there is a significant form-factor effect which causes the scattering from X-rays to be quite weak at high angles. The form-factor for X-ray diffraction is described by the equation

$$f_0 = \int_0^\infty U(r) \frac{\sin kr}{kr} dr \quad (2.5)$$

where $k = 4\pi(\sin \theta)/\lambda$ and $U(r) = 4\pi r^2 |\psi|^2$. ψ is the wavefunction of the atomic electrons and so $U(r)dr$ is interpreted as the probability of finding an electron between r and $r + dr$ from the nucleus.

Magnetic neutron scattering occurs from the valence electrons of an ion which are much more diffuse than the core electrons. The form-factor has a similar form to that for X-ray scattering, but falls off much faster with scattering vector. The fall-off with angle is indicated for the three types of scattering in Figure 2.4

Neutron scattering cross-sections

A neutron interacting with a nucleus may either be scattered or absorbed. The proportion of neutrons scattered per second is defined as the scattering cross-section, σ_s . The proportion of neutrons absorbed per second is defined as the absorption cross-section, σ_a . The nucleus-neutron interactions may also be described by the scattering length, b which is measured in femtometres ($1 \text{ fm} = 10^{-15} \text{ m}$). The real part of this complex parameter represents elastic scattering and is usually positive, though it is negative for some nuclei. The imaginary part corresponds to absorption.

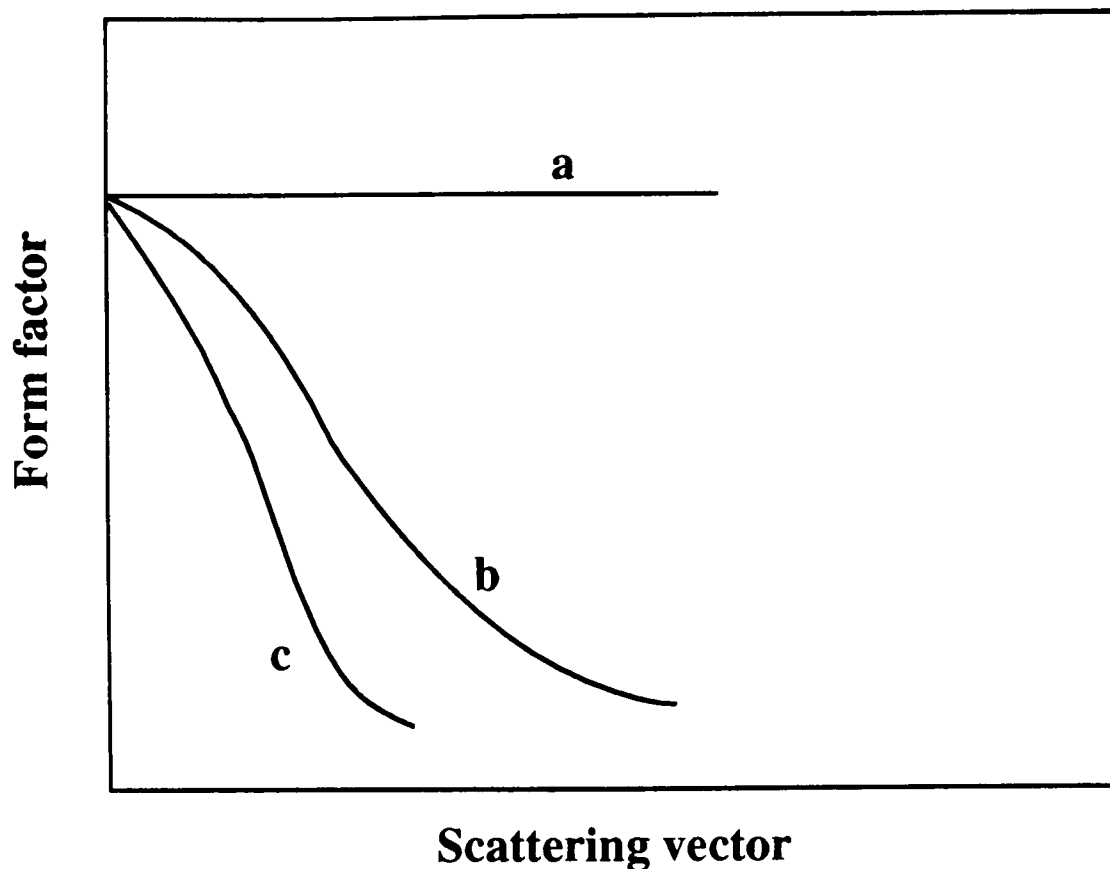


Figure 2.4: The form-factors for nuclear neutron scattering (a), atomic X-ray scattering (b) and magnetic neutron scattering (c). Each form-factor has been normalised relative to its value when the scattering vector is zero.

The scattering cross-section is related to the real part of the scattering length by:

$$\sigma_s = 4\pi b^2.$$

The real part of the scattering length of an element depends on which isotope scatters the neutron and on the spin state of the nucleus. Thus in an elemental crystal, the scattering length at a particular site may be different from that at its neighbours. Diffraction peaks only arise when the scattering from all the nuclei interferes constructively. This *coherent* scattering is proportional to the average scattering length $\bar{b}$ and the coherent cross-section, σ_c is equal to $4\pi|\bar{b}|^2$. Deviations from the average scattering length are randomly distributed and do not give rise to interference. They give rise to *incoherent* scattering which is proportional to the mean-square deviation from the average scattering power: $\sigma_i = 4\pi(|\bar{b}|^2 - |\bar{b}|^2)$. Incoherent scattering usually only contributes to the background scattering. The neutron scattering cross-sections for H and D are tabulated in Table 2.1. The incoherent cross-section for H is exceeded only by that of Gd, and so it is essential to replace all the H in a material by D in order to avoid raising the background immensely, and also to allow determination of the hydrogen atom positions in the structure. D also has a much smaller absorption cross-section and a larger coherent cross-section than H.

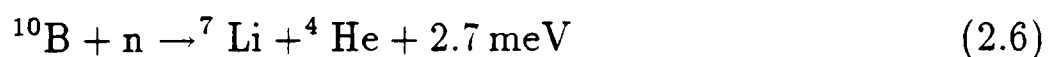
	b/fm	σ_c/barn	σ_i/barn	σ_a/barn
H	-3.7423	1.7599	79.91	0.3326
D	6.674	5.597	2.04	0.000519

Table 2.1: A comparison of the neutron scattering lengths and coherent, incoherent and absorption cross-sections for H and D.

One may determine the scattering length and the cross-sections for coherent and incoherent scattering and for absorption for each nucleus [68, 69]. It is found that these do not vary systematically in magnitude with atomic number and with the number of protons and neutrons in the nucleus.

Detection of neutrons

Neutrons cannot be detected in the same way as other forms of radiation, since they are uncharged and cause virtually no ionisation of the medium through which they pass. One makes use of the fact that certain nuclei have large absorption cross-sections, and that they decay after absorption, to produce ionising fragments. One mode of detection is to use a tube containing BF_3 gas enriched with ^{10}B , through which passes a wire at high potential. The ^{10}B nucleus absorbs a neutron:



and the alpha-particle causes ionisation of the gas which is detected as a current and converted to a signal representing the detection of one neutron. A more efficient device which operates at a lower voltage is the ^3He detector which is a similar device filled with ^3He gas. The reaction is:



and the hydrogen nuclei cause the ionisation in this case. The ^3He detector is newer, and now the most widely used. The spectrometer TAS6 at Risø described in this chapter uses a ^3He detector. The diffractometer C2 at Chalk River considered in Chapter 4 uses a $^{10}\text{BF}_3$ detector.

Use of neutron scattering

Neutron scattering from nuclei is used to elucidate crystal structures and is a complementary technique to X-ray diffraction. It has the advantage of being able to distinguish atoms of similar atomic mass since the neutron scattering power is not proportional to the atomic number. For this reason it may be used to determine the position of hydrogen or other very light atoms in the structure. The fact that magnetic scattering also occurs means that magnetic structures can be determined. Furthermore, magnetic scattering allows one to determine the degree of magnetic ordering and the strength of magnetic interactions in a magnetic material, and hence the magnitude of some of the terms in the Hamiltonian. Work on this is discussed in Sections 2.4 and 2.5

2.3.2 Elastic, quasielastic and inelastic neutron scattering

The most straightforward technique in neutron scattering involves the elastic scattering of the neutron from nuclei and is entirely analogous in geometry to the diffraction of X-rays. The neutron is scattered with no change of energy and the momentum vectors of the ‘initial’ neutron, $\vec{k}_i$, and the ‘final’ neutron, $\vec{k}_f$, are equal in magnitude. The scattering vector, $\vec{Q}$ is defined by

$$\vec{Q} = \vec{k}_i - \vec{k}_f. \quad (2.8)$$

One may picture another case in which $|k_i| \neq |k_f|$, ie. the neutron has lost energy to, or gained energy from the sample. This inelastic scattering may occur when the neutron is scattered by a lattice vibration (phonon) or by a magnetic excitation (magnon). These types of scattering are summarised in Figure 2.5. At a reactor source, an elastic scattering experiment is carried out on a diffractometer or 2-axis spectrometer. From the range of neutron energies emanating from the moderator, a monochromator crystal selects a particular wavelength by diffraction from a chosen lattice plane (eg Graphite (002) or Ge (111)). Diffraction of these neutrons from the sample is detected by the methods described above. For a powder diffraction experiment, a wide-angle detector is usually employed to optimise the proportion of

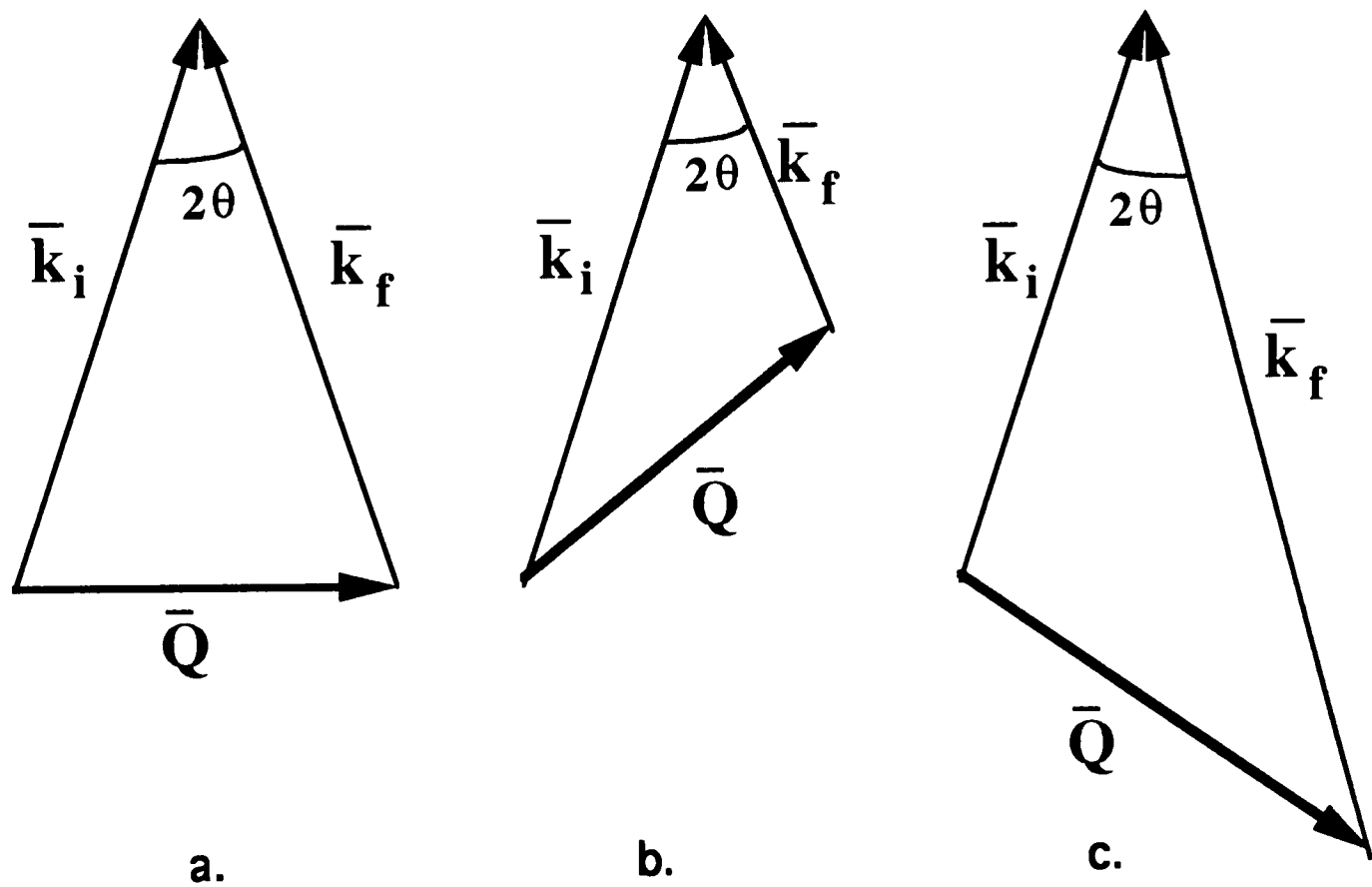


Figure 2.5: A neutron may be scattered elastically (a.), or inelastically (b.) & (c.). For inelastic scattering, the neutron may either lose energy (b.) or gain energy (c.). $\vec{k}_i$ and $\vec{k}_f$ are the initial and final neutron wavevectors respectively. $\vec{Q}$ is the scattering vector, $\vec{Q} = \vec{k}_i - \vec{k}_f$.

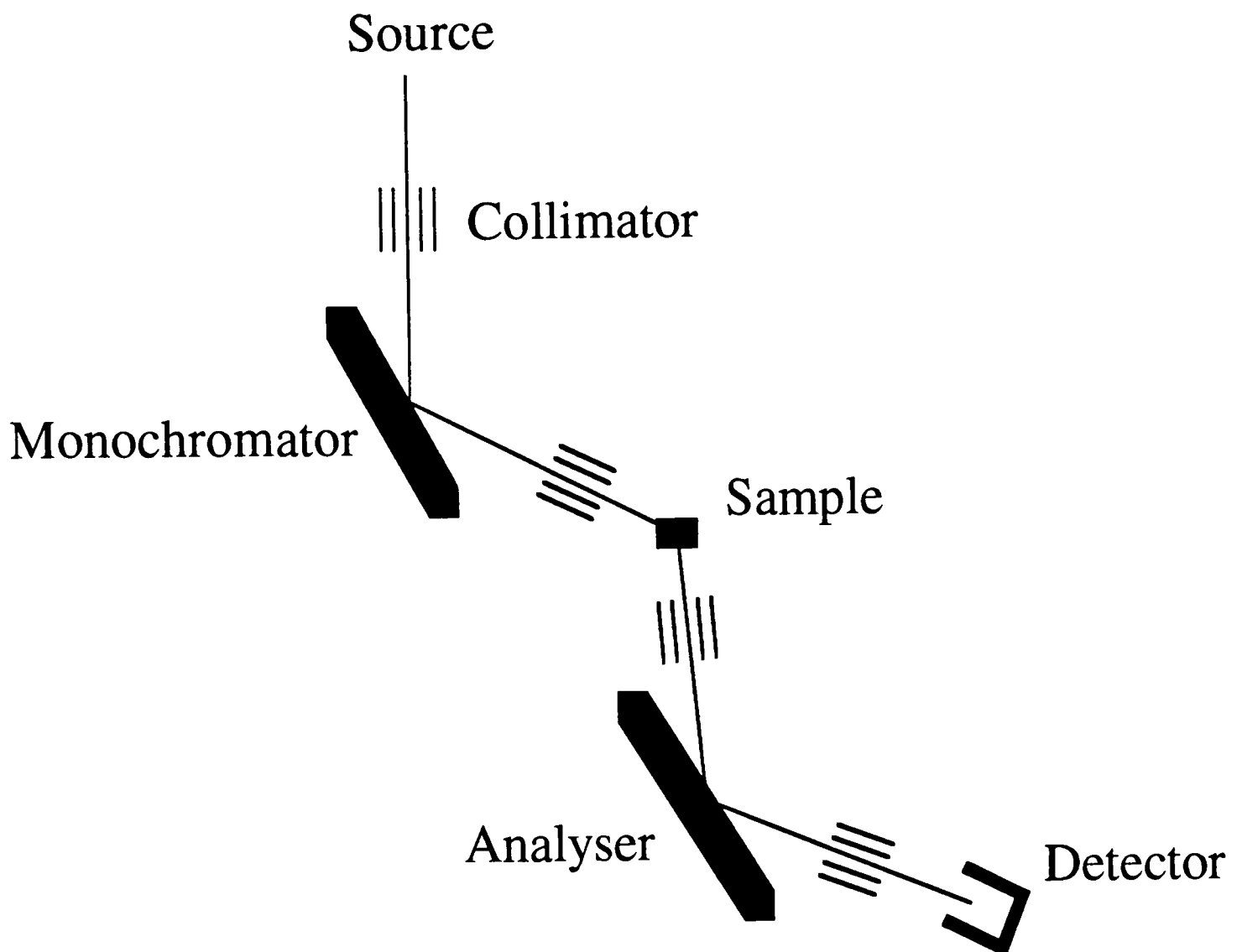


Figure 2.6: A schematic representation of the arrangement of the inelastic neutron spectrometer TAS6 at Risø. The ‘W’ configuration in which the detected neutrons follow a ‘W’-shaped path optimises the resolution by minimising the spread of neutrons.

neutrons detected. The two axes of the spectrometer are the two points at which the neutrons change their momentum — the monochromator and sample crystals.

In an inelastic experiment, there must be a means of determining the relative numbers of neutrons undergoing a particular energy change. This is accomplished by including a third axis between the sample and the detector. This analyser crystal is typically made of the same material as the monochromator and monochromation and energy analysis are often carried out by the same reflection planes. To measure the inelastic spectrum, one may keep the monochromator fixed relative to the source and keep the incident energy, E_i , fixed, and then move the analyser relative to the detector in order to measure different final energies, E_f . Alternatively, one may fix E_f and vary E_i . The arrangement of the triple axis spectrometer TAS6 at Risø, is shown in Figure 2.6. Experiments using this spectrometer are described in Section 2.5.

Note that in Section 2.4.1 a diffraction (2-axis) experiment was performed in 3-

axis mode. In this case, the analyser was used to ensure that only elastically scattered neutrons were detected (ie. that there was zero-energy transfer).

In a conventional inelastic experiment using a reactor source, only about 1 in 10^{15} of the neutrons incident on the monochromator reach the detector. Most pass straight through the monochromator, the sample or the analyser, while others are scattered, but not towards the detector. A less wasteful strategy is to use a multi-channel analyser spectrometer such as the instrument PRISMA at ISIS in which neutrons having a range of k_i reach the sample. 16 analysers arranged at different scattering vectors count neutrons of the same k_f . Hence one can measure 16 points in reciprocal space simultaneously, thus increasing the efficiency of the measurement.

The cross-section for inelastic scattering is orders of magnitude less than that for elastic scattering, and in order to increase the signal to noise ratio to a reasonable level, it is necessary to decrease the instrumental resolution and increase the size of the sample. The resolution function can be calculated [70, 71] and is made up of contributions from the mosaic spread in the monochromator, sample and analyser crystals, which smear the energy of the neutrons, and from directional smearing which is only incompletely eliminated by collimators located between the monochromator and sample, sample and analyser, and analyser and detector. The resolution function is an ellipsoid in reciprocal space and the energy dimension; it is shown diagrammatically in the discussion of spin-wave measurements on CFTD (Section 2.5). In an elastic scattering experiment the resolution ellipse is very small because narrow collimations may be used and intense Bragg peaks may still be observed using small crystals. Hence its broadening effect on the diffraction pattern may often be ignored. However in an inelastic experiment, much of the collimation is removed, the larger crystals used often have a larger mosaic spread, and the resolution ellipse becomes so large that it broadens the inelastic peaks considerably. Since the intrinsic width of the peaks is usually an important quantity, it is essential to calculate the resolution function accurately and deconvolve it from the scattering profile to obtain accurate information about the intrinsic nature of the phonon or magnon peaks.

An intermediate form of scattering may also be identified — quasielastic scattering

(QES). This arises from the broadening of elastic scattering by random processes. It may be used in spectroscopy where, for example, QES arises from the Doppler broadening of an elastic peak by translational processes. It may also arise from rotational motion. In a collective magnetic system, quasielastic ‘critical’ scattering arises from the short-range ordered regions present just above the long-range magnetic ordering transition.

2.4 Measurement of magnetic ordering and fluctuations

Elastic and quasielastic neutron scattering experiments were performed on CFTD using the triple-axis neutron spectrometer D10 at the High Flux Reactor (HFR) of the Institute Laue-Langevin, Grenoble (ILL). D10 is situated on a neutron guide emanating from the thermal source of the HFR. This work has been described previously [72, 73], but will be discussed here in some detail as it is relevant to the measurement of spin-waves discussed in Section 2.5, and to the determination of the terms in the magnetic Hamiltonian. We will compare the results with early neutron scattering experiments on La_2CuO_4 [33, 34].

A crystal of dimensions $5 \times 3 \times 2.5$ mm was wrapped in Al foil to prevent dehydration and sealed in a can filled with ^4He exchange gas which was mounted in a ^4He flow cryostat on the Eulerian cradle of D10. This allows the crystal to be oriented about four different axes in three dimensions. A vertically focussing Pyrolytic Graphite (PG) (002) monochromator was used together with a PG filter to produce a wavelength of 2.36 Å.

2.4.1 Magnetic ordering

Experimental

Measurements of the (200), (002) and ($\bar{2}$ 20) nuclear reflections indicated that there were two crystallites separated by 0.45° in the direction of c^* which is perpendicular to the planes of copper ions. The twinning merely complicates the analysis slightly

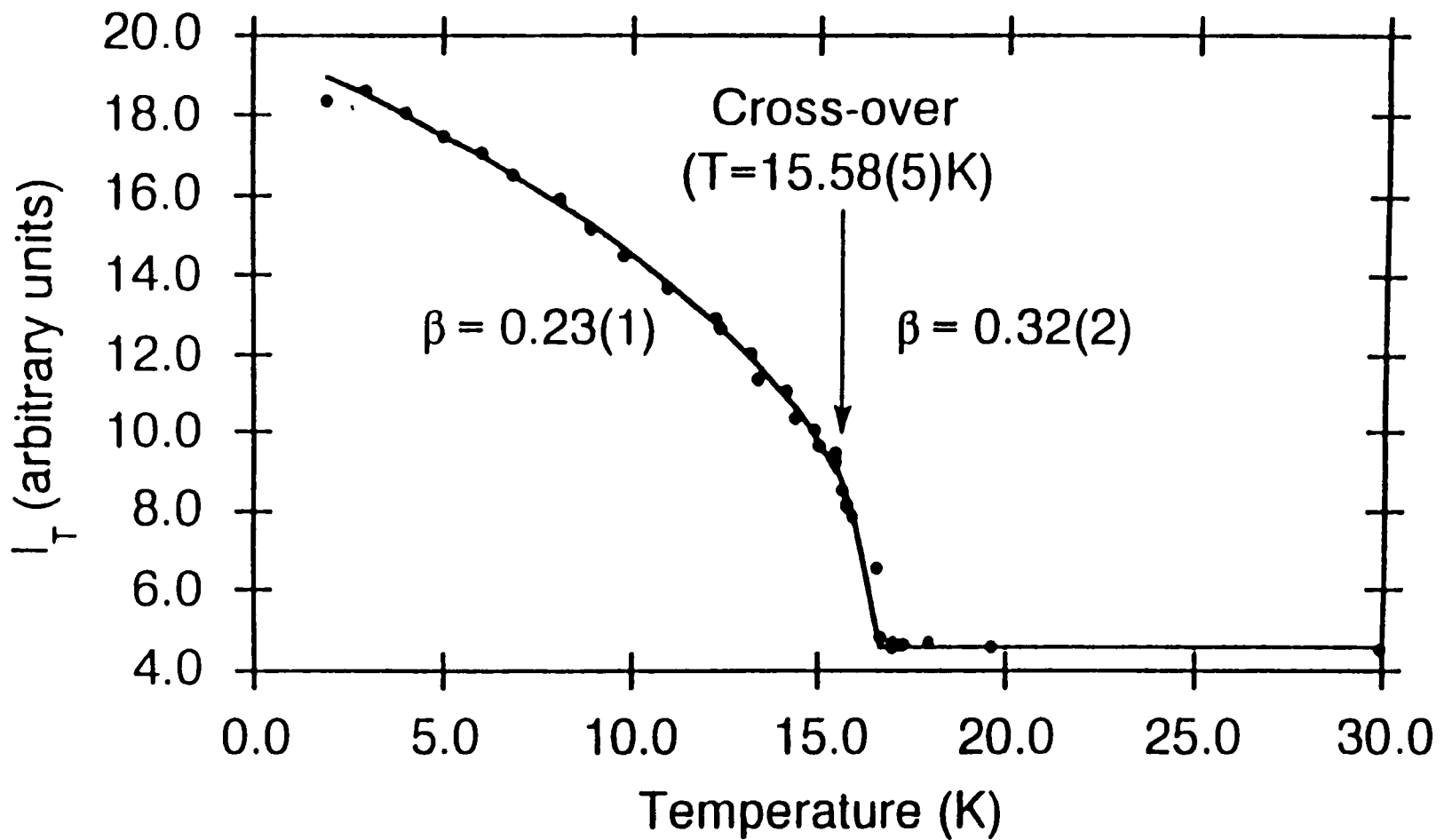


Figure 2.7: The intensity of the (0-11) magnetic Bragg peak as a function of temperature. The solid line is a fit to Equation 2.11. T_N is the temperature at which the plot becomes flat.

and does not affect the results. The twinned crystal was used because it was the largest available. The (0-11) magnetic Bragg peaks of both crystals was measured at 50 temperatures between 2.0 and 30 K using the PG (002) analyser to ensure that only elastically scattered neutrons were detected. At each temperature the 25 points of the scan were counted for 70 seconds each. A time of 15 minutes was allowed at each temperature for thermal equilibration.

The intensity, I_T of each of the identical scans was obtained by summing the number of neutrons detected at each point in the scan. The variation of intensity with temperature is shown in Figure 2.7. The flattening out of the magnetisation curve allows one to determine the background scattering intensity, I_B , for the scans and the value of the transition temperature to the magnetically ordered state, T_N .

Analysis

The sublattice magnetisation of the antiferromagnet is related to the scattering intensity thus:

$$\left(\frac{M_T}{M_0}\right)^2 \propto I_T - I_B \quad (2.9)$$

where M_T and M_0 are the sublattice magnetisations at temperatures T and 0 K respectively.

The magnetisation ratio is related to the reduced temperature, $(T_N - T)/T_N$ by

$$\left(\frac{M_T}{M_0}\right) = \left[\frac{(T_N - T)}{T_N}\right]^\beta \quad (2.10)$$

where β is the critical exponent of the magnetisation. This expression describes the way in which the magnetisation behaves in the critical region below the transition temperature. β adopts different values according to the spin and lattice dimensionalities. Combining Equations 2.9 and 2.10 produces

$$I_T - I_B = A \cdot \left[\frac{(T_N - T)}{T_N}\right]^{2\beta} \quad (2.11)$$

where A is a constant. A plot of $\log(I_T - I_B)$ against $\log[(T_N - T)/T_N]$ is shown in Figure 2.8. T_N is defined as the point at which the magnetisation curve becomes flat. T_N was estimated from Figure 2.7 to be about 17 K. It is difficult to determine T_N accurately by this method because there is a small amount of quasielastic scattering at temperatures just above T_N which produces a small ‘tail’ in the size of the magnetisation. The use of the value of 17 K in Equation 2.11 indicated that below T_N there were two regions characterised by different values of β . Independent least-squares fits of the points in the two regions to Equation 2.11 were used to refine T_N and find the value of β in each region. The values of T_N obtained in this manner were equal within experimental error. T_N was determined to be 16.54 ± 0.05 K. Between this temperature and 15.5 K the value of β is 0.32 ± 0.02 . Below 15.5 K β is 0.23 ± 0.01 . These values are quite similar to those obtained by Koyama *et al.* [74] of 0.30 ± 0.01 and 0.22 ± 0.02 using proton NMR. Burger *et al.* obtained a value of 0.22 ± 0.04 in the lower temperature region, but failed to notice the cross-over in behaviour. The cross-over must indicate a change in the dimensionality of the lattice. The value of 0.32

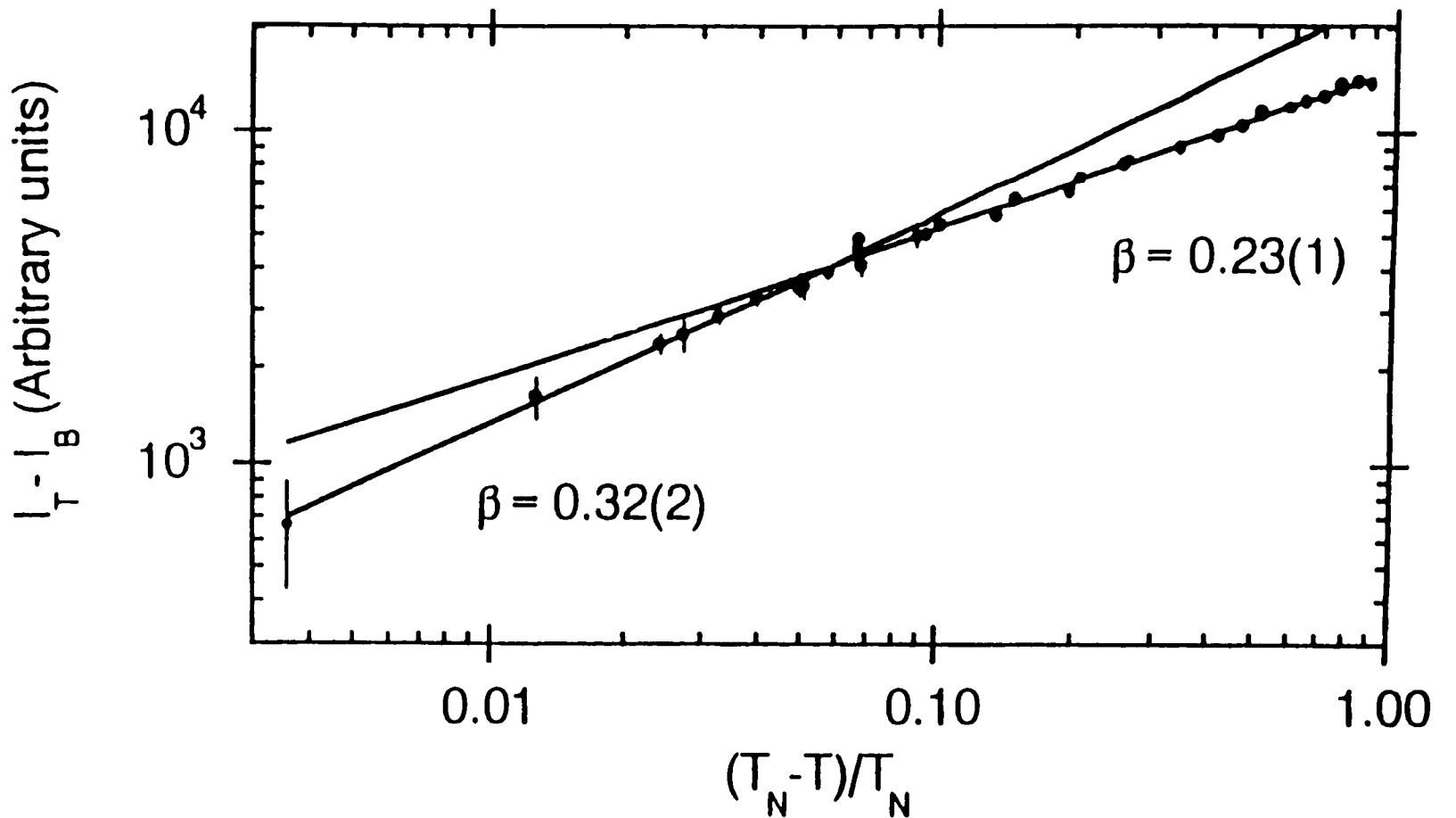


Figure 2.8: A plot showing the cross-over from 3D behaviour just below T_N to 2D behaviour at lower temperatures. The solid line are fits to Equation 2.11 in the two regimes.

is characteristic of a 3D system, while recent theoretical work [24, 25, 26] suggests that the value of 0.23 is characteristic of 2D systems with XY character (see below). The transition is not truly 2D because for ions with Heisenberg or XY symmetry, an ordering transition can only take place at a very low temperature [25] which becomes zero in the limit of an infinitely large sample [20].

Rationalisation

As one cools the system down, the strong in-plane exchange causes islands of ordered moments to form in the planes. When these islands are sufficiently large, the weaker inter-plane exchange can force ordering between the correlated regions in neighbouring planes and this starts to happen at T_N . This means that the initial critical behaviour of the sublattice magnetisation will be three dimensional and will display a 3D critical exponent (about 0.3). As cooling continues, all the planes become correlated with their neighbours so no further inter-planar ordering can occur. However, in the planes, further ordering can still take place, and does so, being characterised by a 2D critical

exponent for the magnetisation.

The principle of ‘Universality’ developed by Kadanoff [2] states that close enough to T_N , the behaviour will be determined by the weakest term in the Hamiltonian (Equation 2.2) and providing that the weakest term is sufficiently large, a cross-over in properties will be experimentally observed at a temperature close to T_N . One could visualise two ways in which this can occur in a 2D system. In the case considered here, the weak term in the Hamiltonian is that containing J' and so this drives the transition and the exponent in the critical region just below T_N is characteristic of a 3D system. In magnets such as K_2NiF_4 , K_2MnF_4 and Rb_2MnF_4 , the Ising anisotropy is greater than J' and drives the LRO ordering which is allowed in the 2D Ising case. The critical exponent for the magnetisation in these cases is $\frac{1}{8}$, which is characteristic of Ising systems.

Recent theoretical work by Bramwell and Holdsworth [24] suggests that the curious value of $\beta=0.23$ observed below the cross-over just below T_N has a theoretical basis. With the aid of Renormalisation Group (RG) theory, they have deduced that for XY magnets or Heisenberg magnets with an XY -type anisotropy, the exponent β will be $3\pi^2/128 \simeq 0.231$. Further, experiments on a number of 2D systems with XY character, including thin film magnets, and Monte-Carlo (MC) simulations, have all produced values for β of around 0.23. We conclude from this that there is a small XY -type anisotropy in CFTD which is observable below T_N . This anisotropy is not apparent at higher temperature in the region above T_N nor in the spin-dynamics. However it should be noted that when CFTH is studied by Electron Spin Resonance spectroscopy (ESR) (Chapter 3) there is clearly an anisotropy in the g -value of the ion.

The value of β of 0.23 is not a conventional critical exponent. It is not observed at the point where the sublattice magnetisation approaches zero. All the magnets investigated experimentally display 3D behaviour in the region immediately below the transition temperature. $\beta = 0.23$ holds in a region below the transition [25]

2.4.2 Theory of Paramagnetic Fluctuations in the 2D-HAF

Above T_N there are short-range magnetic correlations and these have a characteristic length ξ which depends on temperature in the following way:

$$\xi = A \exp(-B/k_B T) \quad (2.12)$$

The constants A and B are known to depend on properties such as the magnitude of the spin quantum number, S , and the strength of the intraplanar coupling, J . Chakravarty, Halperin and Nelson [38] (CHN) have developed a model for the 2D-HAF with $S=\frac{1}{2}$ which allows the precise values of A and B to be related to terms in the magnetic Hamiltonian. They have used their model successfully to describe the correlation length, ξ , and the static sublattice susceptibility at the centre of the magnetic Bragg peak, $S(\vec{q} = 0)$, for La_2CuO_4 . Their model is described as a Quantum Non-Linear Sigma Model (QNL σ M) which is derived from classical theory using a renormalisation group analysis. The QNL σ M has d spatial dimensions ($d=2$ in this thesis) and one of imaginary time which reflects the quantum fluctuations and has a thickness proportional to $1/T$, where T is the temperature, which tends to infinity as T tends to zero. The aim of this work was to compare the predictions of the model with the results of experiments. In order to do this, it is not necessary to have a full appreciation of the details of the model. The model has two independent parameters: the spin-wave stiffness constant at $T=0$, ρ_s , and the local uniform magnetic susceptibility perpendicular to the sublattice magnetisation, $\chi_\perp^0$. A fuller discussion of what a spin-wave is is left until Section 2.5. The spin-wave stiffness and the spin-wave velocity, c , essentially measure the resistance of the coupled spins to a disruption, ie. they are measures of J .

A two-loop Renormalisation Group analysis together with computer simulation of the classical lattice rotor model allows ξ to be computed with no adjustable parameters:

$$\xi = \sqrt{32} e^{\pi/2} \cdot (2\pi C_\xi^L) \cdot \left(\frac{\hbar c}{2\pi \rho_s} \right) \cdot \exp(2\pi \rho_s / k_B T) \quad (2.13)$$

where C_ξ^L is a constant and k_B is Boltzmann's constant. Oguchi [75] obtained expres-

sions for $\chi_{\perp}^0$ and for the spin-wave velocity, c :

$$\chi_{\perp}^0 = \frac{\hbar^2}{8Ja^2} \cdot Z_x \quad (2.14)$$

$$c = \frac{\sqrt{8}JSa}{\hbar} \cdot Z_c \quad (2.15)$$

where a is the separation between nearest neighbour Cu^{2+} ions and Z_x and Z_c are functions of S given by:

$$Z_x = 1 - \frac{0.552}{2S} + O\left(\frac{1}{2S}\right) \quad (2.16)$$

$$Z_c = 1 + \frac{0.158}{2S} + O\left(\frac{1}{2S}\right). \quad (2.17)$$

The terms $O(\frac{1}{2S})$ represent corrections which are of higher order in $\frac{1}{2S}$. $\rho_s = c^2 \chi_{\perp}^0$ [38], so using 2.14 and 2.15 we may write:

$$\rho_s = \frac{8J^2S^2a^2}{\hbar^2} Z_c^2 \cdot \frac{\hbar^2}{8Ja^2} Z_x \quad (2.18)$$

$$= JS^2Z_c^2Z_x \quad (2.19)$$

and if the $O(\frac{1}{2S})$ terms in Z_x and Z_c are ignored then:

$$\rho_s \simeq 0.15J \quad (2.20)$$

This gives the relation between the spin-wave stiffness, which can be determined from neutron scattering experiments, and the in-plane exchange constant.

The equation, $\rho_s = c^2 \chi_{\perp}^0$ can be reformulated using Equations 2.14 and 2.15:

$$\begin{aligned} \rho_s &= \frac{\sqrt{8}JSa}{\hbar} Z_c \cdot \frac{\hbar^2}{8Ja^2} Z_x \cdot c \\ &= \frac{SZ_cZ_x}{\sqrt{8}} \cdot \left(\frac{\hbar c}{a}\right) \end{aligned}$$

so

$$\begin{aligned} 2\pi\rho_s &= \frac{2\pi SZ_cZ_x}{\sqrt{8}} \cdot \left(\frac{\hbar c}{a}\right) \\ &= 0.576 \left(\frac{\hbar c}{a}\right) \end{aligned} \quad (2.21)$$

and this relates the spin-wave stiffness to the spin-wave velocity. The spin-wave velocity will appear again in Section 2.5 in relation to the determination of the exchange constant from the spin-wave dispersion.

The experimentally determined correlation length, ξ , can be related to ρ_s using Equation 2.13. Then, Equations 2.20 and 2.21 can be used to determine the in-plane exchange constant, J , and the spin-wave velocity, c .

Combining Equation 2.13 with Equation 2.21 we find:

$$\begin{aligned}\xi &= \sqrt{32}e^{\pi/2}(2\pi C_\xi^L) \cdot \left(\frac{\hbar c}{2\pi\rho_s}\right) \cdot \exp(2\pi\rho_s/k_B T) \\ &= \sqrt{32}e^{\pi/2}(2\pi C_\xi^L) \cdot \left(\frac{\hbar ca}{0.576\hbar c}\right) \cdot \exp(2\pi\rho_s/k_B T) \\ &= \frac{\sqrt{32}e^{\pi/2}(2\pi C_\xi^L)}{0.576} \cdot a \cdot \exp(2\pi\rho_s/k_B T)\end{aligned}$$

$2\pi C_\xi^L$ lies between 0.010 and 0.013 [38] so:

$$\xi = C_\xi a \exp(2\pi\rho_s/k_B T) \quad (2.22)$$

where $C_\xi \simeq 0.5$

The static structure factor at $\vec{q} = 0$, $S(\vec{q} = 0)$, is given by:

$$S(\vec{q} = 0) \simeq C_s a^2 \left(\frac{k_B T}{2\pi\rho_s}\right)^2 \cdot \exp(4\pi\rho_s/k_B T) \quad (2.23)$$

where $C_s = B_s C_\xi^2 N_0^2$. Shenker and Tubochnik [76] find $B_s=180$.

A number of arguments [14, 77, 78, 79, 80] have concluded that N_0 , the sublattice moment per spin in the ground state, is significantly less than the expected value of $N_0=\frac{1}{2}$ for the fully aligned Néel state of a 2D-HAF with $S=\frac{1}{2}$. Reger and Young [77] used Monte Carlo simulation and determined N_0 to be 0.30 ± 0.02 . Huse [78] used a perturbation series analysis in the limit of zero Ising anisotropy to produce $N_0=0.313$. Anderson [14], Kubo [79] and Stinchcombe [80] used spin-wave theory to estimate N_0 and the latter author obtained a value of 0.326. ^{55}Mn NMR studies of 2D systems with $S=\frac{5}{2}$ by Walstedt *et al.* [81] showed that the spin reduction in their systems would correspond to $N_0=0.33$ for $S=\frac{1}{2}$ and a similar analysis of a $S=1$ system produced $N_0=0.30\pm0.03$ [82]. These results are all consistent with one another. They clearly show that the properties of a collection of spins are very different from those of isolated spins, and that the moment can be reduced by quantum fluctuations.

If N_0 is taken to be approximately 0.31, and C_ξ to be 0.5, then $C_s \simeq 4.3$. Shenker and Tubochnik [76] carried out renormalisation group analysis which suggested that

the expressions for ξ and $S(\vec{q} = 0)$ should actually be replaced by:

$$\xi = \frac{C_\xi a \exp(2\pi\rho_s/k_B T)}{[1 + (k_B T/2\pi\rho_s)]} \quad (2.24)$$

and

$$S(\vec{q} = 0) \simeq \frac{C_s a^2 (T/2\pi\rho_s)^2}{[1 + (T/2\pi\rho_s)]^4} \cdot \exp(4\pi\rho_s/T) \quad (2.25)$$

The correction to $S(\vec{q} = 0)$ is significant.

Chakravarty, Halperin and Nelson [38] and Yamada *et al.* [65] found that they could achieve good fits to the correlation length and sublattice susceptibility in La_2CuO_4 using Equations 2.24 and 2.25.

2.4.3 Elastic and quasielastic neutron scattering

In CFTD magnetic Bragg scattering occurs below T_N . The magnetic Bragg peaks coincide with nuclear Bragg peaks because the magnetic unit cell is coincident with the crystallographic unit cell. According to Equation 2.11, the intensity of the elastic magnetic neutron scattering is temperature dependent. The dependence follows a power law, and the exponent in the power law, β , called the order parameter, is characteristic of the spin dimensionality and lattice dimensionality of the system being studied [1, 2, 16, 69] and Section 2.4.1.

In CFTD above T_N , there are islands of 2D ordering. They have a characteristic length ξ which CHN theory relates to the temperature and the strength of the magnetic interactions. Scattering from these regions is weak and broad due to the disruptive effect of magnetic fluctuations.

A 3D magnetic system gives rise to magnetic Bragg points in reciprocal space corresponding to the real-space scattering planes. In the paramagnetic region just above T_N , the correlations in a 2D magnetic system are exclusively within the planes. These planes in real space correspond to rods in reciprocal space perpendicular to the planes from which magnetic scattering can occur. In the case of CFTD, in which the 2D correlations are in the ab plane, the magnetic rods extend along c^* and the scattering profile represents a cross-section through the rod when c^* is in the scattering

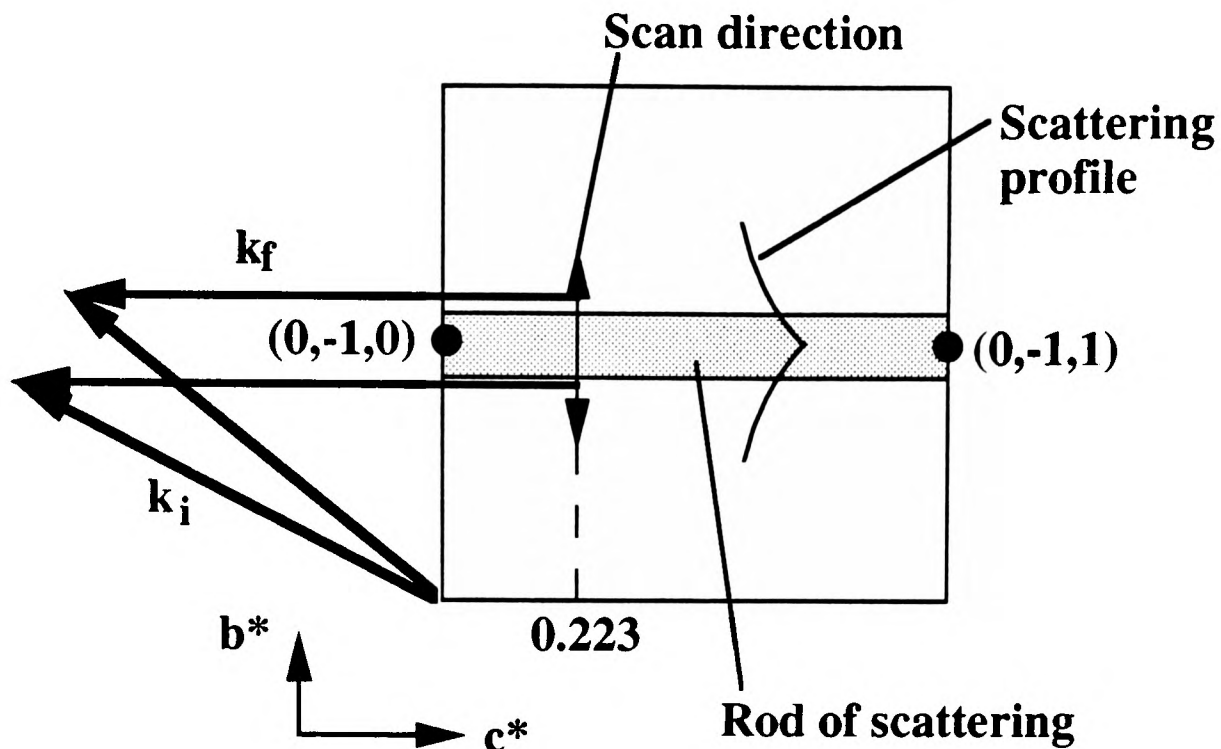


Figure 2.9: A diagram of the reciprocal space of CFTD showing the position and direction in which scans were made to determine the 2D correlation length. The neutron wavevectors at two different points in the scan are shown

plane. CFTD orders three dimensionally at T_N and the rods shrink to points at this transition.

We measured the quasielastic scattering from the rods at $(0-1\ 0.223)$, which is away from the incipient magnetic Bragg peaks since these coincide with nuclear Bragg peaks which would produce elastic scattering which would swamp the quasielastic scattering. A diagram of the reciprocal space of the crystal showing how the scans were performed is presented in Figure 2.9. b and c^* were in the scattering plane.

2.4.4 Correlation length

The correlation length of a magnetic system is a measure of the length scale over which interacting magnetic moments are ordered. At high temperatures, thermal fluctuations dominate the magnetic interactions (ie. $kT \gg J$) and the system is paramagnetic. As the temperature is lowered, one reaches a regime in which $k_B T \simeq J$, and here the 2D magnetic interactions can cause regions of ordering on the scale of a few hundred Ångstroms. Eventually, in our system, the correlation length becomes large enough that the effect of J' acting between correlated regions becomes signifi-

cant, and magnetic long-range order (LRO) occurs. According to the results of MF theory [16], J' is related to ξ and T_N by

$$J' = \frac{k_B T_N}{(\xi/a)^2} \quad (2.26)$$

where a is the separation of nearest-neighbour magnetic ions in the plane (about 5.7 Å in CFTD). Quasielastic neutron scattering is a good probe of the critical region above T_N . The moments in the islands of ordering are fluctuating rapidly, but the region can give rise to sufficient coherent magnetic scattering that peaks form corresponding to cross-sections through the rods of scattering. These peaks are broad and of low intensity. Measurement of the way in which the width and intensity change with temperature in the critical region allow one to compare the behaviour of the inverse correlation length (peak width) and the sublattice susceptibility (height of peak maximum) with theory and to determine an approximate value for J .

Experimental

In CFTD we used D10 in 2-axis mode (without an analyser) and measured the frequency-integrated paramagnetic critical scattering between 16.8 K and 37 K (ie between T_N and about $2T_N$). A cross-section through the scattering rods was measured at (0-10.223) so that the nuclear Bragg peak at (0-10) did not obscure the quasielastic scattering. In order to integrate the low frequency fluctuations, the final scattering vector, k_f , was set parallel to the c^* direction (ie. along the rods) throughout the scan [34, 83] as shown in Figure 2.9.

The critical scans above T_N were fitted to Lorentzian curves. Some of the fits are shown in Figure 2.10. The critical scattering becomes very much more intense as the sample is cooled towards T_N because the sublattice susceptibility, $S(\vec{q}=0)$, which is equal to the peak height, increases as the regions of correlated spins become larger. The increasing correlation length, ξ , is reflected in a narrowing of the critical scans on cooling. The intrinsic width of the critical scattering Lorentzian is proportional to the inverse correlation length, κ . Once the resolution function had been determined as described in Section 2.5.3, the intrinsic width and peak heights of the scans

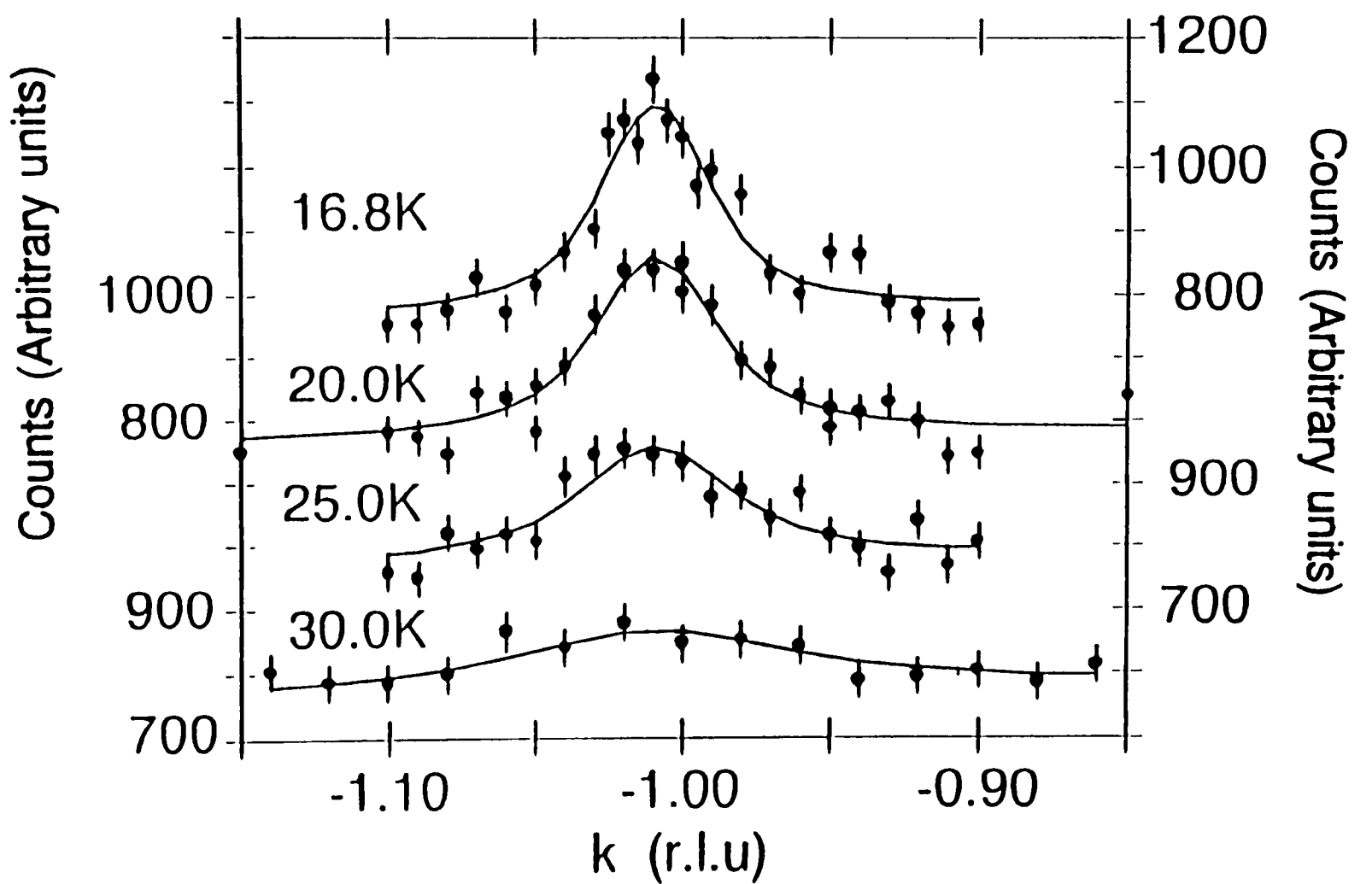


Figure 2.10: Critical scans for CFTD. The scans were performed along the $(1\ k\ 0.223)$ direction as shown in Figure 2.9. The lines are Lorentzian fits. All the plots are on the same scale, but each is shifted along the vertical axis for clarity.

were determined by fitting the scans using the FORTRAN program RESCONV [84] running on the Oxford University Computing Service (OUCS) VAX-6600 mainframe computer. The program calculates the Lorentzian representing the critical scattering from height, width and background parameters estimated by the user and then convolves this with the calculated Gaussian resolution function. It then compares the convolution with the experimental scattering profile and uses a least-squares fitting routine to refine the parameters of the Lorentzian.

Analysis

The inverse correlation length, $\kappa=1/\xi$ measured in $\text{\AA}^{-1}$ is the peak width of the Lorentzian in reciprocal lattice units multiplied by $2\pi/b$. b is the in-plane dimension of the magnetic unit cell in $\text{\AA}$. According to the CHN theory [38, 85] outlined in Section 2.4.2, κ can be fitted to the following form:

$$\kappa = \xi^{-1} \simeq \frac{(1 + (T/2\pi\rho_s))}{C_\xi a} \exp(-2\pi\rho_s/T) \quad (2.27)$$

which is simply an inversion of Equation 2.24 in which $2\pi\rho_s \simeq 0.942J$, C_ξ is a dimensionless constant $\simeq 0.5$, a is the separation of antiferromagnetically coupled Cu ions ($a = b/\sqrt{2}=5.7 \text{\AA}$ in CFTD) so

$$\kappa \simeq \frac{(1 + (T/0.942J))}{2.85} \exp(-0.942J/T) \quad (2.28)$$

and J is measured in units of temperature. Yamada *et al.* [65] have successfully used this formula to fit the correlation length of La_2CuO_4 . They obtained a value of J of 140 meV (1600 K) which agrees well with the estimate of 130 meV from an analysis of the magnetic excitations using neutron scattering [86] and 128 meV using Raman scattering [88].

The data for CFTD were fitted to Equation 2.28 using a least-squares analysis and treating J as the only variable in the fit. The value of J was found to be insensitive to the value of C_ξ within the theoretical limits of 0.47 and 0.61. The fit is very successful and is shown in Figure 2.11: it is sensitive to the value of J and despite the large error bars in the data at high T , the value of J can be pinned down quite precisely

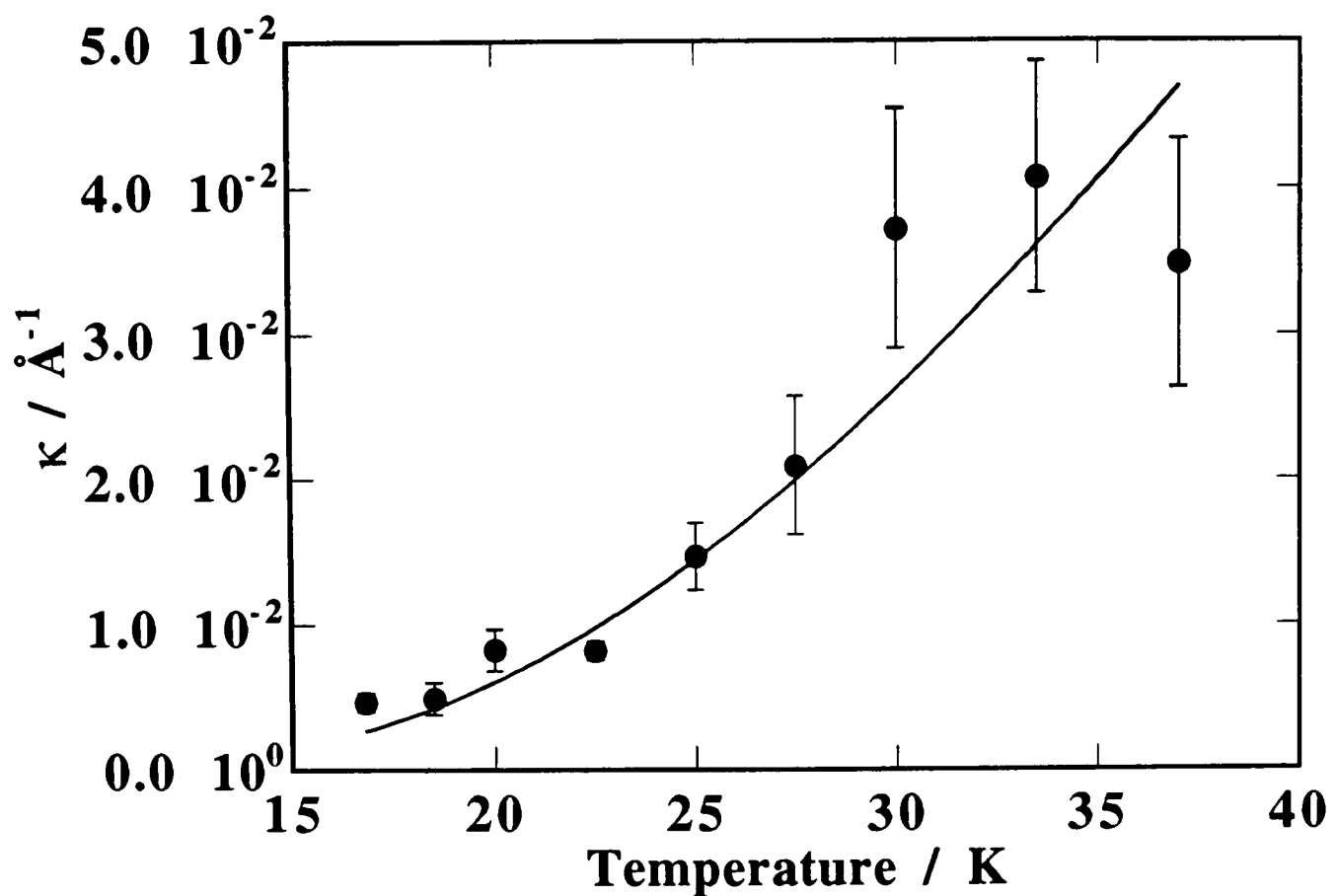


Figure 2.11: The inverse correlation length, κ determined from the width of quasielastic scattering in the critical region plotted against temperature. The solid line is a fit to Equation 2.27.

to be 89 ± 2 K which corresponds to 7.7 ± 0.2 meV (the more usually quoted units of energy).

The fit does not require a knowledge of the value of T_N , unlike in other systems where the correlation length is fitted to a power law. In our case, T_N does not represent a transition to LRO of the 2DHAF and so it is not valid to fit the correlation length data to a power law. A fit to the conventional power law which one would use for a 3D magnet, $\kappa = A[(T_N - T)/T]^{-\nu}$ was attempted but produced a non-linear fit unless T_N was assigned a value of about 13 K, which is clearly incorrect.

The value obtained for J agrees fairly well with the previous result from susceptibility measurements [62], in which J was found to be 6.1 ± 0.1 meV (72 K). The value of J was subsequently tested by determining the magnon dispersion as described in Section 2.5.

Comparison with experiments on La_2CuO_4

The value obtained for J in CFTD is much less than that obtained for La_2CuO_4 , and this means that it is a more convenient system to study experimentally because the lower energy scale involved makes measurements easier. In our determination of the critical exponent β in Section 2.4.1 in which the spectrometer was set up to detect elastic neutrons only, a small amount of quasielastic scattering is visible just above T_N in Figure 2.7 because there is a small energy window arising from the resolution function of the instrument. Much more quasielastic scattering is observed when the analyser crystal is removed and magnetic fluctuations of different energies are integrated as in the determination of ξ . Compare this with La_2CuO_4 [33, 34]. The extremely large exchange constant in La_2CuO_4 increases the range of energies over which magnetic fluctuations occurs. Because the energy window for the quasielastic experiment was very small compared to this range of energies, no quasielastic scattering was observed in the early experiments [34, 33], and the fluctuations were determined to be entirely inelastic which led to the view that the RVB state or something akin to it had been observed.

2.4.5 Sublattice susceptibility

The peak height of the critical scans is proportional to the sublattice susceptibility at the centre of the scattering rod, $S(\vec{q}=0)$. According to CHN theory, $S(\vec{q}=0)$ is given by Equation 2.25:

$$S(\vec{q}=0) \simeq \frac{139(T/0.942J)^2}{[1 + (T/0.942J)]^4} \cdot \exp(1.884J/T)$$

where $C_s \simeq 4.3$. The heights of the Lorentzian fits to the critical scattering were fitted to this equation using the value of J derived from the temperature dependence of κ . The only variable parameter in the fit was an arbitrary intensity scaling factor. The fit is successful and is shown in Figure 2.12.

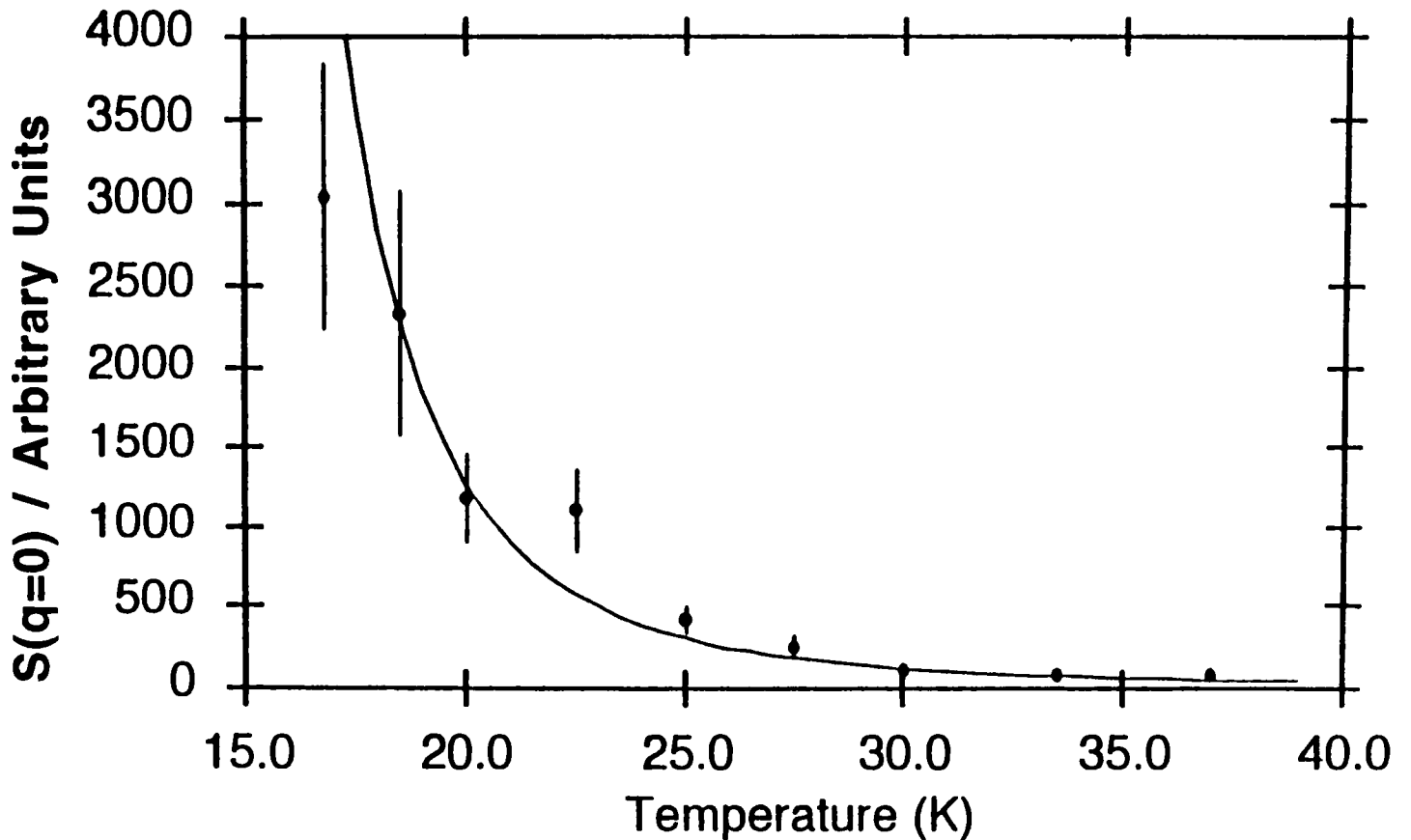


Figure 2.12: A fit of the sublattice susceptibility, $S(\vec{q} = 0)$, determined from the height of the critical scattering to the temperature using Equation 2.25 derived from CHN theory.

2.4.6 Adjustment of the basic Hamiltonian

The determination of the correlation length has enabled determination of the in-plane exchange constant to be made. It also allows one to determine the approximate size of the inter-planar exchange, J' , using MF theory. Following Thio *et al.* [64],

$$J' = \frac{1}{\chi_{2D}(T_N)} \quad (2.29)$$

where $\chi_{2D}(T_N)$ is the 2D magnetic susceptibility at T_N . The 2D susceptibility is obtained from the correlation length:

$$\chi_{2D}(T) = \frac{(\xi/a)^2}{k_B T} \quad (2.30)$$

where the symbols are as defined already. Combining Equations 2.29 and 2.30 produces

$$J' = \frac{k_B T_N}{(\xi_{T_N}/a)^2} \quad (2.31)$$

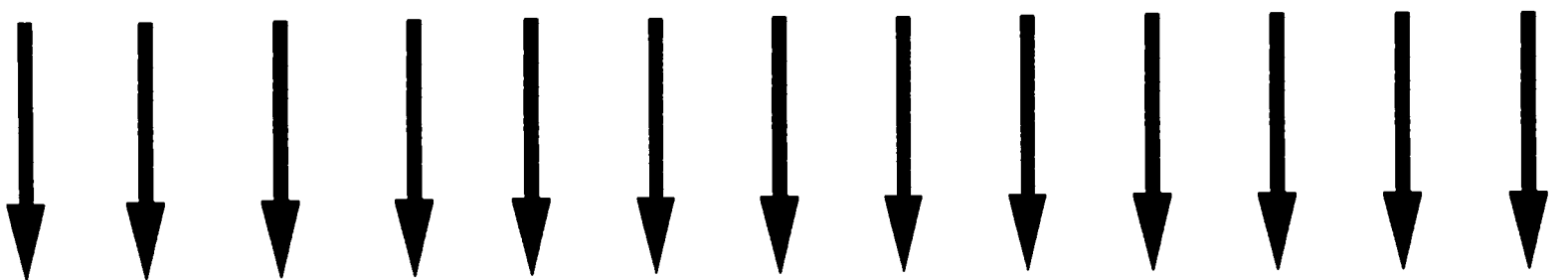
The correlation length at T_N in CFTD is approximately 400 Å, a is 5.7 Å, and so $J' \simeq 3.1 \times 10^{-4}$ meV (0.00358 K). This means that J/J' is about 3×10^4 which suggests that CFTD is a good approximation to a 2D material.

The measurements described in this section do not allow a determination of the other parts of the in-plane nearest-neighbour exchange Hamiltonian, since they do not probe the magnetic interactions directly, but measure a thermodynamic average for the system. The spin-wave measurements in the next section are used to give a more accurate estimate of J and to determine the other terms in the Hamiltonian (Equation 2.2) such as antisymmetric exchange. However, they are less good at measuring the value of J' . The DC magnetic susceptibility and electron spin resonance measurements described in Chapter 3 may also be used to determine the terms in the magnetic Hamiltonian.

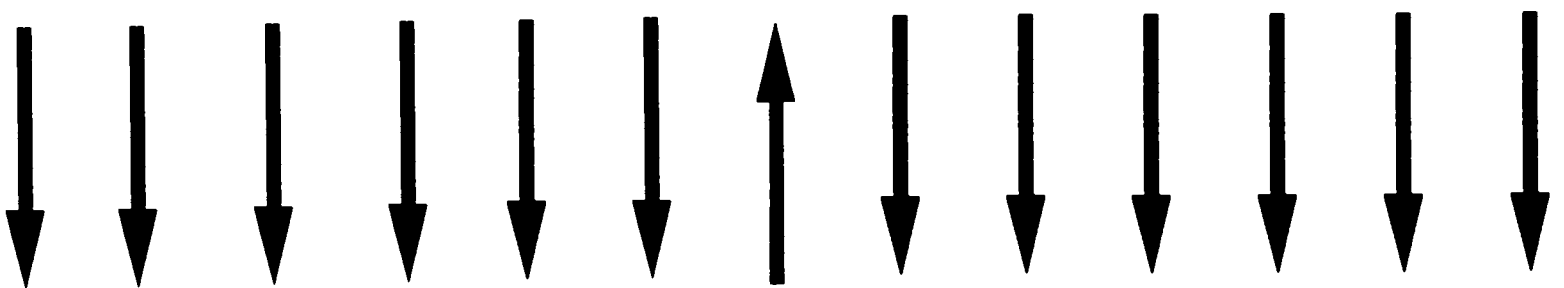
2.5 Measurement of Spin-waves

2.5.1 Introduction

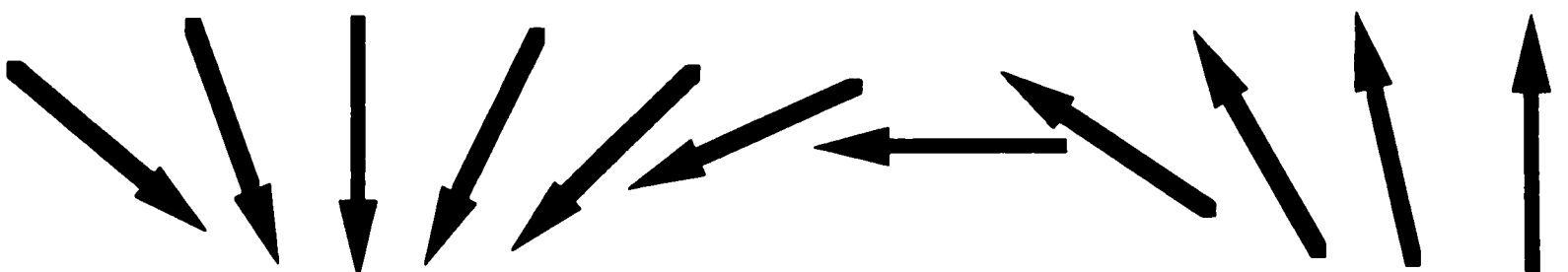
Imagine a one-dimensional (1D) ferromagnet in its ordered state.



Now imagine that one of the spins is flipped over with respect to its neighbours.



This simple form of magnetic excitation, called a soliton, costs twice the exchange energy for creation. In general, a magnetic excitation is called a magnon or spin-wave and the spin deviation is shared by all the spins on the lattice.



The shortest wavelength magnon resembles a series of neighbouring solitons and has a wavelength of $2a$ where a is the nearest neighbour separation. The longest wavelength magnon corresponds to no excitation at all and has zero energy in the simple example. There is a spectrum of magnon energies corresponding to different magnon wavelengths. The reciprocal space coordinate $\vec{q}$ is the displacement in reciprocal lattice units from the magnetic zone centre which coincides with a point on the magnetic reciprocal lattice. $\vec{q}$ is also the inverse of the wavelength of the spin-wave. At $\vec{q}=0$, no energy is required to excite an excitation of infinite wavelength. At $\vec{q}=\pi$, the boundary of the Brillouin zone, the maximum energy is required since this corresponds to flipping a spin relative to its two neighbours. The entire magnon spectrum is condensed into the $\vec{q}$ range $0 \leq \vec{q} \leq \pi$.

This spectrum, referred to as a dispersion relation, is a plot of the magnon energy as a function of $\vec{q}$. For the basic antiferromagnetic Hamiltonian in Equation 1.5, the shape is sinusoidal as shown in Figure 2.13. Careful measurement of the dispersion curve allows one to determine the values of parameters in the magnetic Hamiltonian such as the exchange constant. This method is the best way of measuring J because it is a direct probe of the strength of the interaction between neighbouring moments. In principle magnons can be excited and measured with electromagnetic radiation, for example in a Raman scattering type experiment [88]. Usually one uses neutron scattering and measures the scattering intensity at a series of scattering vectors, $\vec{Q}$, where $\vec{Q} = \vec{\tau} + \vec{q}$, and $\vec{\tau}$ is a reciprocal lattice vector corresponding to a Brillouin zone centre. One can map out the spin-wave energy as a function of $\vec{q}$ and probe the nature of the magnetic interactions.

2.5.2 Summary of early measurements of the dispersion

An initial exploration of the dispersion curve was carried out on the triple axis neutron spectrometer TAS1 situated on the cold neutron source of the 10 MW research reactor DR3 at the Risø National Laboratory, Denmark. This work is fully described elsewhere [72, 89]. The configuration of TAS1 with a fixed incident energy of 5.0 meV

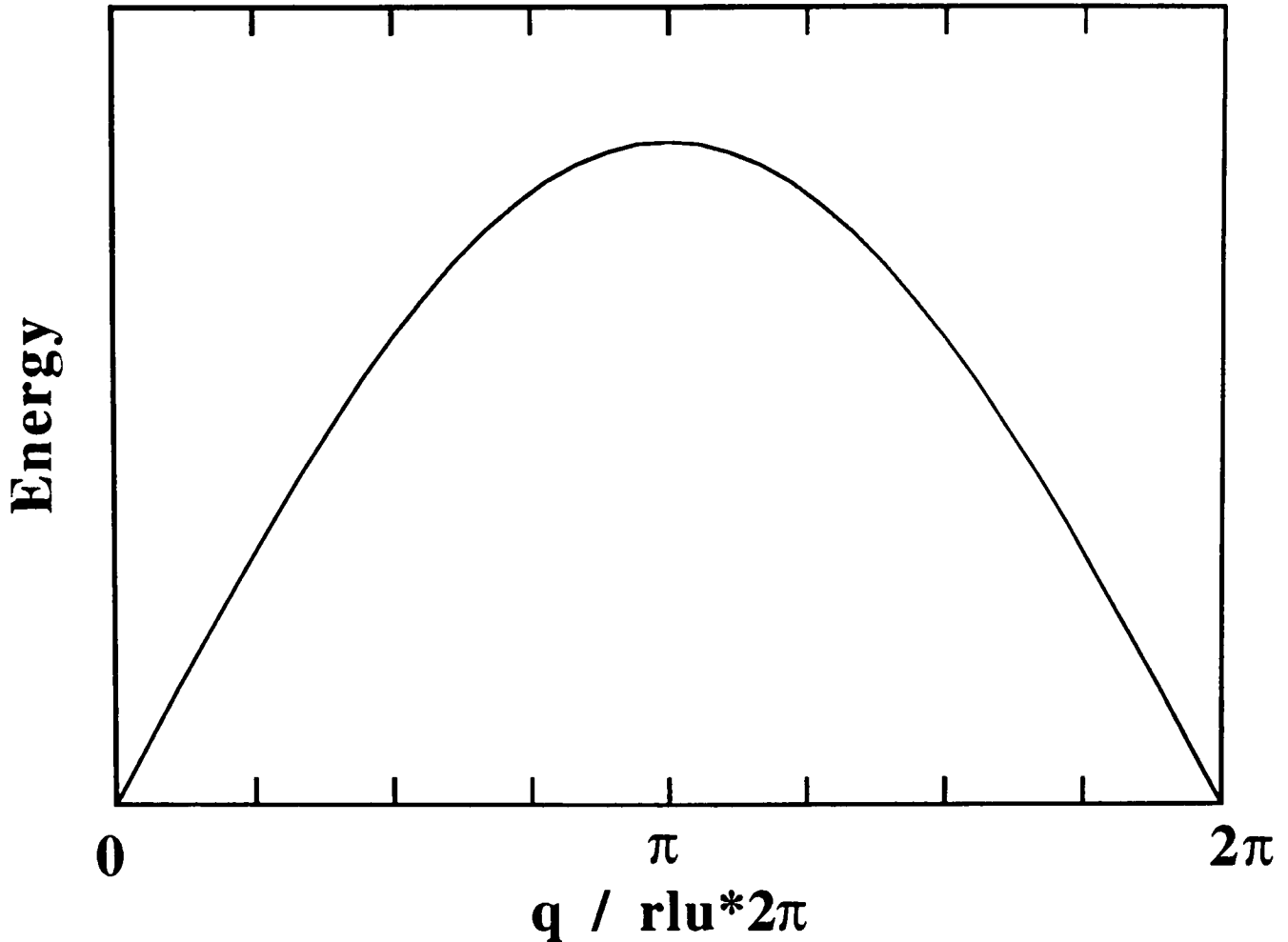


Figure 2.13: The sinusoidal dispersion relation for an antiferromagnet calculated using classical spin-wave theory using the Hamiltonian of Equation 1.5.

allowed a maximum energy transfer of 2.0 meV to be used and hence only the low-energy spin-waves close to the $[0-11]$ antiferromagnetic zone-centre could be measured. The experiment indicated that there was strong in-plane dispersion characterised by an exchange constant, J , of 9.3 ± 0.5 meV. Also there was no measurable dispersion of spin-waves in the out-of-plane direction indicating that the material has a high degree of 2D character. The excitation at the zone centre has an energy of about 0.55 meV (not zero as depicted in the simple dispersion relation in Figure 2.13. This is principally a result of the antisymmetric exchange term, J_D in the Hamiltonian (Equation 2.2).

The dispersion relation obtained from the TAS1 experiment is shown in Figure 2.14. This clearly shows the gap at the magnetic zone centre which persists along the out-of-plane direction, c^* . There is no measurable dispersion along c^* , which confirms the 2D behaviour. We can place an upper bound on the value of J' of about 0.1 meV (1.2 K), but the large size of the resolution function, which is

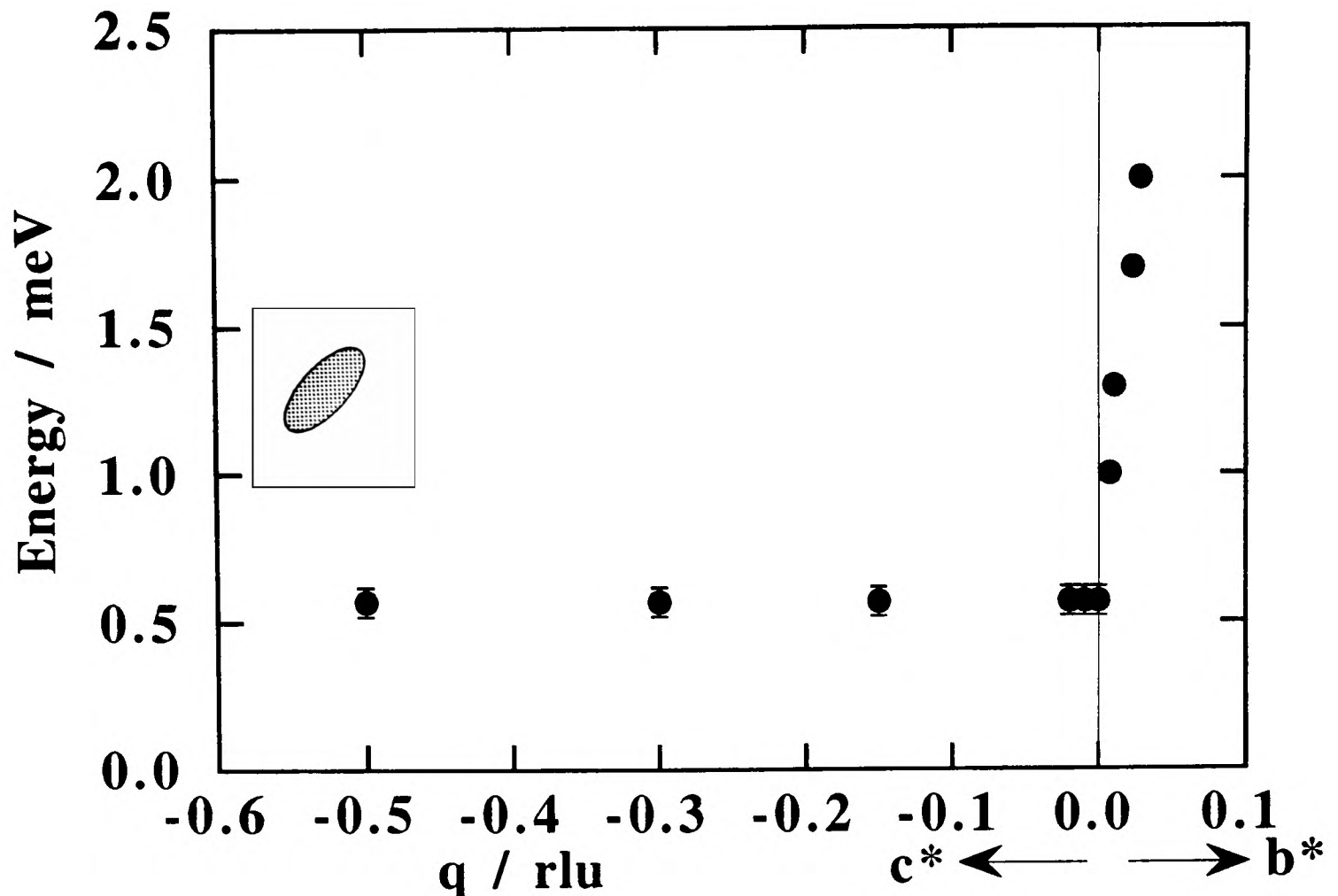


Figure 2.14: The dispersion curve for CFTD obtained using the TAS1 spectrometer at Risø. This clearly shows the gap at the antiferromagnetic zone centre which persists along the out-of-plane direction. There is no measurable dispersion in the out-of-plane direction. The resolution function is represented by the shaded ellipse.

depicted in the figure prevents us from measuring its value accurately; the resolution function is far greater in size in the energy dimension than the small dispersion in the out-of-plane direction which would be caused by J' . The measurements of the correlation length allow us to estimate J' to be more than two orders of magnitude smaller than this upper bound.

2.5.3 Detailed measurement of low-temperature spin-waves

Further inelastic neutron scattering on CFTD was performed using the triple-axis neutron spectrometer TAS6 also at Risø. The experiment using TAS1 had indicated that the whole of the dispersion curve would be accessible using the larger range of incident energies (3.7 to 25 meV) available on TAS6 and allow us to determine J and J_D with some accuracy. This work is described in reference [90].

The sample and its environment

Five good-quality crystals ranging in size from 0.3 to 1.0 cm³ were wrapped in aluminium foil to prevent dehydration and were stacked vertically on an aluminium mount (Figure 2.15). Approximate alignment of the crystals with respect to one another was carried out to within five degrees by eye using the characteristic crystal morphology. Each crystal was then aligned in turn to better than one degree using the (020) and (20 $\bar{1}$) nuclear reflections so that the a and b directions were horizontal and hence the planes of magnetic ions were in the scattering plane. Polaroid photography of the image of the straight-through beam incident on the sample indicated that one of the crystals at the extremity of the sample was composed of twins about 8° out of alignment with one another and so was masked off using Cd foil which readily absorbs neutrons due to its large absorption cross-section. The volume of useful crystal remaining was about 2.5 cm³. The aligned sample was then sealed with an indium gasket inside an aluminium can filled with ⁴He exchange gas at a pressure of one atmosphere. The reason for using an aluminium container rather than one made from vanadium which is used in neutron powder diffraction is as follows. The primarily incoherent nature of the scattering from vanadium makes it ideal as a container material for powder neutron scattering; it has Bragg peaks of very low intensity, and the incoherent background is relatively unimportant since Bragg scattering is intense. In an inelastic experiment, the scattering intensity is low and so background scattering must be minimised. In this case the container material should not have a large incoherent cross-section, although the presence of additional Bragg peaks presents no problem in most cases. Aluminium has a low incoherent cross-section (0.0085 barn c.f. 5.19 barn for V) when compared with most elements and is thus the usual container material for inelastic neutron scattering experiments. The can was mounted in a Cryogenic Associates Inc. CT14 ⁴He flow cryostat with a base temperature of 4.3 K. The temperature stability at 4.3 K was ± 0.05 K and in the range 10 K to 30 K, which is the vicinity of T_N , the stability was better than ± 0.005 K.

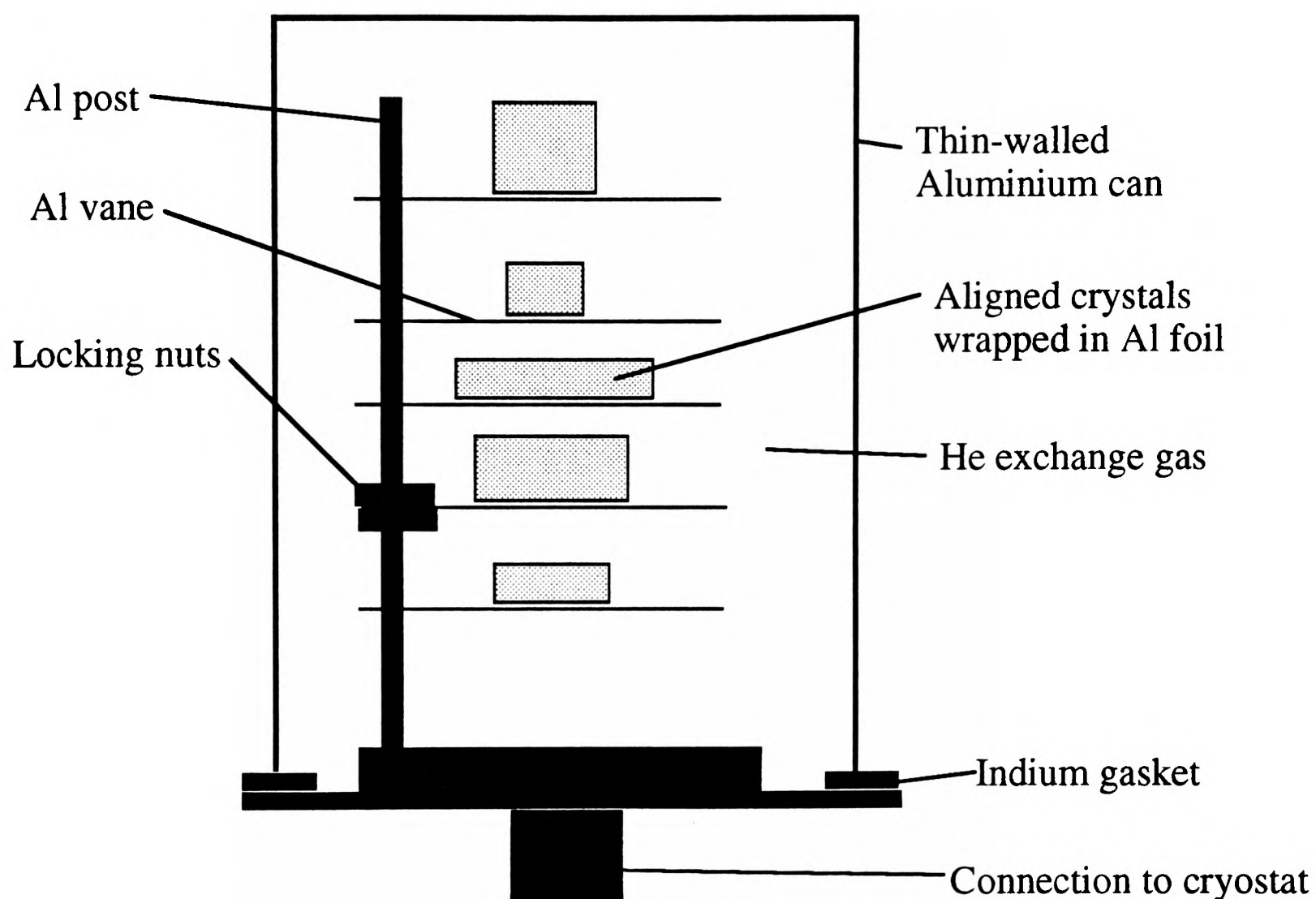


Figure 2.15: The sample-mount used to align 5 crystals of CFTD on the TAS6 spectrometer. The crystals were aligned one at a time from the bottom up, by adjustment of the aluminium vanes to which they were attached using aluminium wire. Aluminium was used as it has a small incoherent scattering cross-section, and so does not contribute greatly to the background.

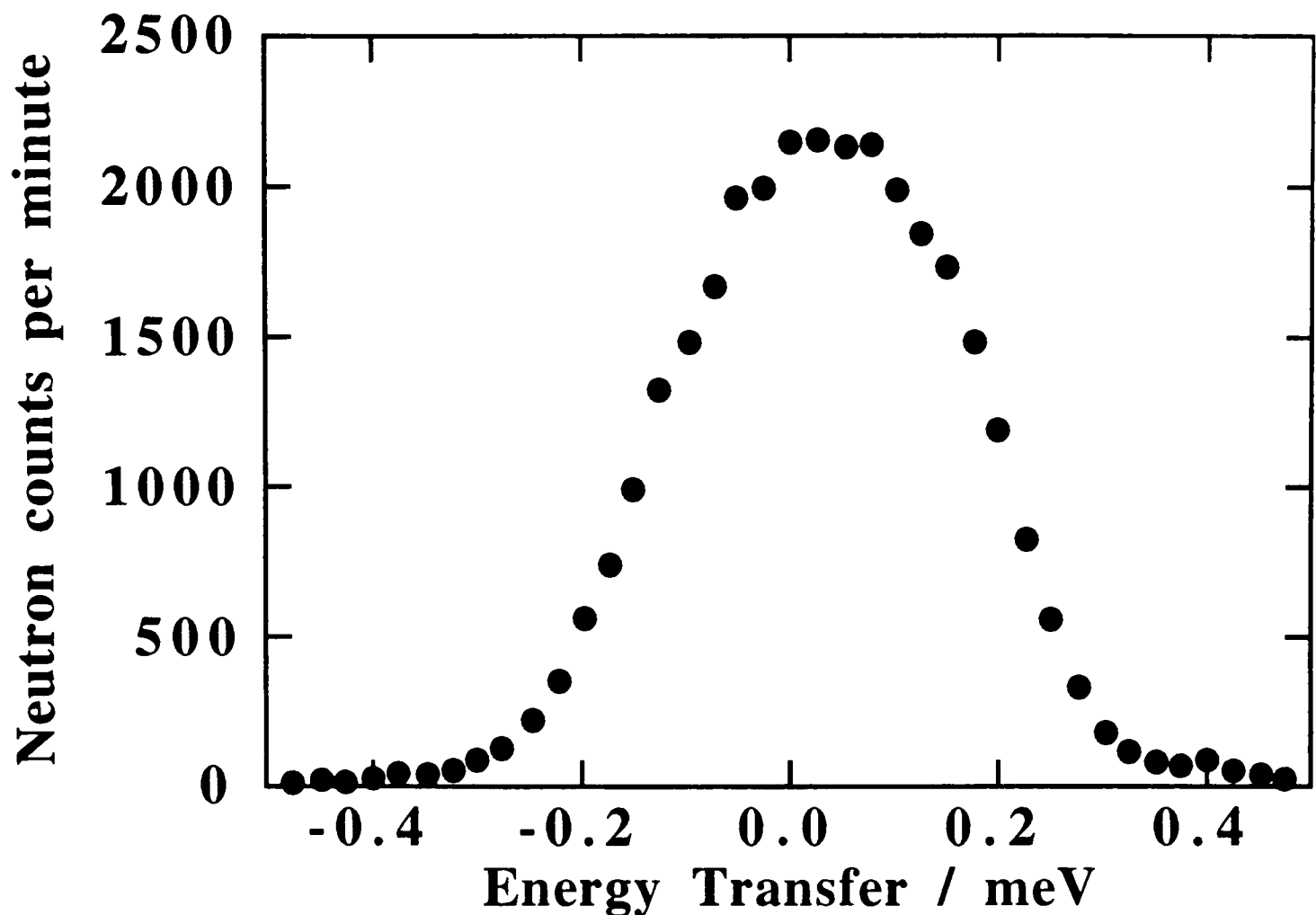


Figure 2.16: The vanadium scan used to determine the zero-point for the energy transfer in the inelastic experiment on TAS6. The energy resolution was determined from the FWHM of this scan to be 0.32 meV.

Spectrometer alignment

In an elastic or inelastic neutron scattering experiment, it is necessary to measure the wavelength and zero-angle of the detector accurately. This is conveniently performed using a powdered Al_2O_3 sample with known d -spacings. In an inelastic experiment it is also necessary to set the zero point for the energy transfer. This is done by using a powdered vanadium sample, and making use of the large incoherent scattering cross-section. In a vanadium scan, the energy transfer is varied and the peak in the incoherent elastic scattering defines the zero for the energy transfer. The vanadium scan obtained on TAS6 is shown in Figure 2.16. The width of such a scan is the width of the instrumental resolution function in energy units, ie. it is a measure of the range of energy transfers over which elastically scattered neutrons can reach the detector.

We employed TAS6 with a variable incident energy, E_i , and a fixed final energy,

E_f , of 5.0 meV. This E_f corresponds to a λ of 4.0 Å. At a given configuration of the pyrolytic graphite monochromator, the monochromator selects a given neutron wavelength by Bragg scattering from the (002) reflection. Bragg scattering from the (004) reflection by neutrons of half that wavelength ($\lambda/2$) occurs at the same angle. Hence the beam incident on the sample consists of neutrons of wavelength λ contaminated by $\lambda/2$ radiation. On TAS6 the intensity of $\lambda/2$ radiation at the sample is roughly equal to that of λ radiation due to the range of neutron energies produced at the source. The $\lambda/2$ radiation can be useful for orienting the sample since more reflections are accessible to a shorter wavelength, however for the inelastic work, this radiation would produce an unwanted addition to the background. Since the inelastic scattering is quite weak compared to the background scattering, the $\lambda/2$ radiation must be removed before it reaches the detector.

Removal of $\lambda/2$ radiation

A powdered Be filter cooled to liquid nitrogen temperatures with built-in 100' collimation was placed between the sample and the pyrolytic graphite analyser to eliminate about 98% of the neutrons of wavelength $\lambda/2$. Be metal has a largest d -spacing d_{max} of just 1.97 Å. The diffraction condition cannot be satisfied for radiation with λ greater than $2d_{max}$, hence neutrons with λ of 3.94 Å or greater cannot be diffracted by Be. In this case, with $\lambda=4.0$ Å, 98% of the $\lambda/2$ radiation is diffracted away from the detector while 80% of the λ neutrons pass through — some being lost to absorption. Higher order contamination ($\lambda/3$) is present only at the level of a few % of the flux of λ on TAS6; this is also filtered out by the Be.

Resolution considerations

In an elastic scattering experiment, one scans through reciprocal space (scanning $\vec{q}$) while the energy transfer is fixed (at zero). In an inelastic experiment, one may also perform constant-energy scans, with the energy transfer fixed at some value not equal to zero. There is also the possibility of scanning the energy transfer at a fixed point in reciprocal space (a constant- $\vec{q}$ scan). Which of these is used in practice

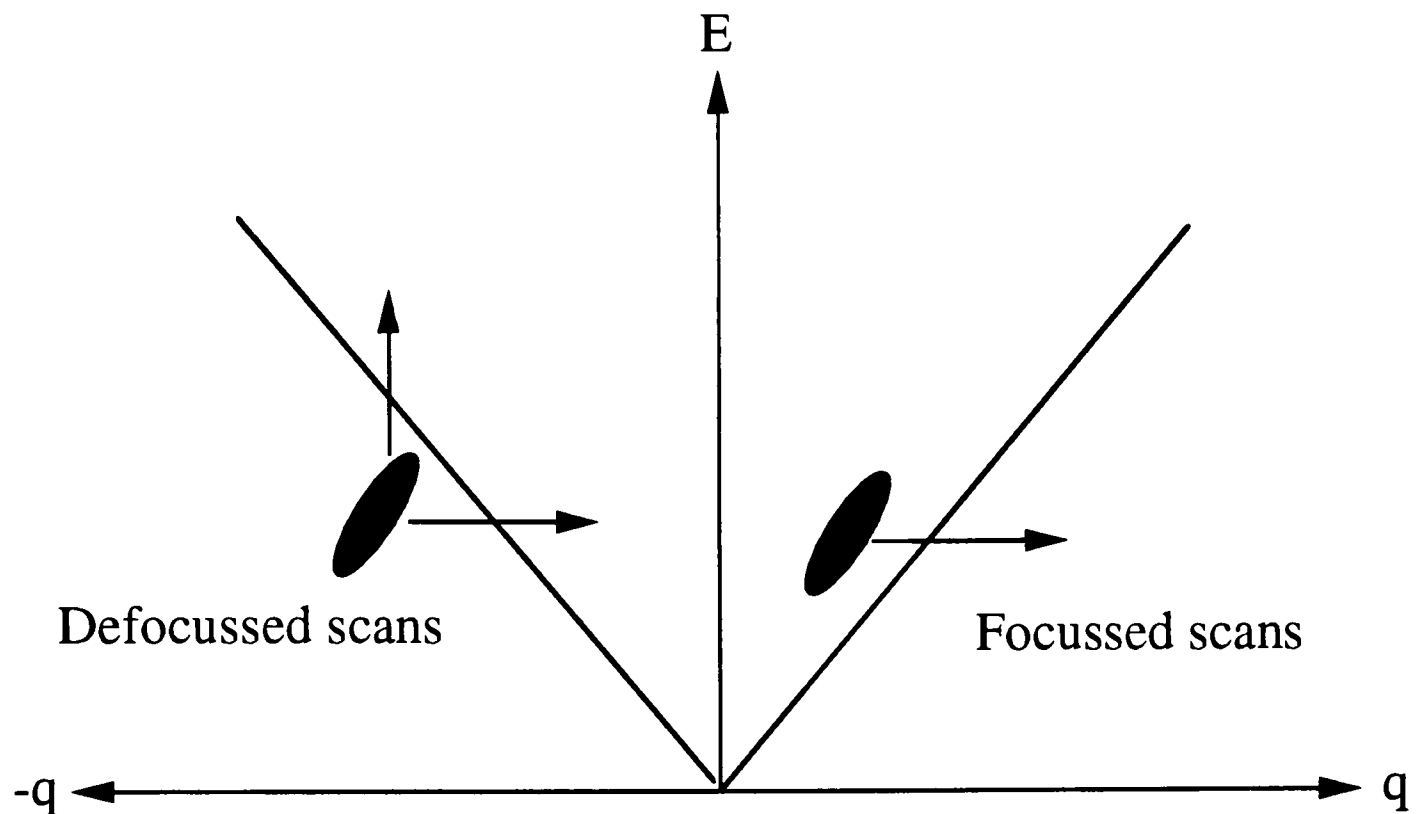


Figure 2.17: One may scan across the dispersion surface keeping the energy transfer constant, or by keeping the scattering vector constant. While the dispersion is symmetric about the antiferromagnetic zone centre ($\vec{q} = 0$), the instrumental resolution function, represented by the shaded ellipse is not, so focussed scans in which the ellipse crosses the dispersion surface ‘quickly’, and defocussed scans in which it crosses ‘slowly’ are possible. Calculating the resolution function from instrumental parameters allows focussed scans to be used throughout the experiment.

depends primarily on the shape of the dispersion curve at a particular $\vec{q}$ relative to the orientation of the resolution ellipsoid. If the dispersion curve (E vs. $\vec{q}$) rises steeply, then a constant-energy scan will cause the instrumental resolution function depicted by the ellipse in Figure 2.17 to pass through the dispersion surface faster than a constant- $\vec{q}$ scan would. If the dispersion curve is relatively flat, as will probably be the case close to the zone boundary, a constant- $\vec{q}$ scan will have the better resolution.

The instrumental resolution function arises from the mosaic spread in the monochromator, sample and analyser crystals, the collimations applied to the beam in horizontal and vertical directions and the scattering geometry. All these factors cause the neutron beam to exhibit a spread in both energy and reciprocal space. In general, the collimations are kept as tight as possible to keep the resolution function small, and in an elastic experiment in which the Bragg peaks are intense, it is possible to make the spatial resolution function so small that it may be ignored to a first approxima-

tion. In inelastic work, where the scattering intensity is small, the resolution must be lowered and the magnon or phonon peaks will be broadened. It is thus essential to deconvolve the resolution function from the intrinsic spin-wave cross-section. The resolution function may be calculated from a knowledge of the instrumental configuration [70, 71]. The shape of the instrumental resolution function must be calculated before the experiment is carried out as this determines how best to scan through the dispersion surface. The Fortran program *RESCAL* developed at Brookhaven National Laboratory was used to determine the size and shape of the resolution ellipsoid in the two spatial directions defined by the scattering plane and the energy direction using the instrumental parameters. The focussing effect of the resolution function is shown in Figure 2.17. If the principal axis of the resolution function is roughly parallel to the dispersion curve, as in the right-hand portion of the diagram, it can be seen that the resolution function will pass quite rapidly through the dispersion surface during a constant-energy or constant- $\vec{q}$ scan and the spin-wave peak will be narrow or 'focussed'. If the principal axis of the ellipse is roughly perpendicular to the dispersion curve, then it will pass more slowly through the dispersion surface and the scan will be broader or 'defocussed'. A spin-wave measurement should be made in focussed mode.

Experimental details

The vertically-focussing pyrolytic graphite monochromator selected incident energies of between 7.0 and 19 meV (energy transfers of between 2.0 and 14 meV) for the constant-energy scans and this was sufficient to map out the entire dispersion curve. The full width at half maximum of the constant- $\vec{q}$ scans was determined to be 0.32 meV from the vanadium scan. The horizontal collimations used along the path reactor-monochromator-sample-analyser-detector were 60'-58'-100'-200'. This gave a relatively high flux at the expense of horizontal resolution. However, the relatively coarse resolution was not a big disadvantage as the spin-wave peaks on either side of the magnetic zone centre were well resolved from one another at as little as 2 meV energy transfer.

To measure the dispersion we used mainly constant-energy scans in which between 3 and 14 meV was transferred to the sample from each neutron. E_f was always fixed and had a value of 5 meV unless stated. Constant-energy scans were performed in two equivalent magnetic zones centred at $[010]$ and $[210]$. The reason for this is indicated by reference to the diagram of reciprocal space in Figure 2.18. This shows that when one wishes to transfer much more than 50% of the neutron energy to the sample, it may not be possible to complete the scattering triangle even at $2\theta = 0$ if the scattering vector is small. In practice, very small values of 2θ are unattainable because of the physical size of the components of the spectrometer ie. they will bump into one another! In order to transfer the desired energy, it may be necessary to move to an equivalent region of reciprocal space further from the origin, ie. at a larger scattering vector, and hope that the decrease in the intensity of the magnetic scattering arising from the reduction of the magnetic form-factor with increasing scattering vector is not too great. In this experiment, with E_f fixed at 5 meV, it was necessary to move from the $[010]$ zone to the $[210]$ zone when the energy transfer exceeded 6 meV.

Scans were performed along both the a^* and b^* reciprocal lattice directions as indicated in Figure 2.18. The spin-wave cross-section convolved with the instrumental resolution function was of the form:

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k_f}{k_i} |f(\vec{Q})|^2 A(\vec{Q}) \left[\exp \left[- \left(\frac{E-E(\vec{q})}{w} \right)^2 \right] - \exp \left[- \left(\frac{E+E(\vec{q})}{w} \right)^2 \right] \right] \quad (2.32)$$

where k_f and k_i are the final and initial neutron wavevectors respectively, $f(\vec{Q})$ is the magnetic form factor, $A(\vec{Q})$ is the magnetic structure factor and w is the width of the constant-energy scans.

The spin-wave energy, $E(\vec{q})$, was described by an expression with two variable parameters: the spin-wave velocity, c and a parameter Δ which produced the energy gap at the zone centre which is directly observable in this experiment, and which we had initially detected using TAS1 [72, 89].

$$E(\vec{q}) = [(c + \Delta)^2 - (c\gamma_{\vec{q}} - \Delta)^2]^{1/2} \quad (2.33)$$

where $\gamma_{\vec{q}} = \cos(\vec{q} \cdot \vec{a}/2) \cdot \cos(\vec{q} \cdot \vec{b}/2)$. Δ probably arises from an antisymmetric exchange

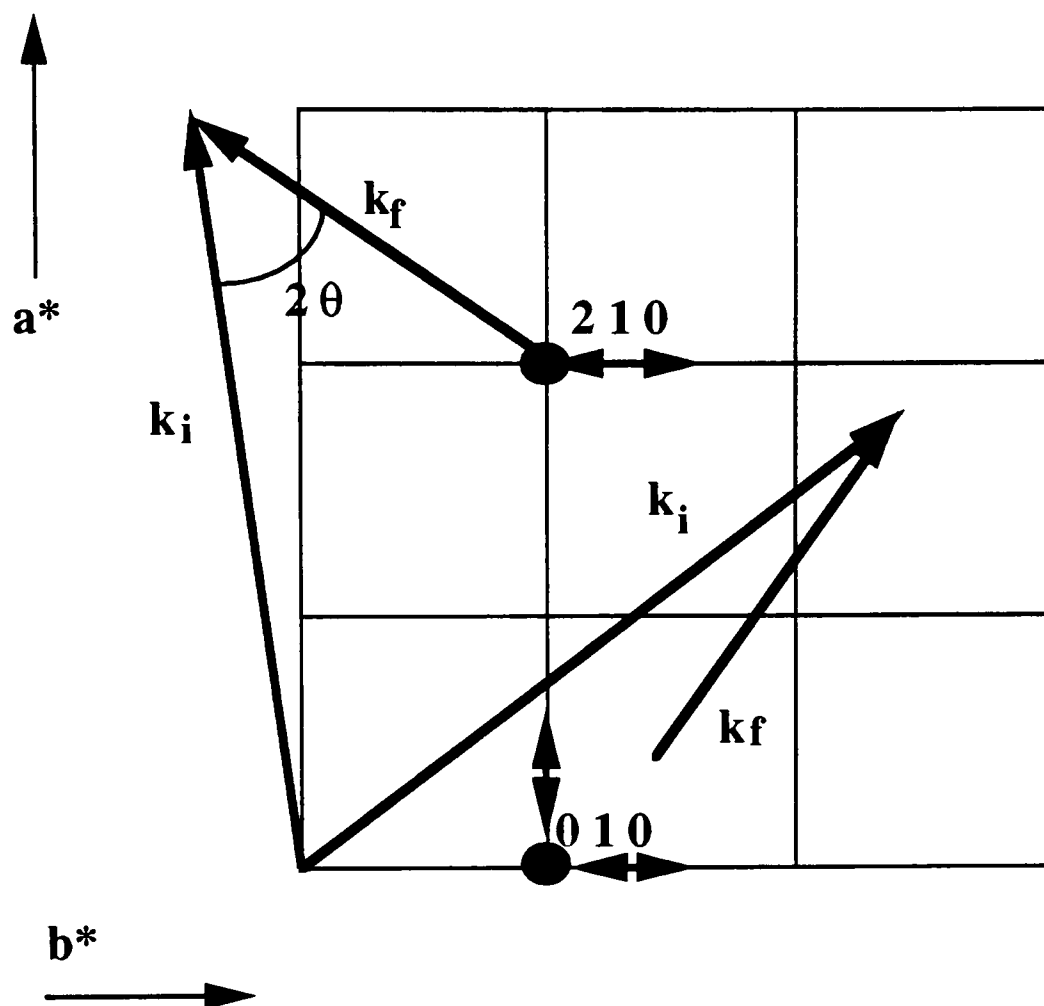


Figure 2.18: A diagram of the reciprocal space for CFTD in the ab plane showing how the scans to determine the spin-wave dispersion were performed (double-headed arrows). The figure also shows that when k_f is fixed in magnitude, it may not be possible to transfer a large proportion of the neutrons' energy at a low scattering vector even when $2\theta = 0$. Hence one must move to an equivalent region of reciprocal space with a larger scattering vector.

term in the Hamiltonian, such as that arising from the Dzyaloshinsky-Moriya (DM) interaction. Other terms could give rise to the gap, but we are unable to distinguish them from the DM case in the absence of polarisation analysis of the spin-waves. Antiferromagnetic resonance measurements [91] indicate that the DM interaction is the dominant source of additional terms in the Hamiltonian. Least squares fits to Equation 2.33 together with deconvolution of the resolution function were carried out using a 10 000 point Monte Carlo Integration (MCI) [92] which was found to be faster than the common analytical method. The program used was developed by Thom Mason at the University of Toronto, and is called FIT3AX [93]. It calculates the experimental resolution function from the spectrometer configuration and then generates 10 000 points inside the resolution ellipsoid with a Gaussian distribution. Calculation of the spin-wave energy at each of these points using a set of approximate parameters in the Hamiltonian produces the calculated scattering intensity at a particular point in $(\vec{q}, E)$ space which is then least-squares fitted to the observed intensity. Typical fits to the constant-energy scans are shown in Figure 2.19.

The fits to the constant-energy scans produced a value of the spin-wave velocity of $14.9 \pm 0.1 \text{ meV \AA}$. The large size of the resolution function meant that while the value of the spin-wave velocity could be determined quite precisely, the scans were insensitive to the value of Δ because it is very small compared to c . The value of Δ used in the fits was fixed at a value of 0.005 meV which corresponds to the size of the gap at the zone centre. The size of the gap at the zone centre was determined using constant- $\vec{q}$ scans at and near the zone centre with $E_f = 4.0 \text{ meV}$ rather than the 5.0 meV used for most of the scans. This resulted in a tighter resolution, which allowed the gap to be measured more precisely. The size of the gap was determined to be $0.55 \pm 0.05 \text{ meV}$ which is very similar to the value obtained using constant- $\vec{q}$ scans on TAS1. A constant- $\vec{q}$ scan at the zone centre is shown in Figure 2.20. The dispersion curve obtained is shown in Figure 2.21. A constant- $\vec{q}$ scan was also used to obtain the point at the zone boundary; constant-energy scans are too broad near the zone boundary where the dispersion is flat.

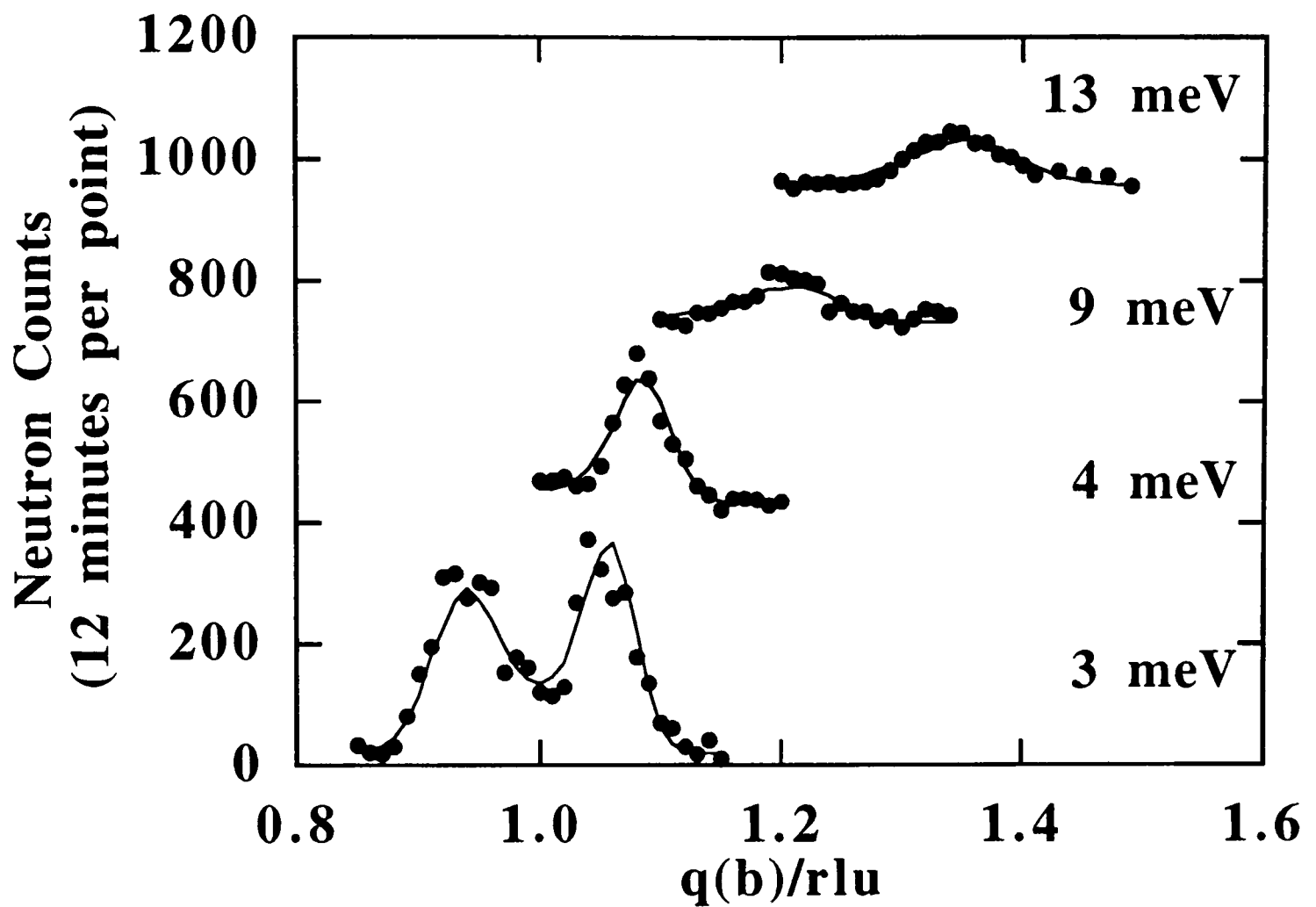


Figure 2.19: Some of the constant energy scans used to establish the dispersion relation. The solid lines are fits to the classical spin-wave expression, Equation 2.33, convolved with the instrumental resolution function. The scans at 4, 9 and 13 meV are shifted along the vertical axis by 400, 700 and 900 units respectively.

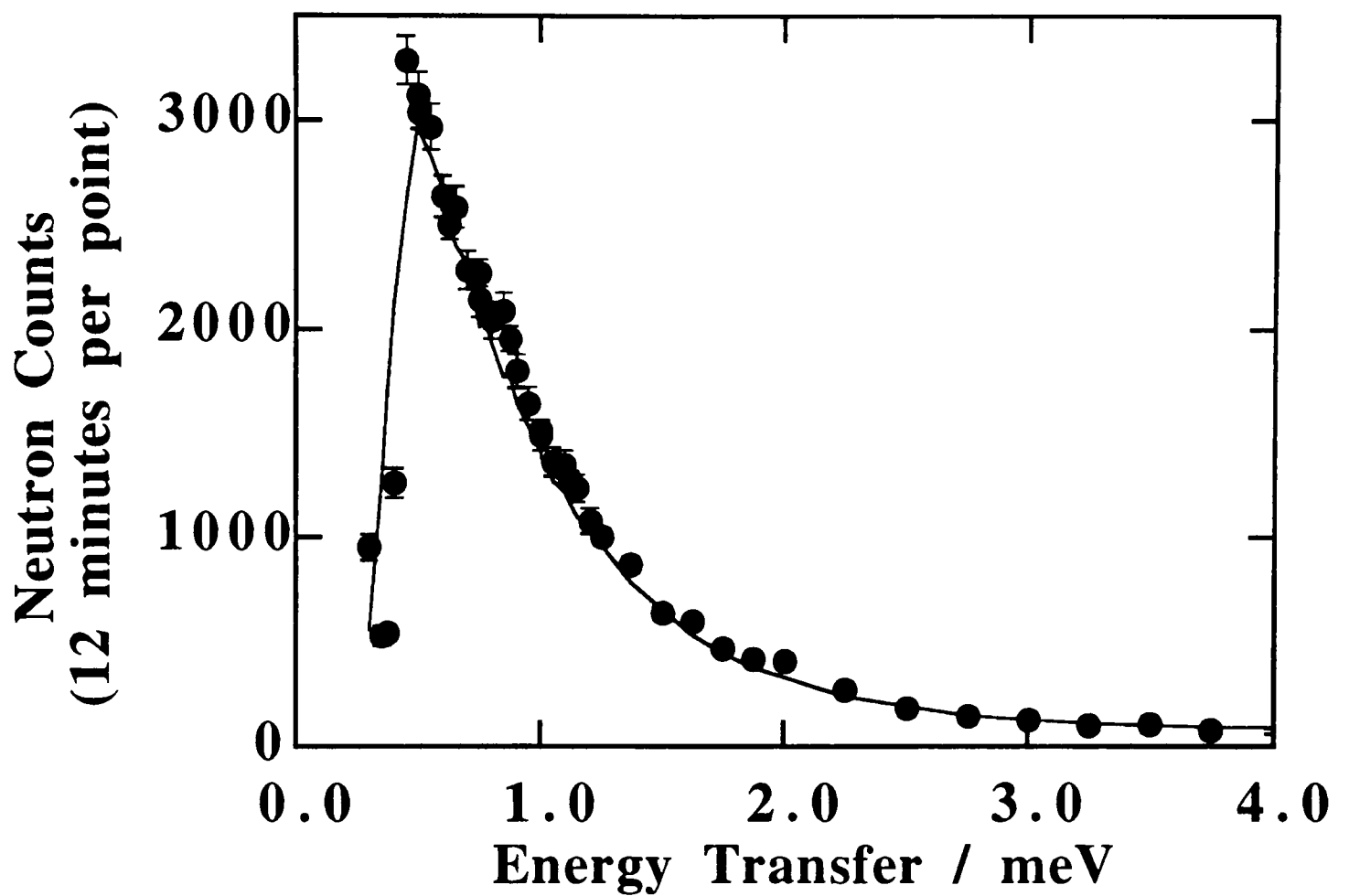


Figure 2.20: A constant- $\vec{q}$ scan at the antiferromagnetic zone centre at (010) at 4.3 K showing the zone centre gap in the dispersion relation. The solid line is a fit to Equation 2.33 convolved with the resolution function.

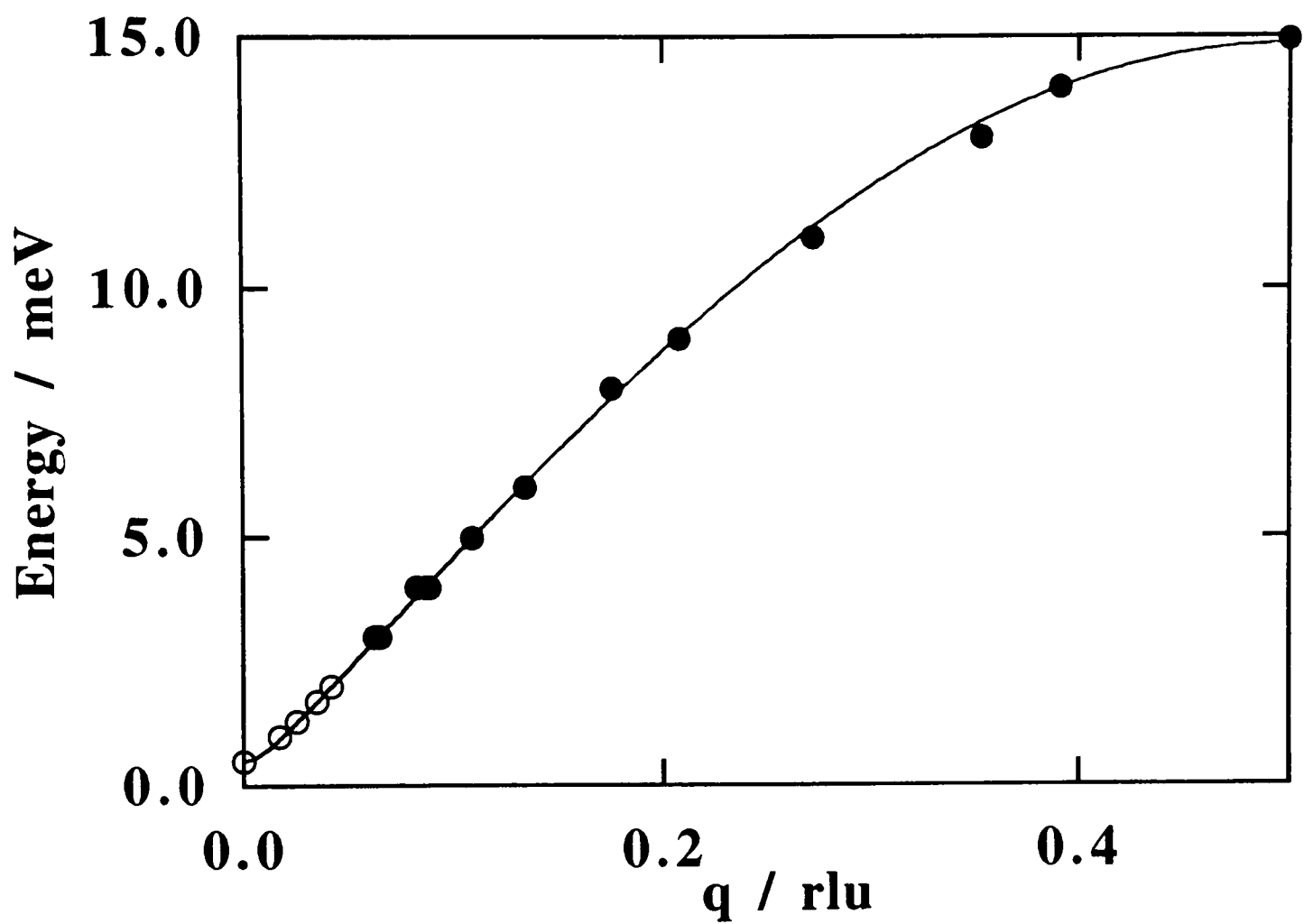


Figure 2.21: The Dispersion curve for CFTD. The four points designated by open circles are data from our previous measurements of the dispersion [89]. There is a clearly-defined gap at the zone-centre of 0.55 ± 0.05 meV. The solid line is a fit to the dispersion relation: Equation 2.34.

Analysis

Equation (2.33) is equivalent to the expression

$$E(\vec{q}) = 4S[(D + J(1 - \gamma_{\vec{q}}))J(1 + \gamma_{\vec{q}})]^{\frac{1}{2}} \quad (2.34)$$

which is a simplified version of the form used by Peters *et al.* [94] for La_2CuO_4 where $S = \frac{1}{2}$. J is the intraplane exchange constant and D performs an equivalent role to Δ . Fitting the dispersion relation to Equation 2.34 produces a value for J of 7.4 ± 0.2 meV and D of 0.0051 ± 0.0005 meV. At the magnetic zone centre, $\vec{q}=0$, so $\gamma_{\vec{q}}=1$, hence

$$E(0) = 4S(2JD)^{\frac{1}{2}} \quad (2.35)$$

so we see that the gap in the dispersion arises from J and D in combination. Thio *et al.* [64] identify the gap in La_2CuO_4 as being due to the DM antisymmetric exchange term, J_D in the Hamiltonian, and state that $E(0) = 4J_D S_0$ where S_0 is the reduced value of the spin of about 0.3 (see Section 2.4.2). We can thus determine an approximate value for J_D using

$$J_D = \frac{(2JD)^{\frac{1}{2}}}{0.6} \quad (2.36)$$

from which we deduce $J_D = 0.46 \pm 0.04$ meV which is similar to the value in La_2CuO_4 of 0.7 ± 0.1 meV [64]. The value for J should be corrected [75, 95] for the leading terms in the $1/2S$ expansion which are neglected in linear spin-wave theory:

$$J = J_{corr.}(1 + 0.158). \quad (2.37)$$

This correction produces a value for J of 6.5 ± 0.2 meV. This value is very similar to the value obtained by Seehra [62] using static susceptibility measurements (6.1 ± 0.1 meV) and to that obtained by an analysis of the inverse correlation length in the region $T_N < T < 2T_N$ (7.7 ± 0.2 meV) [73]. The value for J obtained by analysis of the whole dispersion curve is slightly smaller than that which we obtained by studying the spin-waves close to the zone centre ($0 < |\vec{q}| < 0.03$) using TAS1 [89], but the points from that experiment lie on the current curve which indicates that the difference arises from the relatively large influence of the parameter D close to the magnetic zone centre.

2.5.4 Spin-wave excitations around T_N

Experimental

Using the temperature dependence of the intensity of the (210) magnetic Bragg peak, we established the Néel temperature to be 15.95 ± 0.05 K using this particular cryostat and temperature controller. The *measured* temperature in this experiment was slightly lower than the value of 16.5 K recorded in previous work [73, 96] due to calibration differences between the cryostats used. One of the connections to the thermocouple of the CT14 cryostat had accidentally become detached. Fortunately the thermocouple was constructed such that this only produced a small error at the temperatures of interest.

Constant-energy scans with energy transfers of 3.0 and 5.0 meV were performed at temperatures of 10, 13, 17, 19, 21.5, 25 and 30 K. Constant- $\vec{q}$ scans at (0 1 0), (0.03 1 0) and (0.05 1 0) were performed at these temperatures and, additionally, at 15 K. The constant-energy scans and those at the zone centre at each temperature were fitted simultaneously to Equation 2.33. This simultaneous procedure was used because the constant- $\vec{q}$ scans are relatively insensitive to changes in the spin-wave velocity but are slightly more sensitive to changes in the width of the spin-wave peaks. The results of these fits are shown in Figures 2.22 and 2.23.

Both constant- $\vec{q}$ and constant-energy data show that the spin-waves soften (the spin-wave velocity decreases) and become damped (the peaks become broader). The softening and damping are presented quantitatively in Figure 2.24. The spin-wave softening is approximately linear. The damping increases rapidly above T_N .

Comparison with theory

There has been great interest in the study of the spin-waves in this class of magnet because of the opportunity it presents to test the strength of theoretical understanding of such systems [31, 97, 98]. Measurement of spin-waves allows one to determine the major terms in the Hamiltonian and to test theoretical models of the magnetic class. Comparison with other 2D systems can point out similarities and any differences

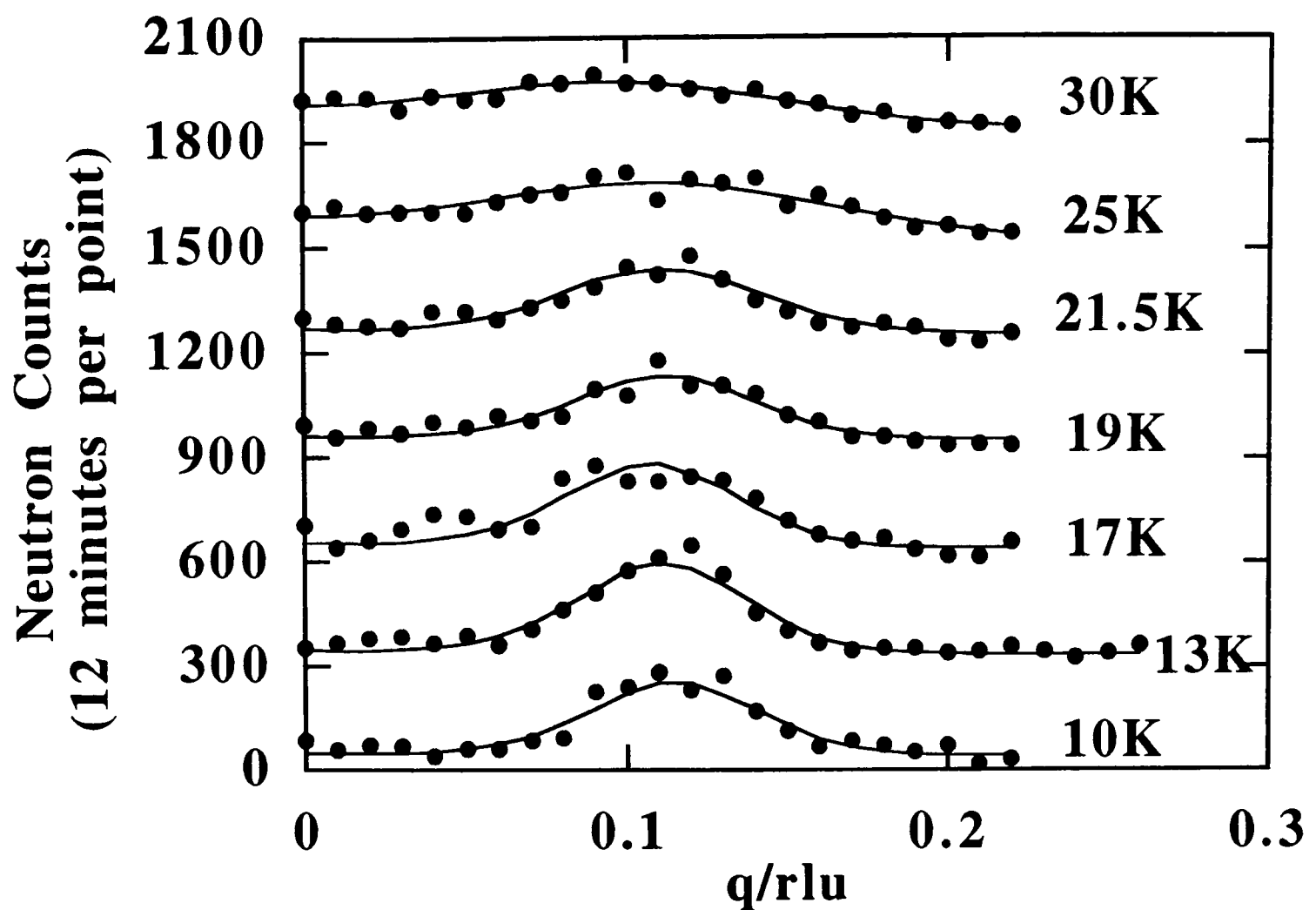


Figure 2.22: Constant-energy scans with 5 meV energy transfer at temperatures around T_N . These show clearly the softening and damping of the spin-waves as temperature is increased. The solid lines are fits of the data to the spin-wave expression Equation 2.33 convolved with the instrumental resolution.

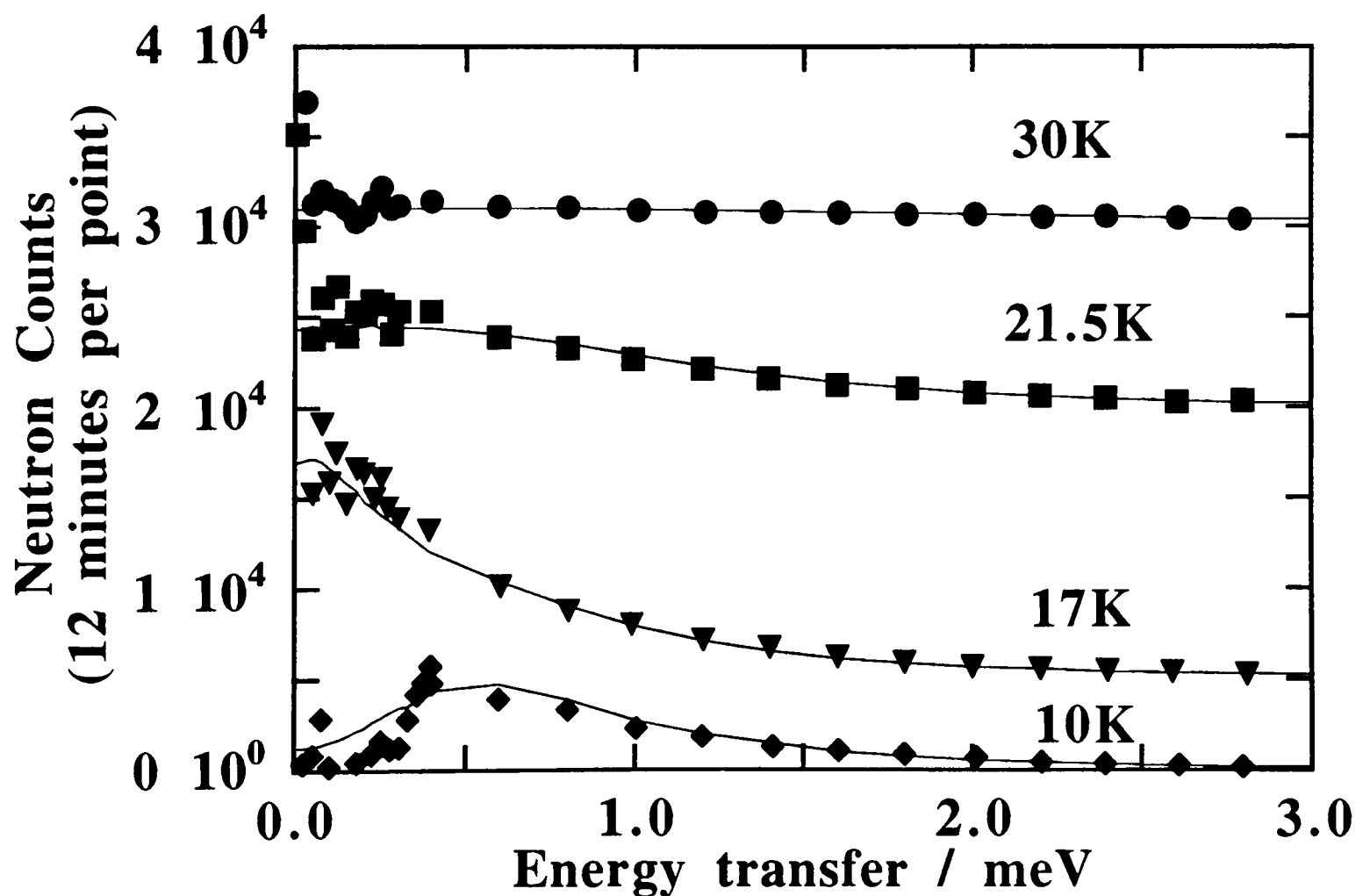


Figure 2.23: Constant- $\vec{q}$ scans at 010 at a range of temperatures from 10 K to 30 K ($T_N=16$ K). These clearly show the spin-wave damping. The solid lines are fits to Equation 2.33 convolved with the resolution function.

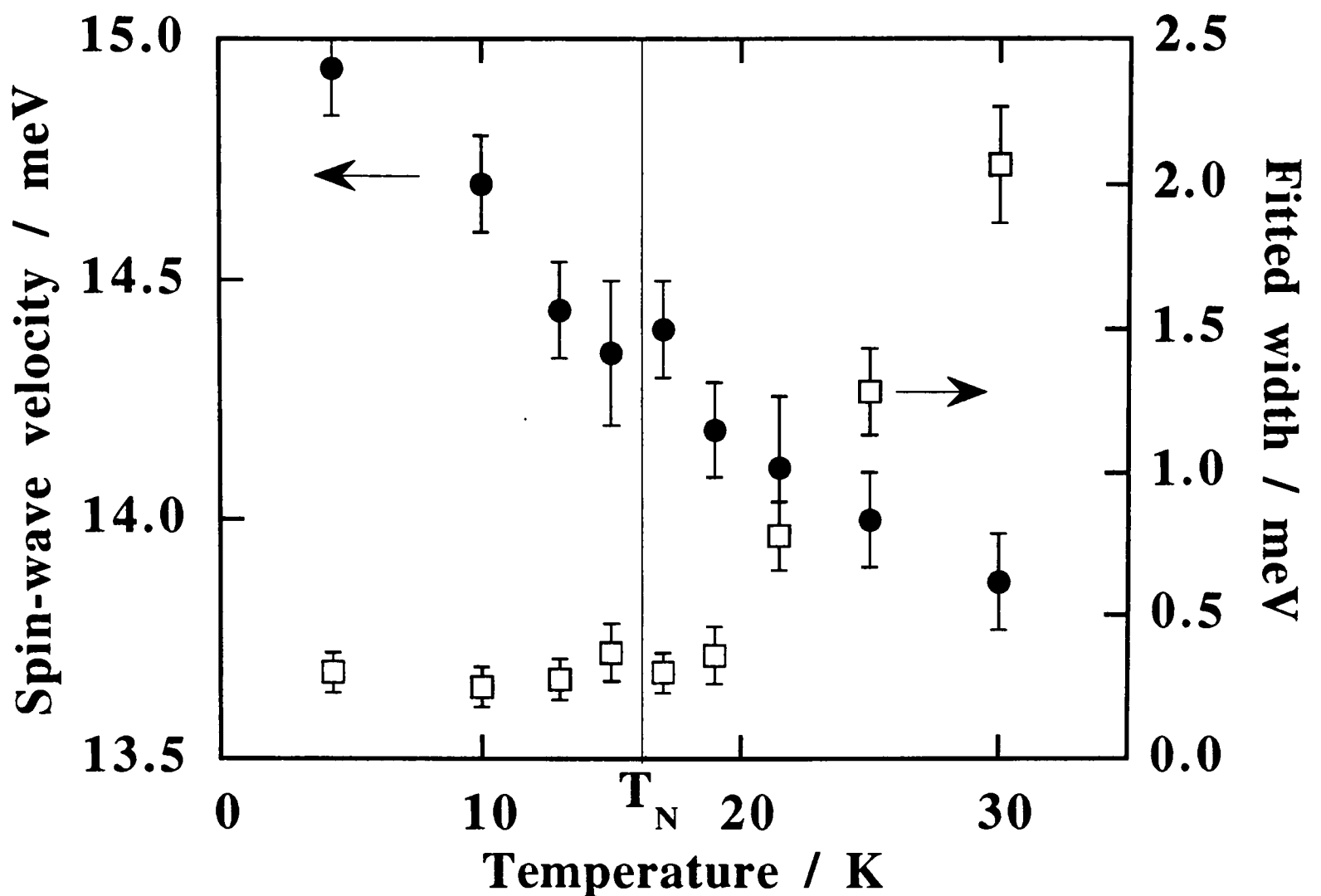


Figure 2.24: The temperature dependence of the spin-wave velocity (filled circles) and the fitted width of the spin-waves (open squares) in the range $T_N/4$ to $2T_N$.

associated with the low moment.

We found that the spin-wave excitations are well defined above T_N . Appreciable softening and damping of the excitations are not apparent until above $1.2T_N$. Well defined excitations above T_N have also been observed in the 2D systems K_2NiF_4 [18] and K_2MnF_4 [83] and many 1D systems. This may be understood by the fact that in order for 3D ordering to be precipitated in a low-dimensional system, the in-plane (or in-chain) correlation length has to become so large that excitations can propagate within the 2D (or 1D) correlated regions even well above T_N . This effect is magnified as the size of the spin is lowered. The out-of-plane exchange energy decreases as S decreases, and so the size of the correlated regions needed to precipitate ordering must increase to compensate. Thus, the smaller the spin, the higher the temperature relative to T_N at which well defined zero-temperature type excitations persist. This is borne out by the experiments on CFTD, K_2NiF_4 and K_2MnF_4 .

Tyč and Halperin [97] find that spin-wave excitations are well defined when the

condition $|\vec{q}|\xi \gg 1$ is satisfied. They also find that for 3D compounds, short wavelength spin-waves are primarily responsible for damping. However in 2D they find that the longer wavelength spin-waves dominate the damping. Our spin-waves of 3 meV and 5 meV have relatively long wavelengths, but remain well defined as far as $1.2 T_N$ due to the very large correlation length which has the effect of suppressing the damping. The correlation length is approximately 100 Å at $1.3 T_N$ [73].

Theoretical predictions [31, 97, 98, 99] have primarily focussed on the spin-wave damping. This is the width in energy units of the excitation at a particular temperature and wavevector; it depends on the lifetime of the excitation and is given the symbol Γ_q . In a conventional 3D magnet, the dominant factor in determining Γ_q is other spin-waves of short wavelength which broaden the excitations appreciably close to and below T_N and make them very poorly defined at higher temperatures. In 1D and 2D, well-defined excitations are known to persist to temperatures well above T_N provided that their wavelength is significantly smaller than the magnetic correlation length at that temperature. Our experimental work supports this and allows us to draw further qualitative conclusions. However, the large uncertainty in the experimental value of Γ_q prevents a detailed comparison with the predictions of theorists.

Γ_q increases with temperature as summarised in Figure 2.25. There is no discernable change in Γ_q as the wave-vector changes from zero to 0.05 because the errors in the fitted widths are quite large, as a result of the large size of the resolution function. For this range of temperature relative to the exchange field in CFTD, we expect the predictions of Grempel [98] to be appropriate, and these are also reproduced in the figure. It is clear that the predicted widths are substantially smaller than the widths which we measured. The more extensive theoretical work of Tyč and Halperin [97] may also be used to predict the dependence of Γ_q on T : substitution of appropriate values of the exchange and lattice constant for CFTD in the appropriate expression for the HAF with $S=\frac{1}{2}$ also provides values for Γ_q which underestimate the experimental values to a larger extent than Grempel's expression.

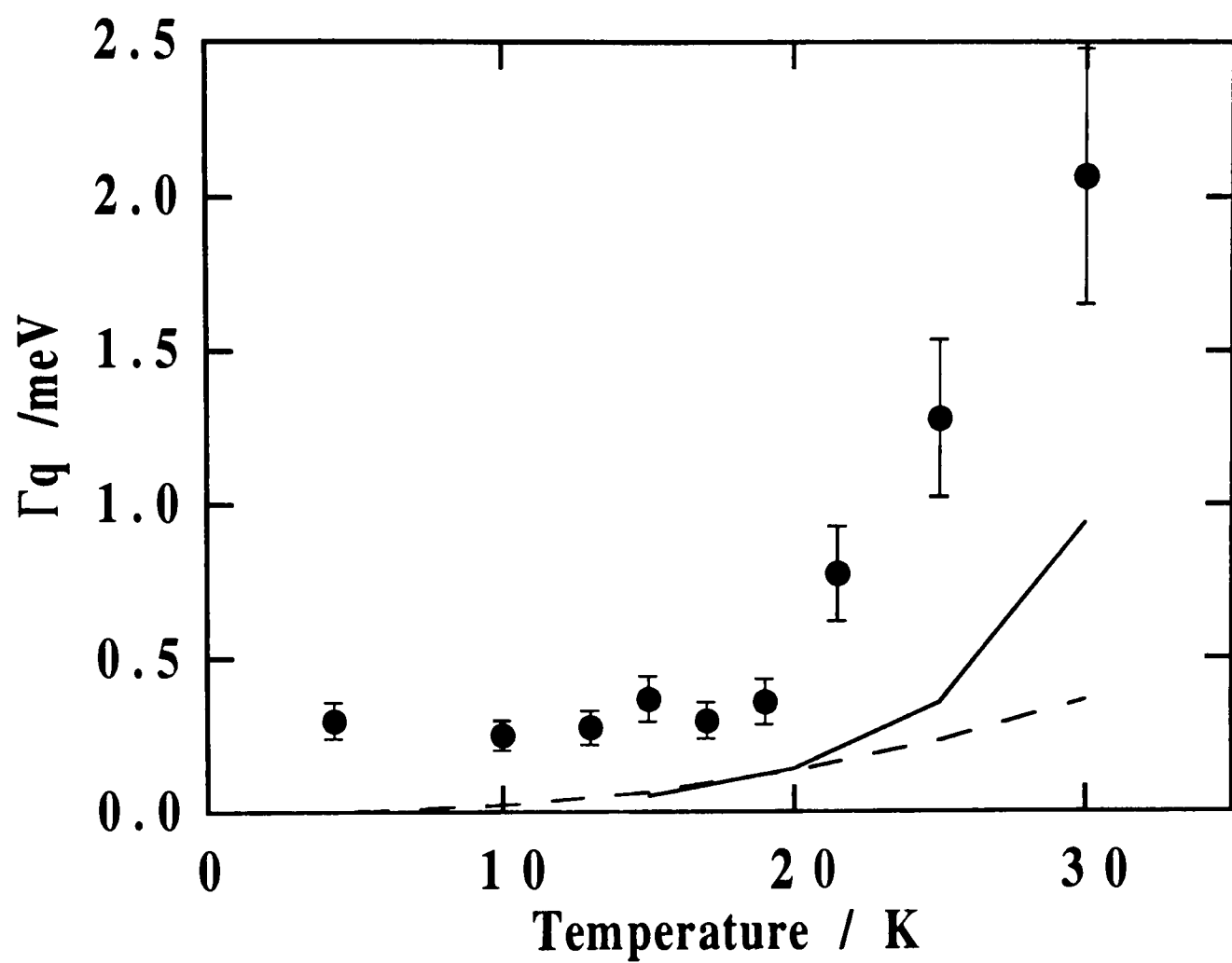


Figure 2.25: A comparison of the fitted width of the spin-waves (closed circles) with the predictions of the theories of Grenpel [98] (dashed line) and Tyč and Halperin [97] (solid line).

2.6 Conclusions

2.6.1 Summary of the behaviour of CFTH

This chapter has described neutron scattering experiments on copper (II) deuteroformate tetradeuterate. Quasielastic scattering above the long-range ordering transition was used to measure the length-scale of the correlated regions and the sublattice susceptibility as a function of temperature and this showed very good agreement with the predictions of the Quantum non-linear sigma model developed by Chakravarty, Halperin and Nelson [38]. The fact that La_2CuO_4 also shows good agreement with this model indicates that the leading terms in the exchange Hamiltonians of CFTH and La_2CuO_4 are very similar and that the CHN model is a valid one to use for the 2D Heisenberg antiferromagnet. We determined J to be $7.7 \pm 0.2 \text{ meV}$ and J' to be $3.1 \times 10^{-4} \pm 0.2 \times 10^{-4} \text{ meV}$.

Below T_N , the intensity of elastic scattering from the (0 -1 1) magnetic Bragg Peak as a function of temperature was used to determine the critical exponent, β for the magnetisation. The cross-over from a 3D value to what appears to be a universal value for 2D-XY systems at a temperature a little below T_N was rationalised in terms of the interplay of intra- and inter-planar exchange.

Studies of the magnetic excitations below and above T_N showed that they may be treated using classical spin-wave theory, with no need to invoke exotic ground states such as the RVB state. Hayden *et al.* [86, 87] demonstrated that this is also the case in La_2CuO_4 . The in-plane exchange constant in CFTH was determined to be to be $6.5 \pm 0.2 \text{ meV}$, which is consistent with all previous measurements, including that obtained by analysis of the correlation length. There is a gap at the zone centre of $0.55 \pm 0.05 \text{ meV}$ which is suggested [67] to arise from an antisymmetric exchange term, J_D , of $0.46 \pm 0.04 \text{ meV}$ in the Hamiltonian. In principle one can determine J' from the out-of-plane dispersion, but our experiment was unable to do better than put an upper bound on its value.

We have investigated the evolution of the spin-waves with temperature and found that they persist well above T_N , although they soften approximately linearly as the

temperature is raised from $T_N/4$ to $2T_N$ and are considerably damped above about $1.2T_N$. This is in keeping with previous studies of 2D materials. The widths of the spin-wave peaks at high temperature appear to be larger by a factor of about 2 than those obtained by a theoretical treatment.

Gathering the results of the neutron scattering experiments together we conclude that the magnetic Hamiltonian has three main terms:

$$\mathcal{H} = -J \sum_{ij} \vec{S}_i \cdot \vec{S}_j + J_D \sum_{ij} \vec{S}_i \times \vec{S}_j + J' \sum_{ik} \vec{S}_i \cdot \vec{S}_k \quad (2.38)$$

in which J is about 7 meV, J/J_D is about 15 and J/J' is about 2×10^4 .

2.6.2 Comparison of CFTH with other model materials

Our determination of the main three terms in the magnetic Hamiltonian of CFTH allows us to make a direct comparison with La_2CuO_4 , the most studied model material for the 2DHAF, and with $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, which has been less well studied, but seems to be a more ideal system because it contains fewer terms in its magnetic Hamiltonian.

Comparison with La_2CuO_4

The symmetric superexchange constants of CFTH and La_2CuO_4 are very different: $J_{CFTH} \simeq 10$ meV, while $J_{\text{La}_2\text{CuO}_4} \simeq 130$ meV. One might expect that this difference could be wholly explained by the larger separation between magnetic ions in CFTH. The separation is 3.8 Å in La_2CuO_4 , but 5.7 Å in CFTH. If the size of the superexchange simply fell off as r^{-12} , one would expect J_{CFTH} to be about 1 meV. The delocalised nature of the formate group causes the fall-off to be much less rapid than predicted. The *effective* separation of Cu^{2+} ions in CFTH is calculated to be about 4.8 Å using the relation $J \propto r^{-12}$.

In La_2CuO_4 , J/J' is slightly larger than in CFTH, but both materials are ‘good’ 2D systems. Thio *et al.* [64] have determined J_D in La_2CuO_4 to be 0.7 meV from the measurement of the gap in the spin-wave spectrum, and from an analysis of the magnetic susceptibility. This value is quite similar to that in CFTH (0.46 meV), and so in La_2CuO_4 , the antisymmetric exchange is smaller relative to the symmetric

exchange. This is expected on the basis of the fact that the Cu environment in CFTH is less symmetric than in La_2CuO_4 .

Comparison with $\text{Sr}_2\text{CuO}_2\text{Cl}_2$

This material has recently been studied by Greven *et al.*. The structure is similar to that of La_2CuO_4 , but has a higher symmetry and is much more like the K_2NiF_4 structure. The space group is $I4/\text{mmm}$ and the lattice parameters are $a=3.967 \text{ \AA}$ and $c=15.59 \text{ \AA}$. a is equal to the nearest Cu–Cu distance which is similar to the separation in La_2CuO_4 ($3.8 \text{ \AA}$). The exchange constant measured by Raman spectroscopy was determined to be $125 \pm 6 \text{ meV}$ which is very similar to the value in La_2CuO_4 . The presence of an inversion centre relating corner-sharing CuO_4Cl_2 units precludes any antisymmetric exchange term in the Hamiltonian [6, 7]. Also, the net inter-planar exchange field at a particular Cu^{2+} ion is zero because the Cu^{2+} ion in one plane lies above the centre of antiferromagnetically coupled square plaquettes in the two neighbouring planes. The ordering at T_N must arise from a single-ion anisotropy which Greven *et al.* [37] identify as an XY term in the Hamiltonian which they represent as

$$\mathcal{H} = -J \sum_{ij} \vec{S}_i \cdot \vec{S}_j + J^{XY} \sum S_i^z S_j^z. \quad (2.39)$$

J/J^{XY} is about 7×10^3 from spin-wave measurements [37]. The size of this term relative to J makes J/T_N about 6 which is quite similar to the values of about 5 in CFTD and about 7.5 in La_2CuO_4 . The identification of the extra term in the Hamiltonian as an XY term may be an error. There should probably be some Ising component which will drive the transition since the 2D Ising magnet can order at a finite temperature [17] while the 2D XY system cannot order in the thermodynamic limit [20, 25].

It seems that $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ may well have the simplest Hamiltonian of any of the model materials studied thus far.

We conclude that although CFTH is easier to measure unambiguously due to the smaller value of the exchange, the departure from the ‘ideal’ Hamiltonian (Equation 1.5) is larger than in La_2CuO_4 and $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ primarily due to the large size of

the antisymmetric exchange term in the Hamiltonian, which arises from the relatively low symmetry.

In the following chapter, we make use of the expression for the magnetic correlation length in the critical region to explain the results of electron spin resonance spectroscopy and DC susceptibility measurements. We also determine the value of J_D from a measurement of the susceptibility and additionally compare the responses of the two materials to replacement of some of the Cu^{2+} ions by a diamagnetic dopant.

Chapter 3

Measurement of pure and doped CFTH using DC magnetometry and electron spin resonance spectroscopy.

This chapter describes experiments on pure samples of CFTH and those in which some of the Cu^{2+} ions have been replaced by Mg^{2+} or Zn^{2+} . DC susceptibility and Electron Spin Resonance (ESR) spectroscopy measurements are described. Further comparisons of CFTH with La_2CuO_4 are made.

3.1 Introduction

3.1.1 Magnetic dilution and percolation

The proposal that the ground state of the 2DHAF is non-classical has led to speculation that there may be novel behaviour associated with diamagnetic doping of such a material. Also, early measurements of the response of the Néel temperature of La_2CuO_4 to diamagnetic doping indicated extreme sensitivity [100] which has since been recognised [101] as being spurious.

When a diamagnetic ion is substituted for some of the magnetic ions in a 2D material, the effect is to dilute the magnetic interactions and disrupt the correlated regions in the planes. When the transition to a 3D ordered state is driven by the interaction of correlated regions in adjacent planes, the correlation length in diluted material must be larger than in undiluted material before 3D ordering can occur.

Lattice	z	p_s	p_b
Honeycomb	3	0.700	0.653
Square	4	0.590	0.500
Triangular	6	0.500	0.347
Diamond	4	0.425	0.388
Simple cubic	6	0.307	0.247
Body centred cubic	8	0.243	0.178
Face centred cubic	12	0.195	0.119
Hexagonal close packed	12	0.204	0.124

Table 3.1: Table of site (p_s) and bond (p_b) percolation limits for various lattices. z is the number of nearest neighbours to a particular site. Values are smaller for more highly connected lattices.

Hence on increasing the dilution, the Néel temperature decreases.

If the dilution is continued, then eventually the concentration of magnetic ions reaches a critical value p below which they do not form a continuous network which extends from one side of the lattice to the other. This point is called the percolation limit. At the percolation limit, the ordering temperature becomes zero, if one assumes that only nn interactions are important. The percolation limit depends on the dimensionality and the geometry of the lattice. Values of percolation limits for different lattices are given in Table 3.1. As the connectivity of the lattice increases, the percolation limit decreases since more dilution is required to achieve a particular level of disruption. We can define percolation limits for site dilution (p_s) which is the replacement of sites, and for bond dilution (p_b) which is the replacement of bonds between sites. Replacement of a site disrupts z bonds, where z is the coordination number of a site. Hence the site percolation limit is always *larger* than the bond percolation limit. On dilution, the manner in which the ordering temperature approaches zero at the percolation limit of the particular lattice under consideration is dependent on the spin dimensionality of the system. While many experiments such as the measurement of short-range correlations using neutron scattering can usefully be performed at or near the percolation limit, that was not possible with CFTH, as it was found that the highest doping level which could be achieved was 15%.

The way in which T_N changes as a 2D material is doped with diamagnetic ions,

can be quantified by Equation 3.1 which is a general case of Equation 2.26 used to determine an approximate value for J' in Chapter 2.

$$T_N(x) = \alpha J' \left(\frac{\xi_{2D}(x)}{a} \right)^2 (1-x) \quad (3.1)$$

with J' expressed in Kelvin. x is the fraction of diamagnetic ions and $\xi_{2D}(x)$ is the 2D correlation length in a sample characterised by a particular value of x at $T_N(0)$. If $\xi_{2D}(x)$ decreases linearly with dilution, as is predicted by MF theory, then $T_N(x)/T_N(0)$ should also decrease linearly as x increases with a gradient, α of 1. One normally observes a value of α of between 1 and 3. This indicates that usually the value of the magnetic correlation length at $T_N(0)$ decreases on doping faster than the MF theory predicts. Usually one can assume that J' is unchanged on doping, unless there is a large change in the structure.

A number of theoretical and experimental studies have been performed on diluted 3D and 2D systems. At low dopant concentrations, the behaviour is characterised by the value of α , which is system dependent. A general result is that α increases as the number of nearest-neighbours on the magnetic lattice decreases. For example, a theory of the 2D Ising system carried out by Idogaki and Uryû [102] suggests the following behaviour for T_N on doping:

$$\alpha = \left[\ln \frac{(1-x)z}{(1-x)z-2} \right]^{-1} \quad (3.2)$$

where z is the number of magnetic neighbours. In addition, α seems to increase as the spin dimensionality increases. This result comes from work by Stinchcombe [103] on Ising and Heisenberg antiferromagnets. He also finds that ferromagnets and antiferromagnets show very similar behaviour. Landau [104] has carried out a Monte-Carlo simulation of the simple cubic Ising system and has found good agreement with theory which predicts $\alpha=1.1$.

In the case of 2D systems, the theory for the 2D Ising system [102] indicates $\alpha=1.3$ and this is borne out by experiments on K_2CoF_4 in which some of the Co has been replaced by Mg [105].

Experiments on 2D systems with less anisotropic moments such as $K_2Cu_{1-x}Zn_xF_4$

[16] and $\text{K}_2\text{Mn}_{1-x}\text{Mg}_x\text{F}_4$ [105] indicate a larger value of α . The results obtained for La_2CuO_4 and CFTH are compared with these magnets later in this chapter.

3.1.2 Summary of doping experiments on La_2CuO_4

If La_2CuO_4 has a very small amount of the La^{3+} replaced by Sr^{2+} , the effect is to reduce T_N very rapidly ($\alpha \simeq 20$). This is because [100], the hole produced is not very localised and very efficiently disrupts the magnetic ordering process. This complication makes it difficult to compare such dilution studies with conventional dilution problems. Experiments which attempted to replace some of the Cu^{2+} in La_2CuO_4 by a diamagnetic ion have been performed. Chakraborty *et al.* [100] replaced up to about 3% of the Cu^{2+} by Zn^{2+} , and measured T_N for a series of samples using a SQUID magnetometer. Their results indicated an α of about 10. There was no change in the ratio of the a and c lattice parameters which define the square plane, which suggests that J' is not changed significantly on substitution. The value of α is much larger than in other 2D materials, and this suggested that there may be something unusual about the doping properties of the 2DHAF. However, more recent magnetic susceptibility measurements by Cheong *et al.* [101] indicate that the rate of depression of T_N with increasing x in carefully-made $\text{La}_2\text{Cu}_{1-x}\text{Mg}_x\text{O}_4$ is about the same as that of classical magnets and that the results of Chakraborty *et al.* arose from the combined effects of diamagnetic doping and additional oxygen incorporated into the structure during preparation. Cheong *et al.* note several important results:

- Mg^{2+} is a much better dopant than Zn^{2+} for Cu^{2+} in La_2CuO_4 , and a value of x of 0.2 is attainable.
- α is about 3 in the range $0 < x < 0.2$.
- The method of preparation of Chakraborty *et al.* involves annealing under an oxygen atmosphere, which incorporates extra oxide into the structure producing $\text{La}_2\text{Cu}_{1-x}\text{Mg}_x\text{O}_{4+y}$, where y is just greater than 0. This has a similar effect to the replacement of La^{3+} by a small amount of Sr^{2+} and results in the anomalously large value of α obtained.

- The method of preparation of Cheong *et al.* involves annealing under nitrogen, and this appears to give material stoichiometric in oxygen.
- There appears to be a similar value of α in all 2D Heisenberg systems at small values of x , which is about 3. This is much larger than the theoretical and experimental work on Ising systems.

3.1.3 Doping experiments on CFTH

In order to compare the behaviour of CFTH with that of classical 2DHAFs, the diamagnetic ions Mg^{2+} and Zn^{2+} were chosen as dopants and T_N was measured using single-crystal ESR spectroscopy and SQUID magnetometry. Mg^{2+} and Zn^{2+} are of similar size to Cu^{2+} ; Mg^{2+} was initially chosen as the dopant ion on the basis that MgO has the octahedrally coordinated rock-salt structure and it was thought that Mg^{2+} would not disrupt the crystal structure as much as Zn^{2+} which adopts a tetrahedral coordination with O^{2-} in ZnO. In fact Zn^{2+} substitutes for Cu^{2+} to a higher degree than Mg^{2+} does. It seems likely that the greater covalency of Zn^{2+} in its compounds makes it a better substitute for Cu^{2+} than Mg^{2+} is. The best substitute for Cu^{2+} would probably be Cr^{2+} because it too is subject to a Jahn-Teller distortion. However, Cr^{2+} is paramagnetic. The possibility of replacing Cu^{2+} with Pd^{2+} which favours a square planar coordination was suggested, but was not attempted, partly due to the expense of Pd compounds.

3.2 Preparation of doped CFTH samples

Samples were prepared by dissolving mixtures of basic copper (II) carbonate and magnesium (II) or zinc (II) carbonate in an aqueous solution of 10% formic acid. Single crystals with sizes ranging from 1 to 1000mm³ were grown by slowly evaporating solutions at room temperature.

The proportion of the Mg^{2+} present in solution which could be incorporated into crystals of $\text{Cu}_{1-x}\text{Mg}_x(\text{HCO}_2)_2 \cdot 4\text{H}_2\text{O}$ (CFTH: Mg^{2+}) was small and a dopant level of

only $x=0.023$ could be obtained by growing crystals at room temperature from a solution containing 30 atom% Mg^{2+} (ie. $x=0.3$). If the solution contained a higher concentration of Mg^{2+} , a multi-phase precipitate was produced which was believed to be a mixture of $\text{CFTH}:\text{Mg}^{2+}$ and magnesium (II) formate. It was possible to grow crystals with $x=0.033$ by elevating the growing temperature to 34.5°C using a water-bath equipped with a thermostat. However, these crystals were of poor quality due to the difficulty of maintaining isothermal conditions and eliminating vibrations from the water-bath during growth.

Crystals of $\text{Cu}_{1-x}\text{Zn}_x(\text{HCO}_2)_2 \cdot 4\text{H}_2\text{O}$ ($\text{CFTH}:\text{Zn}^{2+}$) with x as high as 0.15 could be grown at room temperature from solutions containing up to 30% Zn^{2+} . The characteristic crystal morphology of CFTH [51] shown in Figure 3.1 was unchanged on doping with Mg^{2+} or Zn^{2+} indicating that the diamagnetic ions are incorporated into the structure without distorting it appreciably. However, the samples with $x=0.15$ contained what appeared to be visible planes of dislocation which formed during growth. Single crystals containing Mg^{2+} were prepared with $x=0.009$ and 0.023. Those containing Zn^{2+} had $x=0.023, 0.042, 0.043, 0.059, 0.087, 0.107, 0.111, 0.128, 0.141, 0.145$ and 0.153. It has not yet proved possible to increase further the concentration of Zn^{2+} in the crystals. The relative concentrations of Cu^{2+} and Mg^{2+} or Zn^{2+} were determined spectrophotometrically by the ICL analysis service using about 10 mg of the sample from which the crystal used in the ESR or SQUID measurements had been cut. The total metal ion content was compatible with that expected for a compound with the stoichiometry of CFTH (ie. there was no change of hydration level). The concentration of the dopant ion is smaller in the crystal than in the growing solution. Solutions with a volume of approximately 10^4 times that of the crystals were used to avoid growing crystals with higher values of x nearer their surface.

3.3 Description of ESR spectroscopy

ESR was chosen as the initial probe of the magnetic properties of the doped material because we did not have access to a magnetometer suitable for determining T_N

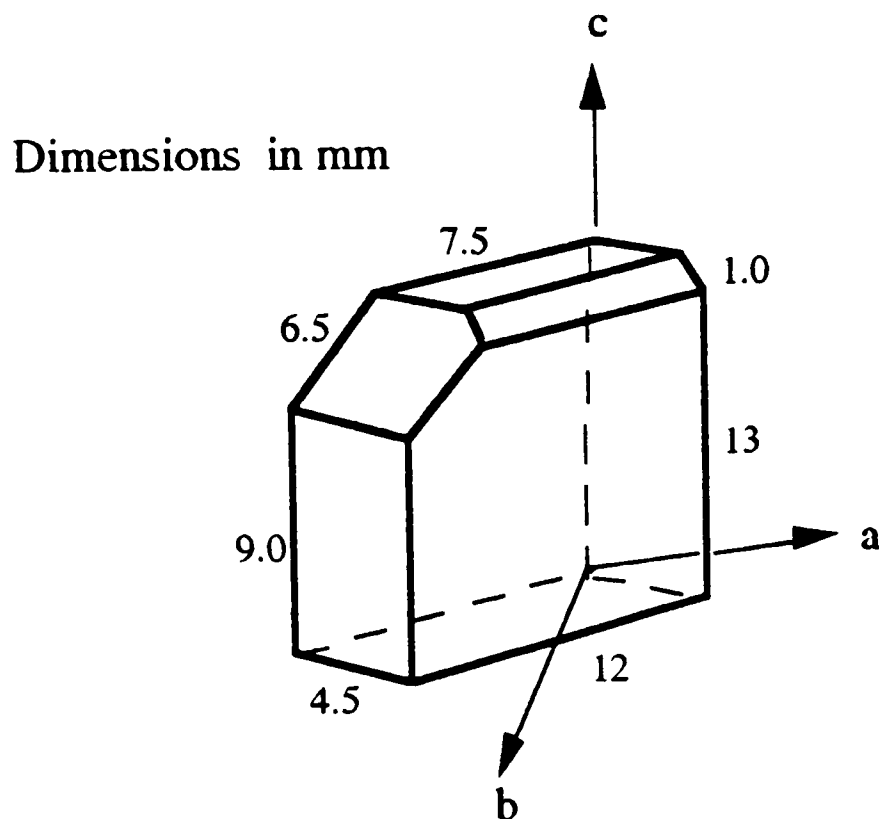
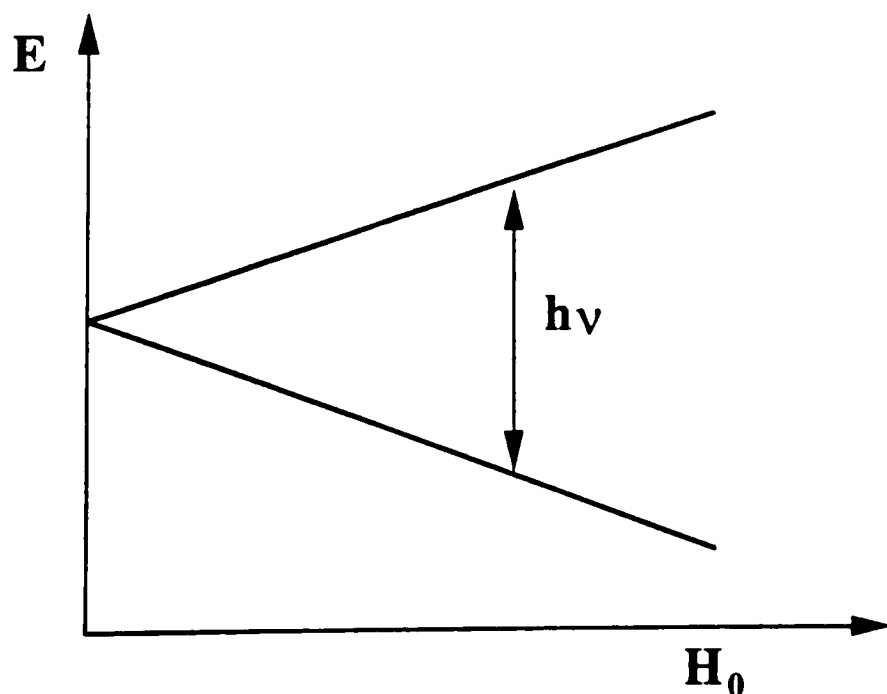


Figure 3.1: The crystal morphology of CFTH which is useful for orienting the crystals accurately by eye.

precisely. The inherent advantages of ESR are that it is a sensitive technique which can, in principle, distinguish between inequivalent magnetic ions and determine any single-ion anisotropy present. There have already been extensive ESR measurements performed on undoped CFTH [67, 91, 106, 107] and on related 2D systems [108, 109]. The results of Seehra and Castner [67, 91, 106, 110] are discussed.

3.3.1 ESR Theory

In an ESR experiment a magnetic field of a few thousand Gauss is applied to the sample. In the case of a metal ion with an odd number of electrons, according to Kramer's theorem, the ground state will consist of a pair of degenerate electronic levels. The degeneracy of these levels is lifted by the application of the field and a Zeeman splitting proportional to the size of the applied field, $\vec{H}_0$, results.



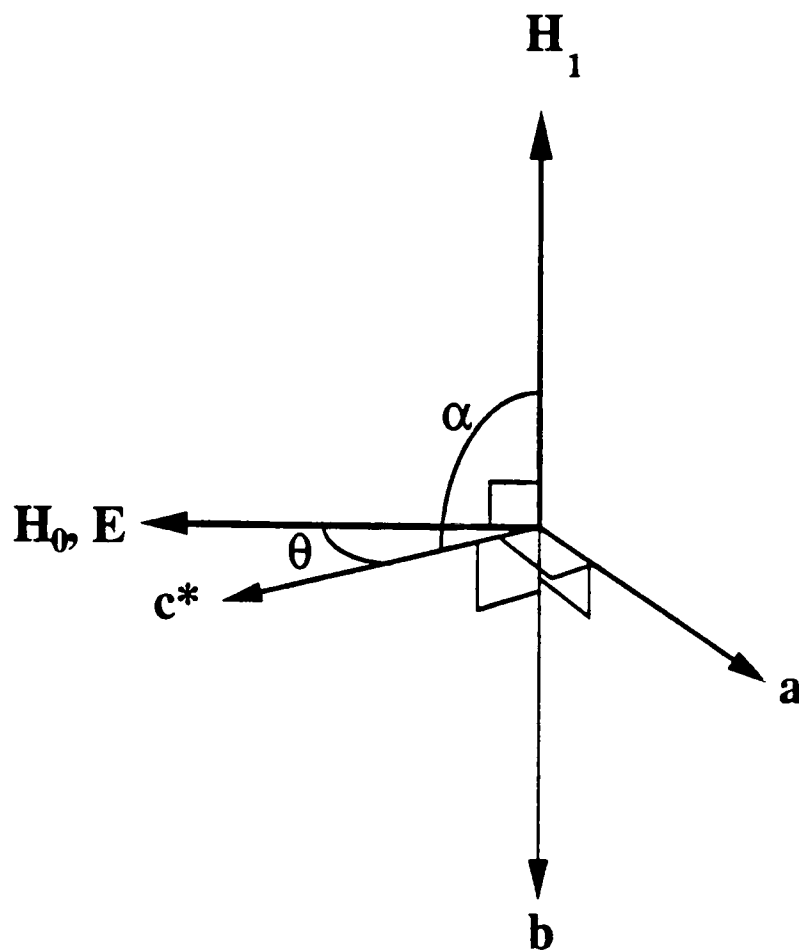


Figure 3.2: The configuration of the ESR spectrometer used at the Inorganic Chemistry Laboratory in Oxford.

The splitting corresponds to energies, $h\nu$ in the microwave region of the electromagnetic spectrum. Application of microwaves produced by a klystron induces transitions between the split levels according to the resonance condition

$$h\nu = g\mu_B H_0 \quad (3.3)$$

where μ_B is the Bohr Magneton and g is the spectroscopic splitting parameter and corresponds closely to the g -factor derived from the angular momentum quantum numbers of the electronic state. There is a net absorption of radiation by the sample because the energy levels have a Boltzmann population. The transitions in ESR spectroscopy are magnetic dipole transitions which involve reorientation of the magnetic moments in the material. They are stimulated by the magnetic component of the electromagnetic radiation, $\vec{H}_1$. In order that the transition probability is non-zero, there must be a component of $\vec{H}_1$ perpendicular to $\vec{H}_0$. In practice $\vec{H}_1$ is usually at 90° to $\vec{H}_0$ as Figure 3.2 shows.

In principle there are similarities between an ESR experiment and a continuous wave NMR (CWNMR) experiment. However, in practice since klystron tubes are only capable of producing radiation with a very narrow frequency range, the microwave frequency is fixed during the experiment and the magnetic field is varied. This contrasts with a CWNMR experiment in which the radiation frequency is varied

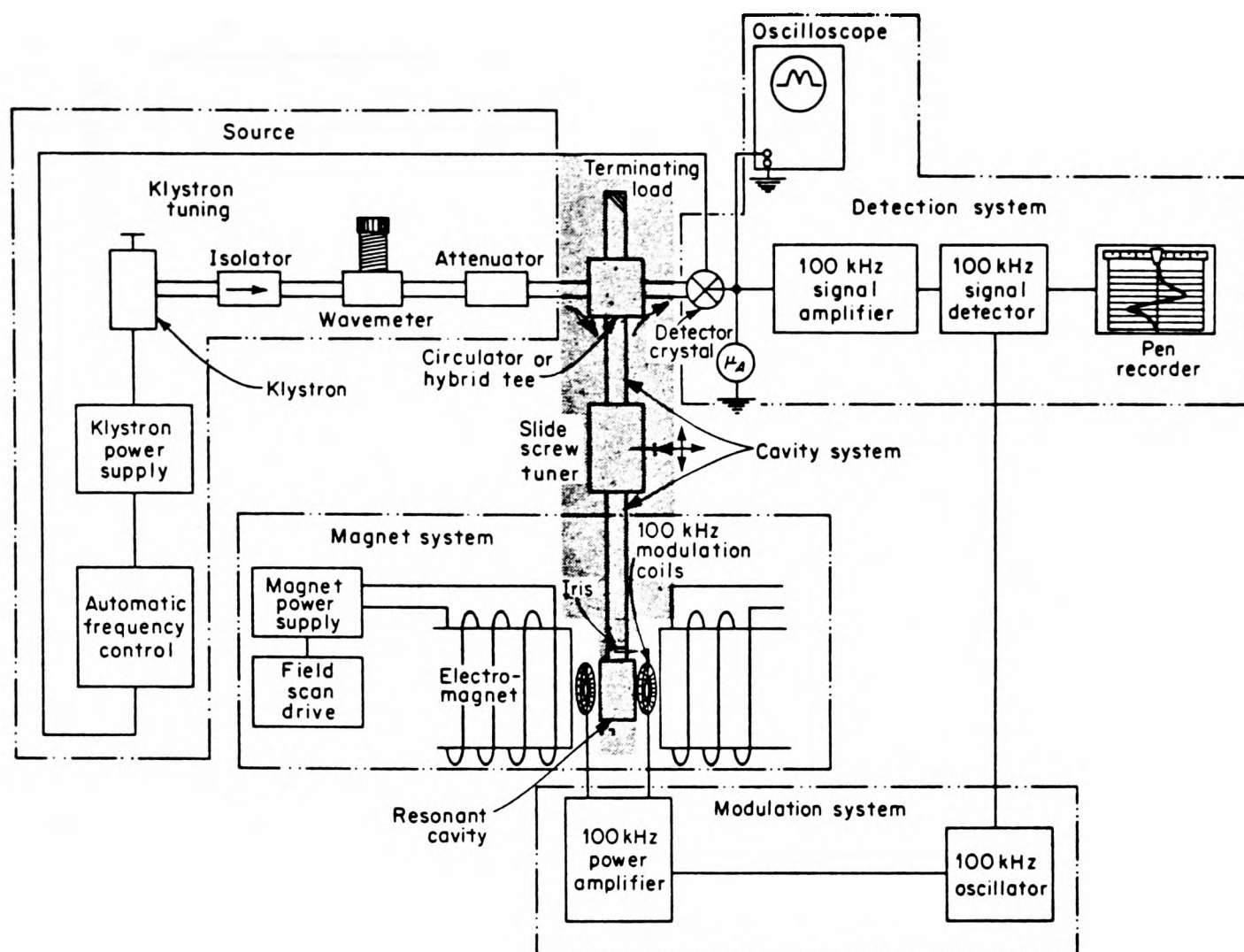


Figure 3.3: A block diagram showing the main components of a continuous wave ESR spectrometer.

and the field is kept constant. ESR can now be performed in the time domain with the advent of solid state sources of microwave radiation which can produce pulses of radiation with a reasonably large bandwidth. These machines are expensive and their development was not consumer driven in the same way as that of the more versatile NMR spectrometers, so unlike modern NMR, much ESR is still carried out in a swept field.

Measurement of the ESR signal

A block diagram of a swept-field ESR spectrometer is shown in Figure 3.3. The sample is placed in a tunable microwave resonant cavity which is mounted between the poles of a variable field electromagnet. In order to measure the spectrum, the applied field is modulated using a pair of secondary coils located next to the cavity and pointing parallel to the applied field. The modulation coils produce a field of between about 0.1 and 10 G which oscillates at a frequency of (usually) 100 kHz. The use of

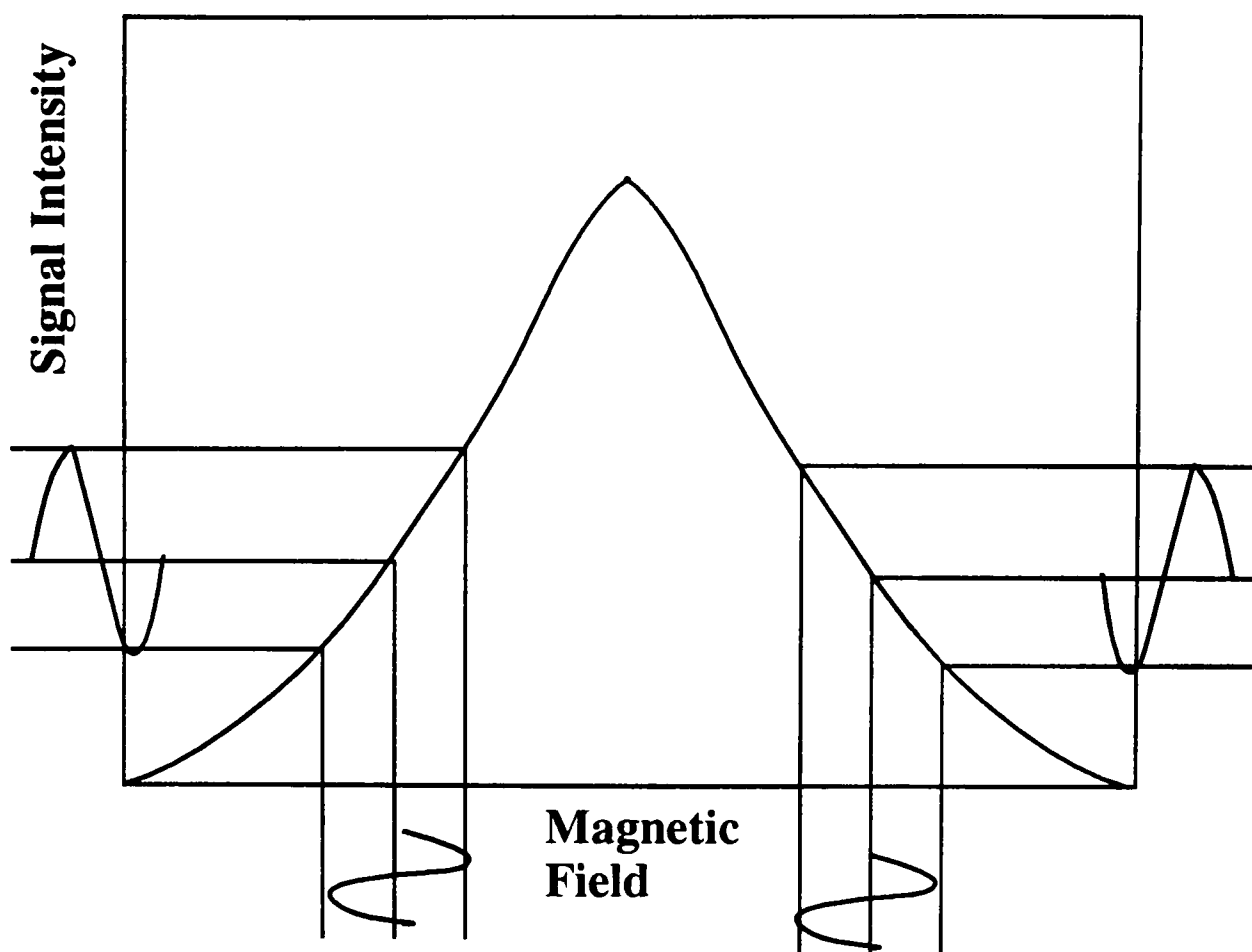


Figure 3.4: The effect of modulation of the field in an ESR spectrometer. A full explanation is included in the text.

modulation reduces the noise contributions of frequencies far from the modulation frequency. The detector system is usually a silicon crystal acting as a microwave rectifier, which detects the signal amplitude modulated at 100 kHz. A further advantage of using a modulation frequency of 100 kHz is that the noise in the silicon detector crystal is low at that frequency. The amplified signal oscillating at 100 kHz is mixed with the output of the 100 kHz oscillator which originally supplied the modulation. If the two signals are in phase, the recorder output is a maximum. If they are out of phase, the recorder output is a minimum. This system of phase sensitive detection further reduces the range of frequencies contributing to the spectrometer noise to a very narrow band of about 1 Hz around 100 kHz.

The effect of modulation is shown schematically in Figure 3.4. The phase of the signal response changes at the centre of the resonance and so the effect of using phase sensitive detection is for the resonance to be recorded as a first derivative lineshape.

The optimal modulation amplitude which should be used in the experiment is determined by the width of the resonance. The modulation amplitude should be less

than $\frac{1}{100}$ th of the line width. If the modulation amplitude is too big, the resonance will be subject to modulation broadening and the lineshape may be distorted. This may prevent the resolution of weak hyperfine coupling. If the modulation amplitude is too low, the signal intensity will be reduced unnecessarily.

The spectrometer is equipped with an automatic frequency control device (AFC). The energy density in the resonant cavity is very sensitive to the frequency of the incident microwave radiation. In order to ensure that the frequency variation is much less than the width of the sample resonance, the AFC locks the klystron frequency to the frequency of the sample cavity.

Interpretation

A wealth of information may be obtained from ESR. The position of the resonance determines the g -value which is equal to 2.0023 if there is only a spin contribution to the angular momentum of the unpaired electron, and deviates from this value if there is an orbital contribution too. The g -value is given approximately by the formula

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad (3.4)$$

which is exact when Russell-Saunders coupling applies, and L and S are good quantum numbers. g is dependent on the electronic state of the ion.

To determine the shape of the ESR spectrum, one solves the Bloch equations which describe the dynamic behaviour of a collection of spins in a magnetic field [111]. The Bloch equations for a system of total magnetisation $\vec{M}$ in a field $\vec{H}_0$ are

$$\frac{dM_z}{dt} = \gamma(\vec{H}_0 \times \vec{M})_z + \frac{M_0 - M_z}{T_1} \quad (3.5)$$

$$\frac{dM_x}{dt} = \gamma(\vec{H}_0 \times \vec{M})_x - \frac{M_x}{T_2} \quad (3.6)$$

$$\frac{dM_y}{dt} = \gamma(\vec{H}_0 \times \vec{M})_y - \frac{M_y}{T_2} \quad (3.7)$$

where M_0 is the equilibrium magnetisation, γ is the gyromagnetic ratio of the electron, T_1 is the spin-lattice relaxation time and T_2 is the spin-spin relaxation time which characterises the loss of phase coherence of the spins.

Solution of the Bloch equations produces components of the magnetisation which are in and out of phase respectively with the microwave field. In fact the response of any linear system to a time dependent perturbation is characterised by a real in-phase component called the *dispersion* and an imaginary out-of-phase component called the *absorption*. These contain the same information but most spectroscopic experiments measure the latter.

So the effects of the microwave field are described by a complex susceptibility:

$$\chi = \chi' - i\chi'' \quad (3.8)$$

where χ' and χ'' are the Bloch susceptibilities.

$$\chi' = \frac{1}{2} \cdot \frac{\gamma M_0(\omega_0 - \omega)}{\gamma^2 H_1^2(T_1/T_2) + (1/T_2)^2 + (\omega_0 - \omega)^2} \quad (3.9)$$

$$\chi'' = \frac{1}{2} \cdot \frac{\gamma M_0(1/T_2)}{\gamma^2 H_1^2(T_1/T_2) + (1/T_2)^2 + (\omega_0 - \omega)^2} \quad (3.10)$$

One relates the out-of-phase susceptibility, χ'' , to the power dissipated in the sample at resonance according to:

$$f(\omega) = \frac{A\gamma M_0(1/T_2)}{\gamma^2 H_1^2(T_1/T_2) + (1/T_2)^2 + (\omega_0 - \omega)^2} \quad (3.11)$$

where A is a proportionality constant dependent on instrumental parameters such as the spectrometer gain, the amount of sample and the modulation amplitude. $f(\omega)$ has a maximum when ω is equal to ω_0 , the natural resonance frequency.

To avoid saturation of the resonance which can occur when the power is large (large H_1) or relaxation is slow (large T_1), one keeps H_1 small and so

$$f(\omega) = \frac{A\gamma M_0(1/T_2)}{(1/T_2)^2 + (\omega_0 - \omega)^2} \quad (3.12)$$

This gives a Lorentzian lineshape which is experimentally observed for a magnetic solid in which the moments are well separated or in solution. The lineshape analysis for a collective magnet is more complicated and will be considered in Section 3.5. The intensity of the resonance determined by double integration of the first derivative spectrum is proportional to the magnetic susceptibility of the material. The full-width at half-maximum of the resonance corresponds to the inverse of T_2 , the spin-spin correlation time. This is equal to the width between the two peaks of the first derivative spectrum.

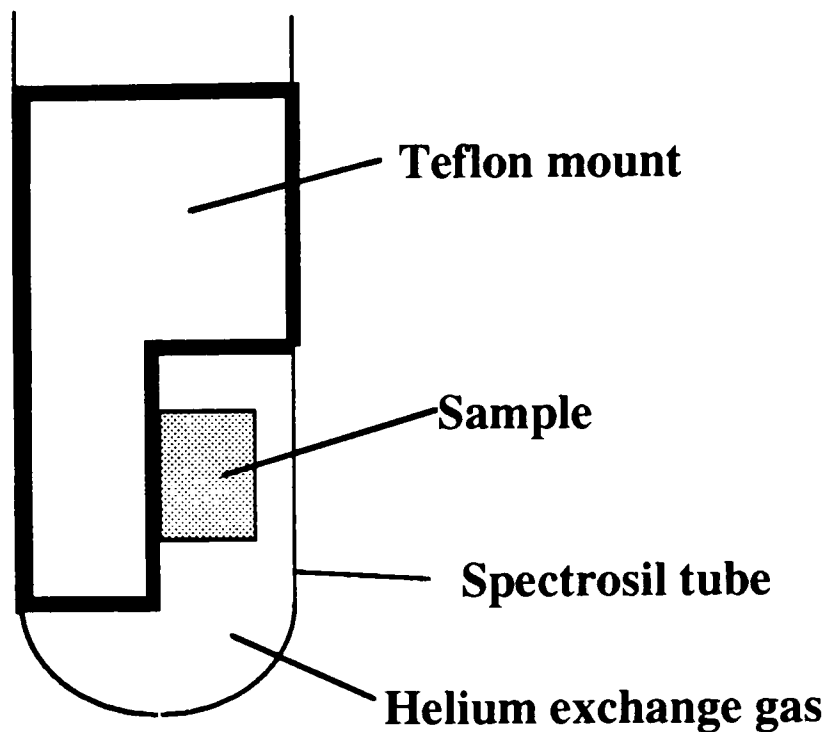


Figure 3.5: The teflon sample mount used in these experiments which allows an air sensitive single-crystal to be oriented accurately within the spectrometer. The sample was attached to the teflon using a small amount of vacuum grease which is not paramagnetic.

3.4 ESR experiments on pure and diluted CFTH

ESR measurements on each sample were carried out using a 9.3GHz Varian E-Line Century Series EPR Spectrometer at the Inorganic Chemistry Laboratory, University of Oxford. A single crystal with approximate dimensions $1 \times 1 \times 2$ mm was mounted on a piece of teflon and this was sealed inside a spectrosil (non-paramagnetic quartz obtainable from Multilab silica glass-blowers) tube in order to prevent dehydration of the sample. The teflon sample mount is shown in Figure 3.5. If a suitable small crystal was not available, one was cut from a larger crystal using a scalpel. The sample was oriented by eye under a microscope using the crystal morphology [51] so that the ab plane, containing the Cu^{2+} ions coupled by J , was vertical. This could be achieved to within about 3° . The magnetic component of the microwave field, $\vec{H}_1$, was also vertical and the applied magnetic field, $\vec{H}_0$, was horizontal.

3.4.1 Measurement of the g -value of pure CFTH as a function of angle

g -value anisotropy

For an ion in a very isotropic environment (eg. one with O_h symmetry), the value of g in Equation 3.3 is independent of the orientation of the crystal with respect to the field. The numerical value of g is determined by the extent of spin-orbit coupling in the ion. If the symmetry is lowered from O_h , the size of the induced orbital component is dependent on the orientation of the ionic site with respect to the applied field. If the site is of a sufficiently high symmetry that a rotation axis of order 3 or greater is retained, the g -value measured in an ESR experiment will arise from two components, $g_{||}$ and $g_{\perp}$, and is given by

$$g_{eff}^2 = g_{||}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta \quad (3.13)$$

where θ is the angle between the applied field and the highest symmetry axis. $g_{||}$ is the g -value measured when the field is parallel to this axis, and $g_{\perp}$ is the value when the field is perpendicular to the axis.

For a system such as CFTH in which the highest order symmetry axis is C_2 , the measured value of g , g_{eff} is expressed as a diagonal tensor

$$g_{eff}^2 = \begin{bmatrix} l_x & l_y & l_z \end{bmatrix} \begin{bmatrix} g_{xx}^2 & 0 & 0 \\ 0 & g_{yy}^2 & 0 \\ 0 & 0 & g_{zz}^2 \end{bmatrix} \begin{bmatrix} l_x \\ l_y \\ l_z \end{bmatrix} \quad (3.14)$$

and $l_x = \cos \theta_x$ etc. where θ_x is the angle between the applied field and the principal axis x . x , y and z are orthogonal axes, although in general one does not know their directions with respect to the crystallographic axes. Thus in order to determine the three components of the diagonal g -tensor, one chooses a set of three orthogonal axes, and uses the relation

$$g_{eff}^2 = \begin{bmatrix} l_x & l_y & l_z \end{bmatrix} \begin{bmatrix} g_{xx}^2 & g_{xy}^2 & g_{xz}^2 \\ g_{xy}^2 & g_{yy}^2 & g_{yz}^2 \\ g_{xz}^2 & g_{yz}^2 & g_{zz}^2 \end{bmatrix} \begin{bmatrix} l_x \\ l_y \\ l_z \end{bmatrix} \quad (3.15)$$

To determine the elements of this tensor, one orients the crystal so that the field is in a plane described by two of these axes, and measures the g -value when each of these two axes makes an angle of $\theta = 0^\circ, 45^\circ$ and 90° with the field. This procedure is then repeated with the crystal oriented in the other two inequivalent orientations. Once all the elements have been determined, the general g -tensor can then be diagonalised to produce the components of the diagonal g -tensor.

Experimental

In order to perform the above analysis on CFTH, a well-formed crystal was chosen and the x , y and z axes for the experiment were defined as nearly as possible to be along the a , b and c^* crystallographic directions respectively. The crystal was then rotated in 10° intervals through an angle θ about a vertical axis and the spectrum was recorded at room temperature as a function of θ . At room temperature, there is a single resonance with a width of about 250 G. This is considerably larger than the linewidth of 40 G for an isolated Cu^{2+} ion in this crystal structure as measured by substituting a small amount ($\simeq 1\text{at}\%$) of Cu into a crystal of the isomorphous $\text{Mg}(\text{HCO}_2)_2 \cdot 4\text{H}_2\text{O}$. The broadening is due to the spin-spin interactions discussed in the next section. The g -value in each orientation was determined relative to that of powdered diphenyl picryl hydrazyl (DPPH) which has a g -value of 2.0036. The variation of the g -value with angle in the three orientations is shown in Figure 3.6. There is clearly anisotropy in all three directions which reflects the low symmetry ($\bar{1} = C_i$) of the Cu^{2+} ion in CFTH. The anisotropy is smallest when the field is confined within the planes of Cu^{2+} ions.

By using the values of g_{eff} at $\theta = 0^\circ$ and 90° in each orientation, we determine the diagonal elements of the general g -tensor to be

$$g_{xx} = 2.14$$

$$g_{yy} = 2.09$$

$$g_{zz} = 2.44$$

Use of the g -value at $\theta = 45^\circ$ to determine the values of the off-diagonal terms

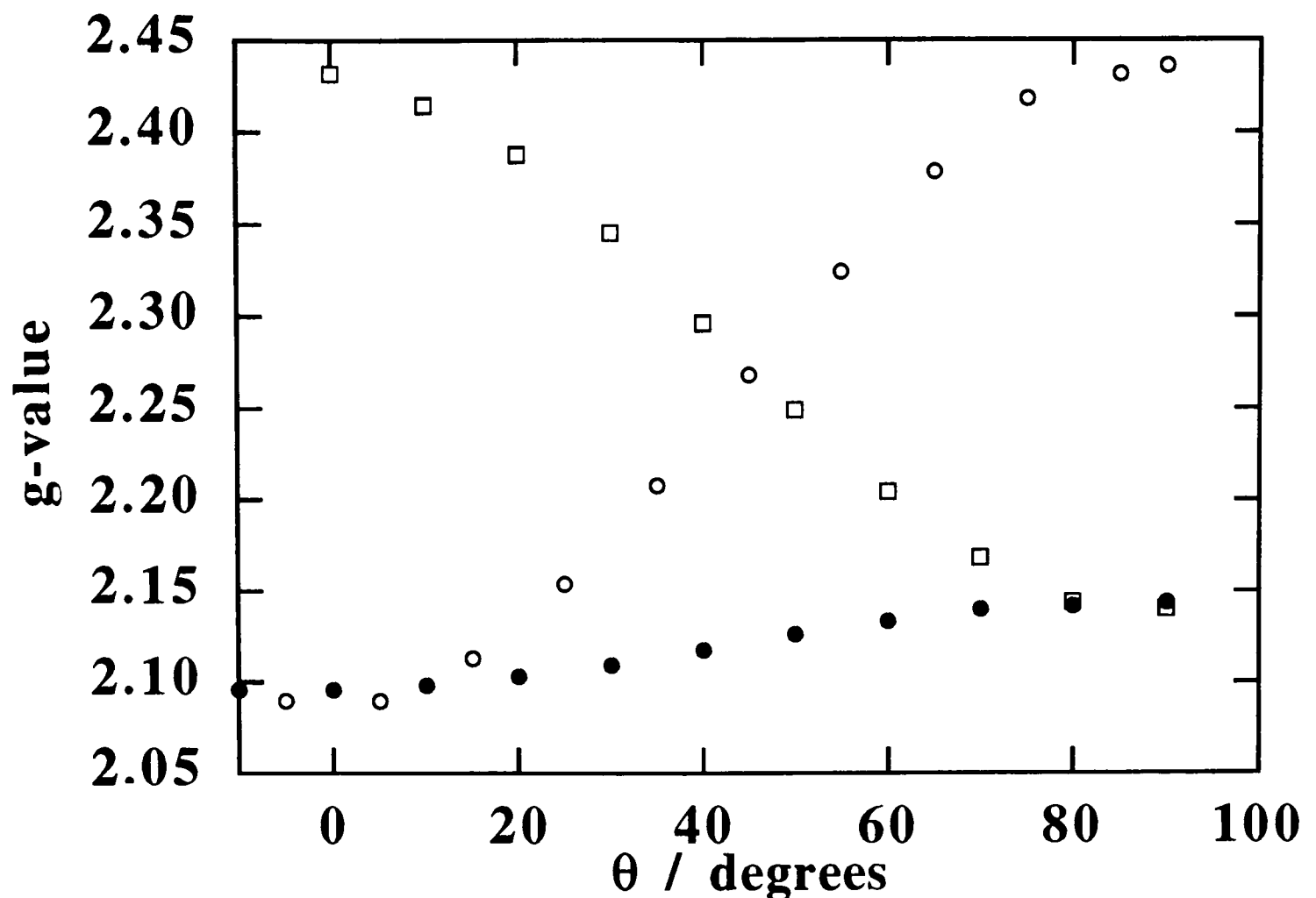


Figure 3.6: The angular dependence of the g -value of CFTH in three mutually perpendicular orientations. Open squares: H is in the bc^* plane and $\theta = 0$ when H is parallel to c^* . Open circles: H is in the c^*a plane and $\theta = 0$ when H is parallel to a . Closed circles: H is in the ab plane and $\theta = 0$ when H is parallel to b .

revealed that these were all close to 0. In fact these terms were so small relative to the diagonal terms that they could not be determined reliably due to the size of the errors (a few degrees) in orienting the samples. This indicates that the axes chosen for the experiment are close to the principal axes of the g -tensor. Equating the diagonal terms listed above with the three components of the diagonal g -tensor is a slight approximation, but a close one, and certainly enables us to remark on the degree of g -anisotropy present in CFTH.

This behaviour was qualitatively and quantitatively the same as that observed by Shimada *et al.* [107]. The variation in g -value can be understood from a knowledge of the relative energies of the d -orbitals in an octahedral ligand field subjected to a Jahn-Teller distortion. The unpaired electron is in the highest energy orbital and this has $d_{x^2-y^2}$ character. Rotation of this half-filled orbital about the z axis leads to an angular momentum contribution along the z direction which in this case is

perpendicular to the plane of Cu^{2+} ions. This is expected to increase the value of g_{zz} relative to g_{xx} and g_{yy} , and this is the observed behaviour.

The fact that the g -value is anisotropic suggests immediately that this is not a true Heisenberg system. There will almost always be departures from truly isotropic spin symmetry, however the g -anisotropy corresponds to an energy of about $3 \times 10^{-4} \text{ meV}$ which is considerably smaller than the nearest neighbour in-plane exchange term in the Hamiltonian of about 7 meV , and is of the order of the interplanar exchange. The inelastic neutron scattering experiments described in Chapter 2 are insensitive to such a small anisotropy and so the moment appears to be Heisenberg. The critical behaviour below T_N suggests that there is some XY-type anisotropy [24].

3.4.2 Temperature dependent ESR spectroscopy

Experimental details

In this series of experiments, the pure and doped samples were oriented with the applied magnetic field perpendicular to the planes of metal ions. The samples were cooled using an Oxford Instruments ^4He flow cryostat and the temperature was measured using an Oxford Instruments ITC4 Intelligent Temperature Controller. The temperature was varied solely by adjusting the flow rate of cold He gas through the cryostat and so the temperature controller was just used as a thermometer. Liquid nitrogen was used as the single fixed reference point for the temperature. Because of the duration of the series of experiments (about one month), the value of this fixed point was found to change by up to 0.4 K due to the effects of atmospheric pressure which fluctuated between 998 and 1035 millibar; the measured temperature was corrected for this, since an error of this size is significant near the 3D ordering transition.

The top face of each sample was mounted in the same position in the tube to within 0.1 mm and the tube was mounted in the same position inside the cryostat to within 0.2 mm . This was in order to eliminate systematic errors in measuring the temperatures of different samples due to them being located in different positions

in the temperature gradient within the cryostat. The tube was purged with He gas before it was sealed to ensure the best thermal contact possible between the sample and the cryostat. The samples were all of the same volume (about 2 mm^3) to within a factor of two. This was not only to ensure that each one reached thermal equilibrium over the same time-scale, but to ensure that there was no difference in the instrumental broadening of the signals of different samples. Such broadening was observed by Seehra and Castner (SC) [67, 106] who used samples varying in size from 0.4 mm^3 to 10 mm^3 and arises from magnetic losses in the sample when it is large compared with the microwave cavity. Comparison of the spectra of two undoped crystals with volumes of 2 mm^3 and 12 mm^3 showed no difference in the linewidths at all temperatures. This indicates that our cavity is sufficiently large for the sample size effect to be small for the samples used. However, we did notice that when the sample was large and the temperature was close to T_N there was appreciable peak asymmetry due to microwave absorption by the sample.

A typical equilibration time of seven minutes was allowed while the temperature was changed by about 2 K in the 25 K region. However the temporal dependence of the sample signal intensity during the change would suggest that thermal equilibration had occurred over about two or three minutes.

The spectrum at each temperature was recorded and fitted to a Lorentzian form (Equation 3.12) using a BASIC program running on a Research Machines 380Z computer.

Treatment of impurity peak

The resonance occurs at $g=2.36$ in this configuration and was recorded at a number of temperatures from about 5 degrees below T_N to room temperature. Very close to T_N , where the resonance is weak, a second peak was observed at a g -value of 2.16. This peak increased greatly in intensity when the sample was allowed to partially dehydrate on exposure to the atmosphere for three hours at room temperature. The peak was thus ascribed to the small quantities of pale blue dehydrated material visible on the surface of the sample. This 'impurity' peak was also observed by SC [106] who

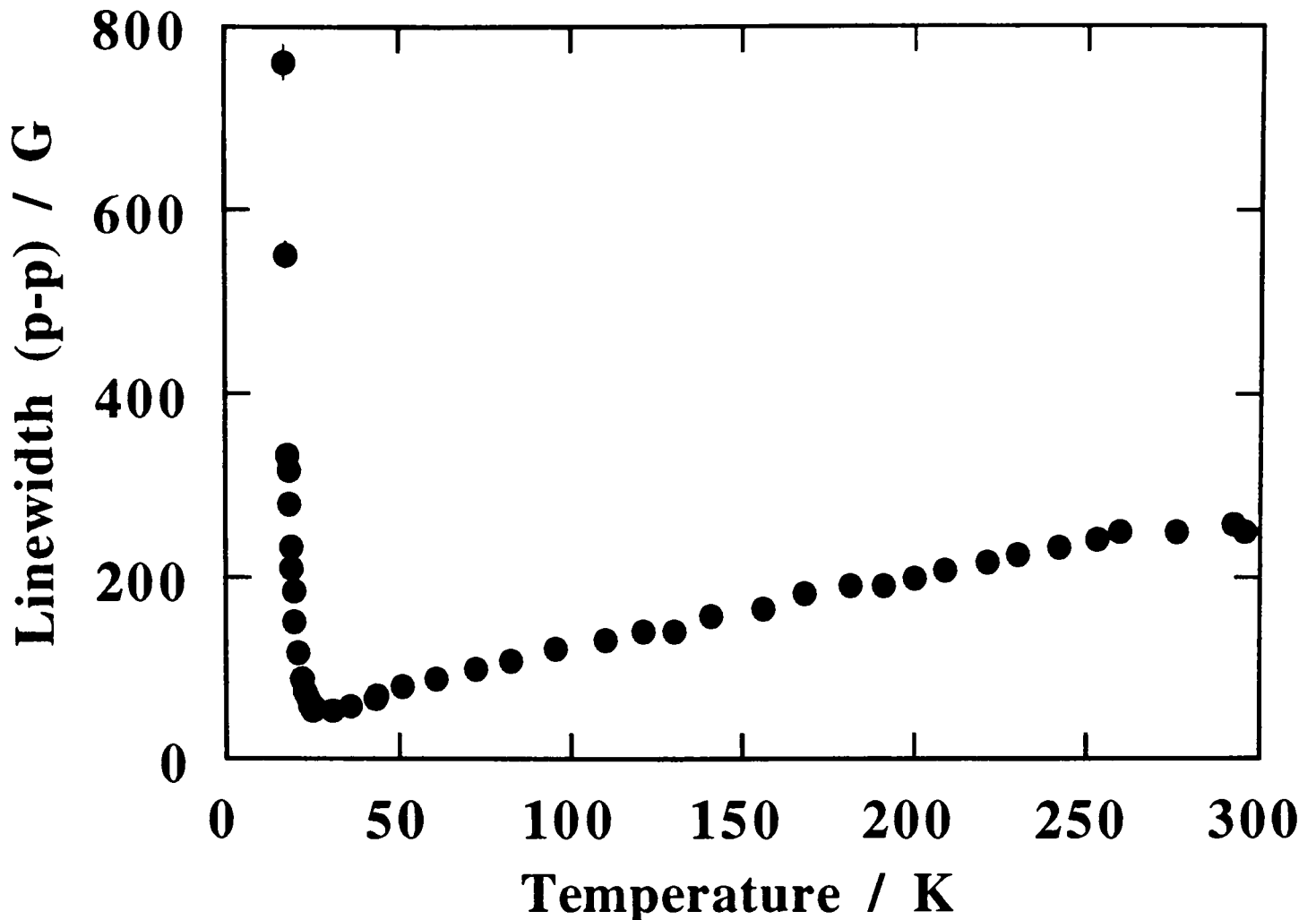


Figure 3.7: The dependence of the ESR linewidth of CFTH on temperature. The linear decrease in width is in agreement with the predictions of theory for the 2D antiferromagnet.

also ascribed it to dehydrated material. If the impurity peak was intense it was found to partially obscure the signal close to T_N , although in all cases at least half of the signal could be fitted. The Lorentzian function used in the fitting program was found to describe the line shape accurately between 300 and 25 K but less well at lower temperatures. The function was used throughout however, because it was found to give an accurate measure of the full width at half maximum (FWHM) at all temperatures. The error in the measurement of the linewidth is typically between 1 and 3 G.

Temperature dependence of the linewidth

For the pure material, the linewidth decreases linearly from 250 G at room temperature to around 100 G at 70 K as shown in Figure 3.7.

From 70 to 30 K, the decrease is still linear, but with a larger gradient. The linewidth reaches a minimum of around 50 G at about 25 K and then increases steeply

as the magnetic correlation length increases rapidly close to T_N . This behaviour is discussed in the next section. The divergence is so steep that it is approximately linear.

SC suggest that the change in gradient at 70 K is related to the susceptibility maximum at around that temperature observed by Seehra [62].

Temperature dependence of the Intensity

The intensity of the resonance determined by double integration of the spectrum increases linearly to a broad maximum before decreasing sharply as T_N is approached. This is shown in Figure 3.8 for CFTH. This susceptibility maximum is ascribed to the gradual onset of in-plane short range ordering. It is much more distinct measured by ESR than by conventional DC magnetometry (Section 3.6.3).

Temperature dependence of the g -value

The position of the resonance with the crystal in a fixed orientation is independent of temperature between room temperature and just above T_N at which point it increases sharply as shown in Figure 3.9. Close to T_N , the correlated regions in the plane are large. The applied magnetic field induces in these regions a field which opposes $\vec{H}_0$ and causes a larger field to need to be applied before resonance will occur. The increase of g -value corresponds to an internal field associated with the ordering of about 300 G.

Effect of dilution on the temperature dependence

As the concentration of the diamagnetic dopant ion increased, there were changes in the behaviour of the linewidth as a function of temperature. Firstly, the temperature at which the divergence occurred decreased linearly with increasing dopant concentration. Since the divergence is linear and very rapid close to T_N , this provides a way of accurately determining the differences in T_N of different samples. Secondly, the resonances of doped samples were found to be narrower than those of the pure material at all temperatures. The Zn^{2+} -doped samples containing about 15% Zn^{2+}

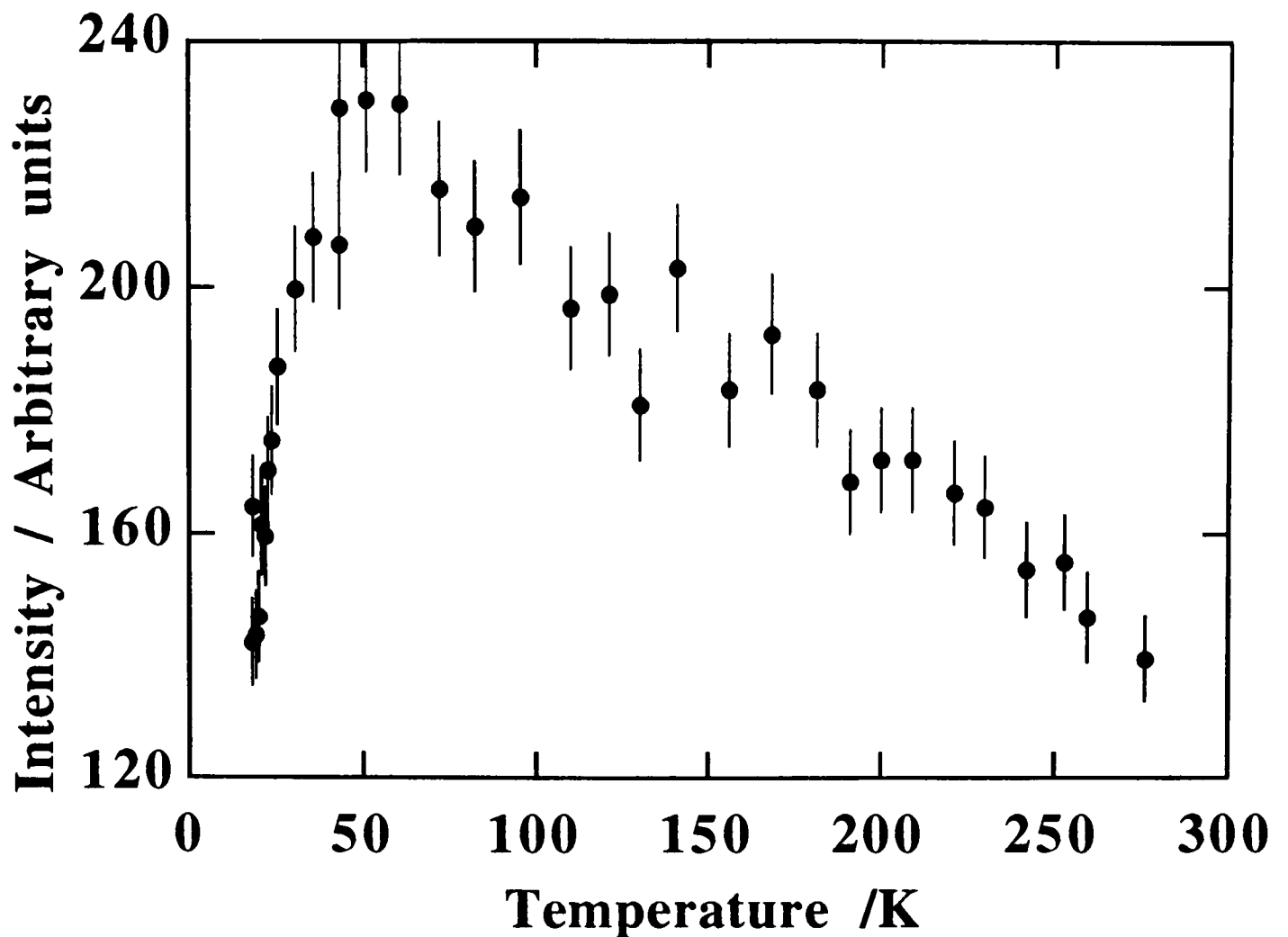


Figure 3.8: The dependence of the ESR signal intensity with the applied field perpendicular to the planes of CFTH on temperature. This is a measure of the magnetic susceptibility.

possess resonances whose widths reach a minimum of about 36 G. The temperature at which the minimum width occurs also depends on dopant concentration because it is linked to the value of T_N .

3.5 Discussion of ESR measurements

3.5.1 Dependence of the ESR linewidth of pure CFTH on temperature

Let us first consider the effects leading to ESR line broadening in collective magnets and the effects of temperature on these. These are well covered by Pake and Estle [112] and by Bencini and Gatteschi [109].

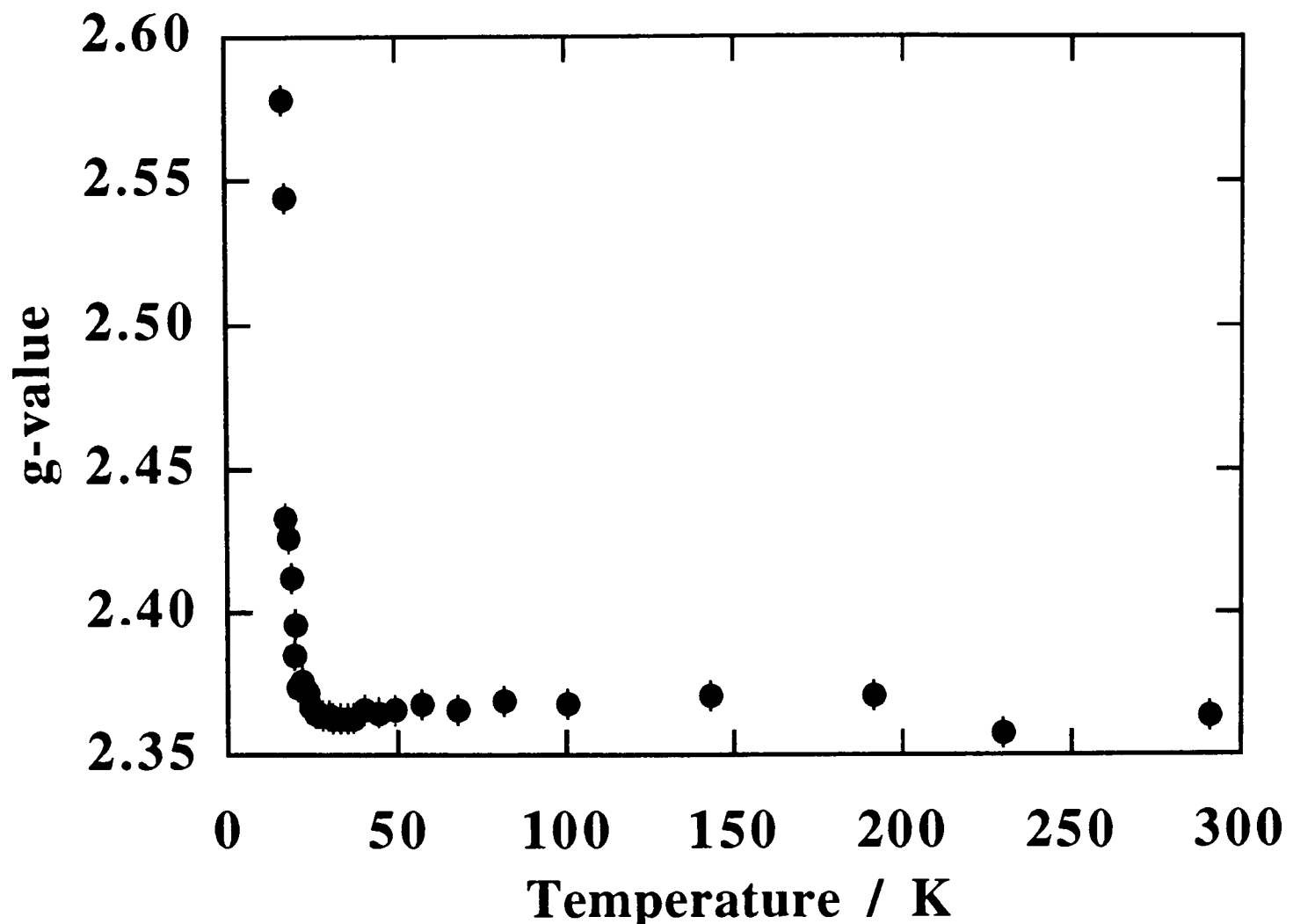


Figure 3.9: The dependence of the g -value with the applied field perpendicular to the planes of CFTH on temperature.

Dipolar Broadening

When a magnetic field is applied to the sample, the Zeeman splitting of the levels produces a term $\mathcal{H}_z$ in the Hamiltonian. There are also terms arising from the dipolar interaction between all pairs of spins in the lattice, $\mathcal{H}_{dip}$, and from the exchange interaction between pairs of nearest-neighbour spins, $\mathcal{H}_{ex}$. So in the absence of other exchange interactions which are present in CFTH, the Hamiltonian in the field is:

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_{dip} + \mathcal{H}_{ex} \quad (3.16)$$

where the different components are as follows:

$$\mathcal{H}_z = g\mu_B \sum_{i=1}^N \vec{H}_0 \cdot \vec{S}_i \quad (3.17)$$

$$\mathcal{H}_{dip} = g^2 \mu_B^2 \sum_{ij} \left[\frac{\vec{S}_i \cdot \vec{S}_j}{r_{ij}^3} - \frac{3(\vec{S}_i \cdot \vec{r}_{ij})(\vec{S}_j \cdot \vec{r}_{ij})}{r_{ij}^5} \right] \quad (3.18)$$

$$\mathcal{H}_{ex} = -J \sum_{ij} \vec{S}_i \cdot \vec{S}_j \quad (3.19)$$

$\mathcal{H}_z$ is a single-ion term, the summation in $\mathcal{H}_{dip}$ is over all pairs of spins in the lattice and $\mathcal{H}_{ex}$ is over all pairs of nearest-neighbour spins. The part of the expression for $\mathcal{H}_{dip}$ inside the summation should be expanded to

$$\begin{aligned}\mathcal{H}_{dip} &= \frac{1}{2}(3 \cos^2 \theta_{ij} - 1)(3S_{iz}S_{jz} - \vec{S}_i \cdot \vec{S}_j) \\ &- \frac{3}{2} \sin \theta_{ij} \cos \theta_{ij}(S_{iz}S_{j+} + S_{i+}S_{jz} + S_{iz}S_{j-} + S_{i-}S_{jz}) \\ &- \frac{3}{4} \sin^2 \theta_{ij}(S_{i+}S_{j-} + S_{i-}S_{j+}) \\ &+ \text{higher terms}\end{aligned}$$

The first term in this expansion couples states with $\Delta M = 0$, the second states with $\Delta M = \pm 1$ and the third states with $\Delta M = \pm 2$. The main transition due to the simple Zeeman splitting has $\Delta M = \pm 1$, but one effect of the dipolar term is to produce other resonances at zero frequency and at frequencies which are multiples of the natural resonance frequency. These weaker resonances will be ignored in the future discussion.

The second effect of the dipolar term is to cause a broadening of the main resonance line. The interaction causes each spin to come into resonance at a slightly different frequency. For a crystal, there will be the order of N_A different transitions, where N_A is the Avogadro number. This produces a symmetric broad line centred around the natural frequency, which is Gaussian in shape because it is the sum of a series of individual sharp transitions. In quantum mechanical terms, one can say that $\mathcal{H}_{dip}$ does not commute with $\mathcal{H}_z$. The linewidth produced by the dipolar interaction is proportional to the dipolar energy:

$$E_{dip} = \frac{g^2 \mu_B^2}{r_0^3} \quad (3.20)$$

Exchange narrowing

It is possible to express the lineshape in terms of so-called moments. The zeroth moment, M_0 is the expression for the intensity of the line. The second moment, M_2 is the mean square width of the line and is equal to the square of the dipolar energy in Equation 3.20. The expression for M_2 does not contain the exchange term in the

Hamiltonian, so this interaction does not lead to broadening of the resonance. ie. $\mathcal{H}_{ex}$ does commute with $\mathcal{H}_z$.

The fourth moment of the lineshape, M_4 (odd moments are zero for a symmetric line) does contain the exchange energy.

$$M_4 = J^2 E_{dip}^2 + E_{dip}^4 \quad (3.21)$$

As J increases relative to E_{dip} , M_4 increases, but M_2 and M_0 remain unchanged. The effect of this is that some of the Gaussian intensity is removed from the wings of the resonance and appears in the centre. This means that the resonance becomes narrowed as an effect of the exchange interaction between nearest-neighbour spins. The shape also changes, becoming increasingly Lorentzian as J increases.

Another way of looking at this is to say that a large exchange interaction corresponds to rapid fluctuation of nearest neighbour spins (at a frequency proportional to the size of the exchange constant) which averages the dipolar field which any electron sees to zero and suppresses the dipolar broadening. Typically, the strength of the dipolar interaction corresponds to a frequency of 10^8 or 10^9 Hz. The exchange interaction can easily be an order of magnitude larger than this in frequency units and so the exchange narrowing regime is usually the norm.

Exchange narrowing of the resonance is analogous to the motional narrowing often observed in solution NMR. As well as depending on the size of J , the efficiency of exchange narrowing depends on the number of exchange pathways through which a moment interacts with its neighbours. Exchange narrowing in 3-dimensions is very effective and leads to lines having a mainly Lorentzian shape, but still being somewhat Gaussian in the wings. In 1D, there are fewer exchange pathways and the lines are generally appreciably Gaussian unless the exchange constant is very large. The 2D case is usually intermediate in behaviour. In the case of CFTH it was found that a Lorentzian fit was generally very good and gave a reliable value for the linewidth.

Other terms in the Hamiltonian which affect the linewidth

As well as the dipolar interaction, significant broadening can arise from other terms in the Hamiltonian. The antisymmetric exchange interaction can be very significant

if it is allowed by symmetry. Additional contributions from symmetric anisotropic exchange and crystal field fine structure are usually small enough to be neglected. Richards and Salamon [113] showed that when the major contribution to linebroadening in a 2D system arises from the dipolar interaction, the relaxation process is dominated by long wavelength phonon modes and this leads to a linear but weak dependence of the linewidth on temperature when $T \gg T_N$. This is the situation in K_2MnF_4 in which the planes are centrosymmetric and there is no possibility of an antisymmetric exchange interaction. In CFTH however, the planes are non-centrosymmetric, as Figure 2.1 in Chapter 2 shows, due to the monoclinic distortion and the resulting cross-terms in the exchange Hamiltonian lead to a Dzyaloshinsky-Moriya (DM) antisymmetric exchange interaction, the evidence for which is discussed in Chapter 2 and in the current chapter. This interaction is significant in CFTH and

$$J_D \simeq \phi J \frac{\Delta g}{g} \quad (3.22)$$

[7] where Δg is the departure of the g -value from the free-ion value of 2 and ϕ is the rotation angle between the CuO_6 octahedra. ϕ is approximately 40° , Δg is 0.12 when the magnetic field is parallel to the planes of copper ions, and so using a value of J of 7 meV, we obtain a value for J_D of 0.32 ± 0.03 meV which is in fairly close agreement with the value obtained from the value of the energy gap in the spin-wave dispersion (0.46 meV).

SC determined [67, 106] that the dominant contribution to line broadening in CFTH arises from the phonon-modulated DM interaction and that in this situation the linewidth is also linear in T when $T \gg T_N$.

SC fitted ΔH , the linewidth measured in gauss, to the empirical form of Equation 3.23.

$$\Delta H = \alpha + \beta T + F(J, T) \quad (3.23)$$

where α is the linewidth extrapolated to $T=0$ from the linear region above 70K and β is the gradient in this region arising from the antisymmetric exchange interaction discussed above. The third term is a function of the exchange constant and the temperature. It is only important very close to T_N and results from the onset of

critical fluctuations which we previously observed in the deuterated material using neutron scattering [73]. This third term is discussed in more detail in the following section. We determined α to be $67 \pm 1\text{G}$ and β to be $0.78 \pm 0.03\text{GK}^{-1}$. These values were unchanged for the samples with small concentrations of dopant ($x < 0.03$). Unfortunately measurements above 70 K were not carried out on the samples with larger x since the main motivation for doing the experiments was to investigate the region just above and around T_N . It is likely that the sample dependence of the variation of linewidth with temperature is most pronounced in the critical region, and that the changes in α and β are relatively small. β is usually close to zero, and the value is large in CFTH, presumably because of the large value of the antisymmetric exchange constant.

SC propose that in the high-temperature linear region, the linewidth is given by:

$$\Delta H = \frac{4}{9} \frac{z}{g\mu_B} \frac{(\lambda a)^2 |\bar{J}_D| J^2}{\rho \hbar^3} \langle c \rangle k_B T \quad (3.24)$$

where z is the number of nearest neighbours at distance a , ρ is the density of the crystal, λ is the expression for the change in exchange constant with Cu-Cu separation, $\langle c \rangle$ is the angular average of the velocities of phonons with frequency J , the symmetric exchange constant. $\bar{J}_D$ is the antisymmetric exchange tensor. Because the CuO_6 octahedra tilt with respect to one another, it is very difficult to determine the individual components of the antisymmetric exchange, and it is best treated as a single parameter. Using this formula in the high temperature region, SC determined [91] that the magnitude of the antisymmetric exchange term is about 0.12 meV. This is quite a lot smaller than the other estimates, but reasonable considering approximations made in determining the values of parameters in Equation 3.24.

SC also proposed that the best approximation for the shape of the resonance line was a Lorentzian times an exponential, although the exact form of the lineshape is unimportant when $J^2 \gg M_2$. We used a Lorentzian lineshape at all temperatures because it was found to give a reliable value for the linewidth, and the resonance only adopted a non-Lorentzian shape well out in the wings.

Behaviour of the linewidth in the critical region

Seehra and Castner [110] have determined that the steep increase in the linewidth on cooling in the vicinity of T_N can be fitted to a form given by a prefactor and the size of the exchange constant, J . The ‘critical’ contribution to the linewidth is obtained from the measured width by subtracting the linear dependence in the region *below* 70 K.

$$\Delta H_c = \Delta H - (\alpha + \beta T) \quad (3.25)$$

where we determined α to be 16 G and β to be 1.1 G^{-1} . These values are in close agreement with those obtained by SC using their data ($\alpha=9 \text{ G}$ and $\beta=1.1 \text{ GK}^{-1}$).

SC fitted their data in the region between $1.5T_N$ and $2T_N$ to the following form which is produced by the theory of Chakravarty and Orbach [114] and of Lazuta [115].

$$\Delta H_c = B \frac{\omega_p^2}{\omega_{ex}} \left(\frac{\xi}{a} \right)^3 \frac{(T/2\pi\rho_s)^{\frac{5}{2}}}{(1 + T/2\pi\rho_s)^4} \quad (3.26)$$

where B is a constant of order unity, ω_p^2 is the second moment of the lineshape which is the dipolar energy squared and ω_{ex} is the exchange energy in frequency units. ξ is the 2D correlation length which is defined in Equation 2.24, and $\rho_s \simeq 0.15J$ is the spin-stiffness constant defined in Equation 2.21 and measured in temperature units. ξ depends on ρ_s according to

$$\xi = 0.5a \frac{\exp(2\pi\rho_s/T)}{1 + T/2\pi\rho_s} \quad (3.27)$$

Substituting in our value of $2\pi\rho_s=84 \text{ K}$ obtained from determination of the inverse correlation length in the region between T_N and $2T_N$ described in Section 2.4.4, we find that we can obtain a good fit to the data between 17 K and 34 K, which is the region between T_N and $2T_N$ in which the CHN theory discussed in Chapter 2 is valid. The fit is shown in Figure 3.10. The prefactor which contains the constant B , the dipolar energy (which is contained in the expression for the second moment) and the exchange energy was determined to be 0.091.

SC found that they could not determine the linewidth for their sample very close to T_N , and so their fit is only in the region $1.5T_N$ to $2T_N$. We have extended their result into the region of temperature where the linewidth varies more steeply with

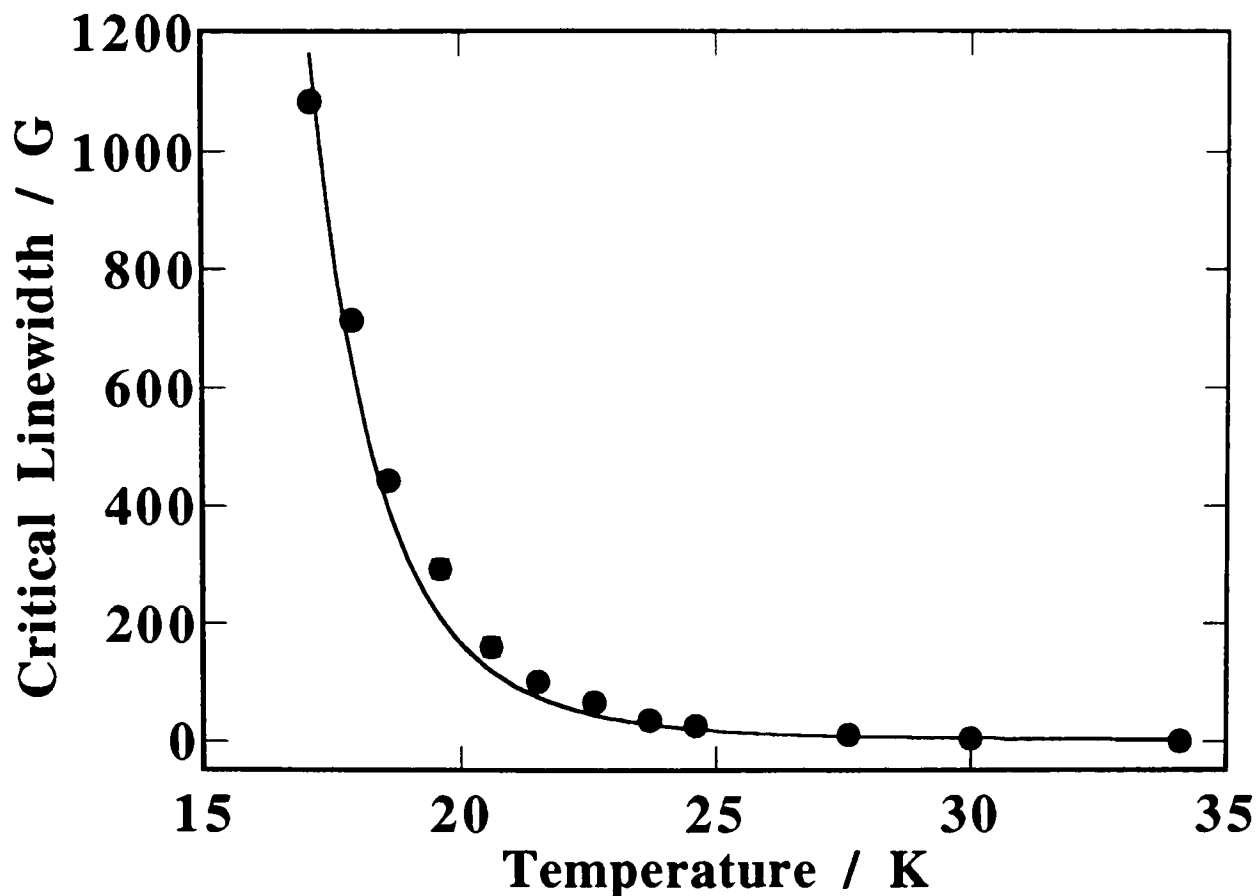


Figure 3.10: The fit to the critical contribution to the ESR linewidth between T_N and $2T_N$ using Equation 3.26.

temperature, and have confirmed that the theoretical dependence of the linewidth on J is valid in this region too.

Behaviour of La_2CuO_4

According to SC, the failure to observe an ESR signal from La_2CuO_4 is due to the extremely large value of J which causes the correlation length to be large well above T_N . The ξ^3 dependence of the critical linewidth means that at all attainable temperatures, the linewidth is expected to be immeasurably large. This is a further advantage of using CFTH as a model. It has been found [116] that while none of the cuprates with linear Cu-O-Cu exchange paths show ESR signals, those with 90° interactions, and poorer overlap leading to a smaller J , such as $\text{Y}_2\text{Cu}_2\text{O}_5$ and Y_2BaCuO_5 do have ESR signals with $g \simeq 2.1$. This value is similar to the value in CFTH when the field lies in the planes of Cu^{2+} ions.

Determination of the antisymmetric exchange constant using antiferromagnetic resonance

SC have carried out antiferromagnetic resonance measurements on CFTH in the region below T_N [91]. They have determined that the value of J_D is about 0.83 ± 0.02 meV which is consistent with the values which we have obtained using neutron scattering measurements and from the size of the tilting of the CuO_6 octahedra with respect to one another.

3.5.2 Effect of doping on the ESR linewidth

We observed that as the concentration of the magnetic ion decreased, the linewidth at a particular temperature in the region close to T_N also decreased. The measurements were not performed over the whole temperature range for all the samples. Since the linewidth calculated by SC is linear in the number of magnetic neighbours of a particular ion, a decrease in the number of magnetic neighbours of some of the ions will be expected to reduce the linewidth. The decrease in the minimum linewidth as the concentration of the magnetic ion decreases is shown in Figure 3.11. Physically one can say that the broadening mechanisms are affected to a greater extent than the exchange narrowing by magnetic dilution.

3.5.3 Effect of doping on T_N

Results for CFTH

Figure 3.12 shows the FWHM of the ESR signal of the sample plotted against temperature in the region around T_N . Due to the weakness and broadness of the signal at temperatures very close to T_N , it was difficult to determine the absolute value of T_N accurately. For the pure material, T_N was estimated to be the temperature at which the resonance could just be discerned at the maximum sensitivity of the instrument. This was 16.1 ± 0.1 K, which compares well with previous measurements. The rate of increase of ΔH in the transition region was the same for all the samples, hence the *differences* in T_N could be determined to within 0.2 K.

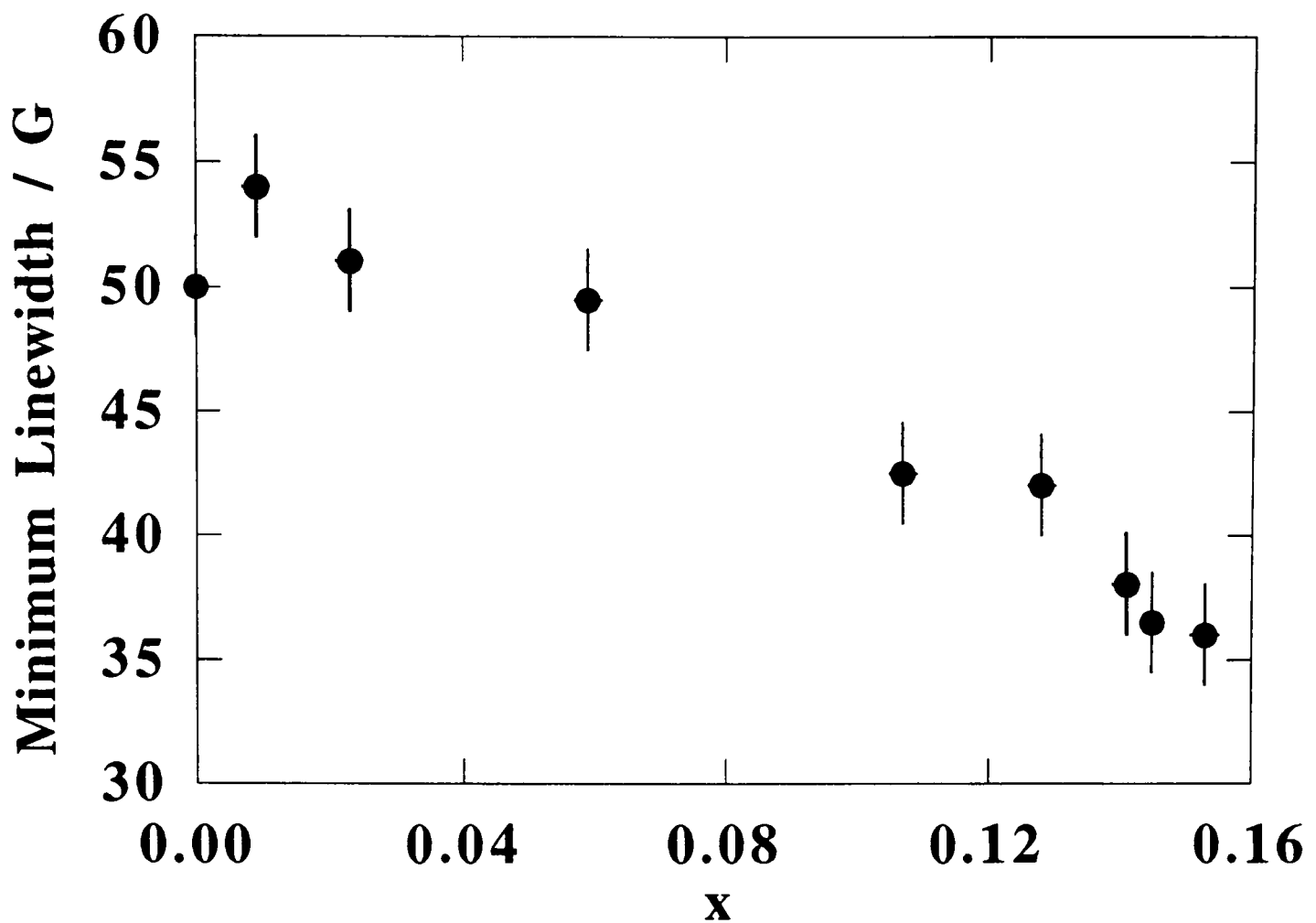


Figure 3.11: The dependence of the minimum ESR linewidth of doped CFTH on the dopant concentration.

x	T_N/K	$T_N(x)/T_N(0)$
0.0	16.5	1.00
0.023	16.1	0.97
0.043	14.9	0.90
0.059	12.6	0.76
0.107	10.5	0.64
0.128	9.6	0.58
0.141	8.1	0.49
0.145	8.3	0.50
0.153	8.6	0.52

Table 3.2: A table of the values of T_N determined for different doped samples of CFTH. $T_N(x)$ was determined by setting $T_N(0)$ equal to the value obtained by neutron scattering measurements, and using the *differences* in T_N obtained from ESR. The data are plotted in Figure 3.13.

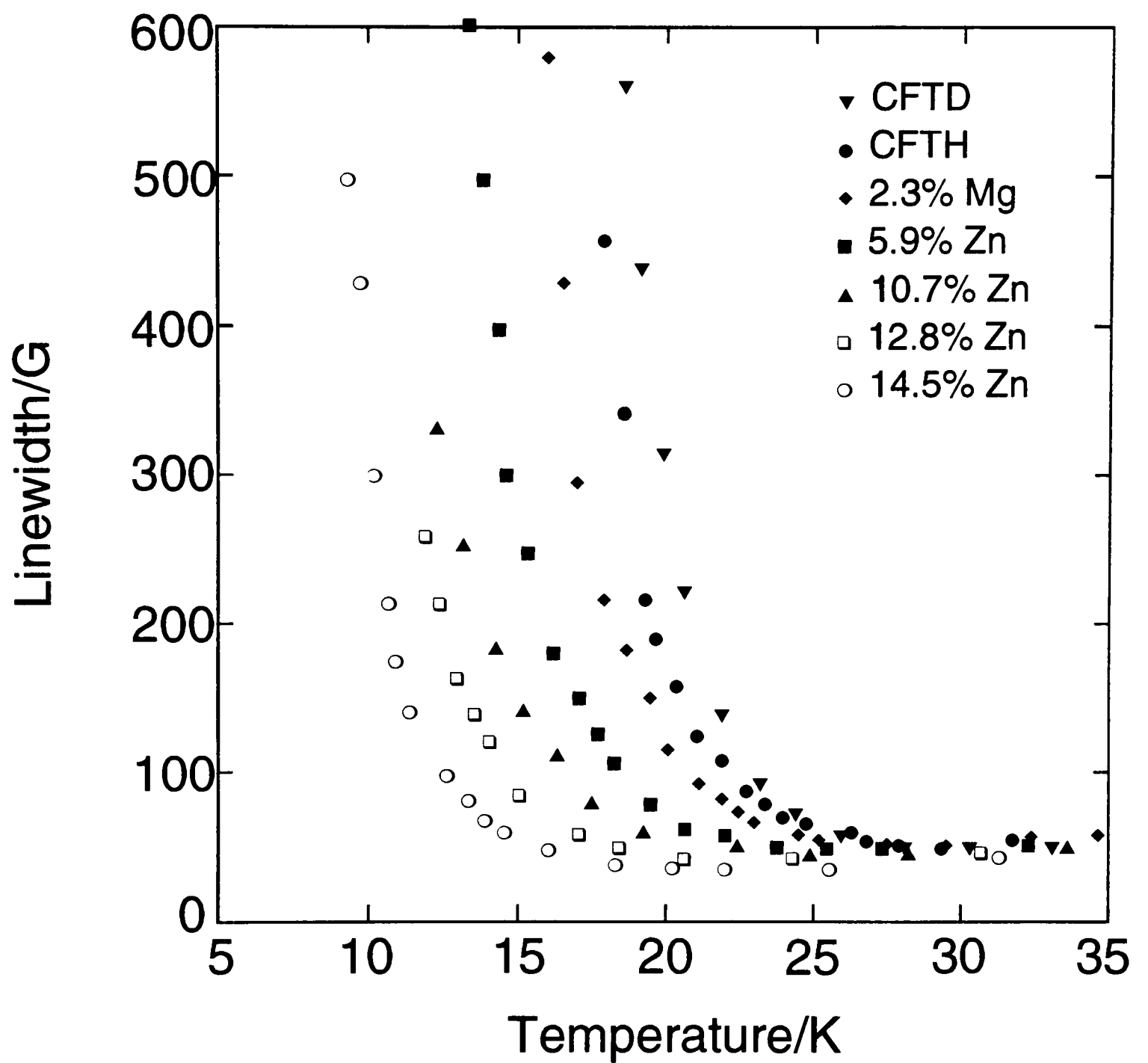


Figure 3.12: The dependence of the ESR linewidth of each of the doped samples on temperature in the region of T_N . The graph shows how accurately one can determine the differences in T_N of compounds with different dopant concentrations.

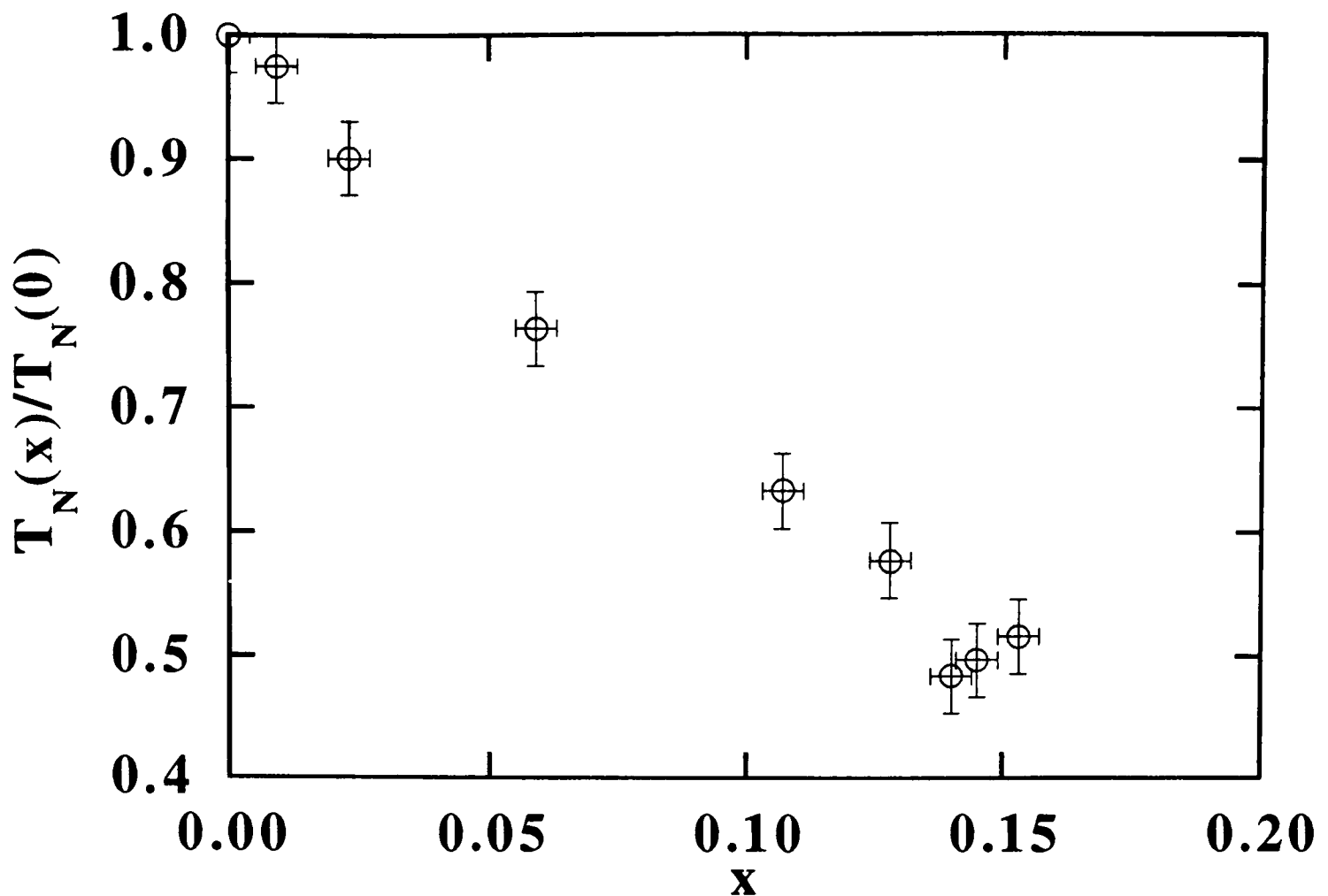


Figure 3.13: A graph showing the rate at which T_N of CFTH is reduced by doping with the diamagnetic impurities Mg^{2+} and Zn^{2+} . x is the mole fraction of the diamagnetic ion in the samples.

The values of T_N in the various doped samples is tabulated in Table 3.2. A plot of $T_N(x)/T_N(0)$, against the fractional concentration, x , of the diamagnetic dopant is shown in Figure 3.13. This plot was found to be very sensitive to the difference in values of T_N but very *insensitive* to the actual values chosen for T_N . The reduction of T_N is linear in x when x is below 0.1 taking the form

$$T_N(x) = T_N(0) \cdot (1 - \alpha x) \quad (3.28)$$

where $T_N(x)$ and $T_N(0)$ refer to the doped and pure material respectively and the constant α is 3.4 ± 0.1 .

The samples containing 2.25% and 4.32% Zn^{2+} were good quality crystals which gave consistent chemical analyses. However, their linewidth behaviour and hence T_N was sample dependent as Figure 3.13 shows. This behaviour cannot be wholly explained by inhomogeneities in the distribution of the diamagnetic ion which are likely to be much larger in magnetically more dilute samples (ie. those containing more Zn^{2+}). Error in positioning the sample in the same place in the temperature gradient of the cryostat by about 2 mm would be required to lead to an error in

measuring the actual temperature of up to 2 K, but considering the precautions taken, the error should not be more than a tenth of this. The source of the discrepancy between different crystals grown from the same solution is difficult to pinpoint.

The transition temperature of the fully deuterated form of the compound CFTD is higher than that of CFTH by about 1.2 K. The lattice constant c is slightly shorter in CFTD [53, 55] because deuterium bonding is stronger than hydrogen bonding. This leads to a slightly stronger inter-planar coupling, J' , in CFTD. It is J' which drives the transition to 3D ordering and so T_N is higher in CFTD.

Comparison with other 2D systems

The value of α in Equation 3.28 for CFTH: Zn^{2+} of 3.4 should be compared with values of between 3.0 and 3.5 obtained for other square Heisenberg ferro- and antiferromagnets [101, 105, 117]. Comparison of the behaviour of a number of 2D systems, including La_2CuO_4 which has been doped with Mg^{2+} and Zn^{2+} [101], is shown in Figure 3.14. CFTH: Mg^{2+} and CFTH: Zn^{2+} show behaviour very similar to other layered Heisenberg systems, including La_2CuO_4 , at low dopant concentrations. The problems encountered when doping La_2CuO_4 discussed at the beginning of this chapter, appear to have been surmounted in the work by Cheong *et al.* [101]. These problems do not arise in CFTH, since the method of preparation cannot lead to oxidation as in the cuprates.

As x increases above about 0.1 it appears that T_N is reduced more rapidly in doped CFTH and La_2CuO_4 than in other Heisenberg systems such as K_2CuF_4 and K_2MnF_4 . This is hard to verify without doping CFTH to higher levels. It is clear that the ordering transition temperatures of all the Heisenberg systems decrease much faster on doping than those of Ising systems whose behaviour can be solved exactly. However the apparently ‘universal’ behaviour displayed by the Heisenberg systems at low dopant concentrations may be fortuitous [16].

In every ‘real’ 2D Heisenberg material, long range order is induced by finite Ising-like anisotropy (as with K_2MnF_4) or finite interplane exchange as in the cases of K_2CuF_4 and La_2CuO_4 . Our evidence is that CFTH falls into the latter category,

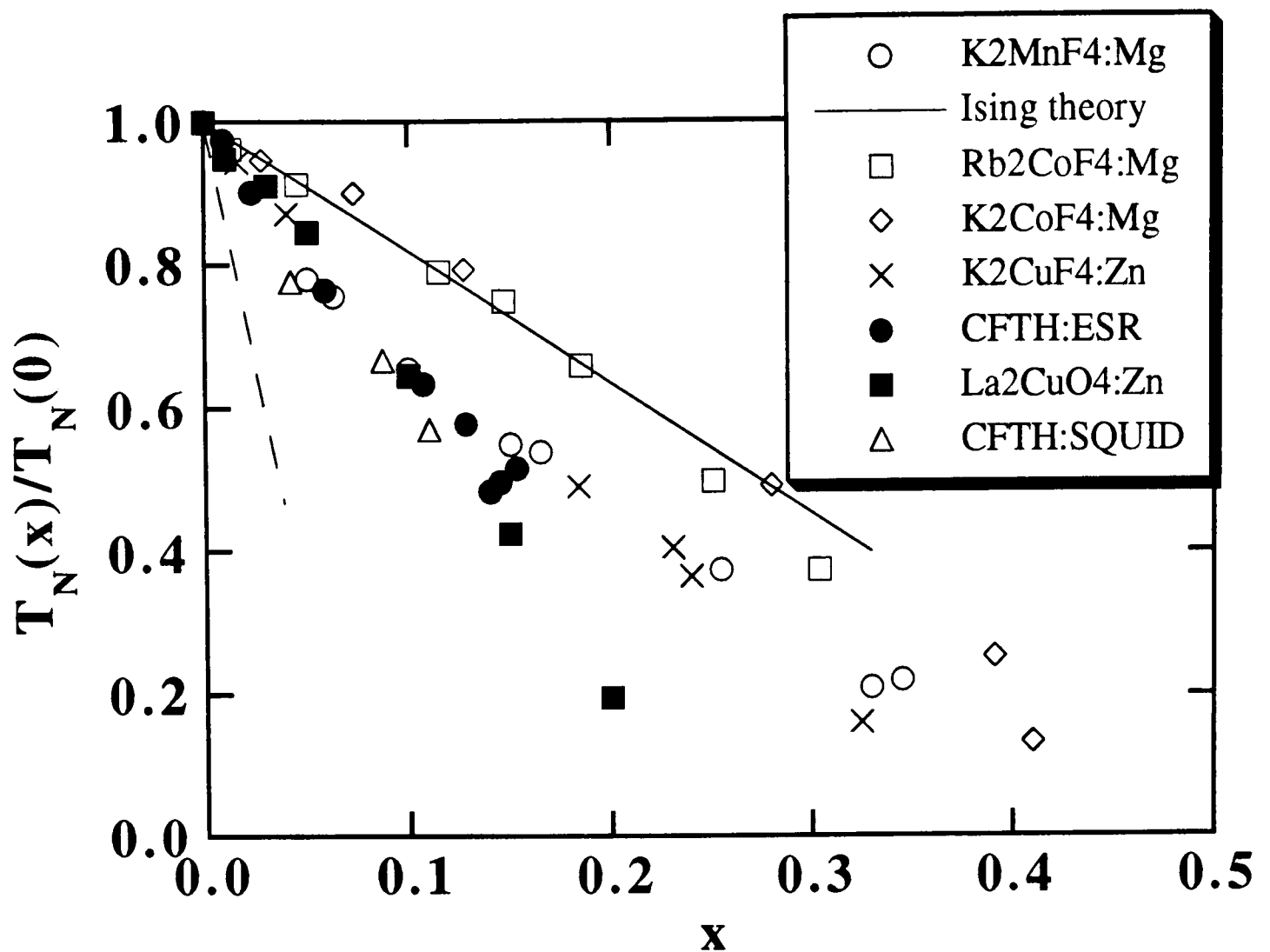


Figure 3.14: A graph showing the relationship of the results from doped CFTH to those obtained from 2D Ising systems, 2D Heisenberg systems, La_2CuO_4 and from a theoretical treatment of the 2D Ising model. x is the mole fraction of the diamagnetic ion in the sample. The broken line indicates the results obtained by Chakraborty *et al.* [100] for La_2CuO_4 .

because, as discussed in Chapter 2 there is no observable Ising-like critical behaviour. There appears to be no reason why systems whose ordering is driven by different mechanisms should exhibit ‘universal’ behaviour in the depression of the ordering temperature by diamagnetic doping. We propose that the Heisenberg systems which have been studied so far may simply show *similar* behaviour on doping and the rate of reduction of T_N is about twice that of the Ising systems. This view is supported by apparent differences in behaviour of different Heisenberg systems when x exceeds 0.1.

3.6 DC susceptibility measurements of pure and doped CFTH samples

3.6.1 SQUID Magnetometry

The volume magnetic susceptibility of a material is defined by

$$\kappa = \left(\frac{\partial M}{\partial H} \right)_T \quad (3.29)$$

If the magnetisation, M , varies linearly with applied field, H , then κ is simply defined by M/H . κ is dimensionless because M and H are measured in the same units (Am^{-1} in the SI system). The magnetisation is defined as the magnetic dipole moment per unit volume, and so we may define the susceptibility of the actual sample to be

$$\chi = \frac{m}{H} \quad (3.30)$$

where m is the magnetic moment of the sample and χ has units of volume. The size of χ is a measure of how sensitive the moment induced by the applied field is to a change of that field. In a collective system, this depends on how the moments interact.

Usually one determines the molar magnetic susceptibility, χ_{mol} , and expresses its value in electromagnetic units (emu) per mole.

$$\chi_{mol}[\text{emu mol}^{-1}] = \frac{m[\text{emu}]}{H[\text{G}]n[\text{mol}]} \quad (3.31)$$

where n is the number of moles of material in the sample. A brief discussion of units in magnetism and of the relation between SI and c.g.s. (emu) units is given in Appendix B.

There are various ways of measuring M or m and hence χ and χ_{mol} . The basis of the Vibrating Sample Magnetometer (VSM) is that when a magnetised sample is moved relative to a coil placed around it, a current is induced in the pickup coil. Alternatively, one may measure the force acting on a magnetisable sample placed in a non-uniform magnetic field (one which has a field gradient associated with it). This is the basis of the Gouy and Faraday Methods.

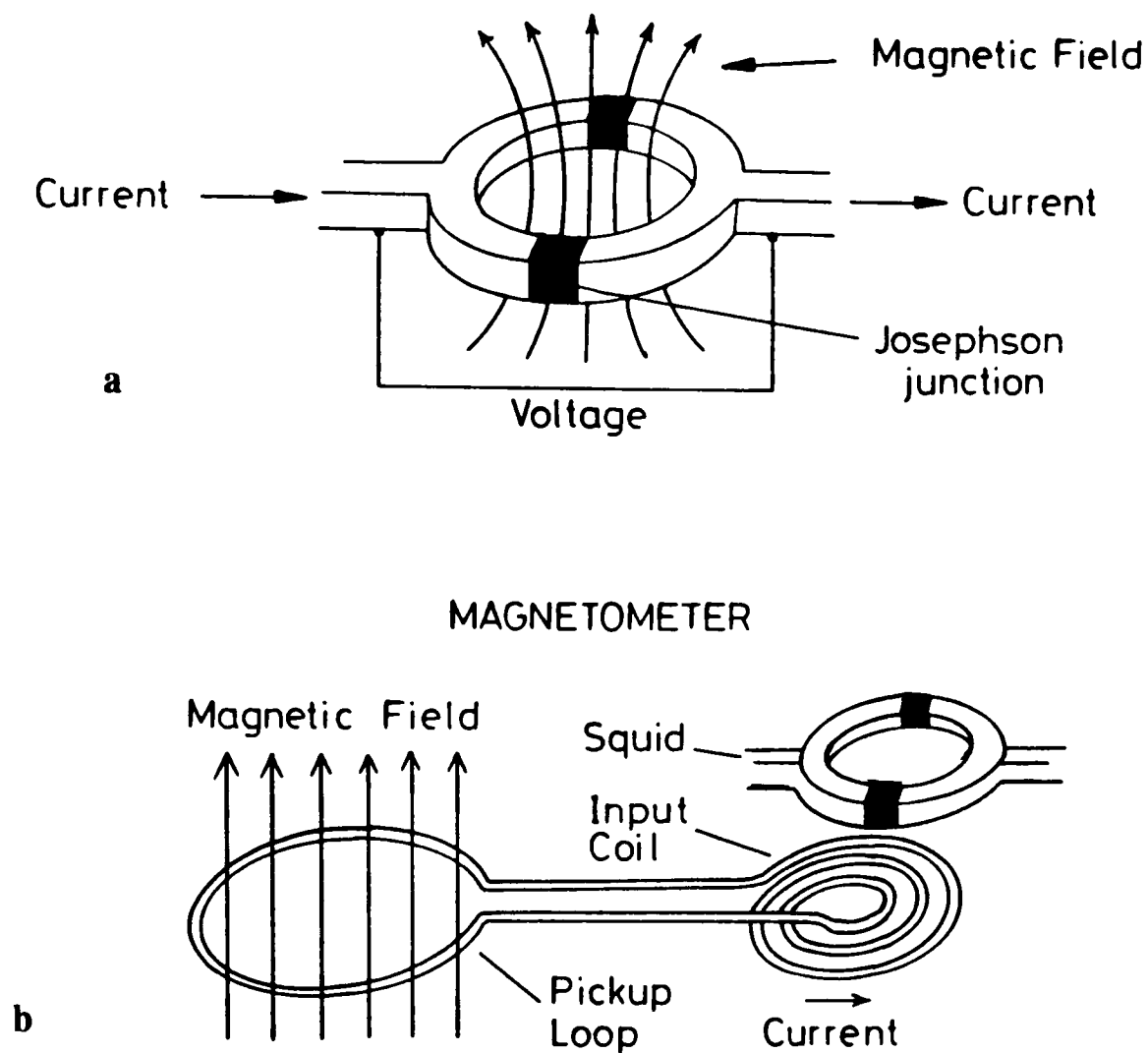


Figure 3.15: The components of the SQUID magnetometer [118]: (a.) The SQUID itself: a ring of superconductor containing two Josephson junctions. (b.) The pick-up circuit acts as a flux transformer. The critical current of the SQUID is dependent on the flux contained within it. This phenomenon enables very small changes in magnetic field to be detected.

The most sensitive method for measuring magnetisation is to use a magnetometer containing a Superconducting QUantum Interference Device or SQUID [118]. The main components of this are shown in Figure 3.15. The DC SQUID consists of a superconducting ring containing two Josephson junctions which are thin regions of non-superconducting material through which the supercurrent can tunnel. When a current is applied to bias the SQUID, it divides between the two junctions and if it is greater than the critical current which is equal to the *maximum* supercurrent which can tunnel through the Josephson junctions, then the ring has a non-zero resistance and a voltage is produced across it. The product of the area of the ring and the magnetic field enclosed by it is called the magnetic flux and it is quantised. The critical current is a maximum when an integer number of flux quanta is contained and a minimum when a half-odd-integer number of flux quanta is contained. Consequently, changes in the magnetic field give rise to changes in the critical current and hence in the voltage measured across the SQUID. This is a quantum interference effect

analogous to Young's double slit experiment in optics. The wavefunctions at the two Josephson junctions interfere producing the oscillations in critical current.

Since one measures a voltage *change* across the SQUID, it is possible to measure a change in flux smaller than the flux quantum and so SQUIDs are extremely sensitive. In order to utilise the SQUID in a magnetometer, the magnetic field produced by the sample is used to induce a supercurrent in a pick-up loop. This loop is part of a circuit, the other component of which is a coil which generates a magnetic field in the SQUID. The use of this arrangement greatly increases the sensitivity of the SQUID because if the input coil to the SQUID is composed of several windings, the pick-up circuit acts as a flux transformer magnifying the field experienced by the SQUID relative to that induced in the pick-up loop. The voltage across the SQUID is measured while the sample is in different positions relative to the pick-up coil. The field which induces a current in the pick-up loop is proportional to the magnetic moment of the sample divided by the cube of the distance between the sample and the pickup loop. Measurement of the way the voltage across the SQUID changes with this distance allows the magnetic dipole moment of the sample to be determined and this can be converted to a magnetisation or a susceptibility.

The magnetometer is usually contained within a cryostat or a furnace to enable the magnetisation of the sample to be determined as a function of temperature. A variable field superconducting magnet is used to apply a field to the sample and magnetise it. Typically the cryostat can reach temperatures of 2 K or less and the magnet a field of up to 6 T or more. The *lowest* field which can reproducibly be applied to the sample in a commercially available magnetometer is of the order of a few tens of Gauss.

3.6.2 Experimental details

The experiments on doped versions of copper formate carried out by ESR were repeated using DC magnetometry in order to verify that the ESR approach is a valid one. The results of the experiment on undoped CFTH were used to test some of the

conclusions about the magnetic Hamiltonian which were reached in Chapter 2.

Sample environment

Crystals of CFTH containing Zn^{2+} with $x = 0, 0.042, 0.087$ and 0.111 were mounted in a gelatine capsule using a small amount of Apiezon M grease and this was sealed by wrapping it in teflon tape. The sample must be in a sealed container in order to prevent dehydration which was found to be rapid inside the magnetometer at room temperature and has a dramatic effect on the magnetic susceptibility. The crystals were mounted with the b direction along the long axis of the gelatine capsule and so that b would be vertical when mounted in the magnetometer.

The gelatine capsule was wedged into a clear drinking straw and this was mounted on the end of a non-magnetic metal rod which was lowered into a Quantum Design MPMS₂ SQUID magnetometer at the Chemistry Department at the University of Edinburgh. The magnetometer was capable of reaching a base temperature of between 1.7 and 1.8 K with a hold time at that temperature of about 40 minutes. The base temperature was reached in less than one hour when cooling in zero field. The temperature stability ranged from 0.7% at 5 K to 0.1% at room temperature. The maximum field which could be attained on this magnetometer was 1.0 T

Measurement of the susceptibility

The magnetisation of CFTH was found to be linear with field at room temperature which is expected for a paramagnetic material. The sample was cooled to 4.2 K in zero field and the magnetisation was measured as a function of temperature up to room temperature at a field of 0.1 T. A maximum in the susceptibility was expected near the 3D ordering temperature, T_N . This temperature was estimated for each of the samples using the ESR results and temperature steps of 0.2 K were used around the transition so that T_N could be defined precisely. The excellent stability of the measured sample temperature enabled these small temperature steps to be taken. The typical equilibration time close to T_N was 3 minutes and this increased to 15 minutes close to room temperature where larger temperature steps were taken and

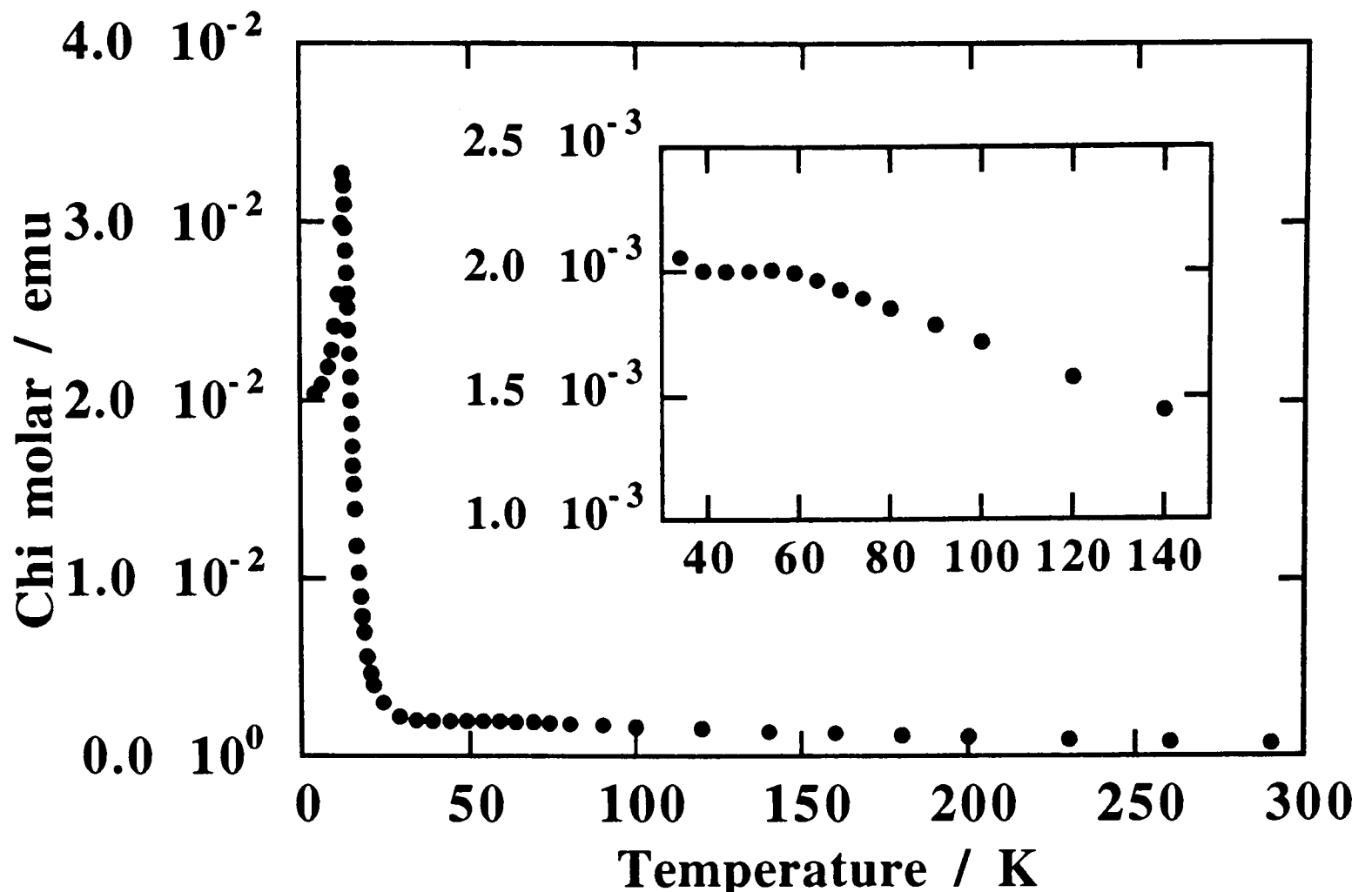


Figure 3.16: The molar magnetic susceptibility of undiluted CFTH as a function of temperature. The inset region shows the broad maximum associated with short-range antiferromagnetic correlations. Other features are described in the text.

equilibration is slower. No additional equilibration time was allowed at any temperature as this was not found to affect the measured value of the magnetisation. The molar susceptibility was calculated using Equation 3.31. The measured magnetisation was corrected for the diamagnetism of the gelatine sample holder. Corrections for the diamagnetism of the sample and for temperature independent paramagnetism (TIP) were not made since these were small compared to the sample's paramagnetism near the transition.

The dependence of the molar susceptibility of undoped material is shown in Figure 3.16 and agrees very closely with those of Flippen and Friedberg [61] who measured the susceptibility below 25 K and those of Martin and Waterman [59] who measured it above 50 K.

The susceptibility rises as the sample is cooled and reaches a broad maximum at between 50 and 70 K which is ascribed to the effect of short range intra-plane ordering. Reference to the magnetic structure [66] reveals that the moments in the plane are

canted slightly along the b and c directions. The canting arises from the tilting of the CuO_6 octahedra and causes the antisymmetric exchange interaction which leads to weak ferromagnetism within the planes [64]. This causes the susceptibility to rise by roughly one order of magnitude below 50 K as the short-range correlated regions increase in size, increasing the magnitude of the canted moment. A maximum is reached at 16.6 K in the pure material. This almost corresponds to T_N where the ordered islands within the planes are sufficiently large for 3D ordering to occur through the effect of the weak inter-planar exchange constant, J' . Equating T_N with the susceptibility maximum is a slight simplification since it assumes that Molecular Field (MF) theory is obeyed. T_N actually corresponds to the point at which the *derivative* of the susceptibility has its maximum value. We have assigned T_N to be equal to the temperature at which it has its maximum value, although this is a slight overestimate. The deviation from MF theory is due to the effect of short range ordering.

Normal behaviour of an antiferromagnet

The rationalisation for the appearance of the χ against T plot for an antiferromagnet shown in Figure 3.17 is that at $T=0$, when the spins are perfectly aligned, a field parallel to them exerts no torque and so $\chi_{||}=0$. On warming, thermal disruption of the alignment causes $\chi_{||}$ to increase reaching a maximum at about T_N . Above T_N , in the paramagnetic phase, χ decreases as T is raised since thermal agitation becomes progressively better at disrupting the alignment of spins in the field. In this region, the Curie-Weiss law predicts that

$$\chi = \frac{C}{T - \theta} \quad (3.32)$$

where C is the Curie constant and θ is the Weiss constant. If below T_N , H_0 is perpendicular to the axis of the spins, there is a tendency for the spins to couple to the field but the resultant acting on a pair of dipoles is zero and so $\chi_{\perp}$ is constant below T_N .

We do not observe exactly this behaviour in CFTH because of the canted moment.

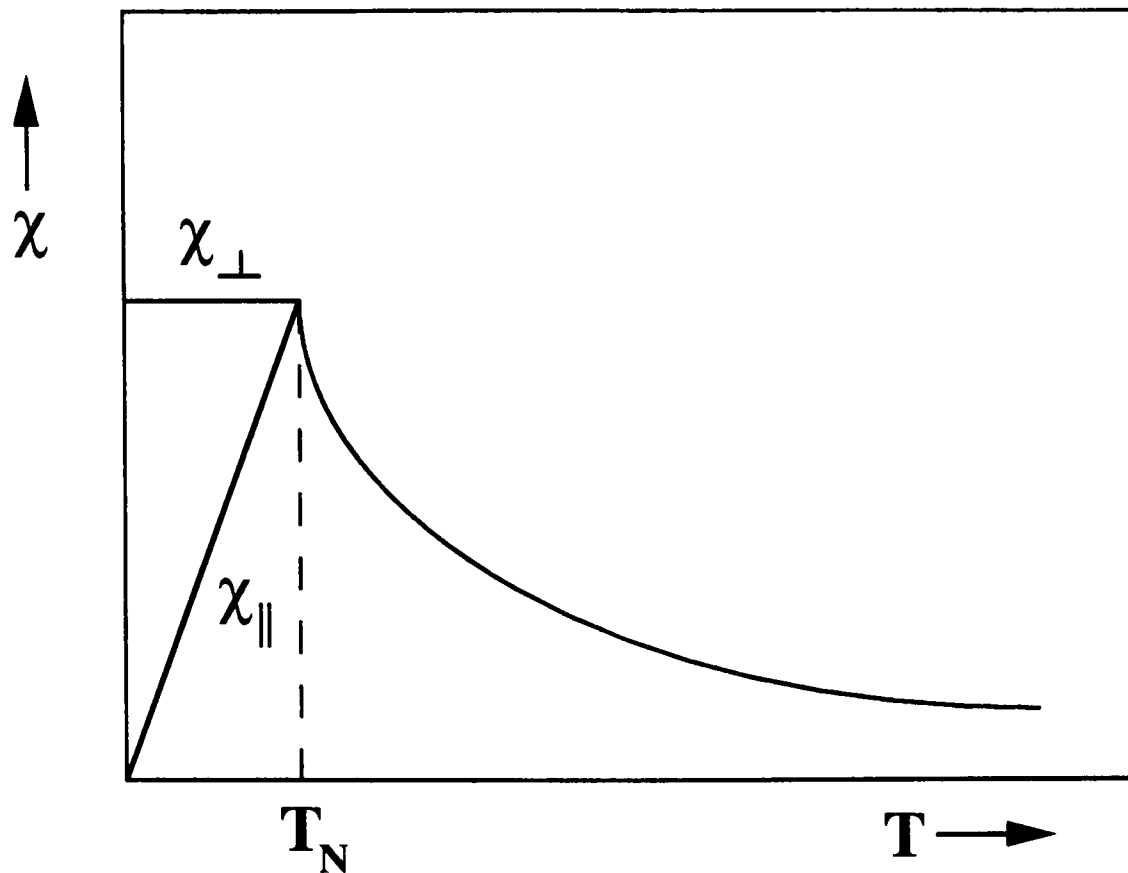


Figure 3.17: The usual susceptibility behaviour of an antiferromagnet. An explanation is given in the text.

The effect of canting is not observed when the susceptibility is measured in the a direction [74]. This indicates that the canted moment has some component along the b and c directions but none in the a direction.

3.6.3 Results

Undoped CFTH

The temperature dependence of the magnetic susceptibility of CFTH shown in Figure 3.16 is strikingly similar to that of La_2CuO_4 [64] which is consistent with the two materials having similar magnetic Hamiltonians. Thio *et al.* [64] performed an analysis of the susceptibility, χ , of La_2CuO_4 close to T_N in which they used the values of the correlation length, ξ , and the interplanar coupling, J' , measured by neutron scattering to estimate the value of J_D , the antisymmetric exchange. χ may be expressed as

$$\chi = 4\chi_0^2 J_D^2 \chi_+ \quad (3.33)$$

where χ_0 is given approximately by $g^2/8J$, and in the region above T_N

$$\chi_+^{-1} = \chi_{2D}^{-1} + J' \quad (3.34)$$

χ_{2D} is described as the 2D staggered susceptibility and is defined by

$$\chi_{2D} = \frac{(\xi(T)/a)^2}{k_B T} \quad (3.35)$$

In the region between T_N and $2T_N$, the CHN theory described in Chapter 2 is valid and so

$$\xi(T) = 0.5a \exp(2\pi\rho_s/T) \quad (3.36)$$

where the terms are as described in Section 2.4.2, $2\pi\rho_s \simeq 0.942J$ is 84 K and J' is 0.0036 K) (Section 2.4.4). Substituting these values in temperature units into Equation 3.33 allows us to fit the susceptibility in the region above T_N to

$$\chi = \chi_0 + \frac{4\chi_0 J_D^2}{4T \exp(-168/T) + 0.0036} \quad (3.37)$$

where χ_0 and J_D are the only variable parameters. The fit is reasonably good and is shown in Figure 3.18. χ_0 is determined to be $8.3 \times 10^{-4} \pm 3.0 \times 10^{-4} \text{ emu mol}^{-1}$ and J_D is $8.9 \pm 2.0 \text{ K}$ or $0.77 \pm 0.2 \text{ meV}$. This value is similar to the others obtained. The relatively large error is due to the difficulty of determining χ_0 precisely when one restricts the fit to the region between T_N and $2T_N$ where CHN theory is valid.

Doped CFTH

The dependence of the molar susceptibility on temperature changes with composition as shown in Figure 3.19. The doped samples show essentially similar behaviour although there are three differences arising from the dilution of the magnetic ion by the diamagnetic ion.

- Most noticeable is the fact that T_N decreases as the dopant concentration is raised. A plot of the ratio of $T_{N(0)}/T_{N(x)}$ where x is the concentration of dopant ion is shown in Figure 3.20, where the rate of decrease is found to be very similar to that found using ESR spectroscopy, and is characterised by a value of α of about 3.4.

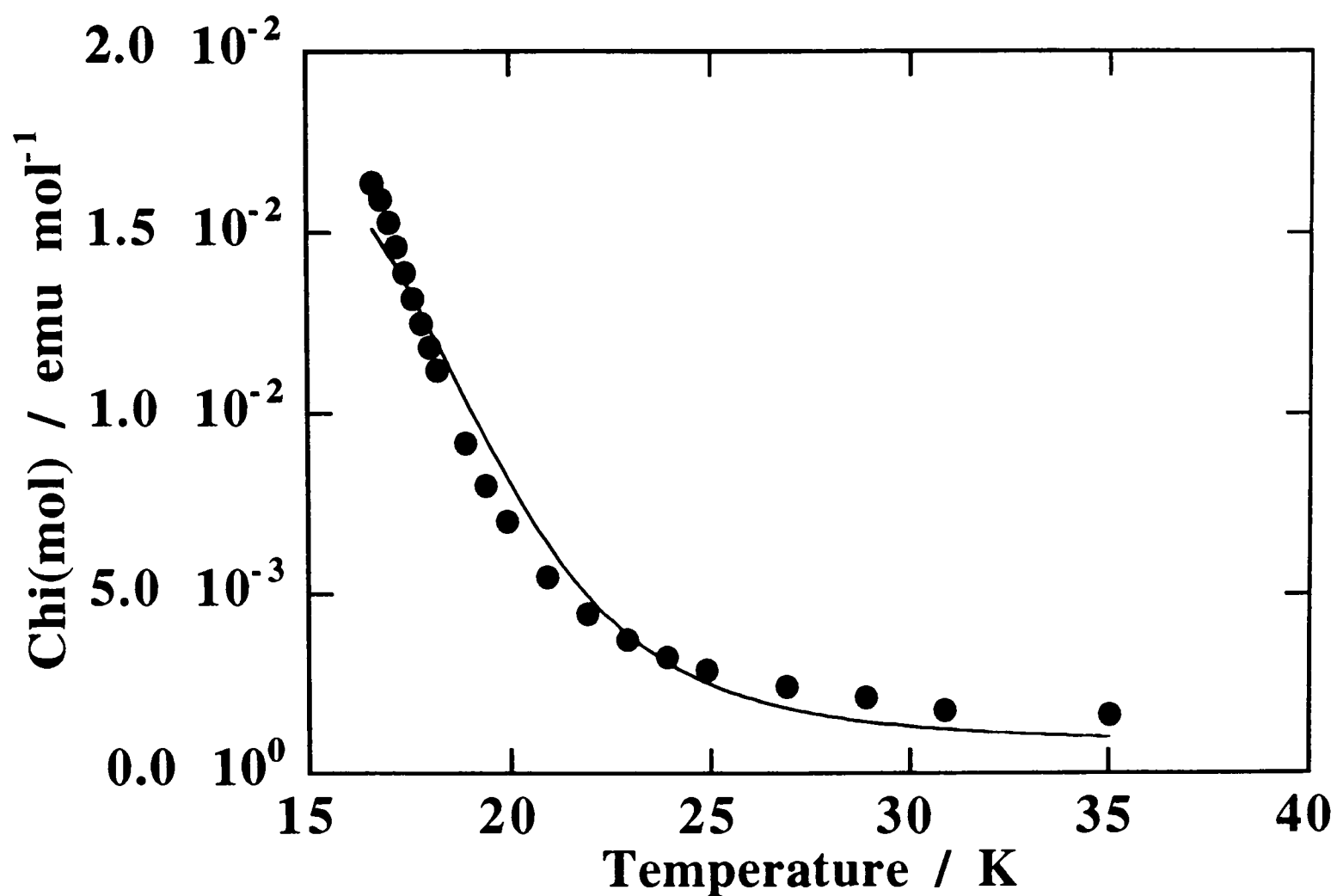


Figure 3.18: The magnetic susceptibility in the critical region fitted to Equation 3.37.

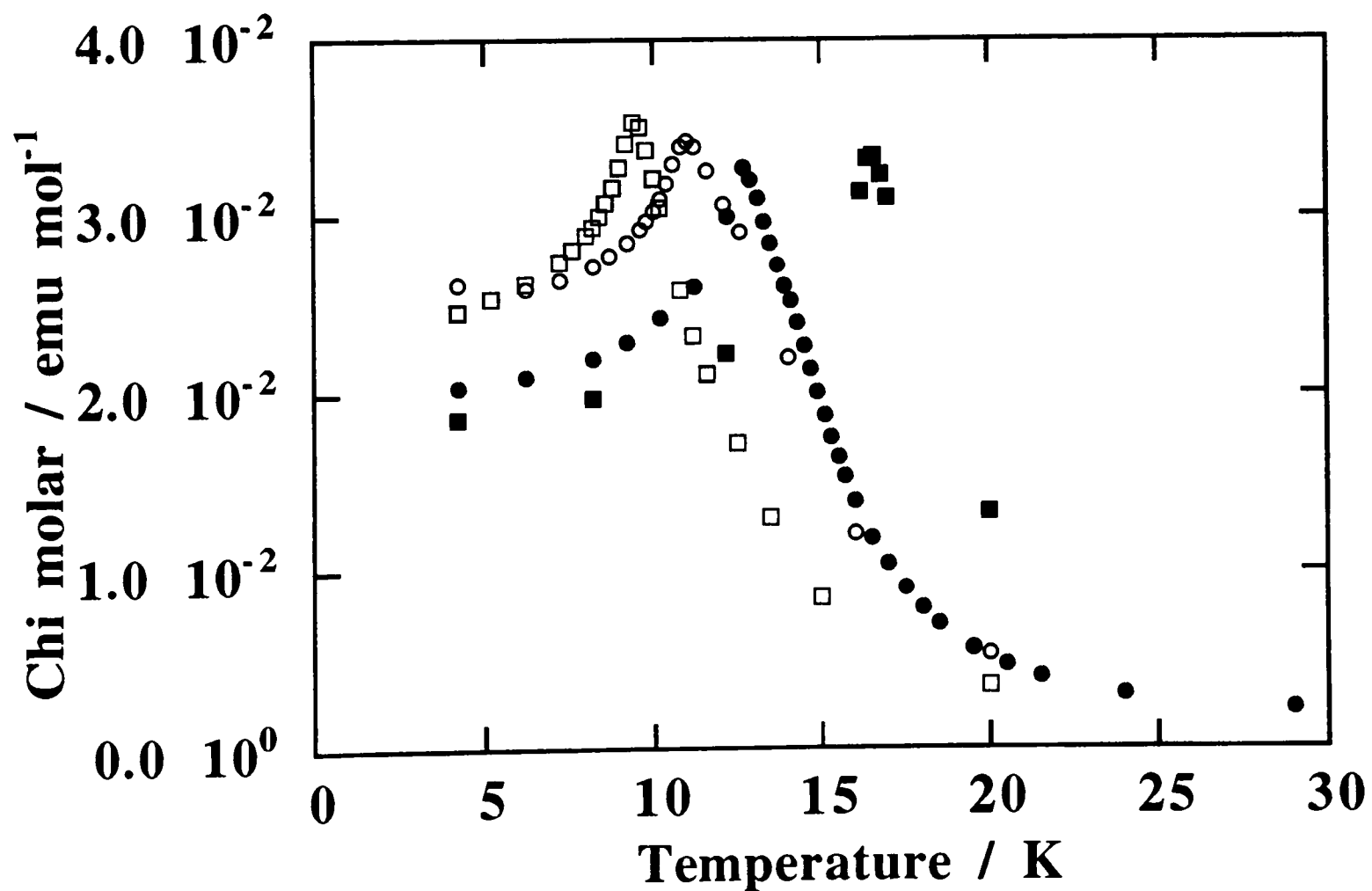


Figure 3.19: Comparison of the magnetic susceptibility behaviour of undiluted and diluted CFTH.

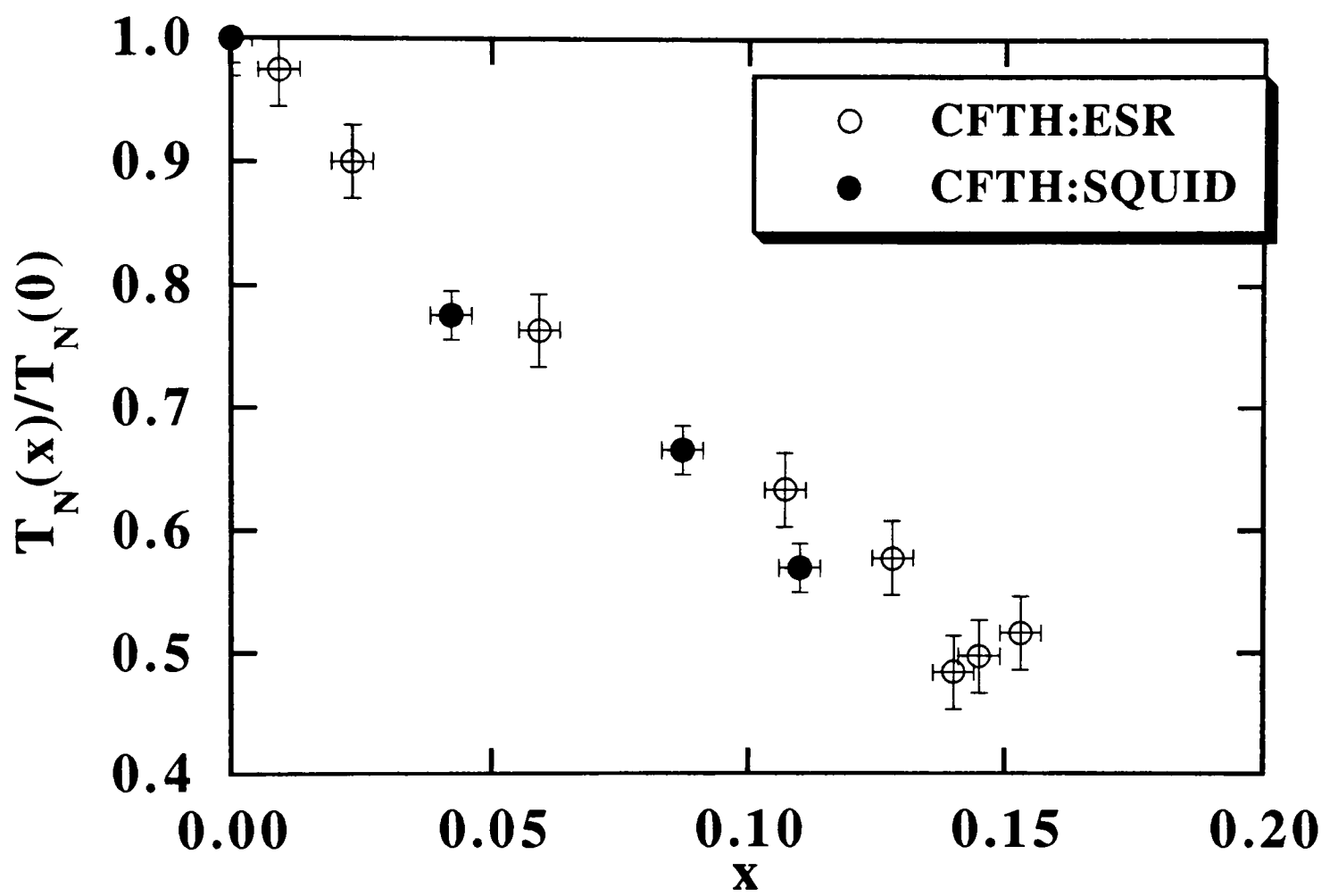


Figure 3.20: The rates of decrease of T_N at low dopant concentrations measured using ESR spectroscopy (filled circles) and SQUID magnetometry (open circles). Both results indicate that the value of α in Equation 3.1 is 3.4 ± 0.2 .

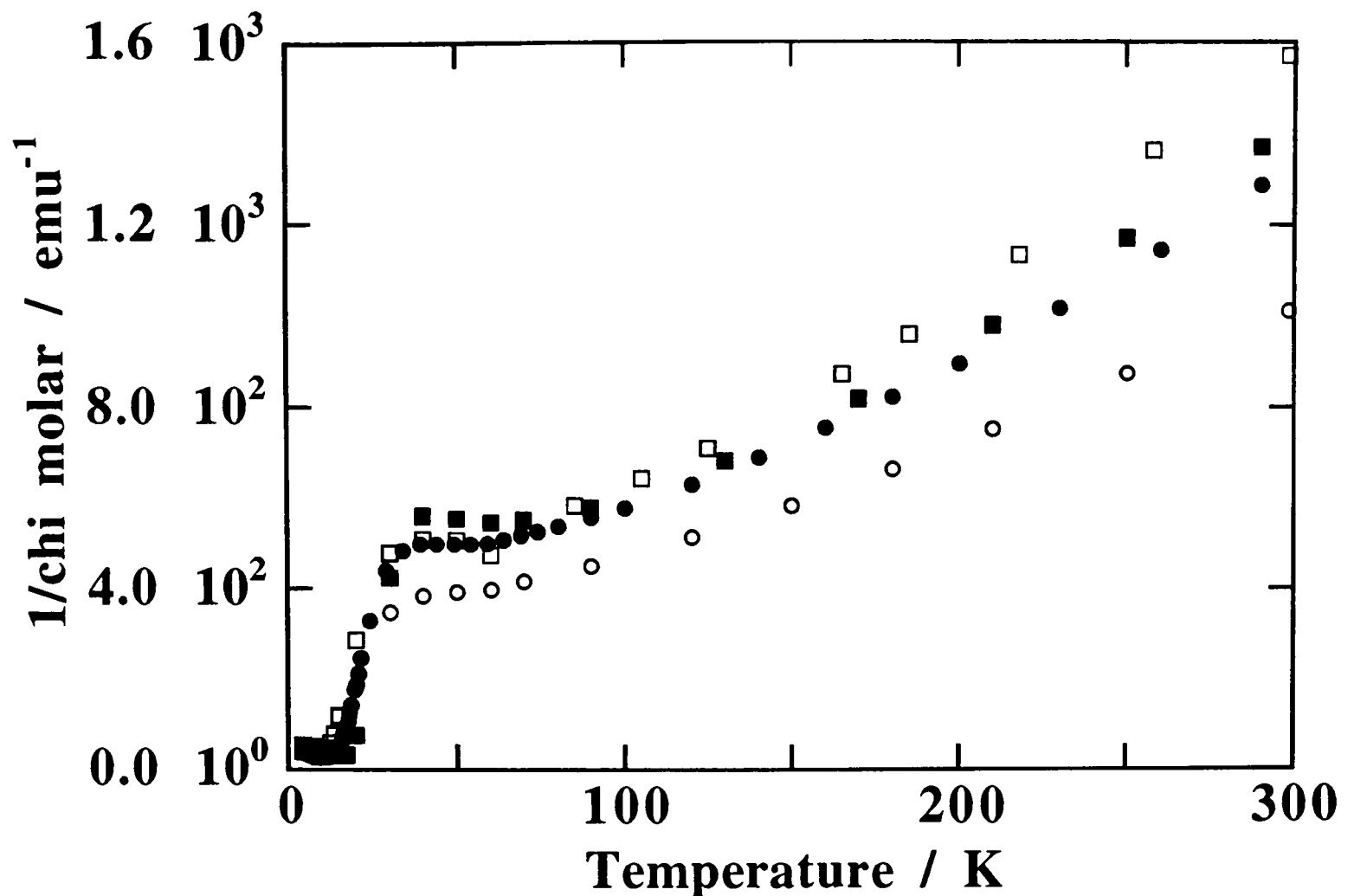


Figure 3.21: The inverse magnetic susceptibility of undiluted and diluted CFTH.

- It appears that there is a systematic increase in the susceptibility at 4.2 K with increasing dopant concentration, and although some of this may be due to errors in orienting the samples [74], this may be explained in terms of Cu^{2+} ions with some Zn^{2+} neighbours experiencing a different exchange field to those of the undoped material and making a larger contribution to the susceptibility.
- One would also expect that on doping, the average in-plane exchange constant, J , would decrease since some ions do not experience the exchange field provided by four near neighbours. This should cause an decrease in the Weiss constant obtained by extrapolation from the linear region of a graph of $1/\chi_{||}$ against T which is shown in Figure 3.21. Unfortunately measurements were not made at temperatures high enough for the plot to be linear. The non-linearity persists to high temperatures due to the effects of short-range ordering.

x	T_N/K	$T_N(x)/T_N(0)$	$\chi_{4.2}/\text{emu mol}^{-1}$
0	16.5	1.00	0.018
0.042	12.8	0.78	0.021
0.087	11.0	0.67	0.026
0.111	9.4	0.57	0.025

Table 3.3: A table showing the change in T_N and the susceptibility at 4 K measured using a SQUID magnetometer.

3.7 Summary

3.7.1 Comparison of ESR and SQUID results on pure and doped CFTH

The techniques of ESR and SQUID magnetometry probe the magnetic properties of a material in fundamentally different ways. Both measure the magnetic susceptibility, but in CFTH the magnetometer picks out the transition from 2D SRO to 3D LRO, while the ESR signal in this region is immeasurably broad. ESR spectroscopy appears to be a more sensitive probe of the changes in the susceptibility which arise from short range ordering phenomena at higher temperatures. ESR may also be used to elucidate results from the SQUID magnetometer. If the CFTH is allowed to dehydrate partially, a second ESR signal appears which is separated from the main signal because the copper in the dehydrated material has a different g -value. If insufficient precautions are taken to ensure that the SQUID sample does not dehydrate, one obtains a temperature dependent susceptibility in which the 3D ordering transition is still visible, but hardly so since the dehydrated material has a rapidly increasing susceptibility in that region and tends to swamp the signal of the non-dehydrated material. In ESR spectroscopy different contributions to the magnetic susceptibility may be resolved while a SQUID magnetometry experiment averages over all the contributions to the susceptibility.

In this series of experiments, ESR and SQUID magnetometry both give similar results for the decrease of T_N with temperature and they also show the presence of a broad hump in the susceptibility at about 50 K due to short range ordering.

3.7.2 Comparison of CFTH with other 2D materials

A graph showing the similarities and differences between the behaviour of the long-range ordering temperature in CFTH and other 2D materials including La_2CuO_4 is shown in Figure 3.14. In all the systems having spins with nearly Heisenberg symmetry, $T_N(x)/T_N(0)$ falls at a rate of αx where α is about 3. This is a faster rate of decrease than in Ising systems ($\alpha \simeq 1$). There are grounds for expecting that the agreement between the Heisenberg systems is coincidental rather than an indication of some universal behaviour, because the systems have different magnetic Hamiltonians. CFTH and La_2CuO_4 behave in very similar ways and we have shown that they also have very similar magnetic Hamiltonians.

3.7.3 Comparison of results on undoped material with those of Chapter 2

The magnetic Hamiltonian of CFTH has been probed by a variety of techniques. The Hamiltonian is of the form

$$\mathcal{H} = -J \sum_{ij} \vec{S}_i \cdot \vec{S}_j + J_D \sum_{ij} \vec{S}_i \times \vec{S}_j + J' \sum_{ik} \vec{S}_i \cdot \vec{S}_k. \quad (3.38)$$

J has been determined to be $6.5 \pm 0.2 \text{ meV}$ from an analysis of the spin-wave dispersion, a value slightly lower than the $7.7 \pm 0.2 \text{ meV}$ obtained from analysis of the magnetic correlation length. J_D has been determined to be $0.46 \pm 0.04 \text{ meV}$ from the spin-wave dispersion. Values of 0.32 ± 0.03 and 0.77 ± 0.20 were obtained from the measurement of the g -value and of the magnetic susceptibility respectively. J' has been determined to be $3.1 \times 10^{-4} \text{ meV}$ from the correlation length measurements. Also the value of the 3D ordering transition has been determined to be $16.5 \pm 0.1 \text{ K}$ and the determination of the critical exponent of the magnetisation, β below this temperature confirms that the ordering is driven by inter-layer coupling and suggests that there is a small XY-type anisotropy in the Hamiltonian.

Quantity	CFTH	La ₂ CuO ₄	Sr ₂ CuO ₂ Cl ₂
J / meV	7	130	125
J_D / meV	0.5	0.6	0
J' / meV	3.1×10^{-4}	2.6×10^{-3}	
T_N / K	16.5	230	230
J/J_D	15	210	
J/J'	2.3×10^4	5×10^4	
J_D/J'	1600	230	
α	3.4	3.0	

Table 3.4: A comparison of the terms in the Hamiltonians and other properties of CFTH, La₂CuO₄ and Sr₂CuO₂Cl₂.

3.7.4 Comparison of CFTH with La₂CuO₄ and Sr₂CuO₂Cl₂

CFTH and La₂CuO₄ appear to have very similar magnetic properties, although the exchange interactions in La₂CuO₄ are larger. A comparison of the approximate values of the terms in the Hamiltonian is presented in tabular form in Table 3.4. This table includes the measured parameters for Sr₂CuO₂Cl₂.

Chapter 4

Structural and magnetic study of the Na_xTiO_2 and Li_xTiO_2 systems

4.1 Outline of chapter

Our work on the Na_xTiO_2 system has revealed a vast number of features, and an attempt has been made to introduce them in the most helpful order. First of all, the structural characteristics are discussed as a function of preparation conditions and composition at room temperature with the help of the results of our X-ray diffraction measurements. This is followed by a description of the magnetic properties measured using a SQUID magnetometer as a function of temperature for each of the samples. The room temperature structural characteristics are then correlated with the magnetic behaviour. In the next section, the structural characteristics of a stoichiometric sample are analysed as a function of temperature using neutron diffraction. Finally, an attempt is made to rationalise all the experimental observations. This also involves comparison with a number of related compounds.

The discussion of Na_xTiO_2 forms the bulk of the chapter. It is followed by a smaller section on lithium-titanium(III) oxides. The behaviour of LiTiO_2 is discussed in the light of the analysis of NaTiO_2 .

4.2 Introduction

As discussed in Chapter 1, the possibility of a frustrated 2D system possessing an unusual ground state has been suggested and a great deal of effort has been expended

on the part of theorists in trying to determine whether states such as the Resonating Valence Bond (RVB) state actually can exist. Experimental evidence that the (non-frustrated) square antiferromagnet with $S = \frac{1}{2}$ behaves classically has been found and is discussed in the preceding two chapters. It was always thought that the triangular lattice would be a better place to look for novel behaviour because of the frustration and the possibility that there is chirality (see Figure 1.6 and [39]) in the 120° Néel state of XY and Heisenberg magnets. There are very few materials which are candidates for the triangular lattice antiferromagnet with a low value of the spin. These are most likely to exhibit exotic behaviour (Chapter 1). The material which has long been thought the most promising is NaTiO_2 [35, 119, 120] and work on this material was motivated by the possibility of unusual magnetic behaviour.

4.2.1 AMO_2 compounds

Compounds of the formula AMO_2 where A is an alkali metal and M is a first row transition metal fall into a number of structural classes and have a range of magnetic properties. Most have structures based on that of NaCl with an FCC array of oxide ions and all octahedral interstices filled. As a general rule, if the two cations have a radius ratio ($r_{A^+}/r_{M^{3+}}$) greater than about 1.1, the size difference is sufficient to produce an ordered structure in which alternating $[1\ 1\ 1]$ planes of the NaCl structure are occupied by one type of cation. This is called the α - NaFeO_2 structure which has the space group $R\bar{3}m$ (No. 166) and is shared by most of the NaMO_2 compounds. In the case of most of the compounds containing Li, there tends to be more disorder between cation sites due to there being much less of a difference in size between the two types of cation. LiScO_2 has a partially ordered structure based on that of NaCl, which has been described [121] as being like an ScO_2^- anatase framework stuffed with Li^+ . LiTiO_2 has a disordered version of the NaCl structure with Li^+ and Ti^{3+} distributed statistically over the single metal ion site. LiVO_2 has the α - NaFeO_2 structure as do most of the later members of the LiMO_2 series. LiNiO_2 was once thought to be a good candidate for a triangular lattice antiferromagnet with $S=1$

[120, 122, 123, 124], although conflicting information about its magnetic properties was obtained before careful work by Reimers *et al.* [125] revealed that there is disorder coupled with frustration which leads to spin-glass behaviour. For the members of the Li series, there appears to be metallic or semiconducting behaviour as far as vanadium, and then a cross-over to insulating behaviour as one passes vanadium and the d-orbitals contract. This contraction causes the energy width of the 3d band to decrease below that required to overcome the electron-electron repulsions associated with the movement of an electron to a neighbouring atom and so the later members of the series are Mott-Hubbard insulators.

4.2.2 Na_xTiO_2

NaTiO_2 was first prepared by Hagenmuller *et al.* [126] who reported a structure of the $\alpha\text{-NaFeO}_2$ type in which alternate planes are occupied by Na^+ and Ti^{3+} . The space group is rhombohedral $R\bar{3}m$ with approximate lattice parameters $a = b = 3 \text{ \AA}$ and $c = 16.3 \text{ \AA}$. The structure is shown in Figure 4.1 where the comparison with the NaCl structure is indicated. The Ti^{3+} ions in each plane form a triangular array with 6 nearest neighbours about $3.0 \text{ \AA}$ apart and neighbouring planes are separated from one another by about $5.4 \text{ \AA}$. A glance at the structure indicates that the in-plane exchange path is very much better than the exchange path between Ti^{3+} ions in adjacent planes and so one would expect 2D magnetic behaviour to be pronounced if the material is a magnetic insulator. Note that the separation of Ti^{3+} ions in neighbouring planes of NaTiO_2 is roughly equal to the nearest-neighbour separation in CFTH. Exchange over such a long distance in CFTH is possible due to the delocalised nature of the formate group. The exchange path between planes in NaTiO_2 would be via Ti-O-Na-O-Ti which would not lead to strong exchange.

The ionic radii of Na^+ ($1.02 \text{ \AA}$) and Ti^{3+} ($0.67 \text{ \AA}$) are quite dis-similar and this leads to segregation and the layered structure. However one cannot rule out the possibility that there exists a small amount of disorder between the Na-planes and the Ti-planes.

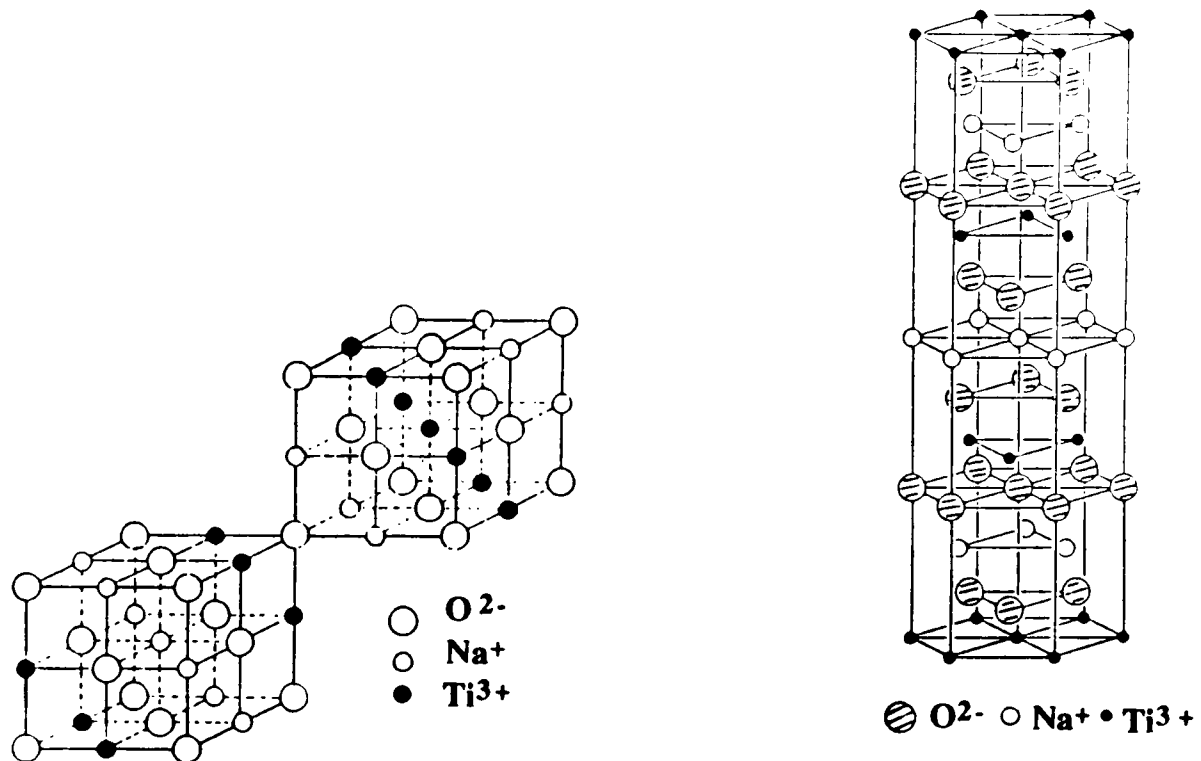


Figure 4.1: The structure of NaTiO₂ compared with that of NaCl. The metal ions occupy alternate $[1\ 1\ 1]$ planes. The spacegroup is the rhombohedral $R\bar{3}m$.

It is possible to deintercalate Na from NaTiO₂ using iodine in acetonitrile or electrolytic oxidation. At room temperature, Maazaz and Delmas [127] reduced NaTiO₂ using a propylene carbonate cell and identified solid solutions in the ranges Na_{0.71}TiO₂–Na_{0.87}TiO₂ and Na_{0.94}TiO₂–NaTiO₂. These conserve the NaTiO₂ structure except for a weak monoclinic distortion for Na-concentrations towards the lower end of this range which is also observed in NaCoO₂ [128]. If further oxidation is carried out to reduce the Na-content below 0.71, Maazaz and Delmas [127] assert that some Ti³⁺ migration to the Na planes takes place and (Na_xTi_y□_{1-x-y})(Ti_{1-y}□_y)O₂ is produced, where □ represents a vacant metal ion site. On reintercalation, the new structure is conserved and on full reduction of the Ti⁴⁺ to Ti³⁺, one obtains (Na_{1-y}Ti_y)(Ti_{1-y}Na_y)O₂.

Measurements of the magnetic properties of NaTiO₂ have produced inconsistent results [119] because the material is difficult to prepare in a pure form and is very air-sensitive. In this chapter, we present a reliable method for making NaTiO₂, carry out a structural analysis of stoichiometric and Na-deficient Na_xTiO₂ samples, and examine the magnetic properties using a variety of techniques, of which DC magnetometry proved to be the most useful. Our results are compared with those of other

workers. All the experiments were carried out on powder samples since it has not yet proved possible to make a single crystal of this material. Some of the experiments, and attempts to make a single crystal are included in an appendix to this chapter (Appendix A).

4.3 Preparation of Na_xTiO_2

Due to the air sensitive nature of NaTiO_2 , all manipulations, unless stated, were carried out in a Braun Labmaster 130 He-filled dry box in which a 25 W light bulb punctured with a 10 mm diameter hole remained illuminated for between 10 and 30 hours indicating a total O_2 and H_2O content of less than 1 ppm. The atmosphere of the box was continually cleaned by circulation through a purifier containing a molecular sieve and a copper metal catalyst. NaTiO_2 was prepared by sealing stoichiometric amounts of sodium metal (99.9% from Aldrich Chemical Company) and finely powdered anatase (99.999% from Aldrich Chemical Company) in an ampoule made from ARMCO soft ingot iron rod (>99.8% purity obtained from Goodfellow Metals Ltd). The ampoules, shown in Figure 4.2, typically had an outer diameter of 25 mm and an internal bore of 17 mm and were 40 mm long. The lid was disk shaped with a central spigot of the same diameter as the internal bore to give a tight fit. The sodium, stored under paraffin oil, was cleaned with hexane and then transferred to the dry-box where the outer surface was cut away and discarded. The ampoule was filled with a total of about 3.5 g of clean Na chunks and powdered anatase. The ampoule was sealed in air soon after removal from the dry box using a Tungsten Inert Gas welding rig. The ampoule was then heated in a flow of dried and deoxygenated Ar gas in a Carbolite STF 16/50 tube furnace to 500°C for one hour. The temperature was then raised to between 900°C and 1000°C for a further 2 to 7 days. Different samples were made under slightly different conditions, and the exact method of preparation was found to have an effect on the structural and magnetic properties. These differences are described fully in later sections and are summarised in Table 4.2. An ampoule with a large external to internal diameter ratio of about 1.4 was used as the temperature

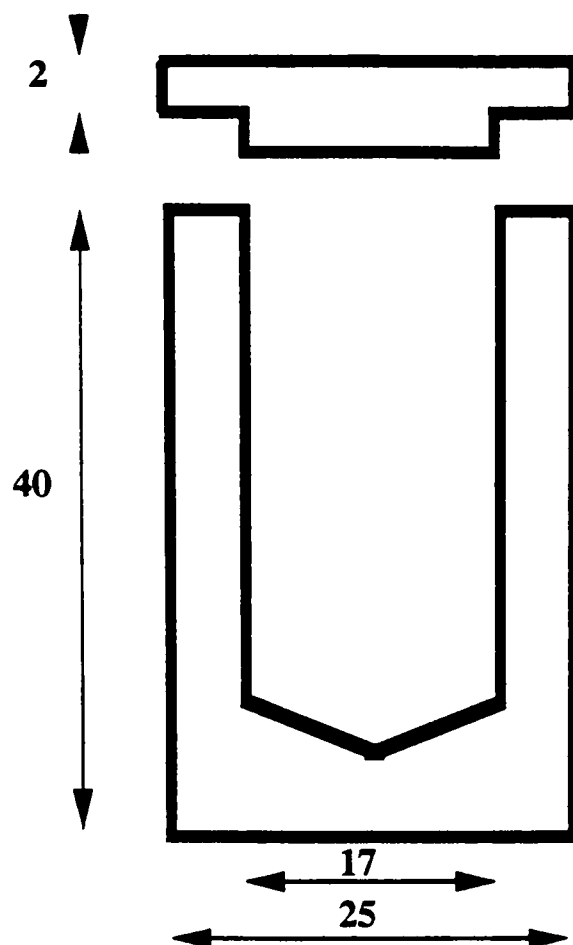


Figure 4.2: The iron ampoules used to make NaTiO_2 . Dimensions are in mm.

is raised to the boiling point of Na (900°C). However, it seems that the intercalation of Na into anatase is largely complete before this point is reached and the pressure in the ampoule never gets very large. The ampoule was cooled to room temperature in the furnace at a rate of approximately 5°Cmin^{-1} . The ampoule was opened in two stages: firstly, a lathe was used to thin the walls in the region of the weld to around 1 mm. Then the ampoule was transferred to the dry-box where a tube-cutting tool was used to cut through the wall. This procedure avoids any contact of the NaTiO_2 with the air. NaTiO_2 formed by this route is black and the X-ray diffraction pattern shown in Figure 4.3 agrees closely with that of Hagemuller *et al.* [126]. On exposure to the air the material degrades quickly, via reaction with atmospheric water, producing NaOH and Na_xTiO_2 ($x < 1$). Eventually, the material is oxidised to TiO_2 by reaction with oxygen in the air and becomes white.

On removal from the ampoules, the mass of the product was typically less than 10 mg smaller than that of the original contents. Some solid remained attached to the inner surface of the ampoule and so it seems that the loss of mass from ampoules made from the ARMCO soft ingot iron is less than 0.3%. A qualitative elemental analysis of some of the samples using energy dispersive X-ray analysis in a JEOL electron microscope indicated that only Na, Ti and O were present and that no Fe

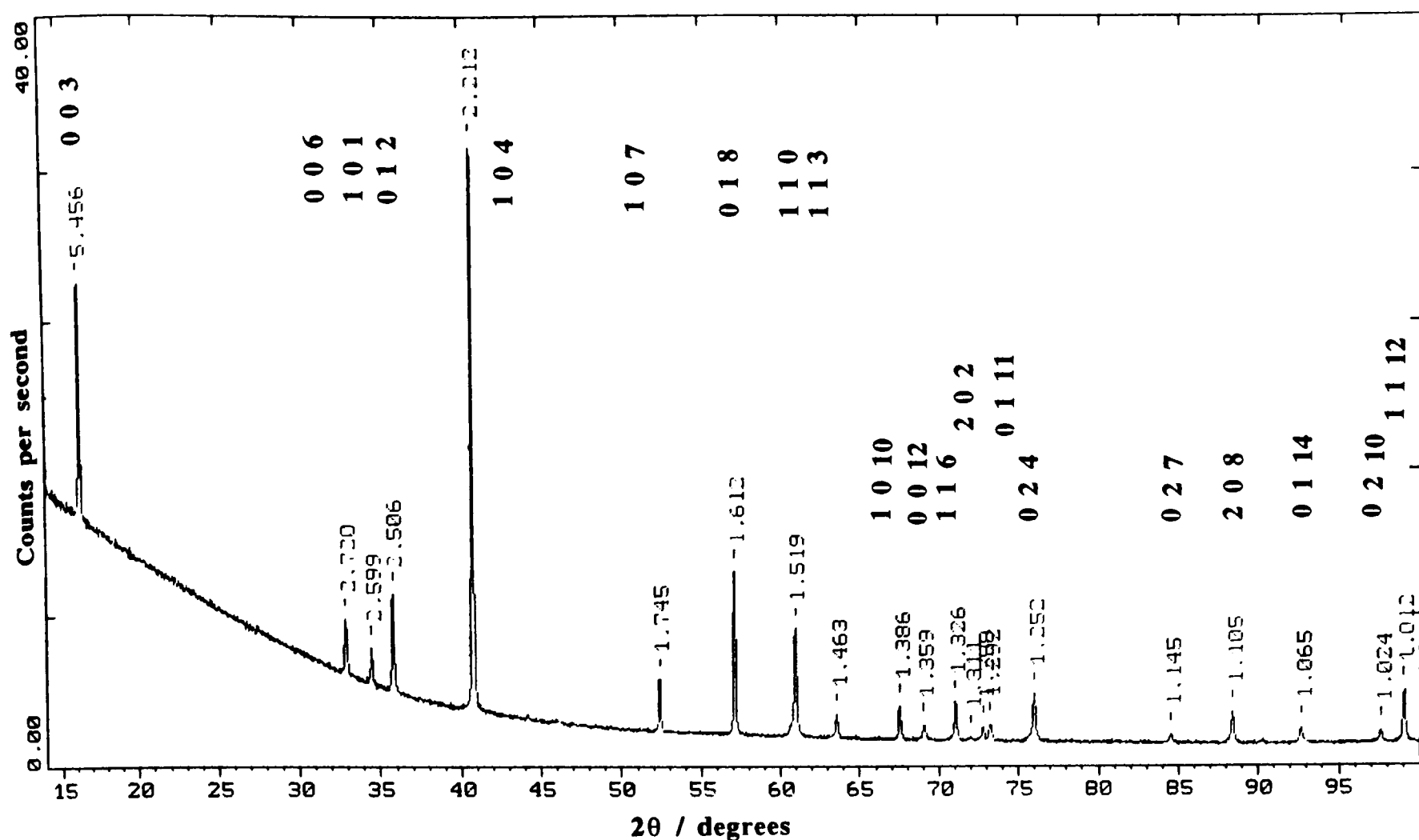


Figure 4.3: The X-ray diffraction pattern of NaTiO_2 measured using a Siemens D5000 diffractometer operating in transmission geometry.

had been introduced from the sample container above the level of about 3%.

Some of the samples were reground and treated under various heating and cooling regimes, including quenching from 1000° and slow cooling. However, these samples were contained in narrow ampoules made from 99.5% iron (from Goodfellow metals) capped by a stainless steel bolt which was then welded on. It was found that there was some loss of mass from these ampoules which indicated that the Na content had decreased and this was presumed to be due to the different type of iron used or to the use of the stainless steel bolt. These samples will not be considered further.

Samples were also prepared in which the nominal stoichiometry deviated from $\text{Na}_{1.0}\text{TiO}_2$. These were prepared in similar fashion but with the initial mixture of starting materials adjusted accordingly. Samples prepared from mixtures containing an excess of Na were prepared in order to see if reduction to Ti^{2+} was possible (The oxide TiO_x with x close to 1 exists), or to avoid the consequences of any Na loss during heating. After heating at 950°C for 7 days, these samples were 'sticky' when ground up indicating the presence of unreacted Na. Accordingly, each of these was washed in entirety with liquid ammonia in order to determine how much Na remained

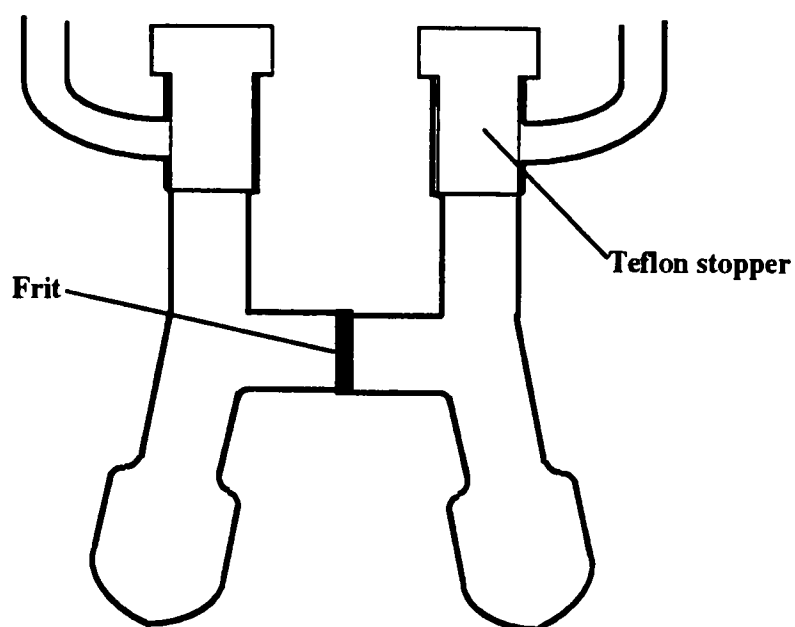


Figure 4.4: An 'H'-cell of the type used for washing a solid with a solvent under inert conditions and at low temperatures. The use of the apparatus is described in the text.

unreacted. The washing was performed in the following manner.

A round-bottomed flask containing a small amount of Na was attached to a Wayda-Dye greaseless vacuum line [129] which was evacuated to a pressure of 4×10^{-4} torr using an Edwards EXT 70/NW 40 turbomolecular pump. Part of the line, including the flask, was then isolated from the pump and a few cm^3 of $\text{NH}_{3(l)}$ from a cylinder was condensed into the flask with the aid of an isopropyl alcohol (IPA)/dry-ice slush bath at -80°C . The ammonia was dried and deoxygenated by leaving it in contact with the Na for about 30 minutes. In the meantime, an 'H'-cell (shown in Figure 4.4) containing the powdered sample (approximately 3 g) in one of its arms was attached to the line via UltraTorr connectors and stainless steel bellows tubing, and was evacuated to a pressure of 4×10^{-4} torr. The part of the line containing both the dried $\text{NH}_{3(l)}$ and the 'H'-cell was then isolated from the pump, and the ammonia was condensed from the round-bottomed flask onto the solid.

Upon contact with the solid, the ammonia turned blue indicating the presence of dissolved Na. The solution was filtered through the frit in the 'H'-cell into the empty side. Although thick-walled glass apparatus was used, care was taken to ensure that the solution did not boil at any point during its passage by pouring the IPA/dry-ice slush over the parts of the 'H'-cell in contact with the solution. The ammonia was

Sample i.d.	Mass washed/g	apparent stoichiometry after washing
Na _{1.3} TiO ₂	0.5	Na _{0.97} TiO ₂
Na _{1.3} TiO ₂	2.5	Na _{1.06} TiO ₂
Na _{1.2} TiO ₂	3.5	Na _{1.01} TiO ₂
Na _{1.1} TiO ₂	0.5	Na _{1.06} TiO ₂

Table 4.1: The results of titration of the excess Na removed from Na_xTiO₂ samples with $x > 1.0$ by washing with liquid ammonia.

then condensed back onto the solid by immersing only the solid-containing chamber in the slush bath. By this means the solid was washed and filtered 3–5 times until the ammonia in contact with the solid did not show any blue colouration, which indicated that a minimal amount of Na remained in contact with the solid, and all of it had been washed into the other side of the ‘H’-cell. The bulk of the ammonia was removed from the ‘H’-cell by condensing it into a storage ampoule and the remainder was removed by pumping the ‘H’-cell to a pressure of about 2×10^{-5} torr overnight. The solid was removed from the ‘H’-cell in the He dry-box. The solid was still black and did not appear to have reacted with ammonia. The X-ray diffraction patterns measured before and after washing were not significantly different. The amount of Na which had been removed was determined by dissolving it in water, adding a measured excess of 0.1 M HCl solution and then back-titrating this with 0.1 M NaOH solution. This procedure was carried out on samples with nominal stoichiometries of Na_xTiO₂ where $x=1.1$, 1.2 and 1.3. The results of titrations are tabulated in Table 4.1. The results indicated a range of x in the products of between 0.97 and 1.06. There are a number of sources of error including the possibility that some of the Na is lost from the iron ampoule during heating. There was evidence that this had occurred in some cases which would account for an apparent value of x greater than 1.0 in a product which was truly Na₁TiO₂. It seems likely that the washed solid has the stoichiometry Na_{1.0}TiO₂. The extreme air-sensitivity of the material makes the standard techniques such as Thermogravimetric Analysis (TGA) difficult, as there is a small but significant change in mass while the material is placed in the TGA apparatus. This makes it difficult to determine small deviations of x in Na_xTiO₂ from 1, which is exactly

what we want to achieve! Although what appear to be good-quality samples can be prepared by mixing stoichiometric quantities of the starting materials, there are reasons for favouring the use of excess Na followed by washing with liquid ammonia:

- The Na_xTiO_2 phase diagram seems to be bounded by $\text{Na}_{1.0}\text{TiO}_2$, ie there is no reduction to Ti^{2+} , so an excess of Na may be safely used.
- The problem that a small amount of Na may be lost from the iron ampoule during the heating of a stoichiometric mixture, resulting in an Na-deficient product is alleviated.
- The lattice parameters and magnetic properties of samples prepared in this way seem to be more reproducible than if a stoichiometric starting mixture is used. (see Table 4.2).

4.4 Analysis of Na_xTiO_2 by X-ray Diffraction at room temperature

4.4.1 X-ray diffractometers

The X-ray diffraction patterns of the Na_xTiO_2 samples were all recorded using a Siemens D5000 diffractometer operating in transmission mode with the sample contained within a sealed glass capillary with an internal diameter of 0.3, 0.5 or 0.7 mm and a wall thickness of 0.01 mm. This strategy was used purely because the samples are air sensitive.

Usually for a ternary transition metal oxide one would use a diffractometer operating in symmetrical reflection mode (Figure 4.5) with a large amount of sample mounted on a flat plate. The para-focussing nature of this so-called Bragg-Brentano arrangement means that a large amount of the sample can contribute to the measured intensity without loss of resolution, and when the sample is a relatively good absorber of X-rays (as a transition metal oxide is), there is no resolution penalty for using a thick sample. However, no truly air-tight sample holder suitable for use in the reflection geometry was available to us. A sample of NaTiO_2 contained between

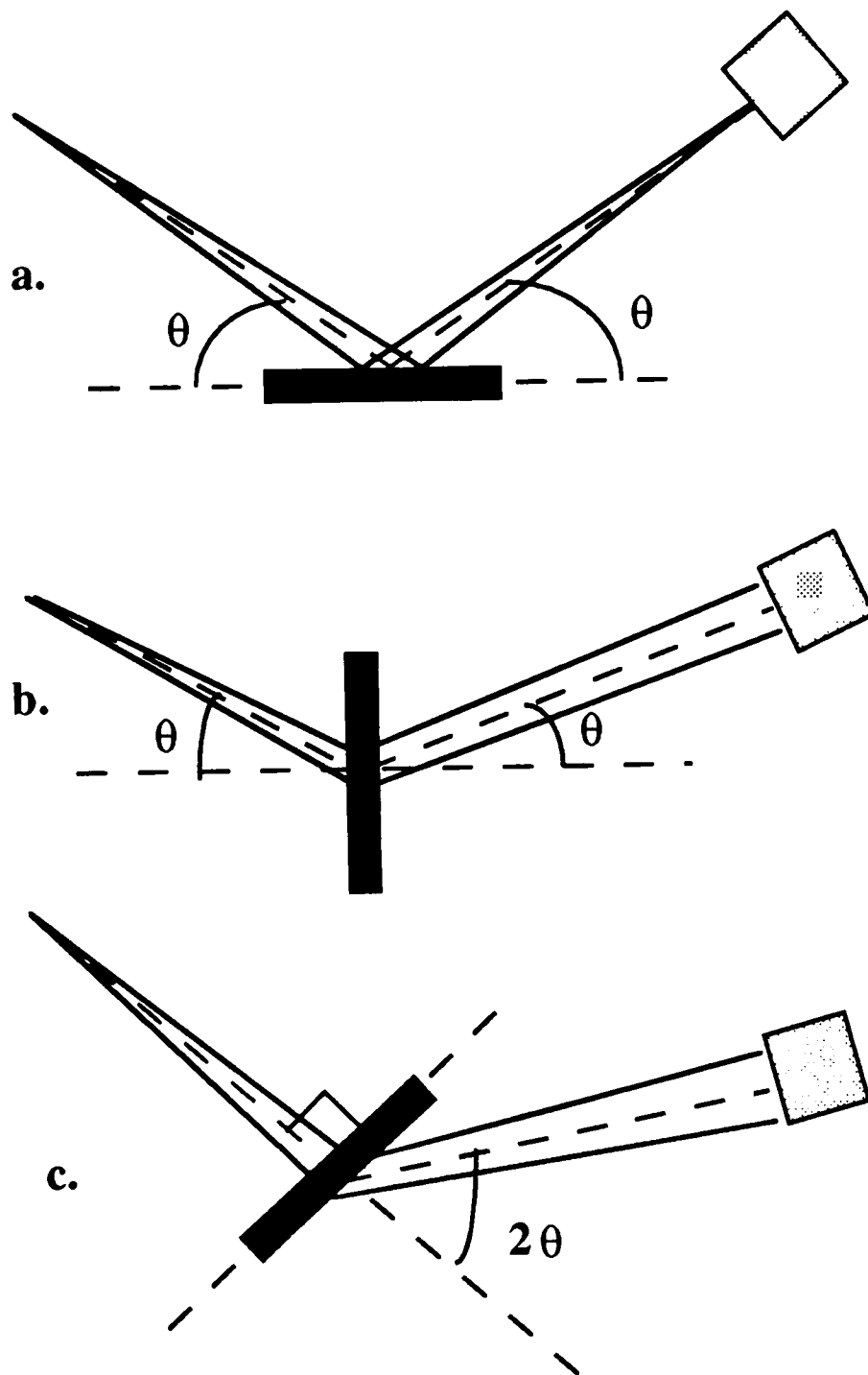


Figure 4.5: The geometries used in X-ray and neutron diffraction. (a.) Bragg-Brentano reflection geometry. (b.) Symmetric transmission geometry. (c.) Asymmetric transmission geometry. For a cylindrical sample, (b.) and (c.) are equivalent.

a flat plate and a sellotape or mylar closure was found to change its diffraction pattern over the course of a few hours, and the covering contributes to the background or has its own Bragg peaks. The alternative to reflection geometry is to use one of two transmission geometries shown in Figure 4.5. These two are equivalent when the sample is cylindrical. Transmission is the favoured geometry when the sample contains mostly light elements such as carbon, which are poor absorbers of X-rays. The beam converges on the detector to avoid loss of resolution due to the absence of focussing. The drawback with transmission as far as NaTiO_2 is concerned is that absorption of X-rays is significant, reduces intensity, and the angle dependent intensity loss must be corrected for by measuring the linear absorption coefficient and calculating the absorption cross-section as a function of angle [130]. Also, the amount

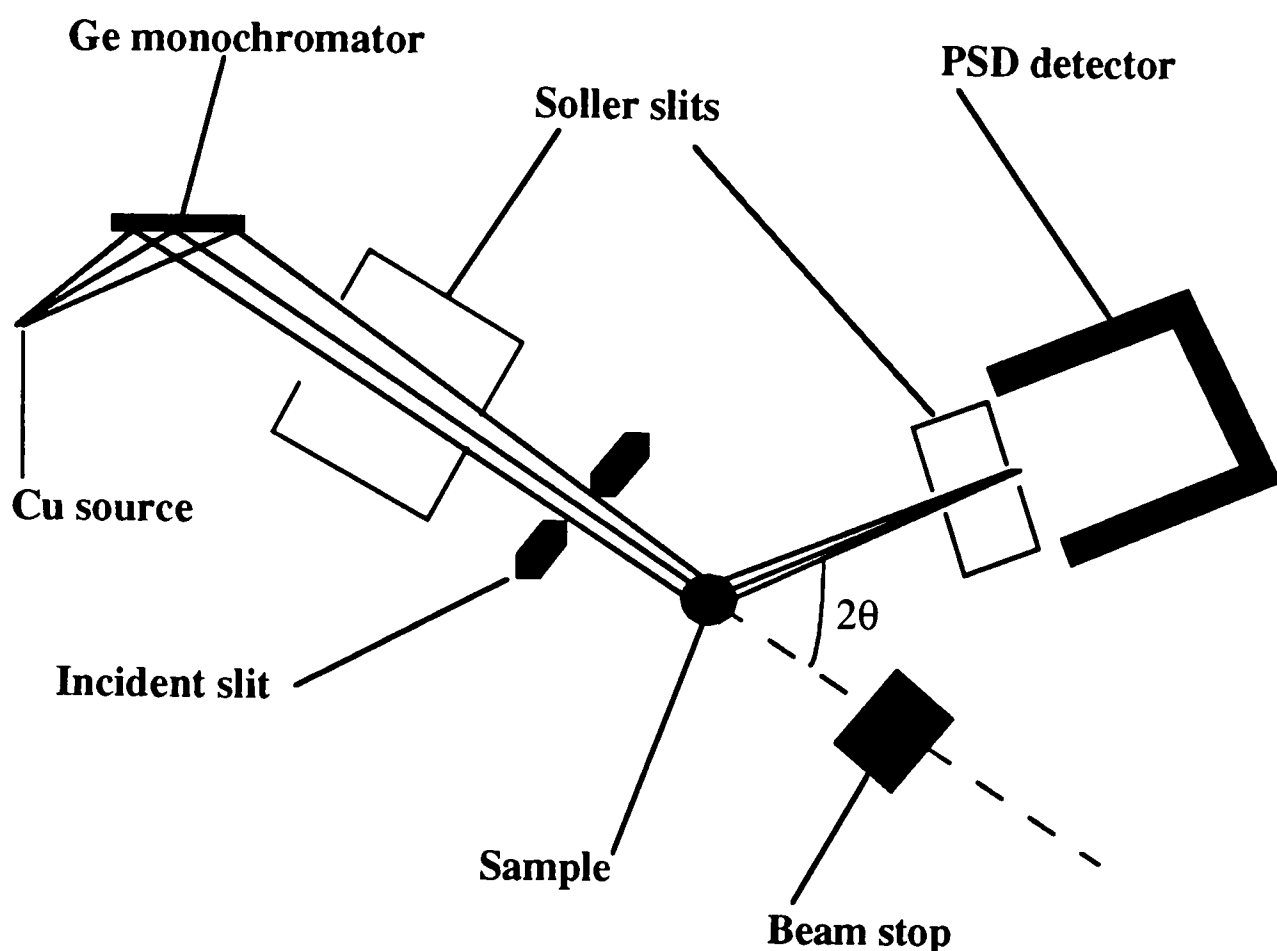


Figure 4.6: The Siemens D5000 transmission geometry diffractometer. The $\text{CuK}\alpha_1$ radiation is selected using a Ge (111) monochromator. It is collimated horizontally using Soller slits, passes through an incident slit which should be about three times the capillary diameter in order to optimise the signal to background ratio for a convergent beam, and is diffracted by the sample. The diffracted X-rays are detected using a wide-angle Position Sensitive Detector.

of sample contained in a capillary is small and this reduces the diffracted intensity below what one could achieve on a reflection machine. Intensity can be improved by integrating the scattering along a significant length (a few mm) of capillary and by the use of a wide-angle detector. A wide-angle, Position Sensitive Detector (PSD) made by Braun was used in these measurements. The PSD may be moved continuously over the 2θ range, and measures the scattering over a 8° angular range at each point. A schematic diagram of the diffractometer is presented in Figure 4.6.

The results of the X-ray analysis of samples with different compositions and prepared in slightly different ways is presented in Section 4.4.2.

4.4.2 Variation of lattice parameters with composition

In order to determine the lattice parameters of the different Na_xTiO_2 samples, each was measured using the D5000 diffractometer. $\text{Cu-K}\alpha_1$ radiation of wavelength

1.54051 Å was selected using the (111) plane of a Ge monochromator crystal. The samples were measured over the angular range 10 to 100° in 2θ and the PSD was moved at about 0.2 deg min⁻¹. The capillary containing the sample was mounted and centred on a goniometer which was rotated during the measurement about the capillary axis in order to minimise the effects of preferred orientation of the crystallites, and to give a good powder average of the sample. Table 4.2 summarises the stoichiometries and preparation conditions of the samples prepared. All the samples could be indexed using a hexagonal cell with approximate lattice parameters $a=b=3.0$ Å and $c=16.3$ Å. In the samples with $x > 0.8$ all the reflections satisfied the rhombohedral condition that $-h + k + l = 3n$ indicating that the choice of spacegroup $R\bar{3}m$ was reasonable. As many reflections as possible (about 15–20) were used in the lattice parameter refinement program REFCEL [131], and the results of the refinement of the lattice parameters and unit cell volume are included in Table 4.2. The samples Na_{0.7}TiO₂ and Na_{0.8}TiO₂ seem to have additional reflections which either arise from a reduction in symmetry or from there being a mixture of two phases.

The variation of the two lattice parameters and the unit cell volume with x is shown graphically in Figure 4.7. As x in the preparation mixture increases so the c -axis of the product decreases and the hexagonal basal plane increases in size; these changes do not compensate one another and the change in volume is dominated by the change in the size of the basal plane. When x is close to 1.0, the lattice parameters are very sensitive to the value of x . It appears that the samples made by mixing stoichiometric ingredients have slightly different compositions, either due to weighing errors or due to loss of some Na from the iron reaction vessels.

4.4.3 Rietveld profile refinement

If the preparation of single crystals is not possible, X-ray or neutron *powder* diffraction must be used for structure determination. The disadvantage of this is that all the information from the three dimensions of reciprocal space is projected onto one dimension and reflections usually overlap one another. The overlap arises either because

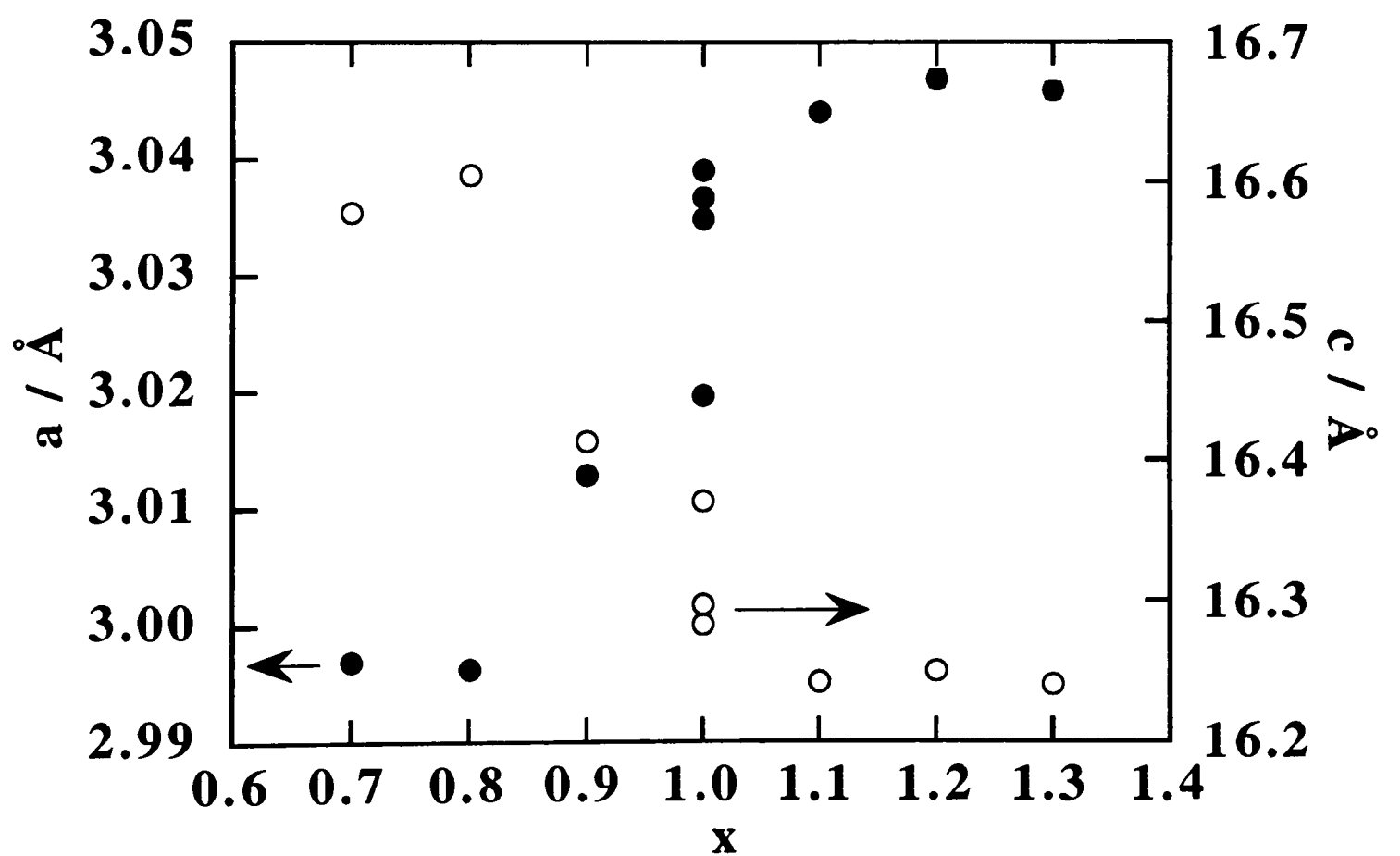
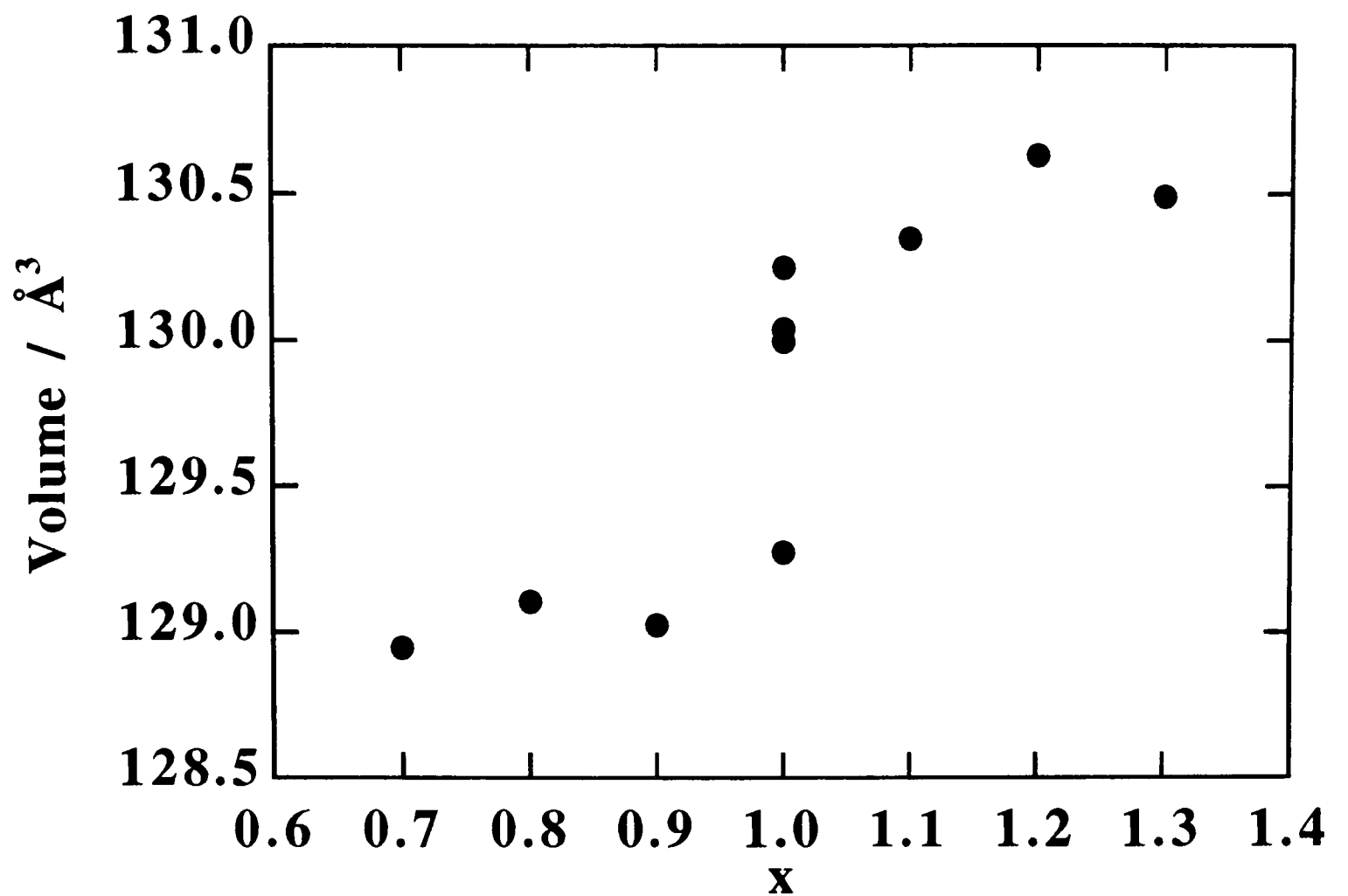


Figure 4.7: Lower: The variation of the lattice parameters $a=b$ and c with composition of the mixtures of Na and TiO_2 used in preparation of the sample. a and b increase with increasing Na-concentration, while c decreases. Upper: The behaviour of the unit cell volume is dominated by the behaviour of a and b .

Sample i.d.	Preparation conditions	$a=b/\text{\AA}$	$c/\text{\AA}$	Vol/ $\text{\AA}^3$
Na _{0.7} TiO ₂	950°C 7 days	2.9969(1)	16.5782(22)	128.95
Na _{0.8} TiO ₂	950°C 7 days	2.9963(1)	16.6052(16)	129.11
Na _{0.9} TiO ₂	950°C 7 days	3.0128(2)	16.4143(26)	129.03
NaTiO ₂ -1	910°C 48 hours	3.0196(1)	16.3719(14)	129.28
NaTiO ₂ -2	920°C 60 hours	3.0349(1)	16.2978(12)	130.00
NaTiO ₂ -3	920°C 80 hours	3.0367(1)	16.2837(10)	130.04
NaTiO ₂ -4	1000°C 7 days	3.0391(1)	16.2837(6)	130.25
Na _{1.1} TiO ₂	950°C 7 days	3.0441(1)	16.2428(10)	130.35
	washed	3.0445(1)	16.2506(6)	130.45
Na _{1.2} TiO ₂	950°C 5 days	3.0469(2)	16.2503(32)	130.63
	washed	3.0458(1)	16.2472(5)	130.53
Na _{1.3} TiO ₂	950°C 5 days	3.0459(1)	16.2407(9)	130.49
	washed	3.0457(1)	16.2425(8)	130.48

Table 4.2: A summary of the Na_xTiO₂ samples investigated, with the conditions for their preparation listed. The conditions marked by an asterisk were carried out in a thin, 99.5% Fe ampoule. All others in thick-walled 99.8% ARMCO soft ingot iron ampoules. The three samples prepared with excess Na were washed with liquid ammonia as explained in Section 4.3.

the structure has high symmetry and several hkl planes have the same d -spacing, or because the structure has a lower symmetry and many reflections at different angles, each with a finite width overlap one another. The overlap hampers the determination of the structure factor amplitude, F_{hkl}^2 , of each reflection. Rietveld developed a method of refinement which used the integrated intensity of a set of overlapping peaks [132]. He then modified this to include the peak profile [133] and finally devised a method [134] of refining a structural model by comparison of the calculated diffraction profile of the model with the entire experimental diffraction profile, which is the best way of compensating for the loss of information resulting from peak overlap. The Rietveld Method does not require the determination of integrated peak intensities. The procedure uses a non-linear least-squares fit. The use of the procedure became practical at the end of the 1960s when sufficiently powerful computers became available. It was originally developed for use with neutron diffraction patterns obtained from the reactor at Petten in the Netherlands, because the peakshape for neutron scattering may be accurately described by a nearly Gaussian function. The development of the method for use with X-ray diffraction data became possible after

the correct functional form for the peak profile was developed [135]. The use of the Rietveld method is summarised by Young [136]. The model should usually be close to the actual structure, and so the method is strictly one for refinement, although it may be used as the main tool to solve structures *ab initio* from a knowledge of the unit cell and an educated guess at the structure [137]. A number of computer programs are available for performing Rietveld refinements [138, 139]. A large number of parameters may be refined, including, as well as all the structural parameters, the background, the peakshape and the absorption by the sample. The quality of fit is quantified by the R-factors defined as:

$$R_p = \frac{\sum_i |Y_{obs}^i - Y_{calc}^i|}{\sum Y_{obs}^i} \quad (4.1)$$

$$R_{wp} = \sqrt{\frac{\sum_i w_i (Y_{obs}^i - Y_{calc}^i)^2}{\sum_i w_i Y_{obs}^{i2}}} \quad (4.2)$$

where Y_{obs}^i and Y_{calc}^i are the observed and calculated intensities of each data point, w is a weighting parameter for each data point, and the summation is carried out over all data points. R_p is described as the *pattern R-factor* and R_{wp} as the *weighted-profile R-factor*. The function which is minimised is the square of the numerator of Equation 4.2 ($\sum_i w_i (Y_{obs}^i - Y_{calc}^i)^2$). One can calculate an expected R -factor, R_{exp} which is determined by the weighted sum of the data points, the number of observables, N_{obs} , the number of variables in the fit, N_{var} , and the number of constraints applied, N_{cons} according to:

$$R_{exp} = \frac{\sqrt{N_{obs} - N_{var} + N_{cons}}}{\sqrt{\sum_i w_i Y_{obs}^{i2}}}. \quad (4.3)$$

The ‘goodness of fit’ parameter, χ^2 is then defined by

$$\chi^2 = \frac{\sum_i w_i (Y_{obs}^i - Y_{calc}^i)^2}{N_{obs} - N_{var} + N_{cons}}, \quad (4.4)$$

and its value after each cycle of refinement gives an indication of how the fit is proceeding. It should be noted that in performing a Rietveld refinement one should pay as much attention to the appearance of the fit as to the size of χ^2 and the R -factors, in order to avoid the problem of the refinement settling in a local minimum.

During refinement, the errors in the refined parameters are represented by the standard deviation which is usually included in brackets as a variation in the last

significant figures of the parameter value. The estimated standard deviation, σ_j in parameter j is defined as:

$$\sigma_j = M_{jj}^{-1} \frac{\sum_i w^i (Y_{obs}^i - Y_{calc}^i)^2}{N_{obs} - N_{var} + N_{cons}} \quad (4.5)$$

where M_{jj}^{-1} is the appropriate diagonal element of the variance-covariance matrix used in the least-squares routine, N_{cons} is the number of constraints applied to the fit, the summation is over all data points and the other parameters are as already defined.

Rietveld profile refinement was carried out using the widely-used General Structure Analysis System (GSAS) [138].

4.4.4 Rietveld refinement of stoichiometric NaTiO₂

The stoichiometric sample NaTiO₂-3 was chosen as one on which to perform Rietveld refinement. The data set used was collected over the angular range 14 to 100° with the PSD moved at a rate of 0.023 deg min⁻¹ in order to maximise the signal to noise ratio. The measured peak width was found to be the same using PSD resolutions of 0.01° and 0.02°, but to broaden at a resolution of 0.05°, and so the 0.02° resolution was used to improve further the signal to noise ratio. The sample was contained in a 0.3 mm capillary in order that absorption was not too severe. The incident slit was set to 1 mm which was found to give the optimal signal to background ratio for a 0.3 mm capillary and a converging beam; a smaller slit decreased the diffracted intensity, while a larger slit increased the background without increasing the diffracted intensity. The absorption coefficient, μ_r of the sample was determined by measuring the integrated intensity of the straight-through beam with and without the sample present using a scintillation counter equipped with a 6 mm copper attenuator and a 0.1 mm collimator. μ_r is related to the measured intensities by the Beer-Lambert law:

$$\mu_r = -\ln(I/I_0) \quad (4.6)$$

where I_0 is the integrated intensity in the absence of the sample. The value of μ_r was determined to be 1.2 for this sample and was used as a constant in GSAS. The procedure followed for Rietveld refinement was as follows

- The diffraction pattern was indexed using the results of Hagenmuller *et al.* [126].
- Approximate values of the lattice parameters and the zero-point error of the D5000 were determined from the angles of the measured, indexed reflections using the program REFCEL [131]. These values of $a=3.0367 \text{ \AA}$ $c=16.2837 \text{ \AA}$ taken from Table 4.2 and a zero-point (Zp) of -0.03° were used in the initial model.
- The atoms were inserted into the unit cell according to the model of Hagenmuller *et al.* [126] which used space group $R\bar{3}m$. The absorption correction was also made at this stage.
- The background was fitted to a cosine fourier series expression with 8–10 variable parameters using the GENLES non-linear least-squares fitting routine in GSAS. A large number of parameters was required because of the steeply varying background at low angle which is due to scattering by the air. The scale factor for the pattern was also refined at this stage. The signal:noise ratio should be as large as possible, since the background is easier to fit than the peaks and if it is too large, relatively too much weight will be apportioned to the background points and R_{wp} will be too small.
- The lattice parameters and zero were then inserted into the refinement.
- The peak profile was refined. This is a function with a Gaussian component of constant width and a 3-parameter Lorentzian component whose width varies with angle as described in references [140] and [135]. A function composed of Gaussian and Lorentzian components is called a pseudo-Voigt function.
- The atomic position parameters were refined according to symmetry. For the spacegroup $R\bar{3}m$, only the position of oxygen along the c -direction could be varied.
- The isotropic thermal parameters for each site were refined. It was found that these became negative (and hence unphysical) if the absorption correction was

not included. The isotropic thermal parameters produce a temperature factor in the structure factor

$$F_{hkl} = \sum_j f_j \exp[-2\pi i(hx_j + ky_j + lz_j)] \exp[-2\pi^2 U(\sin \theta/\lambda)^2] \quad (4.7)$$

where U_j is the thermal parameter of atom j , and the other terms are as already defined.

- The occupancies of the metal ion sites were refined allowing some proportion of the Na to occupy the Ti site and an identical proportion of the Ti to occupy the Na site.
- Between each step in the refinement the R -factors, χ^2 and the visual appearance of the fit were inspected to ensure that the refinement was indeed directing the model towards the global minimum and not settling in an unrealistic local minimum.

The final fit to the $R\bar{3}m$ model is shown in Figure 4.8 and the parameters obtained are listed in Table 4.3. Although it is not possible to determine the actual integrated intensities of the experimental peaks (that is the reason the Rietveld method was employed in the first place), one may determine an ‘observed’ structure factor, $I_{obs'}^{\frac{1}{2}}$, from the results of the refinement. The ‘observed’ structure factors for the reflections were extracted using the program RCALC in the GSAS suite. Comparison of the ‘observed’ and calculated structure factors leads to calculation of the Bragg R -factor, R_B (Equation 4.8) and the Structure Factor R -factor, R_F (Equation 4.9). R_F was determined to be 6.43% which indicates a good quality fit.

$$R_B = \frac{\sum (I_{obs'} - I_{calc})}{\sum I_{obs'}} \quad (4.8)$$

$$R_F = \frac{\sum (I_{obs'}^{\frac{1}{2}} - I_{calc}^{\frac{1}{2}})}{\sum I_{obs'}^{\frac{1}{2}}} \quad (4.9)$$

Reduction of symmetry

One can reduce the symmetry of the structure from $R\bar{3}m$ to the monoclinic space group $C2/m$ by removal of the 3-fold axis of rotation, and the construction of a new

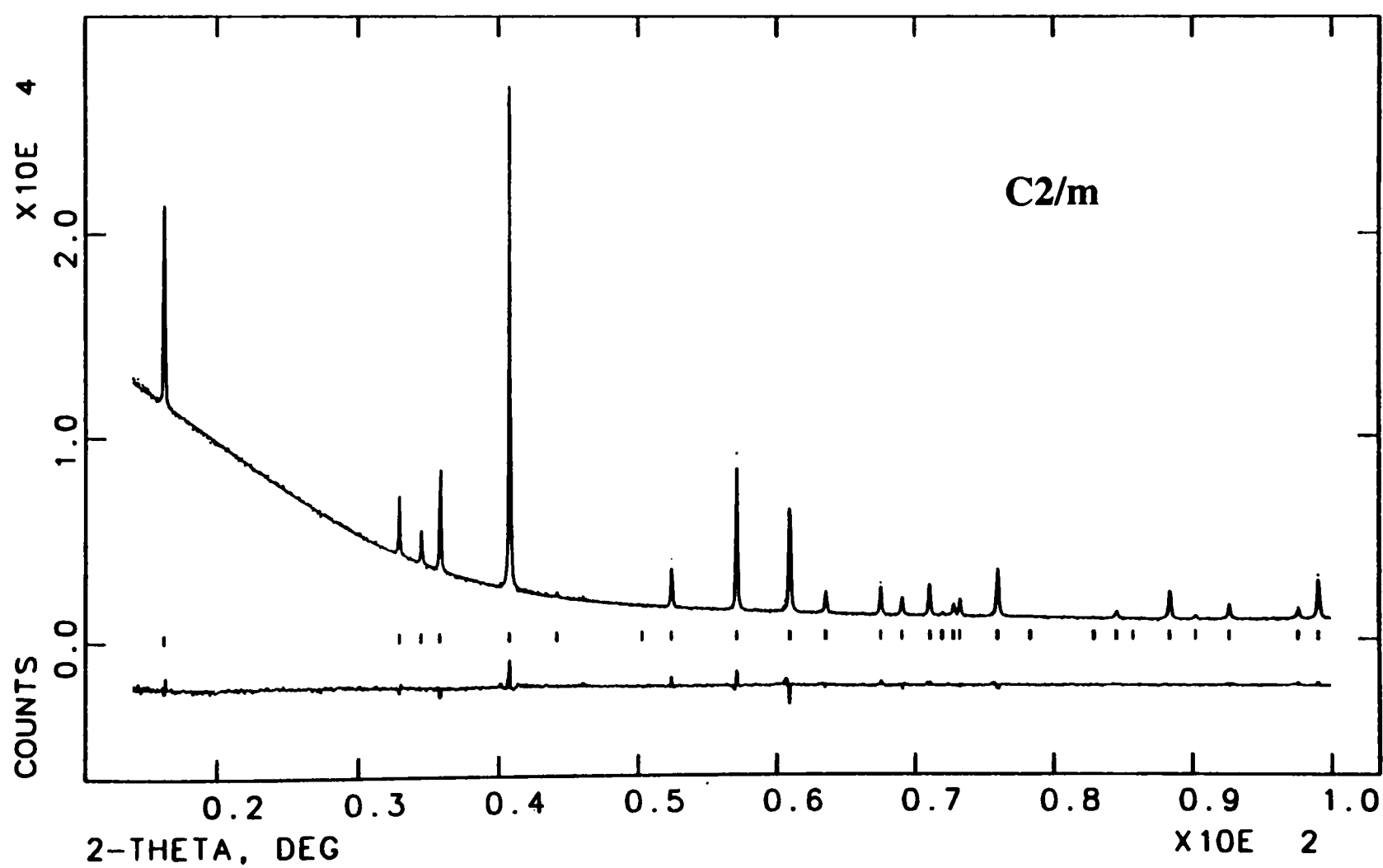
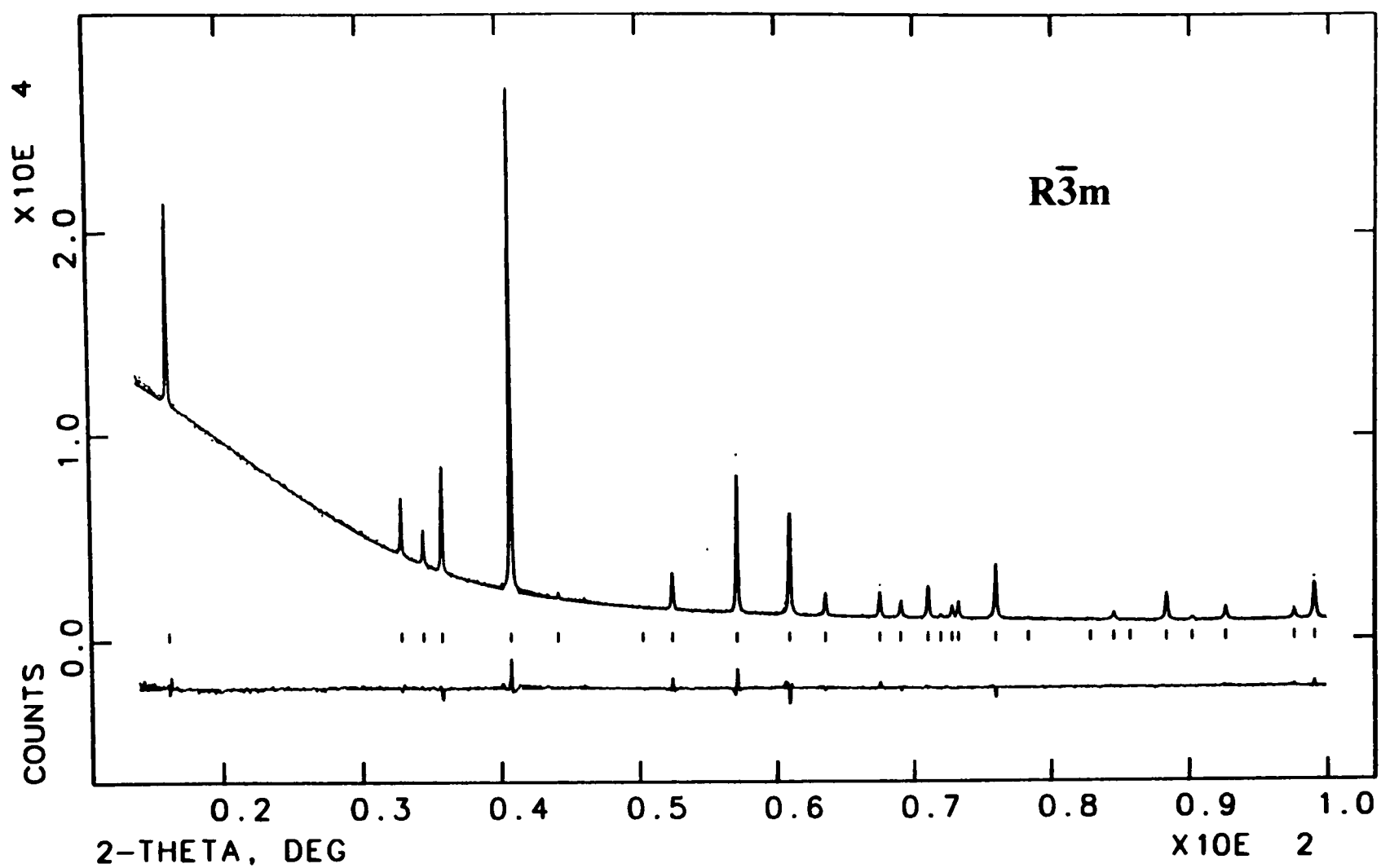


Figure 4.8: The results of Rietveld refinement of NaTiO₂ (sample 3) using the space-groups $R\bar{3}m$ and $C2/m$. The data does not allow one to distinguish between the two models. The cell is very closely hexagonal in the lower symmetry space-group.

unit cell which is $\frac{2}{3}$ of the size of the hexagonal cell. The relationship between the two unit cells is shown in Figure 4.9. The reason for repeating the refinement using the lower symmetry spacegroup was initially because refinements in $R\bar{3}m$ without an absorption correction produced negative temperature factors. However with the realisation that the magnetic anomaly at 250 K discussed in detail in Section 4.5 could be due to some structural change, and in the light of investigations of Na-deficient phases prepared at room temperature [127], we explored the possibility that, although all the observed reflections satisfied the rhombohedral condition that $-h + k + l = 3n$, the room temperature structure may have a slightly lower symmetry than at first thought. This view was reinforced by the fact that NaCoO_2 is subject to this distortion on oxidation [128]. The refinement in $C2/m$ following the procedure above was successful. The oxygen atom has an extra degree of freedom in this spacegroup, but refined stably indicating that the lost symmetry element on which it had been located was not a requirement for good Rietveld refinement. The results for the two refinements are listed in Table 4.3 and the observed, calculated and difference plots for each are shown in Figure 4.8. Note that the refinement using $C2/m$ has the same R_{exp} , a lower χ^2 , a lower R_{wp} and R_p but a slightly larger R_F . Inspection of Figure 4.8 suggests that each model is equally good at describing the X-ray data, as oxygen is a weaker scatterer than either sodium or titanium. The structures obtained by the two refinements are shown in Figure 4.11. The change in the site symmetry of the Ti (and Na) ions is indicated in an exaggerated form in Figure 4.10. The distortion of the sites on lowering the symmetry is very small.

Use of the program RDUCLL in the GSAS suite which determines the relationships between cells of different symmetry indicated that the $C2/m$ cell obtained in the refinement was equivalent to a very nearly hexagonal cell and the lattice parameters for that cell are included in Table 4.3. It appears that the unit cell is hexagonal or very nearly so, but that the *symmetry* may be lower than $R\bar{3}m$. This possibility means that there is no longer the constraint that the Na^+ and Ti^{3+} ions each occupy a triangular lattice, and this loss of symmetry in an insulating system could prevent realisation of a truly triangular 2D magnet.

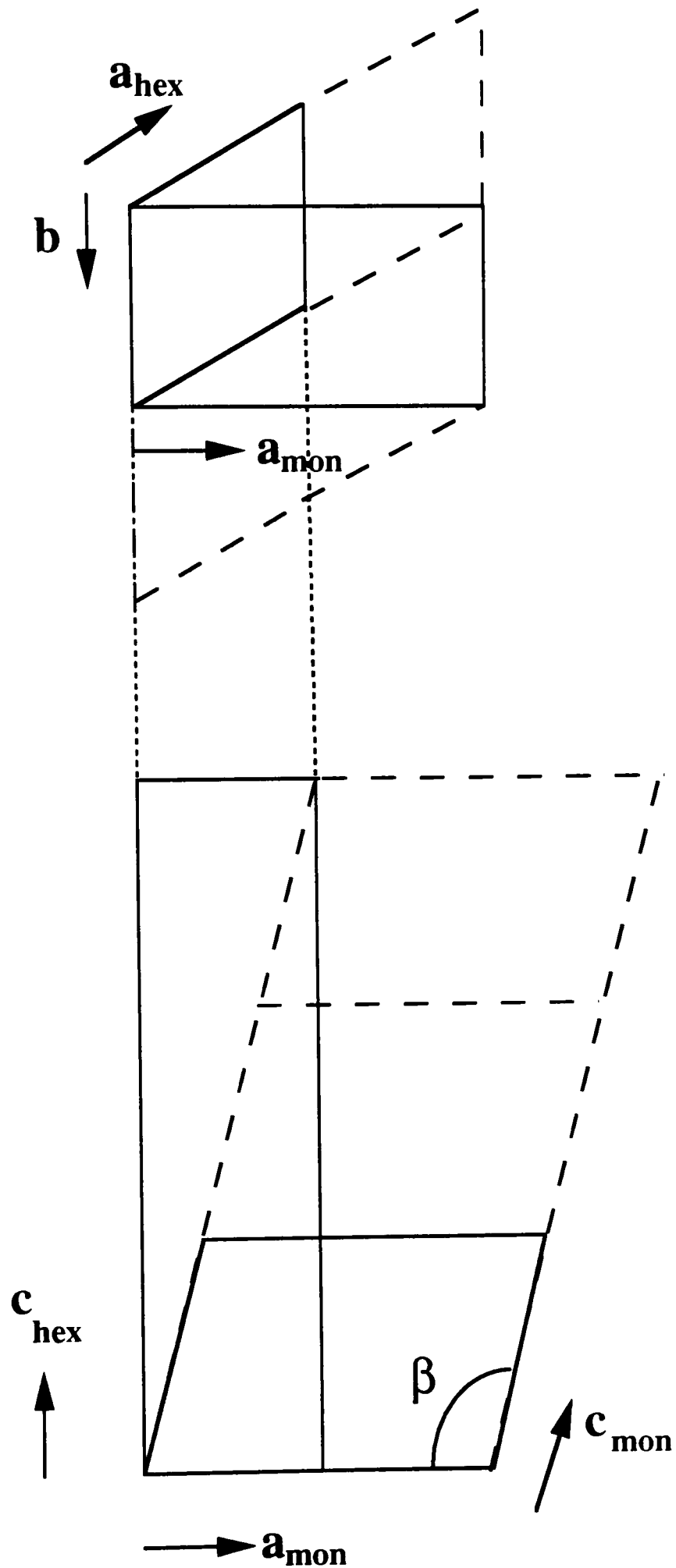


Figure 4.9: The relationship between the unit cells of the two possible space groups for NaTiO₂: the hexagonal/rhombohedral $R\bar{3}m$ and the monoclinic $C2/m$. In the latter, the oxygen atom has an extra degree of freedom. The upper picture is a view down the hexagonal c axis. The lower picture is a view down the b axes of both cells, since these coincide.

Variable	Value in $R\bar{3}m$	Value in $C2/m$	Conversion of $C2/m$ to pseudohexagonal cell
$a/\text{\AA}$	3.03525(6)	5.26117(13)	3.0330
$b/\text{\AA}$	3.03525(6)	3.03301(7)	3.0364
$c/\text{\AA}$	16.29606(31)	5.70799(11)	16.2964
$\alpha/^\circ$	90	90	89.994
$\beta/^\circ$	90	107.886(2)	90.00
$\gamma/^\circ$	120	90	119.963
$Zp/^\circ$	-0.0580(14)	-0.0575(13)	
Na(xyz)	(3a) 0 0 0	(2a) 0 0 0	
Ti(xyz)	(3b) 0 0 $\frac{1}{2}$	(2d) $\frac{1}{2}$ 0 $\frac{1}{2}$	
O(xyz)	(6e) 0 0 0.2352(2)	(4i) 0.7755(20) 0 0.2952(4)	
$U_{\text{Na}}/\text{\AA}^2$	0.0161(9)	0.0148(9)	
$U_{\text{Ti}}/\text{\AA}^2$	0.0076(5)	0.0100(5)	
$U_{\text{O}}/\text{\AA}^2$	0.0056(8)	0.0037(9)	
Abs [*]	1.2	1.2	
U^*	0.0	0.0	
V^*	0.0	0.0	
W	15.2(4)	13.8(5)	
X	3.11(50)	4.7(113)	
Y	10.82(115)	6.30(103)	
Z	-1.02(22)	-1.57(50)	
Asym	0.9(1)	0.9(1)	
χ^2	2.41	1.93	
R_{exp}	1.78	1.78	
R_{wp}	2.75	2.47	
R_p	1.79	1.59	
R_F	6.43	8.09	

Table 4.3: Comparison of the refinement parameters for NaTiO₂₋₃ refined using space groups $R\bar{3}m$ and $C2/m$. The background was described by an 8–10-component cosine fourier series. The U's are the isotropic temperature factors for each type of site. U , V and W define the Gaussian part of the pseudo-voigt lineshape and X , Y and Z define the Lorentzian part. Approximate errors are indicated as standard deviations in the last significant figures in brackets. Parameters followed by an asterisk (*) were not refined.

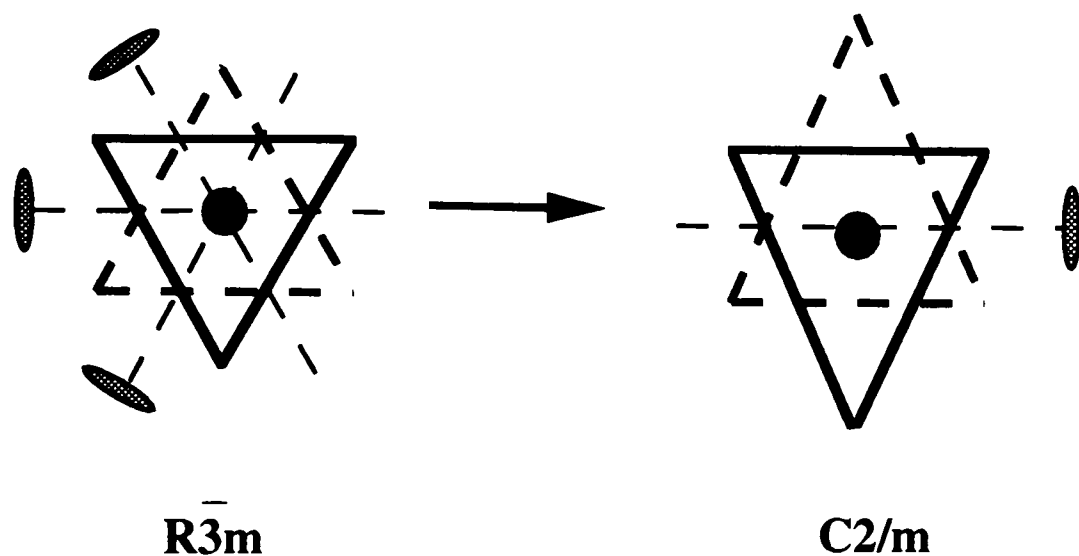


Figure 4.10: The distorted octahedral coordinations of the Na^+ and Ti^{3+} ions in the space groups $\bar{R}3m$ and $C2/m$ used to refine the X-ray data of NaTiO_2 . The site symmetry in $\bar{R}3m$ is $\bar{3}m$ (D_{3d}) and in $C2/m$, it is $2/m$ (C_{2h}). The distortion is shown in an exaggerated form. The C_2 axes of rotation are shown in each case.

Neither of the refinements suggested that there was significant disorder between the Na and Ti sites — ie. the disorder determined was less than 0.5% and zero to within error. The refinement of data collected using the same sample in the same capillary but using a shorter count-time indicated possible disorder at a level of about 3% which was greater than 3σ where σ is the estimated standard deviation in the degree of disorder. However, this must be regarded as a result of trying to refine more parameters than the quality of the data would allow. The refinement program operates in a ‘blind’ manner and will do anything within the constraints provided by the user to lower the value of χ^2 .

4.4.5 Rietveld refinement of Na-‘deficient’ phases

There is some evidence that Na_xTiO_2 prepared by room temperature deintercalation of Na [128] undergoes a distortion to a monoclinic space-group. There is also evidence for solid solutions which exist in the composition ranges $\text{Na}_{0.71}\text{TiO}_2$ to $\text{Na}_{0.87}\text{TiO}_2$ and $\text{Na}_{0.94}\text{TiO}_2$ to NaTiO_2 at room temperature [127]. Reaction mixtures with the compositions Na_xTiO_2 where $x = 0.70, 0.80$ and 0.90 were synthesised according to the method described in Section 4.3. They were heated for 7 days at 950°C .

The reflections of these phases were indexed using the space-group $\bar{R}3m$ and lattice parameters and unit cell volumes were refined using the program REFCEL [131].

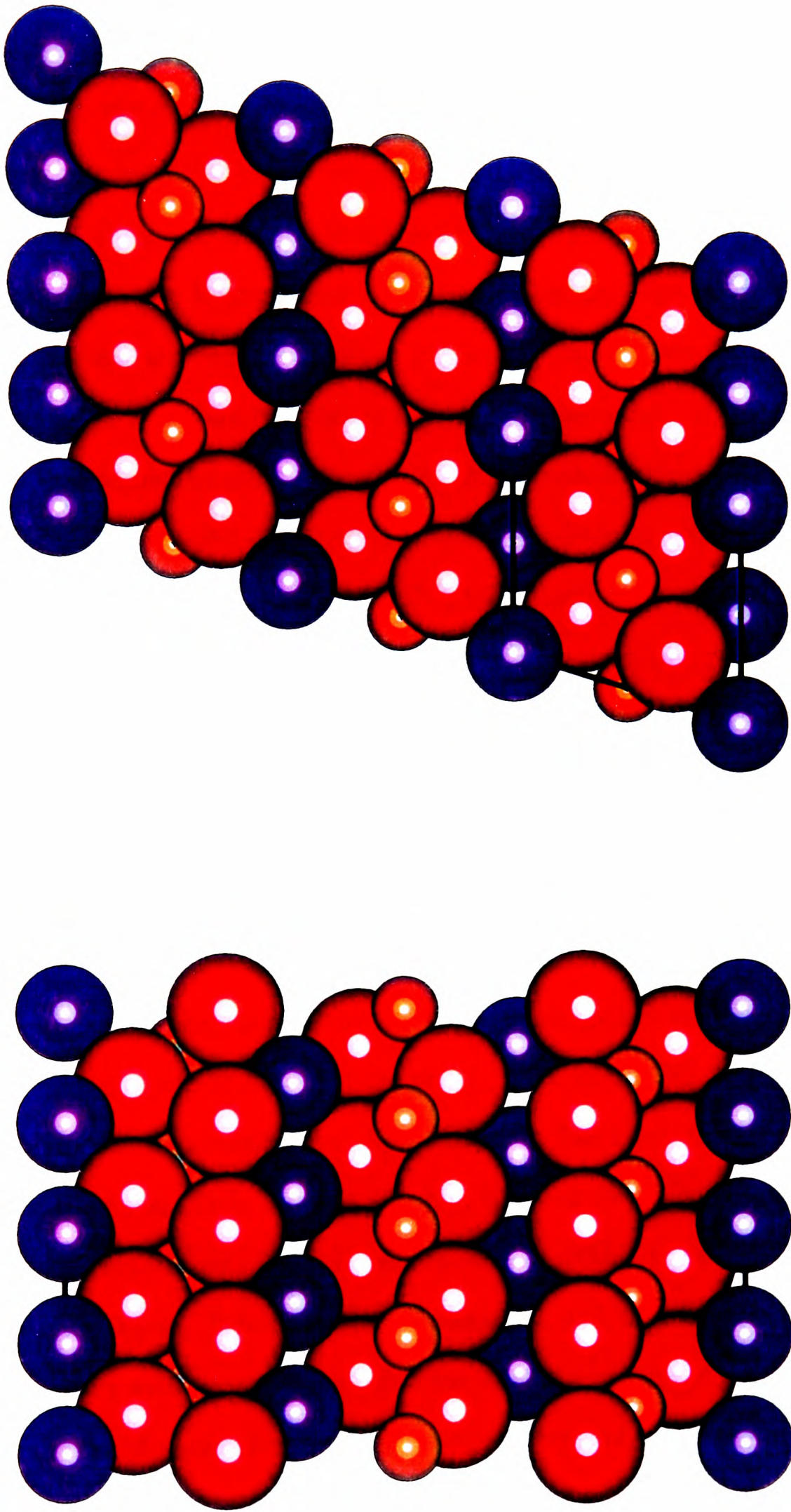


Figure 4.11: The structures of NaTiO_2 obtained by refinement using the spacegroups $R\bar{3}m$ (left) and $C2/m$ (right). Ti are orange, Na are purple and O are red.

The values are tabulated in Table 4.2 where they are compared with those of the samples prepared using a stoichiometric amount of Na or with an excess which was later removed. The variation of lattice parameter with x is presented graphically in Figure 4.7. As x is reduced, there is a decrease in the length of the lattice parameter c which is parallel to the 3-fold axis of the space-group and perpendicular to the planes of metal atoms. This may be explained by a simple consideration of ionic bonding: if some of the cations are removed from a particular plane leaving vacancies, one expects the anions in neighbouring planes to move further apart. If this removal of Na ions were accompanied by migration of some of the more highly-charged Ti^{3+} ions into these vacancies, one might expect the c lattice parameter to decrease as the ionic bonding between anionic planes was increased. This behaviour is observed by Delmas *et al.* [128] when x is reduced below 0.67 at room temperature.

Rietveld profile refinement of $\text{Na}_{0.8}\text{TiO}_2$ was carried out using GSAS on data collected for 3 days on the D5000 transmission diffractometer using a 0.3 mm capillary to contain the sample. Some of the peaks were broader than those of NaTiO_2 which could indicate *slight* distortion to a monoclinic unit cell and consequent overlap of unresolved Bragg peaks. However, not all the peaks which were clearly composed of two partially resolved peaks, such as the (0 0 3) peak of the hexagonal cell shown in Figure 4.12, could give rise to two or more peaks in the monoclinic system. This indicated that there were actually two phases present. The mixture may be a result of the stoichiometry $\text{Na}_{0.8}\text{TiO}_2$ lying in a region between two solid solutions at the high preparation temperature. Rietveld refinement was unable to establish the exact properties of these phases. Treating both as hexagonal, and allowing the Na content of each phase to vary with the constraint that the total Na-content of the mixture was equal to 0.8, produced values for the lattice parameters and the Na-concentrations which are tabulated in Table 4.4. The lattice parameters are probably reasonably accurate while the values obtained for the relative concentrations of Na in each phase should be treated as 'ball-park' figures.

Refinement was attempted using a monoclinic unit cell for one or other or both of the phases. However, this did not improve the refinement and so it proved impossible

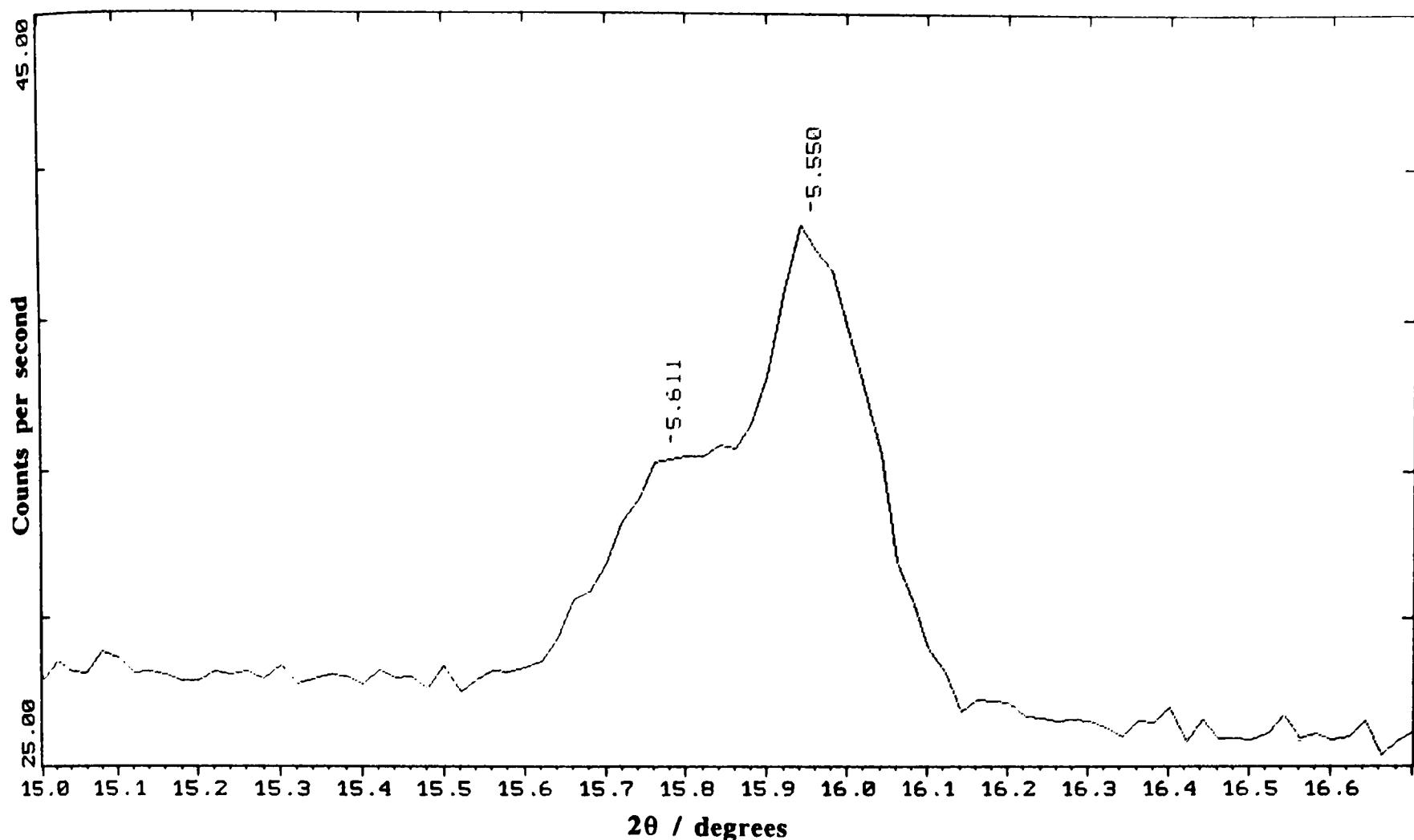


Figure 4.12: The presence of two peaks in the position corresponding to the (003) peak in the hexagonal system cannot be explained by lowering the symmetry of the cell to monoclinic. This reflection corresponds to the (001) reflection in the monoclinic system.

Parameter	1st phase	2nd phase
C	0.78(4)	0.22(4)
x	0.82(1)	0.74(4)
a	2.9955(2)	2.9887(3)
b	2.9955(2)	2.9887(3)
c	16.6002(11)	16.7480(26)

Table 4.4: Comparison of the two phases present in the mixture with stoichiometry $\text{Na}_{0.8}\text{TiO}_2$. C is the relative concentration of the two phases, x is the amount of Na in the formula Na_xTiO_2 . a , b and c are the lattice parameters for the spacegroup $R\bar{3}m$. The c axes of these Na-deficient phases are longer than in $\text{Na}_{1.0}\text{TiO}_2$, and the a and b axes are shorter. The errors in C and x may be underestimates of the true error.

to determine the true unit cells or symmetries of the two phases.

4.5 Magnetic susceptibility of Na_xTiO_2 as a function of temperature

The magnetic properties of Na_xTiO_2 samples were measured using DC SQUID magnetometry, and the stoichiometric samples were also measured using ESR spectroscopy.

4.5.1 DC susceptibility measurements

The DC magnetic susceptibility of different Na_xTiO_2 samples was measured using either a Quantum Design MPMS₂ SQUID magnetometer at the Chemistry Department of the University of Edinburgh or the Cryogenic Ltd SQUID magnetometer in the ICL. The operation of the Quantum Design machine has already been discussed in Section 3.6. The Cryogenic Ltd machine operates in a similar way and has the advantage of being able to reach fields of up to 6.0 T, but is severely limited in its control of temperature, being unable to reach temperatures below 4 K routinely nor being able to control the temperature precisely. The Quantum Design machine had been calibrated using a National Bureau of Standards (NBS) powdered Pd sample and the Cryogenic Ltd machine using a NBS powdered Al sample. The calibration differences between the two machines were determined by measuring the same paramagnetic sample of $\text{Na}_{1.3}\text{TiO}_2$ on each and were found to be negligible.

All the samples made were measured in a SQUID magnetometer in order to relate changes in the magnetic properties to changes in the lattice parameters or the symmetry of the lattice. In each case about 100 mg of sample was loaded, in the He dry box, into a gelatine capsule which had previously had its magnetic susceptibility measured over the same temperature range as would be used for the sample. The filled capsule was kept in He until just before loading into the magnetometer. The capsule was then wrapped in teflon tape before being mounted on the magnetometer whence it is under a He atmosphere. This procedure ensures that there could be no significant degradation of the sample since NaTiO_2 is stable for several minutes in

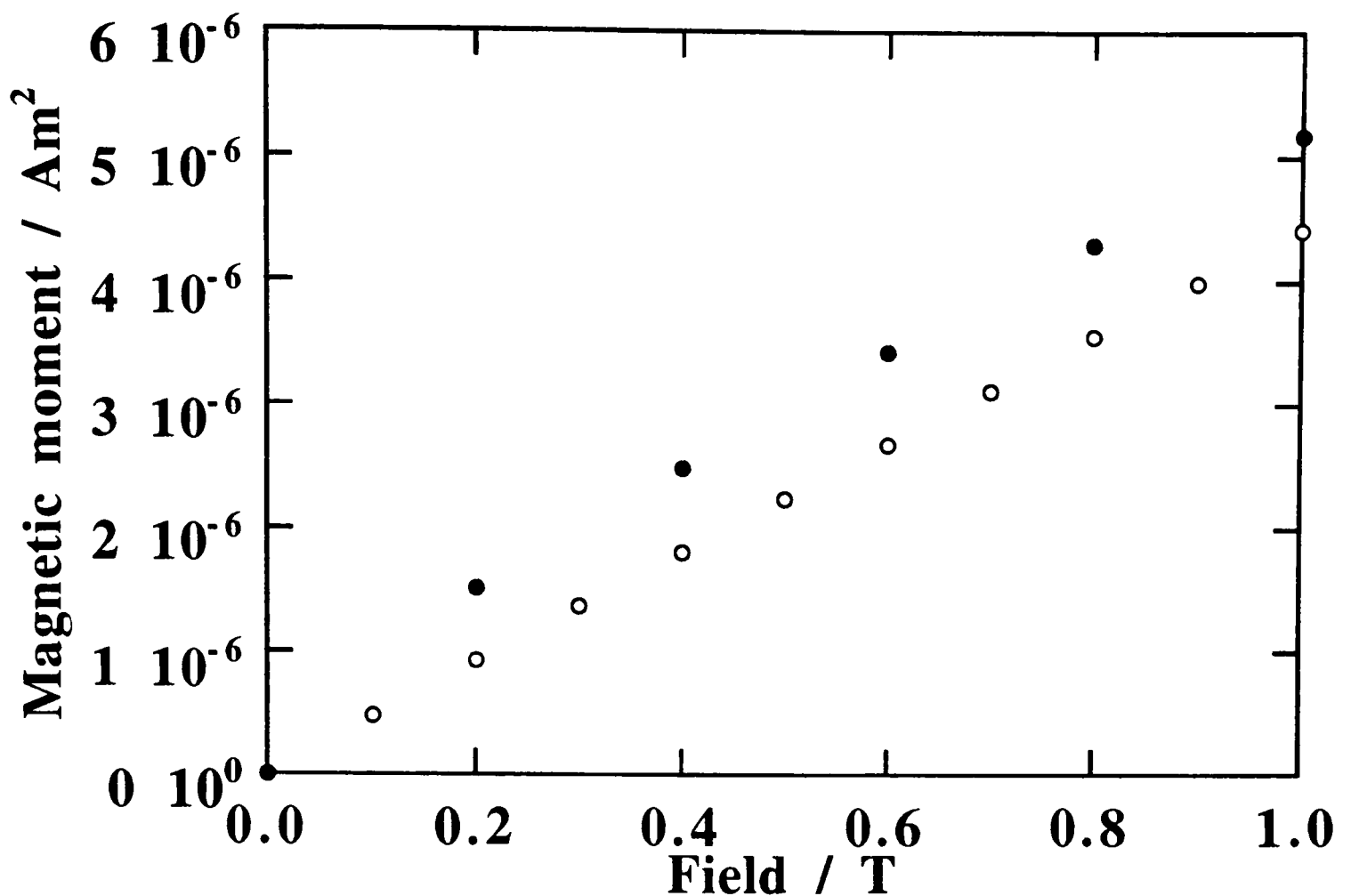


Figure 4.13: A plot of the induced magnetic moment against field for two NaTiO_2 samples. The non-linearity at low field in one of the samples is due to the inclusion of small amounts of ferromagnetic material, either from the iron ampoule or from a nickel spatula. Elimination of this feature was difficult, but was achieved in the case of the other sample shown.

air and the gelatine capsule is very air-tight even without glueing it shut. Samples removed from the magnetometer and kept under a rigorously inert atmosphere before being re-inserted were found not to change their magnetic behaviour indicating that the short time for which the capsule is exposed to air during loading does not lead to significant degradation. Occasionally samples did appear to go off during the short time that the closed gelatine capsule was exposed to the air, if the lid to the capsule was poorly fitting. Gluing the capsule shut using a small amount of polystyrene cement which is about as diamagnetic as gelatine was found to alleviate this problem.

In each case the field dependence of the magnetisation was determined by measuring the magnetic moment as a function of field. This typically had the form shown in Figure 4.13. The dependence is slightly non-linear at fields below about 0.9 T, but is linear above this. This probably indicates the inclusion of a tiny amount of iron

from the reaction vessel or nickel from the spatulas used to handle the material. The use of a large reaction vessel made from ARMCO soft ingot iron seems to minimise the amount of iron impurity included in the sample and which arises principally when the ampoule is opened. If a narrow iron ampoule was used, as was the case when a small amount of sample was annealed, there tended to be a greater amount of Fe impurity incorporated during extraction of the sample. This could be removed to an extent by the use of a magnet. Although the use of EDAX analysis using an electron microscope would not be expected to be sensitive enough to reveal the presence of the tiny quantities of ferromagnetic impurity involved, there is evidence that reaction with the vessel is not the cause of iron impurities, because samples could be prepared whose susceptibility showed no ferromagnetic contamination. This indicates that the main source of impurity is small fragments introduced when opening the ampoules. Care in handling the samples and in opening the ampoules is the key in limiting the amount of ferromagnetic impurity; wrapping Ni spatulas in teflon tape and the use of a Mo foil liner in the iron ampoule were both found to help.

When the samples contained some ferromagnetic impurity, the magnetic moment was measured as a function of temperature at two fields below which the magnetic moment of the impurity had saturated and the plot of moment against field was linear. The molar susceptibility was extracted using the formula

$$\chi_{mol} = \Delta m / n \Delta H \quad (4.10)$$

where Δm is the difference in the induced magnetic moment at the two fields measured in emu, n is the number of moles of sample and ΔH is the difference in the two fields measured in Gauss. The units of χ_{mol} are emu mol^{-1} . The molar susceptibility was corrected for the diamagnetism of the gelatine sample container (measured in each case and approximately $-1 \times 10^{-4} \text{ emu mol}^{-1}$) and of the diamagnetism of the core electrons in the sample. The latter correction is fairly significant, and the value for NaTiO_2 is $-0.4 \times 10^{-4} \text{ emu mol}^{-1}$.

The susceptibility was measured over the temperature range 2–350 K using the Quantum Design magnetometer or over the range 10–320 K using the Cryogenic Ltd

machine. The measurements were carried out after cooling in zero field, applying the measuring field and then warming the sample.

The dependence of the molar susceptibility on temperature for each of the samples investigated is shown in Figure 4.14. There are two main features to the plot in each case, although it is clear that the samples exhibit different characteristics depending on their composition. There is a sharply rising section at low temperature in which the susceptibility increases by a factor of about 10 between 50 K and 2 K. The most noteworthy feature present in all the stoichiometric samples and those made with an excess of Na is an increase in χ_{mol} between 200 and 260 K. The maximum is reached just below room temperature and χ_{mol} is constant from that temperature up to the maximum attainable on either magnetometer. The susceptibility has been measured up to 420 K by Takeda *et al.* [142] and appears to remain flat to that point. Measurements to higher temperatures were not available to us and have not been performed by others, but would be valuable in determining whether the flat shape persists to higher temperatures. If the flat part of the susceptibility corresponds to that of an antiferromagnet below T_N , then T_N would have to be about 500 K. In CFTH and La_2CuO_4 , $J \simeq 7T_N$, which implies that J is about 3000 to 4000 K in NaTiO_2 . This value is more than double the value in La_2CuO_4 and seems unrealistically large. The feature centred at 240 K is both sharper and more pronounced in samples which have been annealed for longer at the preparation temperature and which have been cooled slowly. The feature is absent in samples which are deficient in Na ($x < 1.0$). As the feature increases in size, so the steeply rising section at low temperature becomes less steep. When a sample was measured around the transition during both cooling and warming, there was found to be no hysteresis. This measurement is shown in Figure 4.15.

The susceptibility in the range below 150 K does not obey the Curie-Weiss Law, $\chi = C/(T - \theta)$, but may be fitted very well by the form $\chi = A + C/T$ where $C/A \simeq 100$. Such a fit is shown in Figure 4.16 for the sample $\text{NaTiO}_{2.3}$. A could arise from the second order Zeeman effect if the material is an insulator, or from Pauli paramagnetism if the material is metallic. C is due to the first order Zeeman effect

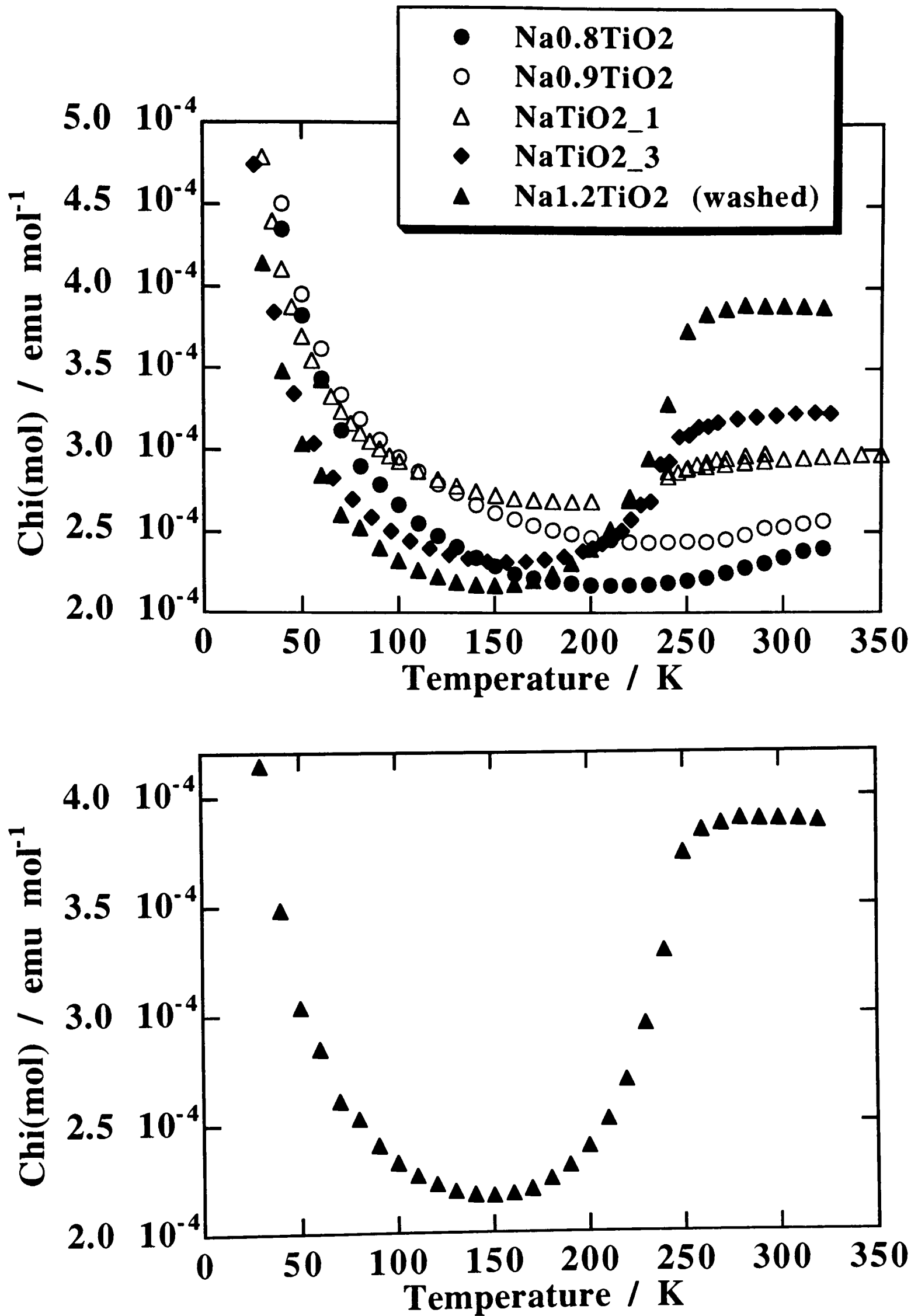


Figure 4.14: The variation of magnetic susceptibility with temperature for several samples of Na_xTiO_2 . Samples with $x=1$ show the magnetic anomaly at 250 K, while those with $x < 1$ do not. The susceptibility has been corrected for the diamagnetism due to the gelatine sample container and the core electrons [141]. We believe that the $\text{Na}_{1.2}\text{TiO}_2$ sample which has been washed is our best sample of NaTiO_2 . The temperature dependence of its susceptibility is shown in the lower part of the diagram.

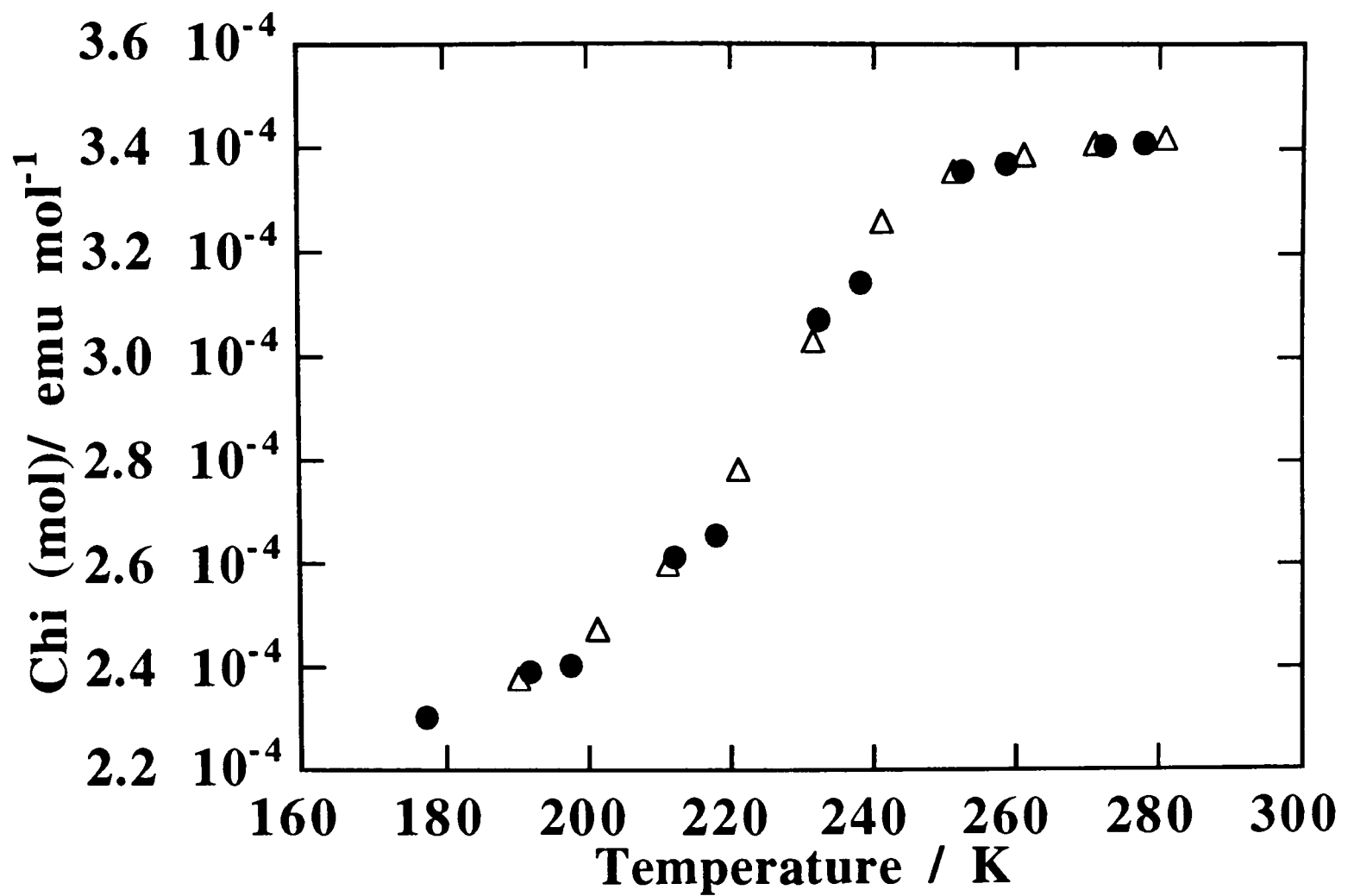


Figure 4.15: The magnetic susceptibility of the sample $\text{Na}_{1.3}\text{TiO}_2$ (washed) measured around the transition on cooling (closed circles) and on warming (open triangles). There is no measurable difference between the two curves.

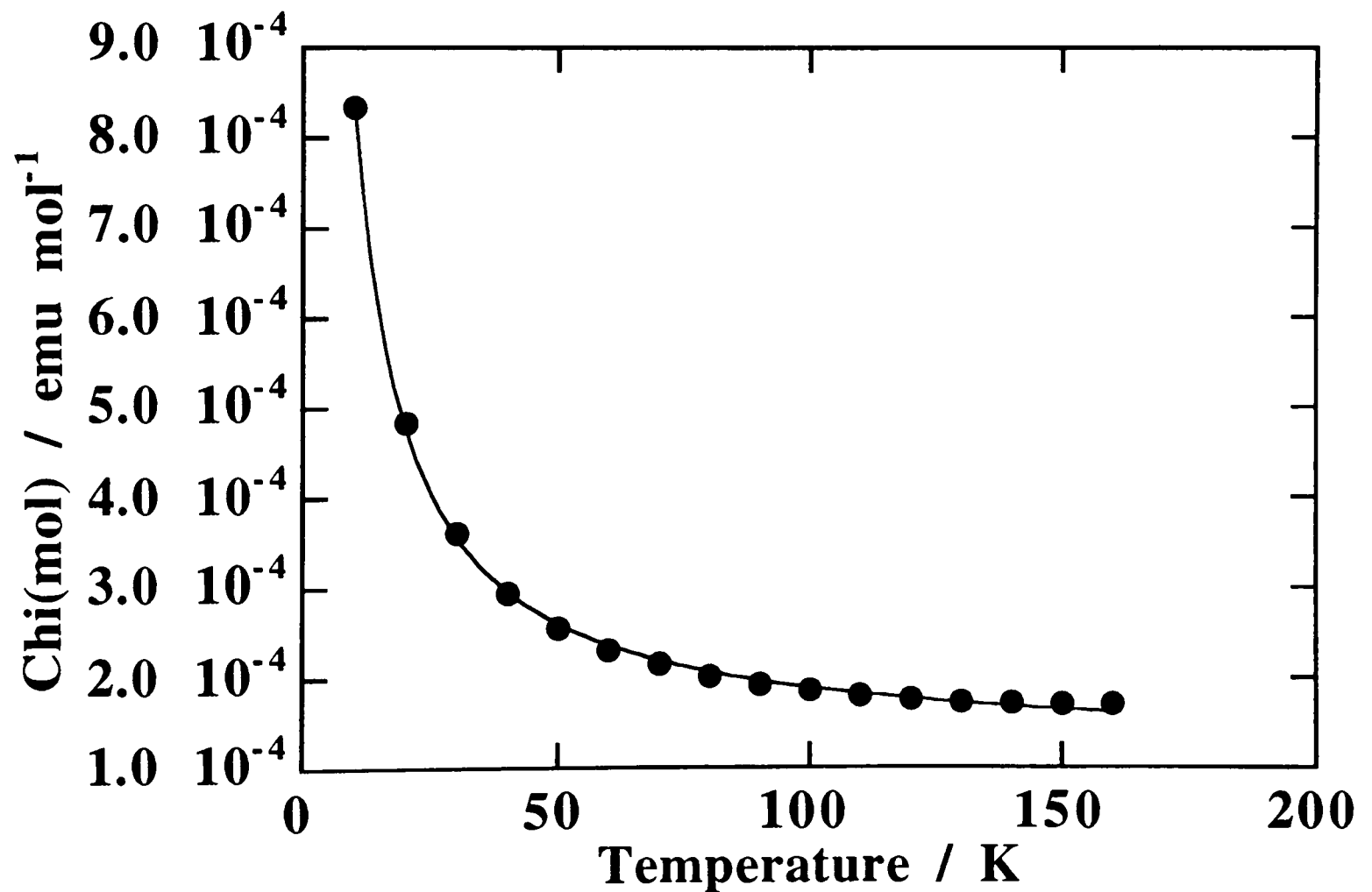


Figure 4.16: The susceptibility of NaTiO_2 below the magnetic anomaly it described by the form $\chi = A + C/T$ as described in the text. The susceptibility has been corrected for the diamagnetism of the gelatine sample container and the diamagnetic cores [141].

Sample i.d.	$10^4 \times A / \text{emu mol}^{-1}$	$10^3 \times C / \text{emu K mol}^{-1}$
Na _{0.7} TiO ₂	2.94(13)	9.67(40)
Na _{0.8} TiO ₂	2.08(4)	12.90(18)
Na _{0.9} TiO ₂	2.24(2)	10.66(10)
NaTiO ₂ -1	2.95(4)	6.26(8)
NaTiO ₂ -2	2.17(13)	6.60(26)
NaTiO ₂ -3	1.74(2)	7.66(3)
NaTiO ₂ -4	1.57(2)	7.19(3)
Na _{1.1} TiO ₂ (unwashed)	1.62(2)	6.42(4)
Na _{1.1} TiO ₂ (washed)	1.52(2)	6.39(64)
Na _{1.2} TiO ₂ (unwashed)	2.85(31)	6.78(20)
Na _{1.2} TiO ₂ (washed)	1.66(2)	7.09(7)
Na _{1.3} TiO ₂ (unwashed)	2.73(25)	5.93(20)
Na _{1.3} TiO ₂ (washed)	1.80(3)	8.26(9)
Hirakawa [120]	4.36	13.4

Table 4.5: The variation of the parameters used to describe the susceptibility of Na_xTiO₂ samples in the low temperature region. $\chi_{mol} = A + C/T$ where C corresponds to a Curie constant and increases slightly as x decreases. A is a temperature independent term. The numbers in brackets are the estimated ($\pm$) errors in the quantities. The value of A determined in the Hirakawa sample [120] is much larger than in our most Na-deficient samples.

and corresponds to a Curie constant. The Curie constant is (see Appendix B)

$$C = \frac{N_A \mu_0 \mu_B^2 g^2 (S(S+1))}{3k_B}, \quad (4.11)$$

and if one assumes that all the Ti³⁺ ions contribute to χ , then S is about 0.015 for the Na_xTiO₂ samples. On the assumption that NaTiO₂ is a magnetic insulator, this suggests that, unless the moment is greatly reduced by quantum fluctuations, only about 3% of the spins contribute to the low-temperature susceptibility. The values of C and A for different samples are tabulated in Table 4.5. C is found to be larger for samples made from mixtures with $x < 1.0$, although the trend is not smooth. The values of C are almost a factor of 100 less than in CFTH which is undoubtedly an insulating magnet with S close to its classical value.

The compound NaSc_{0.98}Ti_{0.02}O₂ which is isostructural with NaTiO₂ was synthesised at the Chemistry Department at the University of Edinburgh in order to assess the size of the paramagnetism arising from 2% isolated Ti³⁺ [143]. The material shows Curie-Weiss behaviour. By scaling the susceptibility with the amount of Ti³⁺ in the material one obtains a value for C comparable to that of NaTiO₂, and this indicates

that the moment of the Ti^{3+} in this environment is probably not reduced below that expected for $\frac{1}{2}$ by the opposing effects of the spin and orbital angular momenta. Such a moment reduction would only be expected for a very highly symmetric octahedral site; as discussed in Section 4.4.3, the environment of the Ti^{3+} ions is a distorted octahedron. The moment is reduced below the expected value by approximately one half when Ti^{3+} is substituted into Al_2O_3 [144], but in other systems, such as when substituted into the zeolite ZSM-5 [146], or in complexes [147], the expected size of moment is observed.

4.5.2 ESR spectroscopy measurements

The ESR spectrum of the stoichiometric $\text{NaTiO}_{2.3}$ was measured using the Varian spectrometer in the ICL. The working of this machine and the principles of ESR have been discussed in Chapter 3. About 20 mg of the sample was sealed in the He-filled dry box inside a spectrosil glass tube with a Young's tap teflon closure. The He atmosphere in the tube prevents the sample from degrading and provides a thermal link between the sample and the cryostat.

The spectrum was measured at temperatures between 5 and 295 K. At room temperature no spectrum could be resolved. At 120 K, the spectrum has a measurable width of about 3000 G and can just be resolved from the background. On further cooling the spectrum sharpens considerably and becomes more intense, reaching a width at 4.7 K of 110 G. At each temperature at which it can be measured, the spectrum consists of a single line which is approximately Lorentzian. The intensity of the observed spectrum was compared to that of an anhydrous copper sulphate standard. This indicated that about 5% of the Ti^{3+} ions present are contributing to the signal. The g -value was measured relative to the standard diphenylpicrylhydrazyl (DPPH) radical and was determined to be 1.96. This does not agree with the results of Yamada *et al.* [145] who obtained a value of 2.16 (although they do not describe their experimental method and may have been measuring an impurity). No signal with a g -value of 2.16 was observed in this experiment. A value less than 2.00 is expected for

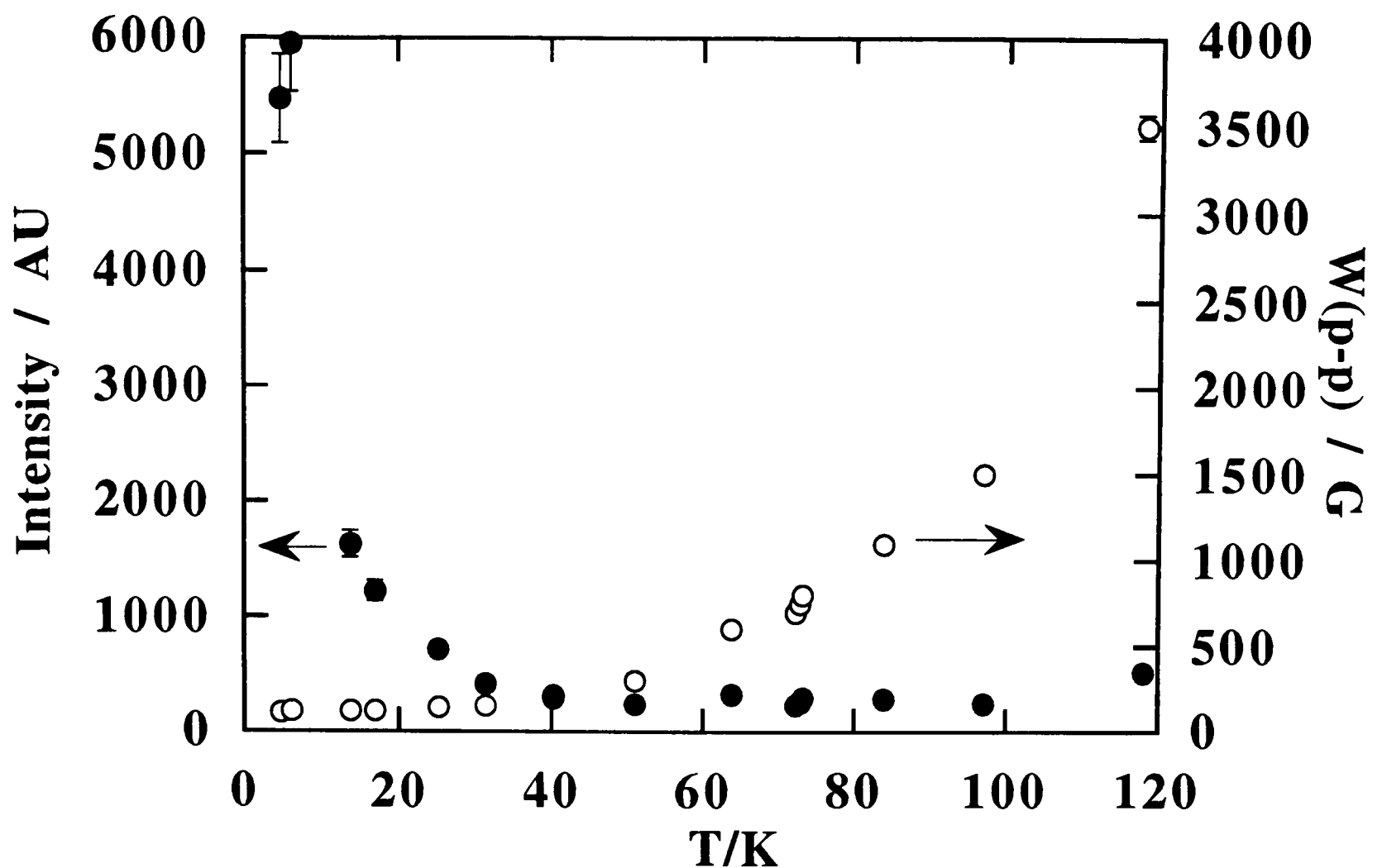


Figure 4.17: The variation of the ESR linewidth of NaTiO_2 with temperature. The signal is unmeasurably broad above about 120 K.

a first row transition metal with a less than half-filled $3d$ -subshell and values of the order of 1.9 are usually obtained for Ti^{3+} complexes [146, 147]. Contrast this with the case of copper formate (Chapter 3) in which the g -value is greater than 2.00. The g -value does not appear to be temperature dependent.

Linewidth measurement

The linewidth of the spectrum was determined by measuring the peak-peak width of the first-derivative spectrum with a ruler from the recording chart. This procedure was adopted because the computer used to collect and fit the data was temporarily unavailable. For a simple Lorentzian curve, this method gives almost identical results when compared with a fitting procedure. The linewidth is plotted against temperature in Figure 4.17. Below about 40 K the increase in linewidth is similar to the high-temperature behaviour of CFTH, but at higher temperatures, the increase in width is very rapid indeed until the signal becomes immeasurably broad.

Susceptibility measured by ESR

The intensity of a Lorentzian ESR signal which is recorded as the first derivative may be determined by an approximation to a double integration procedure.

$$I = \frac{Y(W_{p-p})^2}{MG\sqrt{P}} \quad (4.12)$$

where Y is the peak-peak height of the spectrum measured in units of length, W_{p-p} is the peak-peak width, M is the amplitude of the field modulation measured in Gauss. G is the receiver gain of the spectrometer, measured in arbitrary units, and P is the microwave power measured in mW. The intensity is measured in arbitrary units. Although the intensity represents a susceptibility and can in principle be measured in the appropriate units by comparison with a standard sample, there is always an uncertainty involved in knowing whether the whole sample is located in the field or not, and whether the field is both homogeneous and stable.

The intensity shows a rapid decrease with increasing temperature becoming flat by 100 K where the intensity has become unmeasurable due to broadening. When compared to the susceptibility measured using a SQUID magnetometer, the flattening out occurs at a much lower temperature and the drop from a large value at low temperatures to the flat minimum is much smaller.

The failure to observe a signal at room temperature is unexpected for a magnetic insulator, and indicates that the sample could be metallic. The fact that a signal is observed at low temperatures, but does not appear to be due to all of the Ti^{3+} ions suggests that not all the Ti^{3+} ions are equivalent and that a small proportion behave as paramagnets at low temperatures. ie. there could be partial disorder between the Ti^{3+} and Na^+ ions, and the Ti^{3+} ions in the Na^+ layers would neither see a net exchange field in an antiferromagnet, nor would they lose their moment if the sample is metallic.

4.5.3 The magnetic anomaly

We have determined that there is a strong correlation between the size of the magnetic anomaly and the hexagonal lattice parameters and cell volume. As the size of the basal

Sample i.d.	$a = b/\text{\AA}$ $=r(\text{Ti-Ti})$	$c/\text{\AA}$	c/a	$\text{Vol}/\text{\AA}^3$	$10^4 \times \chi/\text{emu mol}^{-1}$		
					χ_{150}	χ_{300}	anomaly
$\text{Na}_{0.7}\text{TiO}_2$	2.9969(1)	16.5782(22)	5.532(1)	128.95(2)			0.0
$\text{Na}_{0.8}\text{TiO}_2$	2.9963(1)	16.6052(16)	5.542(1)	129.11(2)			0.0
$\text{Na}_{0.9}\text{TiO}_2$	3.0128(2)	16.4143(26)	5.448(2)	129.03(4)			0.0
$\text{NaTiO}_2\text{-1}$	3.0196(1)	16.3719(14)	5.422(1)	129.28(2)	2.946	2.828	0.3054
$\text{NaTiO}_2\text{-2}$	3.0349(1)	16.2978(12)	5.370(1)	130.00(2)	2.466	3.7346	1.2686
$\text{NaTiO}_2\text{-3}$	3.0367(1)	16.2837(10)	5.362(1)	130.04(2)	2.319	3.219	0.900
$\text{NaTiO}_2\text{-4}$	3.0391(1)	16.2837(6)	5.358(1)	130.25(2)	2.115	3.505	1.390
$\text{Na}_{1.1}\text{TiO}_2$ (unwashed)	3.0441(1)	16.2428(10)	5.336(1)	130.35(2)	2.094	3.791	1.697
$\text{Na}_{1.1}\text{TiO}_2$ (washed)	3.0445(1)	16.2506(6)	5.338(1)	130.45(2)	1.982	3.575	1.593
$\text{Na}_{1.2}\text{TiO}_2$ (unwashed)	3.0469(2)	16.2503(32)	5.333(3)	130.65(5)	2.644	3.714	1.070
$\text{Na}_{1.2}\text{TiO}_2$ (washed)	3.0458(1)	16.2472(5)	5.334(1)	130.53(2)	2.167	3.892	1.724
$\text{Na}_{1.3}\text{TiO}_2$ (unwashed)	3.0459(1)	16.2407(9)	5.332(1)	130.49(2)	2.479	4.180	1.701
$\text{Na}_{1.3}\text{TiO}_2$ (washed)	3.0457(1)	16.2425(8)	5.338(1)	130.48(2)	2.375	3.670	1.295
Hirakawa [120]	3.001	16.44	5.478	128.22	5.3*	—	0.0
Takeda [142]	3.04	16.25	5.35	130.06	1.2*	4.0*	2.0

Table 4.6: The sample dependence of the magnetic anomaly compared with the lattice parameters obtained using REFCEL for a hexagonal unit cell. The size of the magnetic anomaly is defined as the difference in molar susceptibility at 150 and 300 K. The anomaly is plotted against the unit cell volume and the ratio of c to a in Figure 4.18. Note that there is evidence that the $\text{Na}_{0.7}$ and $\text{Na}_{0.8}$ samples are not monophasic. The values quoted for the structural parameters refer to the predominant phase. The molar susceptibilities have been corrected for container and sample diamagnetism [141]. The stars(*) indicate that it is not clear whether the work in references [120] and [142] was corrected in this way.

plane contracts and the length of the unit cell increases, leading to a net decrease in the volume of the unit cell, the magnetic anomaly becomes less pronounced. The size of the magnetic anomaly is defined as $\chi_{300} - \chi_{150}$, and its dependence on the lattice constants and the unit cell volume is tabulated in Table 4.6 which also contains a recapitulation of Table 4.2. The behaviour is shown graphically in Figure 4.18. The correlation between the size of the anomaly and the *ratio* of the lattice parameters, c/a is slightly better than the correlation with volume and the two correlations are compared in the table and the figure.

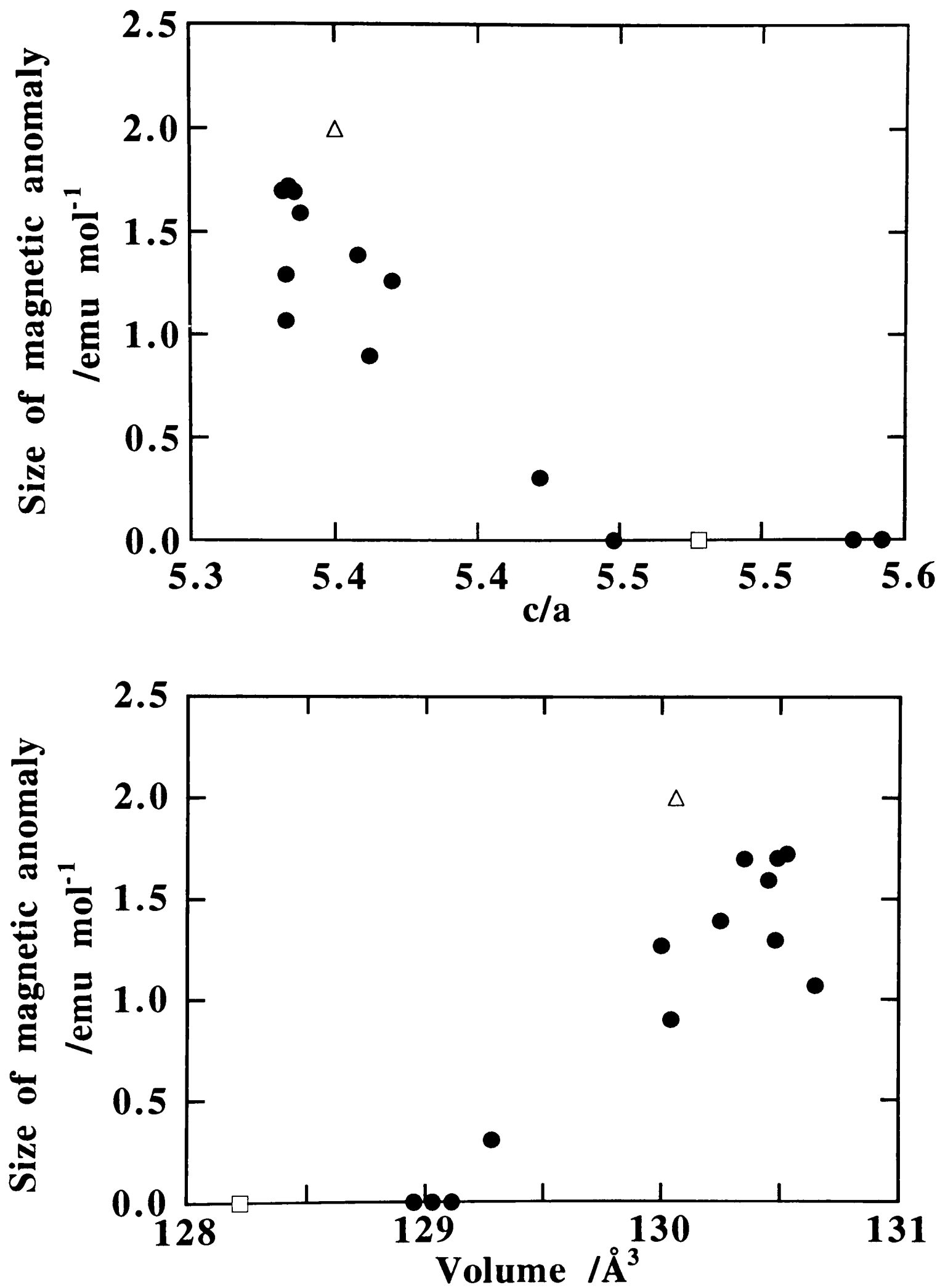


Figure 4.18: The variation of the size of the magnetic anomaly, defined as the difference in the molar susceptibility between 300 K and 150 K, with the ratio of the lattice parameters (Upper) and with the unit cell volume (Lower). The samples of Hirakawa *et al.* [120] and Takeda *et al.* [142] are depicted as squares and triangles respectively.

One can also plot the values of χ_{mol} at 300 K and 150 K and the difference between them against the value of a , which corresponds to the Ti–Ti distance. The relevant values are included in Table 4.6, and the plot is shown in Figure 4.19. The plot indicates a convergence at $a=3.0145$ Å which corresponds to the separation at which one expects no magnetic anomaly to be observed. All the samples which have a Ti–Ti distance less than this critical value are Na-deficient and show no anomaly. This point is returned to after introduction of all the other experimental observations.

Both the dimensions of the lattice and the magnetic behaviour depend on the method of sample preparation. The size of the lattice parameters and the jump in the susceptibility are most reproducible when NaTiO_2 is prepared by using excess Na and washing away what remains. The size of the basal plane and the size of the jump in susceptibility are also largest in these samples. The jump is present in all the samples made by mixing stoichiometric ingredients, but it varies in size. The jump is absent in all the Na_xTiO_2 samples prepared with $x < 1.0$. Despite the interest in this material from the theoretical point of view, no-one has yet bothered to investigate the sample-dependent nature of the magnetic behaviour. This is despite the fact that early samples of La_2CuO_4 showed wildly different magnetic behaviours [148, 149, 150, 151].

4.5.4 Previous magnetic studies of NaTiO_2

Measurements of the susceptibility of NaTiO_2 have been performed before [119, 120, 142]. However, according to our results, many of the samples investigated have clearly been Na-deficient and do not show the transition at 250 K, although they do support the correlation between lattice parameters and magnetic behaviour. Takeda *et al.* [142] appear to have made at least one sample with a substantial magnetic anomaly and ascribe this feature to short range antiferromagnetic ordering of the Ti^{3+} within the planes which reduces the susceptibility. The reason for the sample dependent appearance of this feature may lie in the interplay of this feature with the steeply varying section at lower temperature, which they ascribe to the presence of isolated

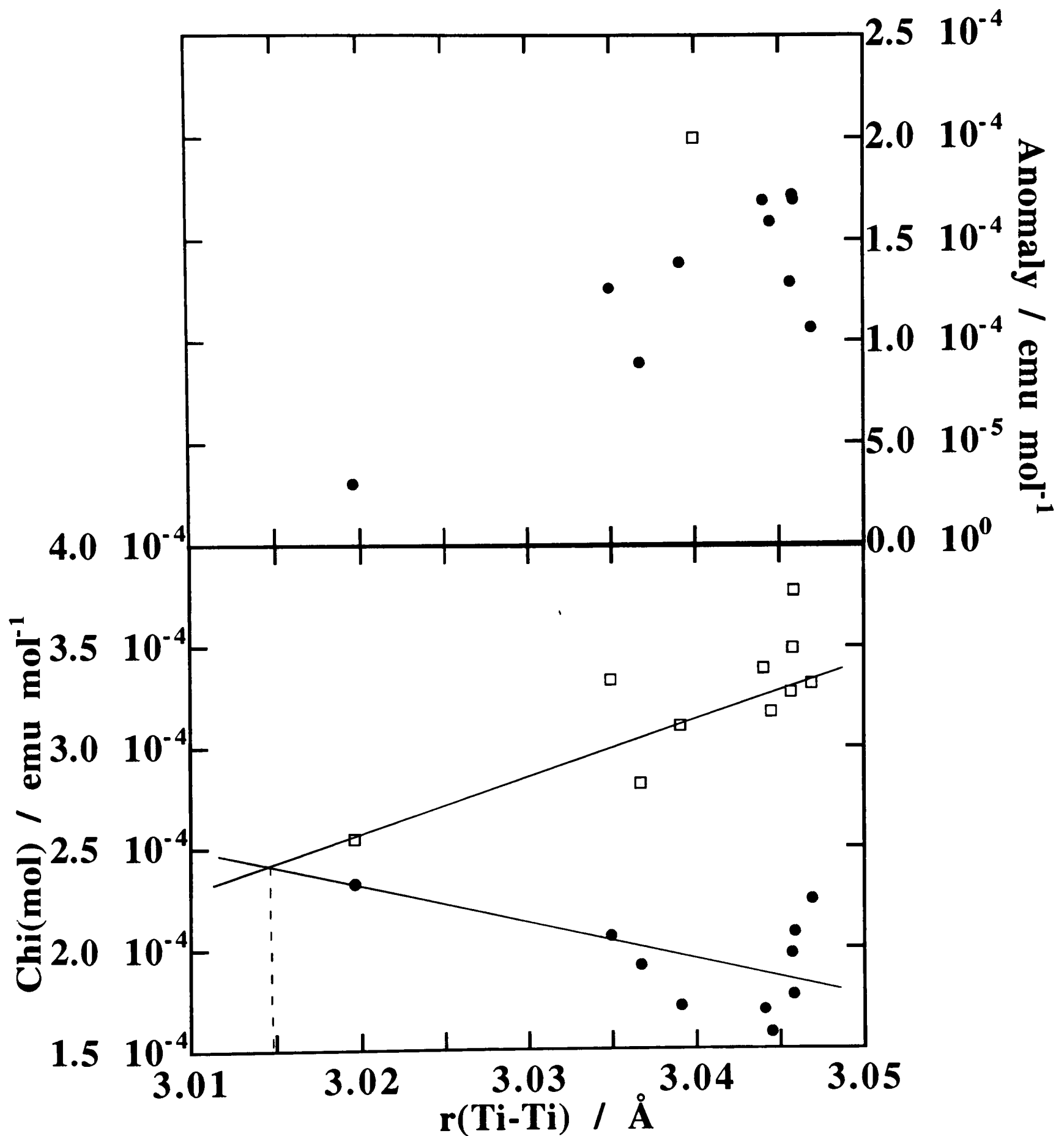


Figure 4.19: Lower: A plot of the molar magnetic susceptibility at 300 K (open squares) and at 150 K (closed circles) for each of the NaTiO_2 samples against the Ti-Ti separation, $r(\text{Ti-Ti})$. There appears to be a trend which indicates that one would expect the values of the susceptibility at the two temperatures to be identical when $r(\text{Ti-Ti})$ is 3.0145 Å. Upper: A plot of the size of the anomaly defined as $\chi_{300} - \chi_{150}$ against $r(\text{Ti-Ti})$. The result of Takeda *et al.* is indicated by the open square.

Ti^{3+} ions in the Na planes. Their conclusion about the origin of the magnetic anomaly is at odds with their results from measurement of the heat capacity which shows a transition at 250 K with an entropy change of about $7 \text{ JK}^{-1} \text{ mol}^{-1}$ (The value was determined from their graph of heat capacity against temperature since they do not state the value!) which is *greater* by a factor of about 1.3 than that expected for ordering of $S=\frac{1}{2}$ moments $R \ln(2S + 1) = 5.7 \text{ JK}^{-1} \text{ mol}^{-1}$.

Measurement of the magnetic moment as a function of field at 4.2 K indicated no hysteresis. Hence the sharply rising section could be ascribed to paramagnetism rather than ferro- or ferrimagnetism. One possible model which assumes antiferromagnetic ordering within the planes and would account for the behaviour seen in NaTiO_2 below 150 K involves a small amount of site disorder between Na^+ and Ti^{3+} . If a small amount of the Ti^{3+} is displaced into the Na^+ planes then those Ti^{3+} will still, in most cases, be surrounded by a trigonal antiprismatic array of other Ti^{3+} in the neighbouring planes on either side, and by a hexagonal array of Na^+ in the same plane. So although these 'isolated' Ti^{3+} ions exchange strongly with the Ti^{3+} in neighbouring planes, the net exchange field is zero, hence these Ti^{3+} ions in the Na^+ planes can behave as paramagnetic impurities.

This is a persuasive model to account for the magnetism, containing as it does the possibility that the Ti^{3+} moments undergo some sort of magnetic ordering on the triangular lattice, The results of Rietveld profile refinement from X-ray data would not be sensitive enough to show the small amounts of Na/Ti disorder required by this model. The model assumes that NaTiO_2 behaves as a magnetic insulator with localised moments.

4.5.5 Comparison with LiNiO_2 and the effects of the ferromagnetic impurity

The material LiNiO_2 [125] is isostructural with NaTiO_2 . It has the lattice parameters $a = b = 2.878 \text{ \AA}$ and $c = 14.19 \text{ \AA}$. It is more correctly expressed as $\text{Li}_x\text{Ni}_{2-x}\text{O}_2$ with x close to 1. LiNiO_2 is disordered, so that even when x is very close to 1, between 2 and 3% of the Ni^{3+} ions occupy sites in the Li^+ planes. This disorder coupled with the

frustration in the triangular planes is sufficient to cause spin-glass behaviour. Reimers *et al* [125] determined that there is a spin-glass freezing transition at 9 K. They postulate that the spin-glass behaviour arises from a frustrated antiferromagnetic in-plane exchange coupled with ferromagnetic exchange between the small number of Ni^{3+} ions in the Li^+ layers. The possibility that NaTiO_2 exhibits similar behaviour was investigated by performing, in sequence, the following experiments which were similar to those performed on LiNiO_2 .

- A zero-field cooled (ZFC) measurement at a measuring field of between 50 and 200 G.
- A field-cooled (FC) measurement at the same field (The field was not adjusted between the measurements).
- A high-field-cooled (HFC) measurement in which the sample was cooled in 50 times the measuring field, the field was then set to zero and then set to the measuring field before a sequence of measurements were taken. This latter procedure was found to give better field reproducibility than going straight from the high cooling field to the measuring field.

Nearly all the samples studied in this way showed similar behaviour — the FC susceptibility was slightly larger than the ZFC susceptibility and the HFC susceptibility was very much larger with a different shape to the temperature dependence as shown in Figure 4.20. The only sample which did not display this behaviour was a sample of $\text{Na}_{1.3}\text{TiO}_2$ which was found to contain no measurable ferromagnetic impurity. In this case, there was a negligible difference between the ZFC and HFC measurements. This indicates that the ferromagnetic impurities present in the other samples are responsible for the different measured susceptibilities. When the measuring field is below the saturation magnetisation of the impurity, one would expect the hysteresis in the behaviour of magnetisation against field for a ferromagnet to cause this behaviour. We conclude that NaTiO_2 does not display the characteristics of a spin glass. This difference in magnetic behaviour between isostructural NaTiO_2 and LiNiO_2 indicates

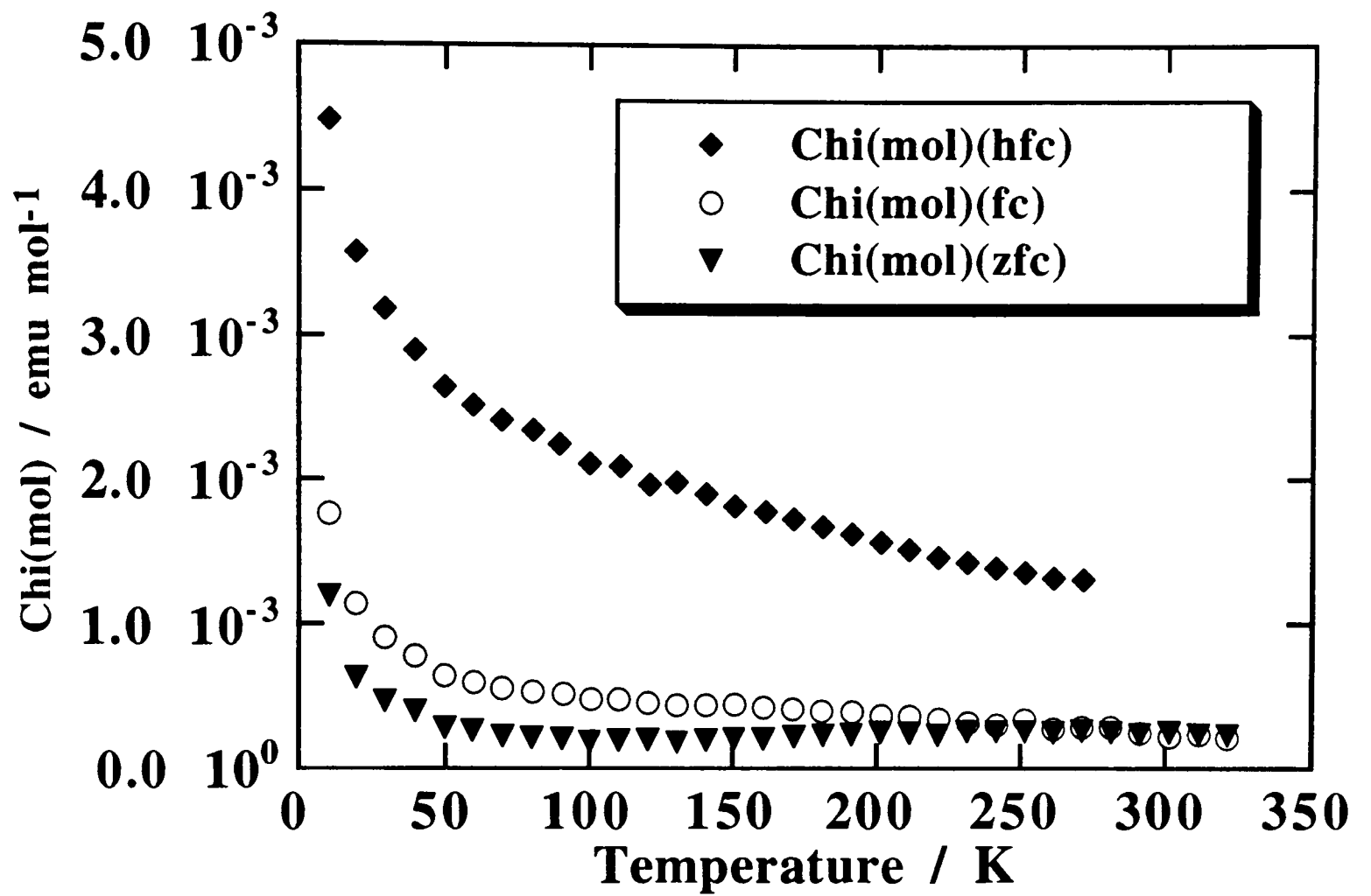


Figure 4.20: Most NaTiO_2 samples showed unusual behaviour when the susceptibility was measured at a low field after cooling in zero-field, cooling in the measuring field and cooling in a much higher field. This behaviour was in fact due to the presence of ferromagnetic material in the samples.

that the systems may have fundamentally different electronic properties due to the much larger $3d$ orbitals of the Ti^{3+} cation. It is possible that while LiNiO_2 is an insulator with localised moments, NaTiO_2 has delocalised $3d$ electrons.

4.6 Analysis of NaTiO_2 using neutron diffraction as a function of temperature

Comparison of the magnetic properties of NaTiO_2 with those of other early transition metal oxides [121, 152, 153], indicated that a structural study should be performed below and through the transition region to investigate whether there is a structural change associated with the magnetic anomaly. Low-temperature X-ray diffraction is not performed routinely because of difficulties in allowing the X-rays to penetrate the cryostat used to cool the sample. All neutron diffractometers may be equipped with a cryostat which allows variable temperature work to be carried out. A further advantage of using neutron diffraction is that the neutron scattering length of oxygen is 5.805 fm which is greater in magnitude than that of Na (3.63 fm) or that of Ti (-3.3 fm). This is in contrast to the X-ray scattering power of O which is less than that of either Na or Ti. Neutron diffraction enables the oxygen positions to be determined more precisely than in X-ray diffraction. A third advantage in this case is that as Ti is one of the few atoms to have a negative neutron scattering length, disorder between the Ti and Na planes should be more apparent than in X-ray diffraction.

4.6.1 Experimental

Neutron diffraction was carried out using the 'High-Resolution Powder Diffractometer' C2, which is part of the DUALSPEC instrument, at the Atomic Energy of Canada Limited (AECL) research centre at Chalk River, Ontario, Canada. 1.7 g of NaTiO_2 was packed tightly inside a 5 cm long thin-walled cylindrical vanadium can with an internal diameter of about 0.6 cm. The can was sealed in the He dry-box using an indium wire gasket. Vanadium has a very low coherent scattering cross-section, hence the nuclear Bragg peaks usually have an immeasurably small intensity, so it is the

best container material for powder samples. The sample can was attached to the end of a stainless-steel rod which was lowered inside the variable temperature insert of an 'ILL Orange'-style cryostat. Two thermal diode sensors were attached to the sample can, one at the top, next to a heater, and the other at the bottom. The space around the sample can was filled with He gas. An incident wavelength of 1.50283 Å which had been measured using a Si standard was selected using a pyrolytic graphite (002) monochromator, and the 5 cm high beam passed through a 0.4° collimator before being incident on the sample. Diffracted neutrons were detected by an 80°, 800 wire multidetector filled with BF₃ enriched with ¹⁰B at a pressure of 2 atmospheres, which performs a similar role to the PSD used on the D5000 X-ray diffractometer. It covers a wider angle and is less wasteful of diffracted particles, but the angular separation of each individual detector is ten times that on the D5000 PSD, and so the resolution is intrinsically lower.

The sample was located at the rotation centre of the sample table, by taking four photographs with the cryostat rotated at 90° intervals and adjusting the position of the cryostat with respect to the beam in the two orthogonal directions. The top and bottom of the sample can were masked off using thin cadmium foil since they contained copper and stainless-steel which would produce extra Bragg peaks. Cd has a very large absorption cross-section (2520 barn compared with 0.530 barn for Na), and does not allow a significant number of neutrons to penetrate it.

The diffraction pattern in the angular range 14° to 94° was measured as a function of temperature, at 100, 150, 180, 200, 210, 220, 230, 240, 250 and 260 K. 1600 points were obtained by measuring the pattern with the detector fixed, and then moving it to a second position 0.05° away (half the angular separation of the detector wires) and repeating the measurement. Data at room temperature (297 K) measured without the use of the cryostat were collected at the same resolution over a period of 12 hours between 10° and 120° which is the full range of the instrument. The FWHM of the peaks was about 0.2°, so there were about 12 points defining a peak. This width is greater than that measured using the D5000 by a factor of almost 2. This indicates that the peaks are resolution limited rather than sample limited in this

case. The cryostat was continuously rotated about the vertical axis of the sample in an oscillatory fashion with an amplitude of $\pm 175^\circ$ to reduce the effects of preferred orientation of the crystallites. The total measuring time at each temperature was about 4.5 hours, and after that time there were about 4000 neutron counts at the most intense point in the pattern. The background contained about 100 counts. This signal to background ratio was found to give a precision in the lattice parameters obtained after Rietveld refinement using GSAS similar to that obtained by counting for 72 hours on the D5000. About 1 hour was allowed for thermal equilibration at temperatures between 100 and 230 K. A slightly longer time was allowed at the higher temperatures. The sensor mounted at the top of the can changed temperature and stabilised in about 15 minutes. The sensor at the bottom of the can changed much more slowly, and at the higher temperatures never reached the same temperature as the top sensor. The resulting temperature gradient of 2 K between the sensors was a shortcoming of the cryostat. The gradient seemed to have a small effect on the determination of the peak profile function in the Rietveld refinement. The problem was not major since the temperature difference along the length of the sample was much smaller than the temperature steps taken.

4.6.2 Rietveld refinement

Rietveld refinement was carried out using the spacegroup $R\bar{3}m$ using GSAS, and was found to give a good refinement at all temperatures, which suggests that there is no change in symmetry which is detectable using this instrument. The values of the parameters obtained by refinement at each temperature are tabulated in Table 4.7. Fits to the data at 100 K and 297 K are shown in Figure 4.21. The fits at all 11 temperatures used are shown in Appendix C. The variation of the lattice parameters and the unit cell volume with temperature are shown in Figure 4.22. The background of all the scans between 14° and 94° was fitted to a 3 parameter cosine fourier series. A larger number of parameters (10) was required to accurately describe the background below 14° where it varies much more steeply. The peak profile used was a pseudo-

T/K	$a/\text{\AA}$	$c/\text{\AA}$	$V/\text{\AA}^3$	$O(Z)$	χ^2
100	3.02528(6)	16.3017(5)	129.21(1)	0.234662(3)	1.72
150	3.02667(6)	16.3084(4)	129.38(1)	0.234496(3)	1.77
180	3.02745(6)	16.3118(4)	129.48(1)	0.234477(3)	1.77
200	3.02794(7)	16.3152(5)	129.54(1)	0.234542(2)	1.84
210	3.02838(8)	16.3160(5)	129.59(1)	0.234533(3)	1.92
220	3.02891(10)	16.3165(7)	129.64(1)	0.234320(4)	2.28
230	3.02977(10)	16.3122(7)	129.68(1)	0.234328(5)	2.59
240	3.03141(8)	16.3022(6)	129.74(1)	0.234290(5)	2.64
250	3.03313(5)	16.2947(5)	129.83(1)	0.234147(3)	2.72
260	3.03429(5)	16.2942(4)	129.92(1)	0.234087(3)	2.85
297	3.03567(3)	16.2992(3)	130.08(1)	0.234207(77)	3.29
T/K	$U_{Na}/\text{\AA}^2$	$U_{Ti}/\text{\AA}^2$	$U_O/\text{\AA}^2$	Disorder/%	
100	0.86(3)	0.68(3)	0.41(2)	1.4(3)	
150	1.05(3)	0.97(2)	0.37(3)	1.9(4)	
180	1.07(3)	0.89(3)	0.38(2)	1.7(4)	
200	1.13(4)	0.93(4)	0.41(3)	1.6(4)	
210	1.00(6)	0.94(8)	0.32(3)	0.9(4)	
220	1.30(6)	1.06(8)	0.43(3)	1.9(4)	
230	1.41(8)	1.05(8)	0.43(4)	1.6(4)	
240	1.47(10)	1.25(8)	0.40(4)	1.6(4)	
250	1.45(10)	1.11(8)	0.45(4)	1.5(6)	
260	1.60(13)	1.07(8)	0.65(5)	2.0(6)	
297	1.05(7)	0.51(6)	0.64(4)	1.7(3)	

Table 4.7: A table of the refinement parameters for NaTiO₂₋₃ at a series of temperatures obtained using GSAS. All refinements were carried out using the spacegroup R $\bar{3}m$.

Voigt with a small Lorentzian component (Equation 4.15).

Disorder between Na and Ti sites

In contrast to Na (and O), Ti has a negative scattering length, which means that their contributions to the structure factor of a reflection are in antiphase, so neutron diffraction is much more sensitive than X-ray diffraction at identifying disorder between Na and Ti. Refinement of the Na and Ti occupancies was carried out with the constraint that the total occupancy of two sites was always 1.0. The thermal parameters of atoms on the same site were also constrained to be identical.

At all temperatures, refinement of the data suggested that about $1.5\pm0.5\%$ of the Ti³⁺ ions were in the Na⁺ planes, which is consistent with the estimate made from DC susceptibility and ESR results assuming that these ions are paramagnetic

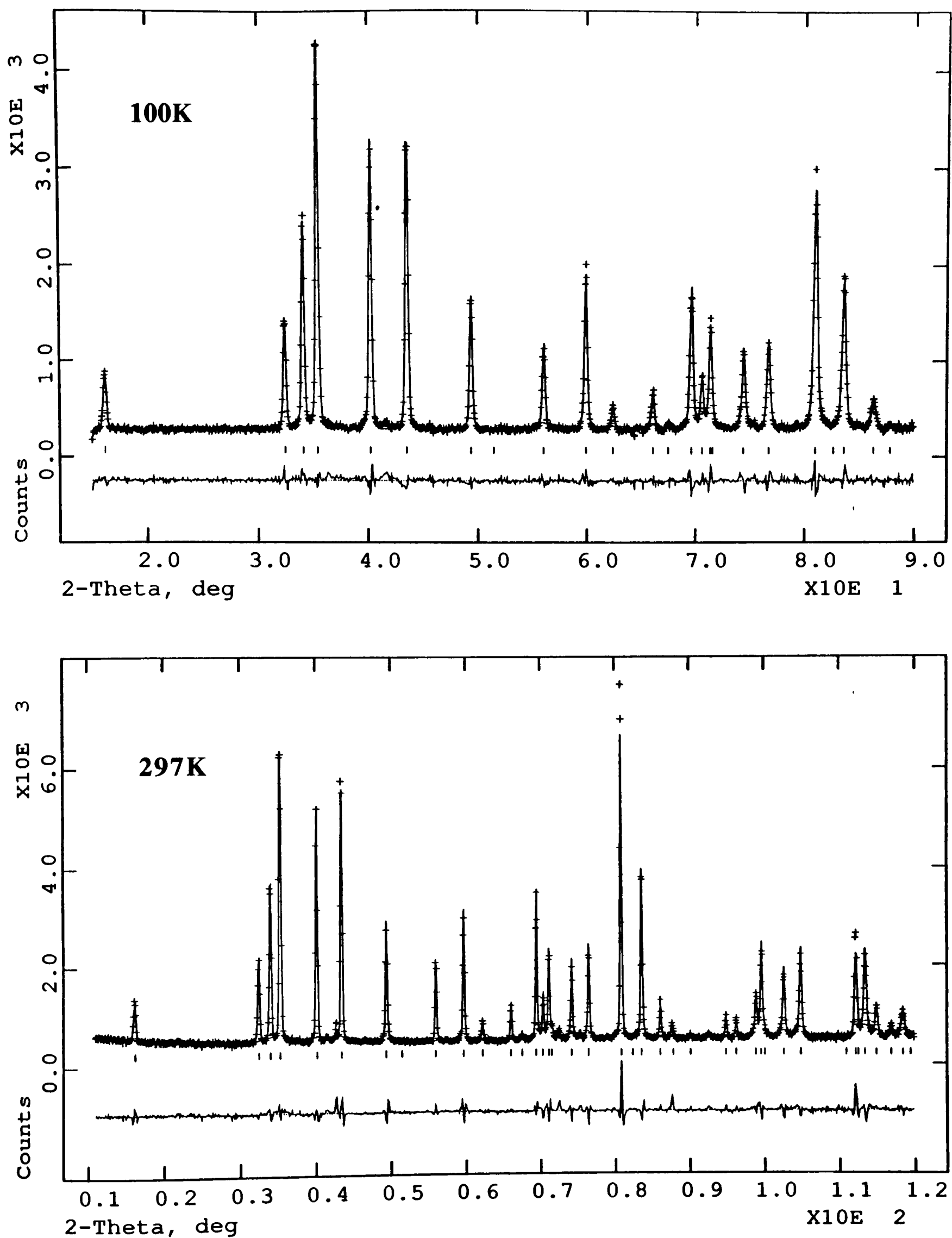


Figure 4.21: Fits to the neutron diffraction data from the instrument C2 on NaTiO_{2-3} . Upper: at 100 K, and Lower: at 297 K. The 2θ scales are different in the two plots. A full set of fits is presented in Appendix C.

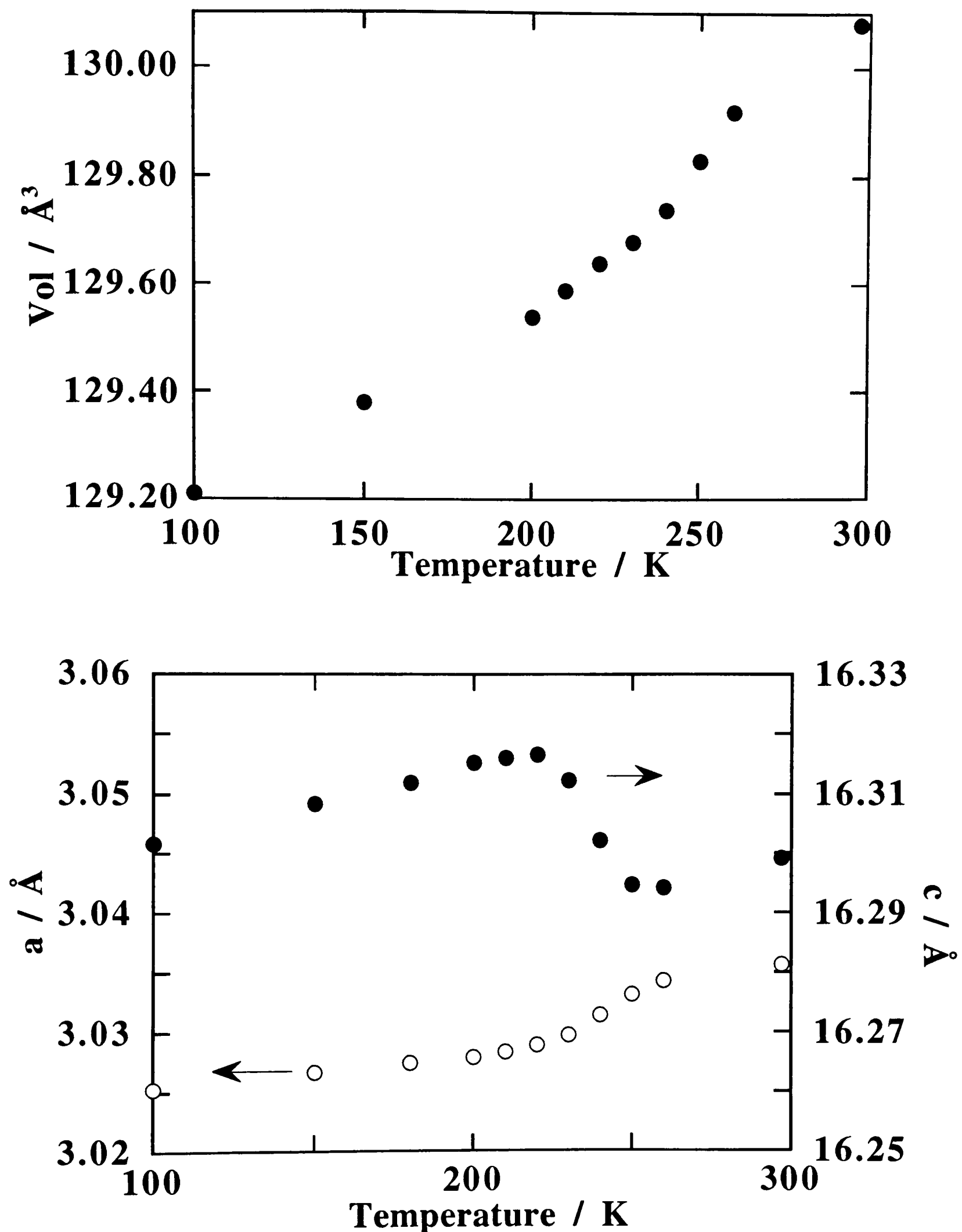


Figure 4.22: Upper: The lattice parameters of NaTiO_{2-3} obtained after Rietveld refinement of the data obtained on C2. On warming, there are two regions of thermal expansion separated by a region in which the lattice parameters change more rapidly and in the opposite direction. Lower: The change in the volume appears to be dominated by the change in the a lattice parameter.

'impurities' with $S = \frac{1}{2}$.

Anisotropic temperature factors

The isotropic thermal parameter, U , defined in Equation 4.7 assumes that the atoms vibrate isotropically. As the symmetry of the site is lowered, the vibrations become more anisotropic and one can define a set of anisotropic thermal parameters which are refined according to symmetry. The anisotropic thermal parameters are the components of the tensor $\overline{\overline{U}}$

$$\overline{\overline{U}} = \begin{pmatrix} U_{11} & U_{12} & U_{13} \\ U_{12} & U_{22} & U_{23} \\ U_{13} & U_{23} & U_{33} \end{pmatrix} \quad (4.13)$$

and produce an anisotropic temperature factor

$$\exp \left[-2\pi^2 (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}lhc^*a^* + 2U_{12}hka^*b^*) \right]. \quad (4.14)$$

The isotropic thermal parameters quoted in Table 4.7 were converted to anisotropic thermal parameters according to symmetry. In the case of $R\bar{3}m$, $U_{11} = U_{22}$ and $U_{23} = U_{13} = 0$. The refinements of the thermal parameters proceeded stably and the values obtained were sensible. However, there was only a reduction of about 1% in the value of χ^2 and the visual appearance of the fit was not changed.

Changes in the lattice parameters with temperature

In the regions below 200 K and above 250 K, the lattice parameters both increase linearly with increasing temperature, which is consistent with thermal expansion on warming. However in the region between 200 and 250 K, the a parameter which corresponds to the Ti-Ti distance, $r(\text{Ti-Ti})$ increases faster than the rate of thermal expansion on warming. The c parameter, which corresponds to the interlayer separation *decreases* rapidly on warming between 200 and 250 K. The combined effect of these two changes is that the volume change is dominated by thermal expansion, but does change slightly in the same manner as the a lattice parameter. This suggests

that the lattice parameters c responds to a change in $r(\text{Ti-Ti})$, but does not fully compensate it. This behaviour seems to be similar to the response of the lattice parameters to changes in the Na content of the system (Section 4.4.2).

The change of the lattice parameters with temperature is most rapid between 240 and 260 K, and it was found that the presence of a 2 K gradient along the length of the sample hampered the determination of the mainly Gaussian peak-shape function that was used:

$$F\omega^2 = U \tan^2 \theta + V \tan \theta + W + L \quad (4.15)$$

where $F\omega^2$ is the full-width at half-height of the mainly-Gaussian peaks. L is a small Lorentzian component. An asymmetry parameter was also included, which takes account of the asymmetry of the peaks. If different parts of the sample are at slightly different temperatures there will be a distribution of lattice parameters, and this will cause an asymmetric spreading of the widths. The fitted asymmetry parameter was large at 250 and 260 K

4.6.3 Change in geometry of Ti between 200 and 260 K

An analysis of the geometry of the TiO_6 pseudo-octahedra at each temperature using the structural parameters obtained by Rietveld refinement shows that at all temperatures, the geometry is that of a trigonal antiprism with its C_3 axis pointing along the c direction and squashed along that axis. The geometry is shown in Figure 4.23. The site symmetry of the Ti^{3+} is D_{3d} . The figure identifies the two different edge lengths of the pseudo-octahedron. For compression l_2 is shorter than l_1 which is equal to the a lattice parameter. Values of $l_1=a$ and l_2 at each temperature are tabulated in Table 4.8. If the compression index is defined as the ratio l_1/l_2 , then it is clear from the plot of l_1/l_2 against temperature in Figure 4.24 that the Ti^{3+} environment becomes more compressed (ie. more distorted from octahedral) on heating. The Na^+ environment is elongated ($l_1/l_2 = 0.8254(5)$), and the degree of elongation does not change by more than the size of the estimated error on heating through the transition. This rigidity probably arises from the bonding in the NaO_6 unit being more

T/K	$l_1 = a/\text{\AA}$	$l_2/\text{\AA}$	l_1/l_2
100	3.0253(0)	2.8223(18)	1.0719(5)
150	3.0267(0)	2.8193(15)	1.0736(5)
180	3.0275(0)	2.8194(18)	1.0738(5)
200	3.0279(0)	2.8216(10)	1.0731(5)
210	3.0284(0)	2.8216(15)	1.0733(5)
220	3.0289(0)	2.8164(12)	1.0755(5)
230	3.0298(0)	2.8167(18)	1.0757(6)
240	3.0314(0)	2.8150(18)	1.0769(5)
250	3.0331(0)	2.8112(10)	1.0789(5)
260	3.0336(0)	2.8096(15)	1.0797(5)
297	3.0356(0)	2.8141(18)	1.0787(5)

Table 4.8: The change in the values of the two O–O distances which define the compressed trigonal antiprismatic environment of the Ti^{3+} ions in NaTiO_2 . l_1 and l_2 are defined in Figure 4.23. The estimated errors in l_1 are negligible since this is equal to the lattice parameter a . The errors in l_2 arise from the uncertainty in the position of the oxygen atom along the c direction.

ionic than that in the TiO_6 unit. NaTiO_2 is thus a much more rigid system than Ti_2O_3 which is discussed in Section 4.7.2.

4.7 Rationalisation of the magnetic and structural behaviour of NaTiO_2

4.7.1 Summary of observations

Almost all the observations which have been described in the preceding sections are at odds with the idea that NaTiO_2 is an insulating magnetic material and the change in the susceptibility is due to the ordering of localised moments.

- The magnetic susceptibility is very small at all temperatures and takes a value roughly corresponding to 5% of the $S=\frac{1}{2}$ Ti^{3+} ions present.
- The Curie-Weiss law is not obeyed over any temperature range studied.
- The susceptibility is invariant with temperature above the transition.
- The shape of the transition is unlike a usual antiferromagnetic ordering transition. These are often broad, especially when they arise from short-range or-

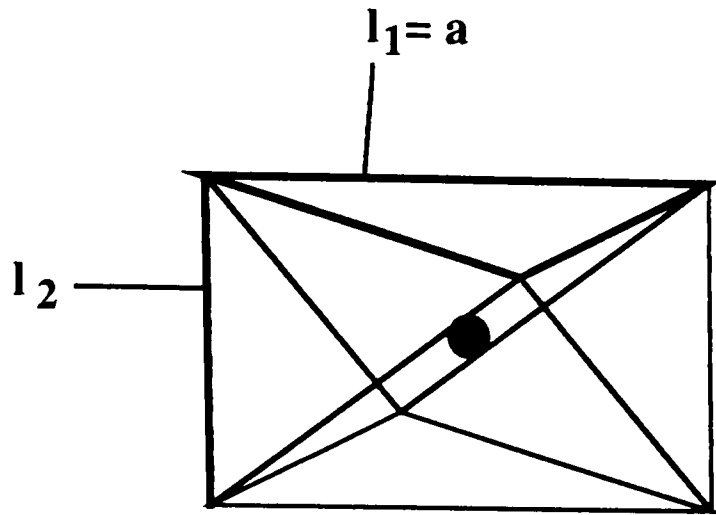


Figure 4.23: The TiO₆ unit is a squashed trigonal antiprism which becomes more compressed on heating through the transition. The compression index plotted in Figure 4.24 is defined as l_1/l_2 .

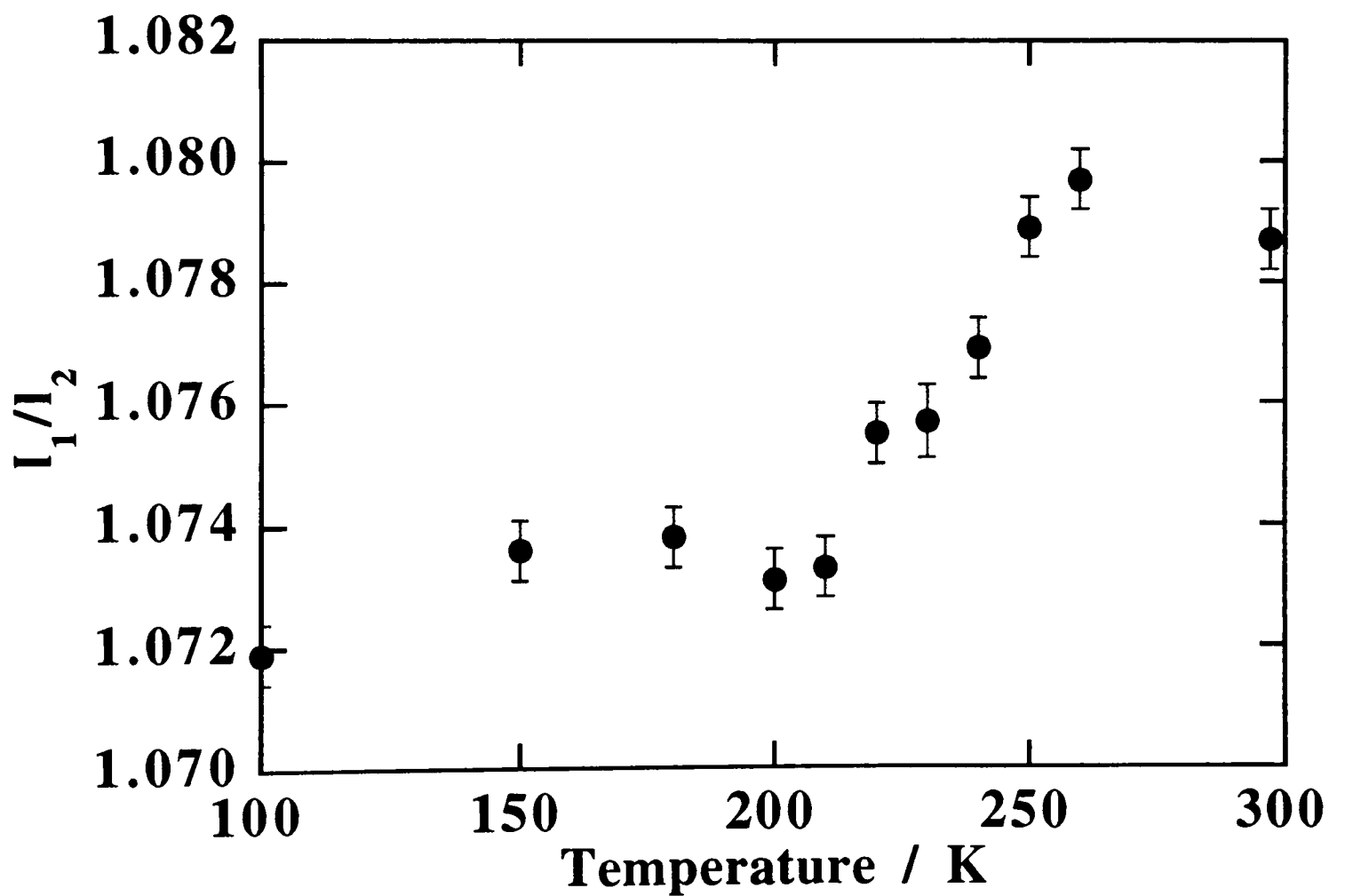


Figure 4.24: The ratio of the O-O distances l_1 and l_2 defined in Figure 4.23 as a function of temperature. The TiO₆ trigonal antiprism becomes more compressed on heating.

dering, and such a transition is observed in CFTH at about 60 K, however they are usually more symmetric than the transition observed in NaTiO₂.

- The material does not show any magnetic similarity with the isostructural material LiNiO₂. In particular, the amount of disorder in LiNiO₂ which produces spin glass behaviour (about 2%) is also present in NaTiO₂ but does *not* produce spin glass behaviour. This is an argument against localised moment behaviour in NaTiO₂.
- The measurement of the heat capacity in the transition region as measured by Takeda *et al.* [142] indicates an entropy change for the transition significantly greater than expected for the magnetic ordering of $S=\frac{1}{2}$ moments.
- The Ti–Ti distance between the centres of two edge-sharing octahedra is about 3 Å. This distance is similar to the distances of between 2.5 Å and 3 Å in oxides such as Ti₂O₃ and LiTi₂O₄ where metal–metal bonding has been identified, and the materials behave as metals. It is shorter than the Ti–Ti separation in LaTiO₃ which also displays metallic character [154] because of Ti–O–Ti overlap in a π sense between corner-sharing octahedra. It seems possible that there may either be direct Ti–Ti σ bonding in NaTiO₂, or metallic character arising from Ti–O–Ti overlap in a π sense between edge-sharing octahedra.
- The magnetic transition is accompanied by a change in the Ti–Ti distance which suggests that the change in the susceptibility is due to a change in the bonding interaction between neighbouring Ti ions. The sample dependence of the Ti–Ti distance and magnetic behaviour supports this view.

As will be discussed below, the observations are all consistent with the material undergoing a transition of the metal to insulator type reviewed by Mott [155] over a broad temperature range.

Such transitions have been confirmed for a number of related materials and some of these are considered below. In most of these cases, the details of the changes in band structure at the transition are controversial. Both NaTiO₂ and the systems

considered below behave superficially in similar ways. However, the differences in the structural characteristics of these compounds are sufficiently large that each must be considered on its own. We have tried to present a picture of the situation in NaTiO_2 which is consistent with all the experimental facts. It is hoped that the picture will be tested more rigorously by conductivity measurements either on the current powdered samples or on a single crystal if one can be grown.

4.7.2 Metal to Insulator transitions in early transition metal oxides and chlorides

Consider some compounds which undergo metal to insulator transitions. Such transitions are common among the binary and ternary oxides of the trivalent early transition metals Ti and V. This observation itself lends credence to the view that such a transition is responsible for the behaviour of NaTiO_2 .

Density of states at the Fermi level of a metal

For a metal, the density of states at the Fermi level, $n(E_F)$ can be deduced from the magnetic susceptibility using the relation

$$n(E_F) = \frac{10e\chi_{mol}}{2\mu_B^2 N_A} \quad (4.16)$$

where e is the electronic charge (1.60219×10^{-19} C), N_A is the Avogadro number, and μ_B is the Bohr magneton. All the constants are expressed in SI units. χ_{mol} is expressed in the familiar c.g.s. units of emu mol^{-1} , and $n(E_F)$ is expressed in units of orbital states eV^{-1} per Ti. The factor of 2 in the denominator arises from the fact that the *total* number of states is twice the number of *orbital* states. We shall later mention the total number of states, $g(E_F)$, where $g(E_F) = 2n(E_F)$. The factor of 10 in the numerator represents the conversion between c.g.s. units and SI units. A fuller discussion of the conversion between c.g.s. and SI units is given in Appendix B. A correlation between $n(E_f)$ and the Ti-Ti separation is included after the discussion of some of the Li_xTiO_2 materials.

Landau diamagnetism

In a metallic compound, the electrons are delocalised throughout the lattice. By analogy with the diamagnetism of the core electrons which arises from the Larmor precession of the electrons in the applied magnetic field, there is a so-called Landau diamagnetism [156, 157] which is an induced diamagnetism arising from the orbital motion of the conduction electrons in the field. For *free* electrons,

$$\chi_{Landau} = -\frac{1}{3}\chi_{Pauli} \quad (4.17)$$

and so the correction which should be applied to the measured susceptibility of a metallic material in order to determine the true magnitude of the Pauli paramagnetism can be large. It is very difficult to calculate accurately the Landau diamagnetism in a material in which the electrons are not completely free. We have not corrected the susceptibility of our samples of NaTiO₂ for this contribution, although if NaTiO₂ is metallic, there will certainly be some contribution, and this means that the values listed will be smaller than the true values.

Ti₂O₃.

This material has received the most attention [153, 158, 159, 160, 161, 162, 163, 164]. The structure is identical with that of corundum at all temperatures [161], and is shown in Figure 4.25. The space group is R $\bar{3}c$ (No.167) with $a=b=5.158$ Å and $c=13.611$ Å. The Ti³⁺ is located on the 12c position with site symmetry 3 (C_3) and the O²⁻ is on the 18e position with site symmetry 2. There are four identical Ti³⁺ ions in the smallest unit cell which can be chosen, and it is in a slightly compressed trigonal antiprismatic site which is of lower symmetry than the site in NaTiO₂ (D_{3d}). There is a short Ti–Ti distance (2.6 Å) joining face-sharing octahedra, which must indicate bonding, and a longer distance (3.0 Å) joining edge-sharing octahedra which is similar to that in NaTiO₂. The molar susceptibility is very similar in magnitude to that of NaTiO₂, and there is a similarly-shaped transition [153] between 400 and 600 K. Consider the behaviour on warming through the transition:

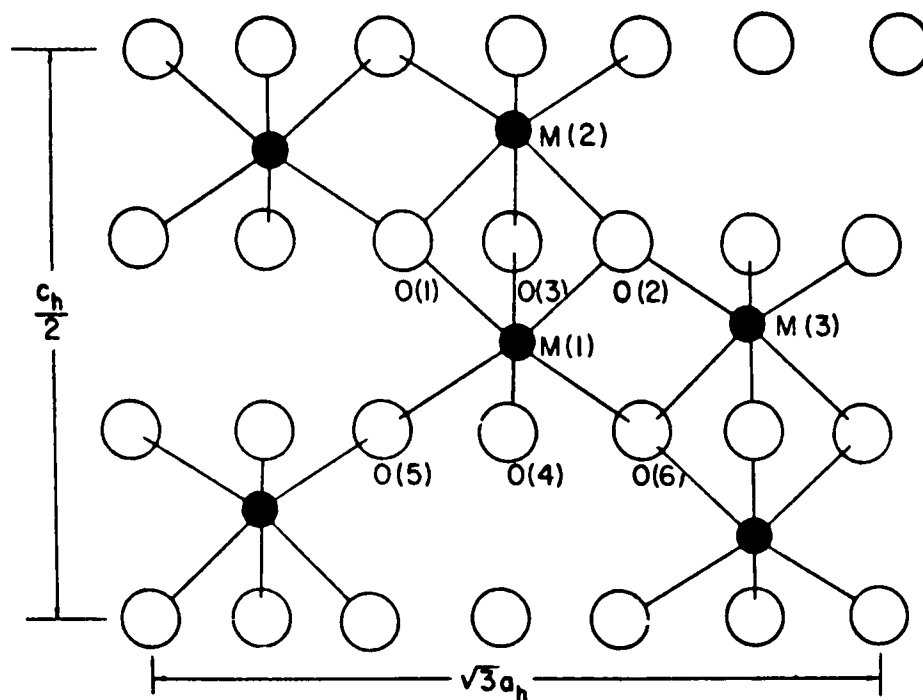


Figure 4.25: The corundum structure adopted by Ti_2O_3 . The metal ions occupy two thirds of the octahedral sites in an FCC array. There are two Ti-Ti distances. The distance between M(1) and M(2) is $2.6 \text{ \AA}$ and is between face-sharing octahedra. The distance between M(1) and M(3) is $3.0 \text{ \AA}$ and is between edge-sharing octahedra.

- The magnetic susceptibility increases [153] from about 1.1 emu mol^{-1} at 400 K to about 2.9 emu mol^{-1} at 700 K. There is then a short plateau region before the susceptibility continues to increase. This is in contrast to the situation in NaTiO_2 in which the flat plateau above the transition extends over a temperature range of at least 150 K. If one assumes metallic behaviour in the high-temperature region, then the susceptibility corresponds to a $n(E_F)$ of 1.5 orbital states eV^{-1} per Ti.
- There is no evidence for any hysteresis in the transition with temperature.
- The trigonal antiprism becomes *less* compressed which is opposite to the behaviour of NaTiO_2 . There is a 0.61% decrease in the in-plane lattice parameter a , and a 2.55% increase in the out-of-plane lattice parameter, c , which indicates a net elongation of the Ti environment.
- The unit cell volume increases by 1.3%, which is about double the percentage increase in NaTiO_2 when it is warmed through its transition.

- The shorter Ti–Ti distance between face-sharing octahedra increases from 2.58 Å to 2.72 Å [161], an increase of 5.7%.
- The longer Ti–Ti distance between edge-sharing octahedra decreases from 2.994 Å to 2.985 Å [161], a much smaller change of 0.33%, which is almost identical to the percentage *increase* in the edge-sharing Ti–Ti distance in NaTiO₂ on warming through the transition.

This behaviour has been rationalised [153, 159] by a band model which is illustrated in Figure 4.26. At low temperature, there are two filled (a_1) bonding bands at lower energy corresponding to overlap of Ti-3 d_{z^2} orbitals along the short Ti–Ti distance to form a bond. At higher energy there are eight empty (e_π) bands corresponding to the 3 $d_{x^2-y^2}$ and 3 d_{xy} orbitals which are bonding with respect to the longer Ti–Ti distance. There is a band gap which arises from the fact that the a_1 is much more bonding than the e_π and so the material is effectively insulating at low temperature. Note that this material *can* be an insulator solely on the basis of band structure arguments, because there are four electrons in the smallest unit cell. These can fill the two a_1 bonding bands corresponding to the two short Ti–Ti bonds in the cell. On warming, the geometry becomes more like a regular octahedron and so the bands move closer together. Whether the bands actually overlap at the higher temperatures to produce a semi-metal is debatable [153]. It certainly seems that the a_1 loses some electrons to become less bonding while the e_π gains some electrons to become more bonding. According to Mott [153], this could result from the material being a semiconductor above the transition with a very narrow band gap. This is consistent with the observation that the susceptibility continues to rise above 700 K.

The conductivity [164] increases on warming by about one and a half orders of magnitude between 400 and 700 K implying an increase in the number of charge carriers. At all temperatures the conductivity in the planes is greater by about half an order of magnitude than the conductivity perpendicular to the planes. This can be rationalised by reference to the structure which shows that although there is better overlap between neighbouring Ti³⁺ ions in the direction perpendicular to the planes,

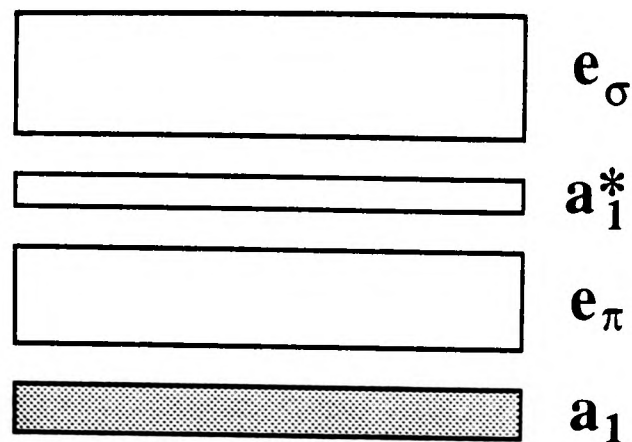


Figure 4.26: The proposed band structure of Ti_2O_3 .

these ions group in pairs along the c axis, so there is no good conduction path in this direction. Conduction along the c axis requires the charge carriers to be delocalised between *corner*-sharing as well as face-sharing octahedra. This is as a result of the two-thirds occupancy of each layer being staggered along the c axis. Electron delocalisation can extend throughout the ab plane via edge-sharing octahedra, so the conductivity is higher in this direction, even though the nearest neighbour orbital overlap is poorer.

This model cannot be used directly to explain the behaviour in NaTiO_2 however. In the smallest unit cell of NaTiO_2 , there is only one Ti^{3+} ion contributing one electron and so no band can be envisaged which is more than half-filled, and there is no evidence for an enlarged unit cell below the transition temperature. Also there is only one Ti–Ti distance. One would expect the band structure of NaTiO_2 to be somewhat similar to that of Ti_2O_3 since the TiO_6 geometry is similar in the two cases. However, note that the comparable Ti–Ti separations in the two materials (that between edge-sharing octahedra) changes in the opposite sense on warming the two materials: in Ti_2O_3 it gets shorter, while in NaTiO_2 it gets longer. The Ti–Ti distance in NaTiO_2 changes in the same sense as the shorter Ti–Ti distance in Ti_2O_3 , but to a lesser degree. This could reflect the fact that in Ti_2O_3 the shorter Ti–Ti distance is between Ti^{3+} ions in *face*-sharing octahedra, while in NaTiO_2 , the distance is between *edge*-sharing octahedra. In both cases, the *shortest* Ti–Ti distance *shortens* through the transition due to increased Ti–Ti bonding. In NaTiO_2 , this shortening could either result from uniform in-plane compression or from dimer formation, which would

have to be disordered since no superlattice peaks are observed. Ti-Ti dimer formation seems unlikely as the thermal parameters determined using neutron diffraction change smoothly and by only a small amount through the transition.

α -TiCl₃

This material shares more similarities with NaTiO₂ than Ti₂O₃ does. The space group is $R\bar{3}$ (No. 148) and the hexagonal lattice parameters are $a=b=6.15$ Å and $c=17.6$ Å. There are six Ti³⁺ ions in the unit cell. The material has a honeycomb lattice, each honeycomb layer being offset from the two on either side of it. The Ti³⁺ ions are all equivalent and there is a single Ti-Ti distance of about 3.5 Å which joins Ti³⁺ ions in the centres of edge-sharing octahedra. This distance is longer than the distance in NaTiO₂ but probably short enough for bonding to occur in the more covalent chloride via a Ti-Cl-Ti interaction. As in NaTiO₂, the coordination is that of a compressed trigonal antiprism with a compression index, as defined above for NaTiO₂, of about 1.03 at room temperature (c.f. 1.08 for NaTiO₂)

The magnetic susceptibility measured as a function of temperature [165, 166] is very similar in both size and shape to that of NaTiO₂, and there is a pronounced transition between 150 and 220 K. The transition looks very similar to that in NaTiO₂, but the increase in warming through the transition is a little larger. Also the susceptibility is not quite flat above 220 K, but drops slowly on warming. On warming through the transition, the lattice parameters change in exactly the same sense as in NaTiO₂, and the compression of the trigonal antiprismatic coordination increases, although insufficient data are available to quantify this with respect to NaTiO₂. At 300 K, the use of Equation 4.16 produces a value of 12.8 orbital states eV⁻¹ per Ti, which is larger by a factor of 3 than in NaTiO₂. This suggests that the overall Ti-Ti interaction is weaker in TiCl₃ than in NaTiO₂. In both cases, the overall interaction is composed of a contribution from direct Ti-Ti overlap, and one from a Ti-X-Ti interaction. It appears that the drop in direct overlap in TiCl₃ as a result of increasing the Ti-Ti separation is not compensated for by the more covalent Ti-Cl-Ti interaction being larger than the Ti-O-Ti overlap. The transition has been interpreted as

the result of a Ti–Ti bonding interaction being present below the transition, although the band structure has not been calculated or measured. According to Hewston and Chamberland [152] the variation of the susceptibility in the high-temperature region indicates that the behaviour is characteristic of a localised electron system, and the transition is between two semiconducting states.

The main difference between TiCl_3 and NaTiO_2 is that a hysteresis in the transition has been observed in TiCl_3 [166] which is not present in NaTiO_2 (Figure 4.15). Tsutsumi *et al.* [166] interpreted this as evidence that the phase transition in TiCl_3 is first order in nature, although rather broad.

$\text{Li}_{0.7}\text{VO}_2$

This material has been investigated by Hewston and Chamberland [152] and they have identified many of the features present in NaTiO_2 . The materials are isostructural, although the mixed valence nature of $\text{Li}_{0.7}\text{VO}_2$ would be expected to lead to differences in behaviour if these were localised insulating magnets. The V^{3+} environment is a trigonal antiprism compressed along the hexagonal axis (Figure 4.23). The lattice parameters of the $\text{R}\bar{3}\text{m}$ unit cell are $a=b=2.846 \text{ \AA}$ and $c=14.87 \text{ \AA}$ at room temperature.

There is a transition in the susceptibility between 400 and 500 K which is very similar in shape to those in NaTiO_2 and TiCl_3 . The susceptibility is flat above the transition temperature as in NaTiO_2 . Warming through the transition is accompanied by an increase in the compression of the V^{3+} site. The compression index (c.i.) defined previously is 1.028 at 297 K and 1.040 at 536 K [167]. These values indicate a lesser compression than is present in NaTiO_2 (c.i.=1.08), which may be due to the fact that V^{3+} and Li^+ are closer in size than are Ti^{3+} and Na^+ . However, the *change* in compression on heating $\text{Li}_{0.7}\text{VO}_2$ is *greater* than that obtained when NaTiO_2 is heated through the transition. It is tempting to suggest that this could account for the slightly larger change in the susceptibility in $\text{Li}_{0.7}\text{VO}_2$ compared to NaTiO_2 . There is no evidence for a change in symmetry or in the size of the unit cell through the transition. Conductivity measurements have been performed on unsintered, pressed pellets of $\text{Li}_{0.7}\text{VO}_2$ [152], and these indicate a 10-fold increase on warming through

the transition.

The observations have been interpreted in terms of a semi-conducting to metal transition which takes place on warming. The suggestion is that there is a 2D covalent cluster at low temperature with a short V-V distance. On heating the distance grows and a narrow band metal results. This conclusion is probably basically correct, but no band structure calculations have been performed which offer a full explanation.

LaTiO₃

Ti₂O₃ and Li_{0.7}VO₂ both appear to contain metal-metal bonds. LaTiO₃ has a perovskite-type structure with space group Pbnm (No. 62) and $a=5.601$, $b=5.590$ and $c=7.906$ [154, 168]. Each Ti³⁺ is in a fairly regular octahedral environment (O-Ti-O bond angles are 90.4, 90.2 and 88.7 °), and the Ti-O bonds are 2.01 Å in length. Each Ti³⁺ is 3.95 Å away from six others in neighbouring *corner*-sharing octahedra, so the coordination about each O²⁻ is Ti-O-Ti with an angle of 157°. This is unlike the other Ti-containing compounds just considered and NaTiO₂. However, temperature dependence of the resistivity of this material is characteristic of a metal above 125 K and of a semiconductor below that temperature [154]. In the metallic region, there is evidence that the charge carriers are not well delocalised and that this material is barely a metal [169]. The magnetic susceptibility is temperature independent above 125 K with a value of 8×10^{-4} emu mol⁻¹. This corresponds to a density of states at the Fermi energy of 12.4 orbital states eV⁻¹ per Ti. This value is similar to that in TiCl₃, but much greater than the values for NaTiO₂ and Ti₂O₃ which is indicative of much smaller overlap and hence a narrow band width. Below 125 K, there is antiferromagnetic ordering and hence each sublattice is subjected to an opposite exchange field. This causes the band to split into two sub-bands, the lower of which is filled, and the upper of which is empty. The band gap is of the order of the exchange interaction. Thus this material undergoes a metal to semiconductor transition on cooling which is associated with the onset of antiferromagnetic order. In the semiconducting region, the susceptibility increases by an order of magnitude and this has been ascribed to weak ferromagnetism with a moment of 7×10^{-3} μ_B mol⁻¹.

The fact that even a material with such a large Ti–Ti distance is metallic suggests that the orbitals are so large in Ti^{3+} that overlap and metallic behaviour is the norm in these materials. This is strong evidence, in the absence of more-conclusive conductivity measurements that NaTiO_2 is metallic. Ti–O–Ti interactions in a π sense are probably important in LaTiO_3 .

TiOCl and TiOBr

These two materials have been described in some detail by Beynon and Wilson [170]. They have proposed that these materials may show some of the characteristics of the RVB ground state [14]. Both compounds crystallise in the orthorhombic space group Pmmm (No. 47), and the lattice parameters are $a = 3.97 \text{ \AA}$, $b = 3.38 \text{ \AA}$ and $c = 8.03 \text{ \AA}$. The structure is composed of puckered sheets of edge-sharing TiO_4X_2 octahedra, and there are weak van der Waals interactions between the layers. Nearest neighbour Ti^{3+} ions separated by $3.10 \text{ \AA}$ in the chloride and $3.19 \text{ \AA}$ in the bromide are at the centres of octahedra sharing O–O edges. Next nearest neighbour Ti^{3+} ions are either at the centres of octahedra sharing O–Cl edges ($r(\text{Ti–Ti}) = 3.38 \text{ \AA}$ in the chloride and $3.49 \text{ \AA}$ in the bromide) or linked via an almost linear Ti–O–Ti linkage ($3.79 \text{ \AA}$ in both materials). The puckering leads to the possibility that, if the materials are insulating magnets, there are next-nearest-neighbour interactions of comparable size to the nearest-neighbour interactions which could cause frustration as discussed in Chapter 1. This was one of the situations in which Anderson [14] proposed that the RVB state would occur.

Beynon and Wilson describe the materials as Mott insulators, and cite as evidence for this the fact that the shortest Ti–Ti distance is $3.10 \text{ \AA}$, which is larger than the $3.05 \text{ \AA}$ proposed by Goodenough [171] to be the critical Ti–Ti separation in the edge-sharing octahedral case below which a material is metallic, and above which it is insulating. Also, they were unable to induce metallic conductivity in the materials even under high pressure, and the materials are flaky brown crystals. The magnetic susceptibility of both materials is flat between 100 and 300 K. Below 100 K in the chloride and 50 K in the bromide, the susceptibility dips slowly to about 90% of its

high-temperature value before rising again slowly below 50 K (25 K in the bromide). This behaviour is reminiscent of, although less pronounced than, the behaviour in NaTiO_2 and the other materials just described at their metal-insulator transitions. It is not clear whether there is any change in the Ti-Ti separation or in the structure on cooling. The susceptibility in the flat region is about twice that of NaTiO_2 above its transition. TiOCl has been included in the correlation of $n(E_F)$ with $r(\text{Ti-Ti})$.

Beynon and Wilson have carried out studies in the two materials in which they replace up to 10% of the Ti^{3+} with Sc^{3+} during preparation. A large paramagnetic tail emerges corresponding to the number of Ti^{3+} ions replaced. They take this as evidence that in the undoped material, there is some dynamic paired state (the RVB state), and that the introduction of some Sc^{3+} ‘freezes’ the Ti^{3+} ions into pairs. It is not clear quite how this causes a number of Ti^{3+} equal to the number replaced to behave as paramagnets, since one would expect that only the very few Ti^{3+} which are completely surrounded by Sc^{3+} would behave in this way.

It is not clear whether these oxyhalides are RVB materials. Beynon and Wilson [170] propose that they may be rare examples of materials which adopt an RVB state as one of the several ‘strategies’ for relieving antiferromagnetic frustration.

4.7.3 The band structure of NaTiO_2

The band structure of Ti_2O_3 has briefly been discussed in the previous section. The picture should be quite similar to that in NaTiO_2 , TiCl_3 and $\text{Li}_{0.7}\text{VO}_2$.

Trigonal distortion of octahedral symmetry

In layered compounds like NaTiO_2 one expects the symmetry of the TiO_6 units to be reduced to trigonal symmetry. The symmetry in NaTiO_2 is D_{3d} with compression along the principal axis due mainly to the presence of the large Na^+ ions in the planes either side of the Ti-layers. The compression has been quantified by the use of a compression index which is the ratio of the O-O distance in the plane perpendicular to the principal axis to the other O-O distance. The reduction in symmetry from

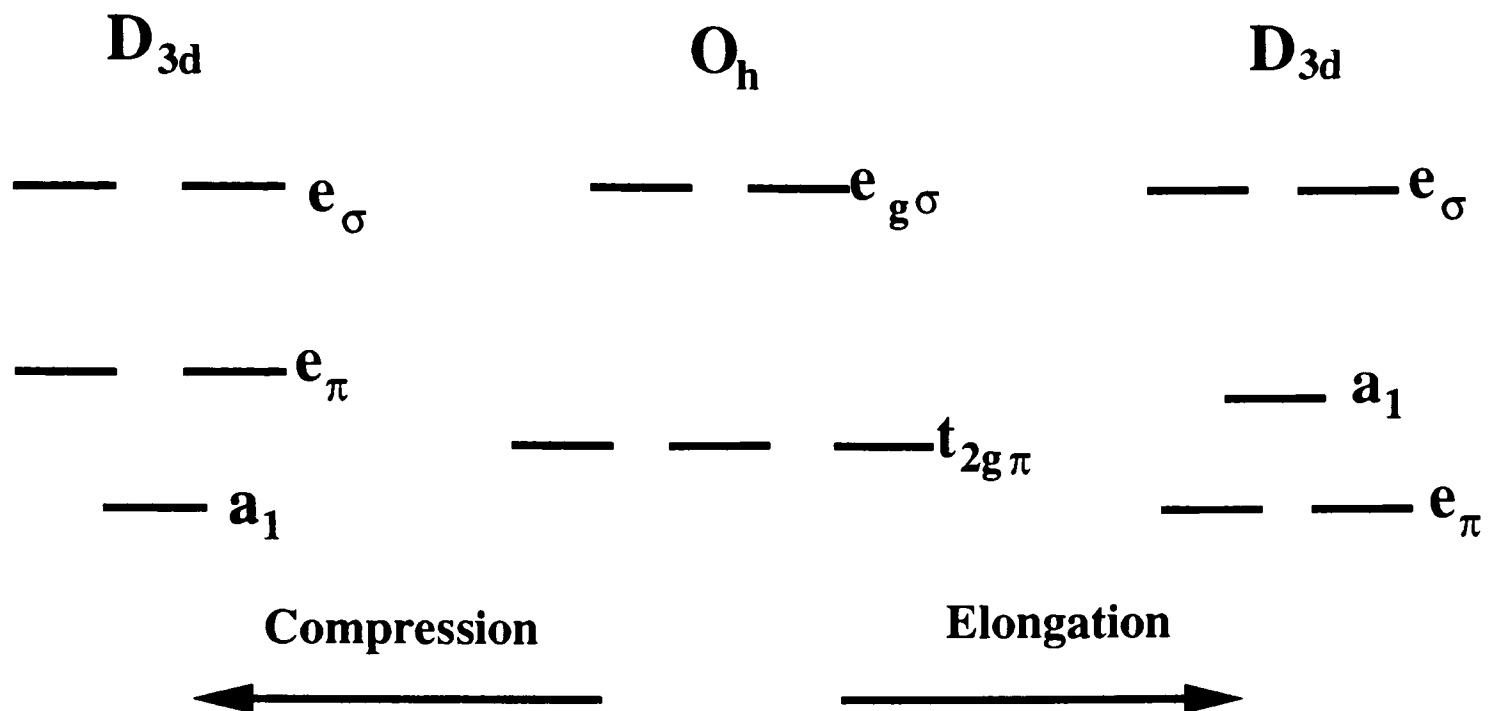


Figure 4.27: Reduction in symmetry from O_h to D_{3d} showing the changing orbital energies [172].

O_h to D_{3d} leaves the e_g^σ orbitals unchanged but splits the t_{2g}^π set into an e_g^π set and an a_1^π orbital. If the geometry is compressed, the a_1^π orbital is expected to be lower in energy than the e_g^π orbitals, but if the geometry is elongated, the reverse is true [172]. This is shown in Figure 4.27. The σ and π labels are assigned according to their symmetry with respect to the surrounding O^{2-} ions.

Arrangement of orbitals

We now consider just the e_g^π and a_1^π orbitals in NaTiO_2 and drop the π label. The $d_{x^2-y^2}$ and d_{xy} orbitals form the e_g set which overlap strongly with the six nearest-neighbour Ti^{3+} . The d_{z^2} orbital has a_1 symmetry and points perpendicular to this plane. This is shown in Figure 4.28.

A greater bonding interaction corresponding to partial occupancy of the e_g orbitals will reduce the Ti-Ti distance and, according to the observations, this is the case at low temperature. Thus the hypothesis is that the energy separation of the e_g and lower-lying a_1 states increases on warming. This is consistent with the observation that the compression increases on heating, since this will cause a greater splitting. The hypothesised change in band structure is indicated in Figure 4.29.

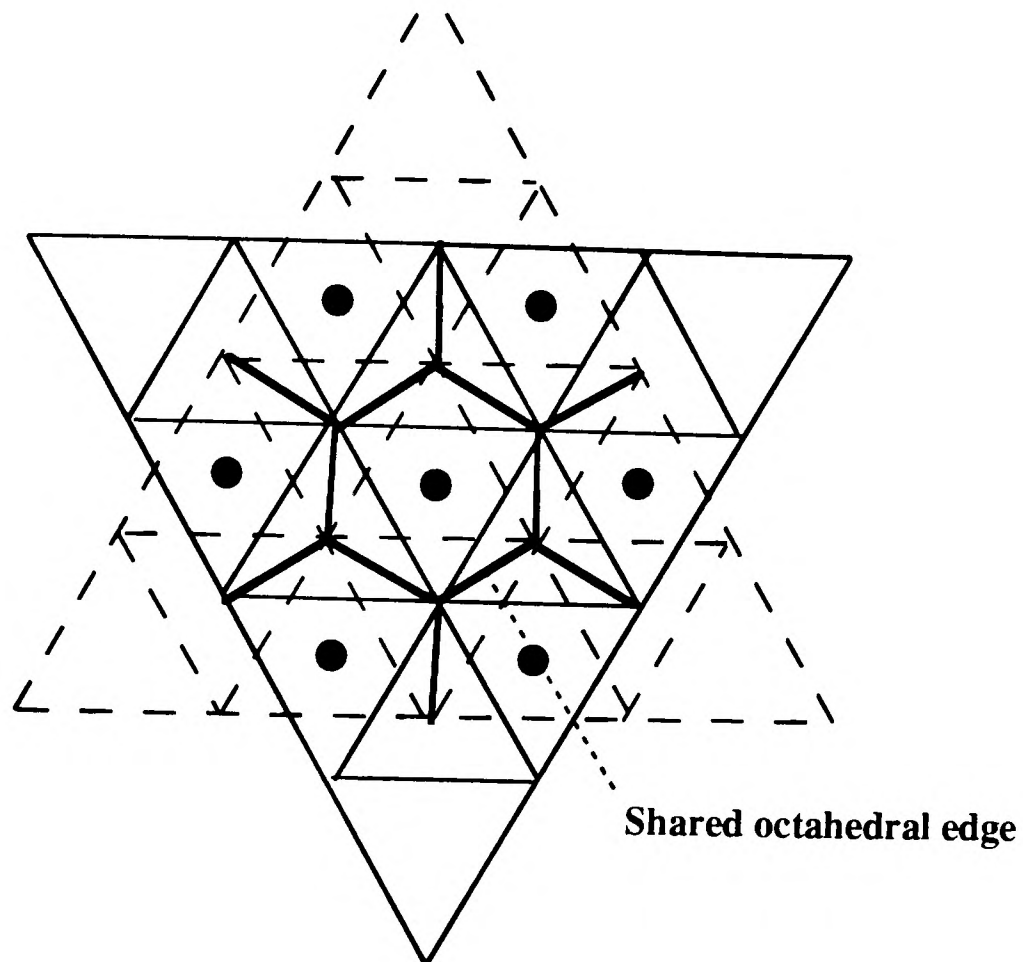


Figure 4.28: The $\text{Ti-}3d_{z^2}$ orbital points perpendicular to the planes in NaTiO_2 . A linear combination of the $3d_{x^2-y^2}$ and $3d_{xy}$ orbitals forms bonds with the six nearest neighbour Ti^{3+} ions in the plane. The Ti^{3+} ions are in the plane of the page. The orbitals are not drawn.

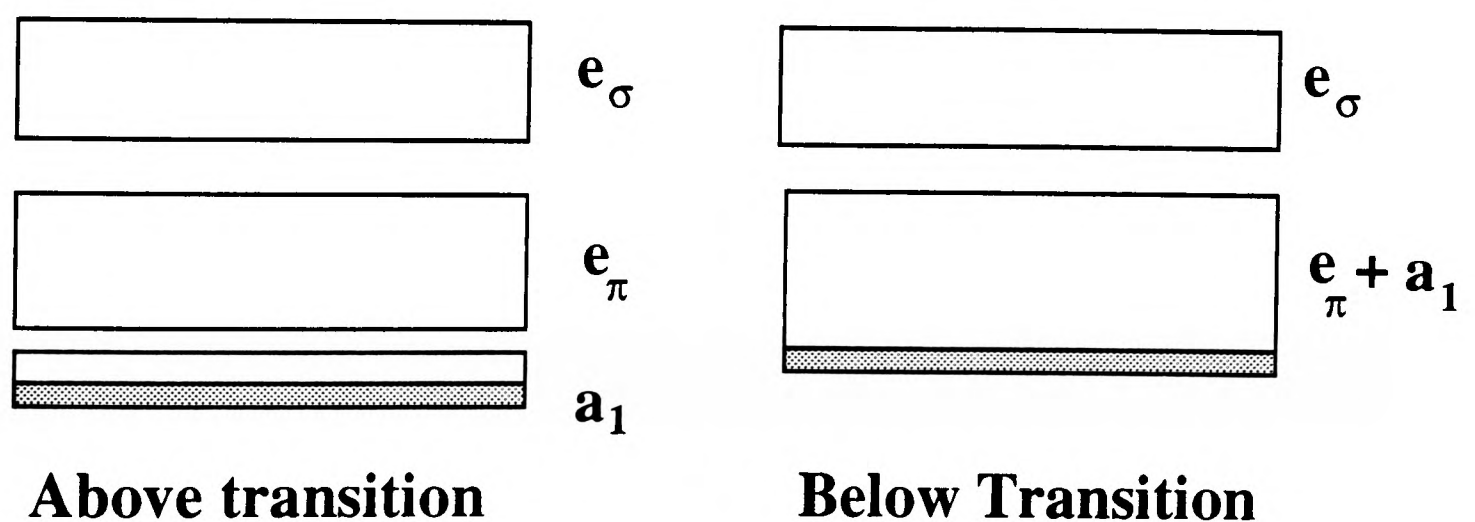


Figure 4.29: The hypothesised band structure of NaTiO_2 , assuming the valence electrons are delocalised. It is likely that the splitting is actually smaller than shown when considered relative to the width of the bands, since the distortion from octahedral symmetry is not very large.

One expects that the e_g band will be broader than the a_1 band because the atomic orbitals it contains are in the Ti planes and are better placed for overlap with those on neighbouring Ti^{3+} ions. The overlap may be direct or be via the intervening oxide ions. At this juncture note that the situation in Ti_2O_3 is *opposite* to this: the compression becomes smaller on heating moving the split levels closer to the degenerate O_h case, so although the magnetic behaviours are superficially similar, they must have slightly different origins.

Application to the magnetic behaviour

From the magnetic susceptibility, we determine that above the transition temperature, the density of states at the Fermi energy is about 5 orbital states eV^{-1} per Ti. This decreases to about half this value below the transition, which corresponds to a narrower band being occupied above the transition. The density of states is slightly larger than that in Ti_2O_3 , which indicates that NaTiO_2 has slightly narrower bands; however it is much smaller than in LaTiO_3 which should have a smaller overlap and very narrow bands. The a_1 band with its narrower width will have a larger density of states than the e_g band, and so the hypothesis about the change in the band occupation is consistent with the susceptibility measurements.

Entropy change at the transition

The heat capacity of a metal is given approximately by

$$C = \gamma T + AT^3 \quad (4.18)$$

where the first term is the electronic contribution and the second term is the contribution from the lattice. γ is given by

$$\gamma = \frac{1}{3}\pi^2 \cdot n(E_F)k_B^2 \quad (4.19)$$

where the energy units used for $n(E_F)$ and k_B must be the same. We can substitute in the expression which relates $n(E_F)$ to χ_{mol} (Equation 4.16) and, ensuring that the units are consistent, obtain

$$\gamma = \frac{10\pi^2 \chi_{mol} k_B^2}{3\mu_B^2} \quad (4.20)$$

The constant term equals $72.9 \text{ JT}^2\text{K}^{-1}$. Notice that the factor of 2 in the denominator of Equation 4.16 has been removed to ensure that we are dealing with the *total* number of states, which is twice the number of orbital states.

The entropy change is related to the heat capacity by

$$\Delta S = \int \frac{C}{T} dT \quad (4.21)$$

so

$$\Delta S_{el} = \int \gamma dT. \quad (4.22)$$

Converting γ to the molar susceptibility.

$$\Delta S_{el} = 72.9 \int \chi_{mol} dT. \quad (4.23)$$

Thus we should be able to correlate the entropy change at the transition determined using measurement of the heat capacity [142] with the magnetic susceptibility above the transition. We must use the same sample in each case due to the differences in magnetic properties of different NaTiO_2 samples.

We take the value of χ_{mol} below the transition to be the value of A in the equation $A + C/T$ (Table 4.5) used to fit the susceptibility in the region below the transition. ie. we subtract out the Curie tail. We take the value of χ_{mol} above the transition to be that in the flat region between about 270 and 420 K. The temperatures between which the integration is performed are estimated to be the temperatures at which the susceptibility flattens out above and below the transition. Takeda *et al.* [142] obtain the following values: $\chi_{mol} = 1.4 \times 10^{-4} \text{ emu mol}^{-1}$ at 230 K and $\chi_{mol} = 4.0 \times 10^{-4} \text{ emu mol}^{-1}$ at 270 K. Substituting these values into Equation 4.23 produces a value for ΔS_{el} of $5.5 \text{ JK}^{-1}\text{mol}^{-1}$. If there is a correction for Landau diamagnetism [157] both above and below the transition, this would scale both susceptibilities by a factor of $\frac{3}{2}$, producing a value for ΔS_{el} of $8.3 \text{ JK}^{-1}\text{mol}^{-1}$. If the material is metallic only above the transition and the constant term in the susceptibility below the transition is due to Van Vleck paramagnetism, as suggested by Takeda *et al.* [142], then we should only correct the value of χ_{mol} above the transition for Landau Diamagnetism, and this produces a value of $9.5 \text{ JK}^{-1}\text{mol}^{-1}$ for ΔS_{el} .

Estimation of the entropy change using the heat capacity data of Takeda *et al.* [142] produces a value of about $7 \text{ JK}^{-1}\text{mol}^{-1}$ which is in good agreement with the calculated values. It should be noted that there are a number of approximations involved in the calculations; the greatest difficulties being associated with the estimation of the different parameters from the graphs of Takeda *et al.* [142].

Our sample labelled as ‘ $\text{Na}_{1.2}\text{TiO}_2$ (washed)’ (Figure 4.14) which we regard as our best sample has a very similar magnetic susceptibility above the transition to the sample of Takeda *et al.* [142], although the transition takes place over a slightly broader range. If we substitute values of χ_{mol} of $3.9 \times 10^{-4} \text{ emu mol}^{-1}$ at 270 K and $1.6 \times 10^{-4} \text{ emu mol}^{-1}$ at 170 K (the latter value obtained by fitting the susceptibility below 150 K), we obtain a value of ΔS_{el} of $5.7 \text{ JK}^{-1}\text{mol}^{-1}$, which is almost identical to that determined for the sample of Takeda *et al.* before correction for Landau diamagnetism.

There is reasonably good agreement between the experimentally determined entropy change using measurement of the heat capacity and the value calculated from the measurement of the magnetic susceptibility on the basis that NaTiO_2 is metallic. This suggests that our model is valid. The use of Equation 4.23 also produces good agreement between the heat capacity and susceptibility data for Ti_2O_3 [153].

Comparison with the completely-free electron model of a metal

For a metal in which the electrons may be treated as free electrons, we can calculate [156] the Fermi energy, E_F , which is

$$E_F[\text{eV}] = 50.1 \times \left(\frac{r_s}{a_0} \right)^{-2} \quad (4.24)$$

where

$$\frac{r_s}{a_0} = 5.44 \times n_{22}^{-\frac{1}{3}} \quad (4.25)$$

and n_{22} is related to the electron density, n , by

$$n = n_{22} \times 10^{22} \quad (4.26)$$

n is the number of electrons per cm^3 . In NaTiO_2 , there are three electrons in the hexagonal unit cell which has a volume of $130 \text{ \AA}^3$ or $1.30 \times 10^{-22} \text{ cm}^{-3}$, and is three

times the size of the rhombohedral unit cell, which is the smallest which can be constructed. n_{22} thus has a value of 2.31 electrons per $100 \text{ \AA}^3$. Substituting this value into Equations 4.25 and 4.24 produces a value for E_F of about 3.0 eV. Note that this analysis strictly applies to electrons in non-degenerate orbitals as is the case in Na. In a transition metal oxide like NaTiO_2 , the electron is delocalised among a degenerate set of T_{2g} orbitals. Including this degeneracy, d , in the calculation produces a value of E_F which is smaller by a factor $d^{\frac{2}{3}}$ than that calculated in the non-degenerate case [174].

The approximate calculation of the Fermi energy allows us to determine the total number of states per Ti at that energy for the free-electron model:

$$g(E_F) = \frac{3n}{2E_F} \quad (4.27)$$

where $g(E_F) = 2n(E_F)$, $n(E_F)$ being the number of *orbital states* per Ti which we considered earlier. n is now the electron density per Ti, which is equal to 1. We calculate $g(E_F) = 0.5 \text{ states eV}^{-1}$ per Ti, which is somewhat smaller than the value of about 10 states eV^{-1} per Ti which we obtained from measurements of the susceptibility above the transition temperature.

This indicates that NaTiO_2 has much narrower bands than one would predict using the free-electron model. By substituting our measured value of $g(E_F)$ into Equation 4.27 we determine the effective Fermi energy of NaTiO_2 to be about 0.15 eV. This is much smaller than for a free-electron metal, but still considerably larger than the thermal energy above the transition which is about 0.02 eV, and so we would expect that metallic conductivity is possible in NaTiO_2 .

If the electrons are completely free, the band width is much greater in energy than the electron-electron repulsions. As the band width decreases and becomes of the order of the repulsions, there is an enhancement of the magnetic susceptibility. This can be thought of as arising from the electrons preferring to align their spins parallel to minimise the repulsions. The so-called Stoner enhancement of the susceptibility [155, 158] is common in early transition metal oxides and can be quantified by the

enhancement factor, I ,

$$g(E_F) = \frac{g(E_F)_{free}}{1 - Ig(E_F)_{free}}. \quad (4.28)$$

Where $g(E_F)_{free}$ is the density of states calculated using the free-electron model. Substituting in our calculated values produces an enhancement factor, I , of about 2. This is a large enhancement, but comparable values have been obtained for other metallic transition metal oxides such as V_2O_3 [175].

This comparison with the free-electron model supports the view that $NaTiO_2$ is a metallic conductor, but with much narrower bands than predicted and strong electron-electron interactions which enhance the susceptibility.

Interpretation

In the absence of any conductivity measurements which may shed more light on the problem, the best interpretation of the behaviour may be summarised as follows:

- At low temperatures, the electrons occupy a band with both e_g and a_1 character. These bands are not degenerate but they overlap. The higher energy e_g band is bonding between nearest neighbour Ti^{3+} ions in the basal plane.
- On warming, the geometry becomes more compressed along the trigonal axis and the bands move further apart. The occupancy of the e_g band decreases and so the Ti-Ti bond weakens and lengthens.
- The narrower a_1 band has a higher density of states than the broad e_g band, and so increasing the a_1 character of the band occupied by the electrons will increase $n(E_F)$, which increases the susceptibility on heating.
- The transition is thus interpreted as a metal-metal transition with a subtle change in the band structure. It seems likely that the behaviour is similar in $TiCl_3$ and $Li_{0.7}VO_2$. The interpretation of $NaTiO_2$ as being metallic is supported by calculations of the entropy change at the transition.

The driving force for the transition on cooling is probably an increase in the in-plane Ti-Ti overlap, which alters the band structure and also causes the interlayer

separation to increase in order to conserve the coordination around the Na^+ ion, which is more rigid in its bonding requirements than the more covalent Ti^{3+} . The size of the volume change is smaller than in Ti_2O_3 (0.6% vs. 1.28%) which is probably due to the greater rigidity of the structure afforded by the presence of the Na^+ ions.

4.8 Investigation of LiTiO_2

There are a number of $\text{Li}_x\text{Ti}_y\text{O}_z$ phases known. The spinel-like LiTi_2O_4 ($\text{Ti}^{3.5+}$) is the best known and is a superconductor below 12 K. The Ramsdellite-type compound $\text{Li}_2\text{Ti}_3\text{O}_7$ (Ti^{4+}) is a 1D ionic conductor. The paper by Murphy *et al* [176] describes soft routes towards the intercalation of Li into anatase using *n*-BuLi, and the paper by Cava *et al.* [177] carries out a detailed structural study of the phases produced. The synthesis of phases in which the Ti^{4+} has been partially or fully reduced to Ti^{3+} is also possible at elevated temperatures between 900 and 1200°C.

The initial objective of this work was to synthesise LiTiO_2 and compare its magnetic properties and structure with those of NaTiO_2 . In NaTiO_2 , the Ti^{3+} and Na^+ ions are sufficiently different in size that they adopt an ordered arrangement, however the smaller Li^+ is very similar in size to Ti^{3+} and the structure is the disordered version of the NaCl structure with space group $\text{Fm}\bar{3}\text{m}$ (No. 225).

The Na-Li-Ti-O phase diagram also seems an interesting area for the study of structural relationships and changes in magnetic behaviour. However, while there was evidence that phases $\text{Na}_x\text{Li}_y\text{TiO}_2$ could be prepared both at high temperatures and by the reaction of *n*-BuLi with Na_xTiO_2 ($x < 1$), this area requires further study.

4.8.1 Preparation of Li_xTiO_2 phases

The compound LiTiO_2 has been prepared by Lecerf [178] via the reaction between Li_2O and Ti_2O_3 and by Murphy *et al* [176] by reducing the anatase polymorph of TiO_2 with *n*-BuLi. We found that a similar reaction to that used to make NaTiO_2 could be employed, ie. $\text{Li} + \text{TiO}_2$ at elevated temperatures. The latter two methods were used for the synthesis to test the hypothesis that the ordering of Li^+ and Ti^{3+}

ions could be influenced by the reaction temperature.

Soft route to LiTiO_2

The method of Murphy was followed closely: this is a multi-step reaction since the intercalation of Li^+ using $n\text{-BuLi}$ into anatase does not allow the formation of phases with a Li^+ to Ti^{3+} ratio greater than 0.7. 10 g of anatase powder (99.999% from Aldrich Chemical Company) were treated with two equivalents of 1.5 M $n\text{-BuLi}$ (99% from Aldrich) in a mixture of hexane and pentane isomers using standard Schlenk line techniques. The reaction was stirred at 25°C for 15 days. The unreacted $n\text{-BuLi}$ was filtered off and the black solid remaining was washed three times with dried, degassed pentane, then filtered and finally dried under vacuum for 12 hours. The solid rapidly deintercalates Li^+ on exposure to the air or to mild oxidising agents such as I_2 in acetonitrile [176]. Anatase is regained from this deintercalation indicating that the intercalation is topotactic. The black solid, $\text{Li}_{0.5}\text{TiO}_2$, was manipulated in the He-filled dry-box. The solid was loaded into a quartz tube, sealed under vacuum and placed in a furnace at 600°C for one hour. The temperature was then increased to 750°C for 9 days to increase the crystallinity of the product and ensure that the Li and Ti ions in the solid were ordered. The blue-black solid resulting from this treatment was also handled in the dry-box. X-ray powder diffraction using a Siemens D5000 diffractometer operating in transmission mode was used to confirm that the phase corresponded to LiTi_2O_4 , which has a spinel-type structure and becomes superconducting below about 12 K. 0.7 g of LiTi_2O_4 was treated with a large excess (>10 equivalents) of 1.5 M $n\text{-BuLi}$ for 16 days at 25°C . This produced a black compound with a very similar structure to the precursor but with a slightly smaller unit cell and peak intensities which corresponded to those of $\text{Li}_2\text{Ti}_2\text{O}_4$. Comparative X-ray powder diffraction patterns are shown in Figure 4.30. This second spinel phase is highly air-sensitive and rapidly turns bright blue on exposure to air. It has the same stoichiometry as the target material and treatment in an evacuated quartz ampoule at 600°C for seven days produced highly crystalline LiTiO_2 . The X-ray powder diffraction pattern of LiTiO_2 is shown in Figure 4.31.

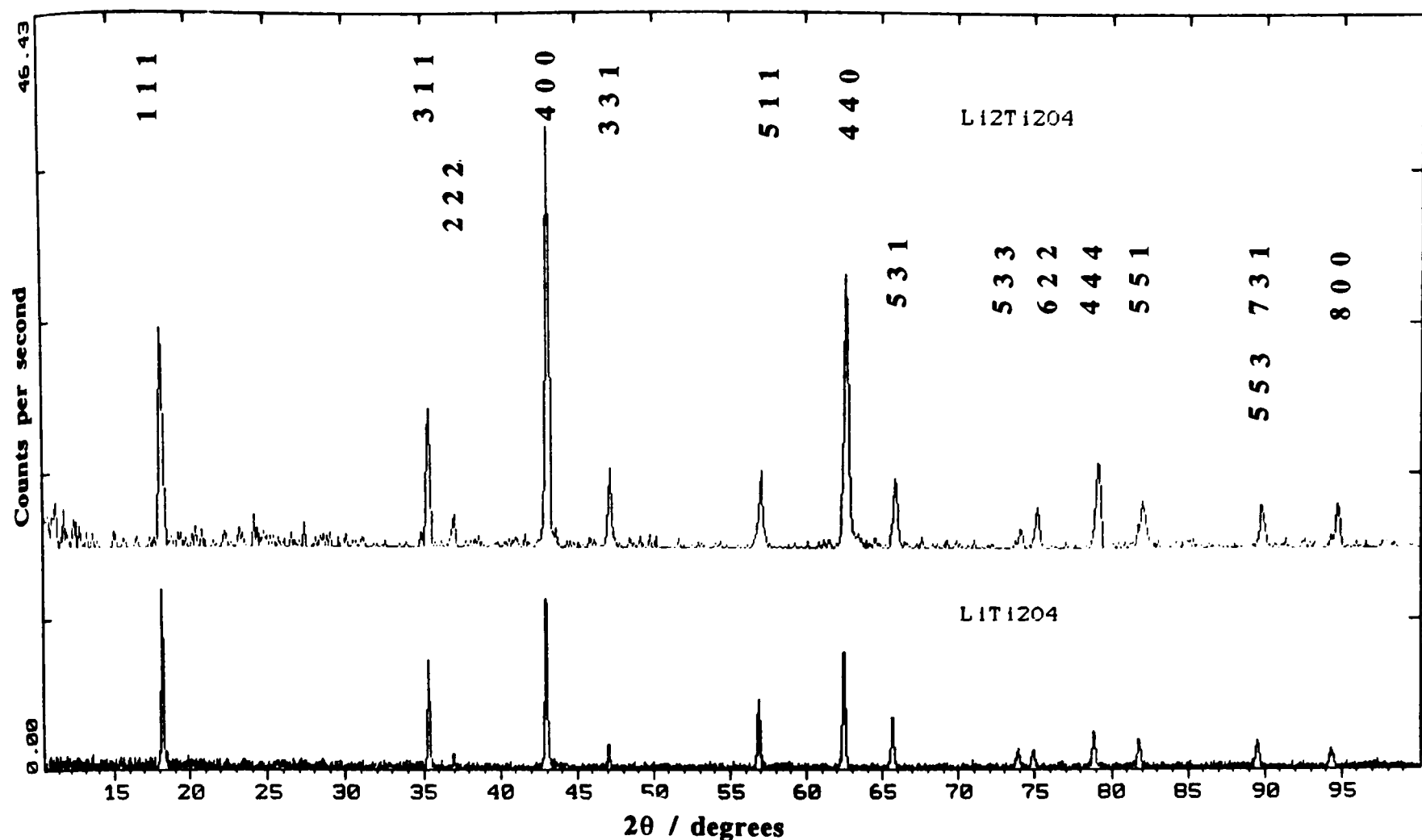


Figure 4.30: The X-ray diffraction patterns of LiTi_2O_4 and $\text{Li}_2\text{Ti}_2\text{O}_4$ samples prepared by the stepwise lithiation of anatase. The patterns are quite similar and agree with the results of Murphy *et al.* and Cava *et al.*. The data have had the background fitted and subtracted for clarity.

The spinel type phase has a unit cell of dimensions $2a \times 2a \times 2a$ when compared to the LiTiO_2 structure. The Ti ions are in edge-sharing octahedra in both cases, and the Li^+ ions are tetrahedrally coordinated in the spinel and octahedrally coordinated in the LiTiO_2 structure.

Care must be taken that the target material is not deficient in Li. If the treatment of LiTi_2O_4 with $n\text{-BuLi}$ was carried out for only 6 days at room temperature with a 2-fold excess of $n\text{-BuLi}$, and the resulting compound was heated for 3 days at 600° , there remained X-ray diffraction peaks corresponding to one of the spinel-like phases. Further heating did not change the intensities of these peaks relative to those of LiTiO_2 indicating that there was excess LiTi_2O_4 present which had not been lithiated.

The structural data on the materials obtained by the stepwise lithiation of anatase powder are summarised in Table 4.9

LiTi_2O_4 has the cubic space group $\text{Fd}\bar{3}\text{m}$ (No. 227) and the lattice parameter of

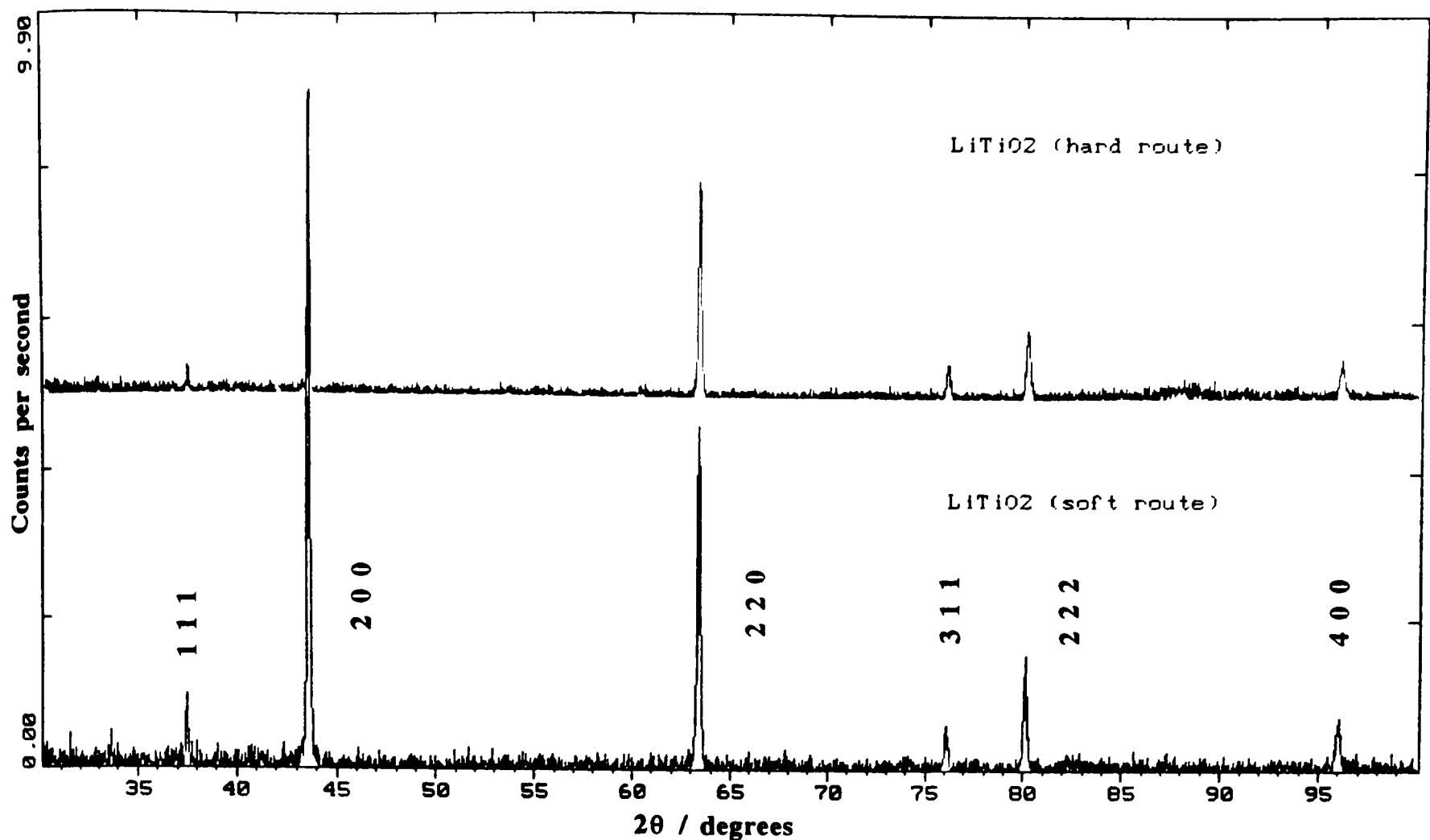


Figure 4.31: The X-ray diffraction pattern of LiTiO_2 obtained by both the soft route with $n\text{-BuLi}$ and the higher temperature route. Neither pattern shows any impurity phases, although a small amount of LiTi_2O_4 was present in the material prepared at 1000° as determined by SQUID measurements. Both patterns have been background corrected for clarity.

hkl	LiTi_2O_4			$\text{Li}_2\text{Ti}_2\text{O}_4$		
	$d\text{-spacing}/\text{\AA}$		$I_0/I / \%$	$d\text{-spacing}/\text{\AA}$		$I_0/I / \%$
	obs	calc		obs	calc	
1 1 1	4.866	4.847	100.0	4.850	4.834	100.0
3 1 1	2.536	2.531	48.1	2.528	2.524	38.4
2 2 2	2.428	2.242	7.4	2.420	2.417	8.3
4 0 0	2.102	2.099	67.4	2.096	2.093	94.2
3 3 1	1.928	1.926	9.2	1.923	1.921	14.4
5 1 1	1.618	1.161	22.6	1.613	1.611	15.1
4 4 0	1.486	1.484	37.8	1.481	1.480	46.6
5 3 1	1.421	1.419	14.0	1.416	1.415	13.2
5 3 3	1.282	1.280	4.6	1.277	1.277	4.5
6 2 2	1.267	1.266	5.0	1.263	1.262	6.3
4 4 4	1.213	1.212	8.8	1.209	1.209	13.5
5 5 1	1.177	1.176	6.9	1.173	1.173	6.9
5 5 3	1.093	1.093	6.5- n	1.091	1.090	6.6- n
7 3 1	1.093	1.093	n	1.091	1.090	n
8 0 0	1.049	1.049	3.7	1.047	1.047	6.3

Table 4.9: Structural data for the phases obtained by lithiation of anatase and subsequent transformations.

	Li + TiO ₂			n-BuLi + TiO ₂		
<i>hkl</i>	<i>d</i> -spacing/Å		<i>I</i> ₀ / <i>I</i> / %	<i>d</i> -spacing/Å		<i>I</i> ₀ / <i>I</i> / %
	obs	calc		obs	calc	
1 1 1	2.394	2.393	9.0	2.395	2.393	8.9
2 0 0	2.073	2.072	100.0	2.074	2.072	100.0
2 2 0	1.465	1.465	71.3	1.466	1.465	57.8
3 1 1	1.250	1.250	10.7	1.250	1.250	6.5
2 2 2	1.197	1.196	22.7	1.197	1.196	17.4
4 0 0	1.036	1.036	12.4	1.037	1.036	8.5

Table 4.10: Structural information for LiTiO₂ prepared by the reaction of Li with anatase and via the reaction of anatase with *n*-BuLi.

8.396(2)Å was obtained from the above data using the cell refinement program *REFCEL*. Li₂Ti₂O₄ is also Fd $\bar{3}$ m and the lattice parameter is slightly smaller (8.373(1)Å) after intercalation of the Li presumably due to the Li exerting a contraction effect on its intercalation site.

High-temperature route to LiTiO₂

The second method of preparation of LiTiO₂ was similar to that used for the preparation of NaTiO₂. Stoichiometric amounts of Li metal (99.9% from Aldrich) and anatase powder were sealed in an ARMCO soft ingot iron ampoule using a TIG welder and heated in a Carbolite 16/50 tube furnace at 1000°C under flowing Ar gas for 12 hours. The ampoule was opened in a He-filled dry box and the product was a black powder. X-Ray powder diffraction showed good agreement with the product of Lecerf [178] and refinement of the unit cell parameters using the least-squares fitting program *REFCEL* [131] produced a value of 4.144 Å for the lattice parameter.

The X-ray diffraction information for LiTiO₂ prepared by the two different routes indicates that they are the same. The patterns are shown in Figure 4.31. The diffraction data are summarised in Table 4.10.

Structural description of the L_xTiO₂ phases

Cava *et al.* [177] have carried out a detailed structural analysis of the phases Li_{0.5}TiO₂, LiTi₂O₄ and Li₂Ti₂O₄. In anatase the Ti–Ti distance is 3.039 Å. On intercalation to

form $\text{Li}_{0.5}\text{TiO}_2$, there are two different Ti–Ti distances of 2.887 Å and 3.128 Å. The former they describe as a bonding distance and the latter as a non-bonding distance. Cava *et al.* [177] suggest that the transformation to the spinel type phase at high temperature is driven by the reduction in strain which accompanies this. In LiTi_2O_4 each Ti ion has 6 neighbours 2.97 Å away in the centres of adjacent edge-sharing octahedra. This material is metallic, and so this provides further evidence that there may be metallic bonding in NaTiO_2 and LiTiO_2 , in which the shortest Ti–Ti distances are similar and the octahedra also share edges. On further reduction, to $\text{Li}_2\text{Ti}_2\text{O}_4$, the distance is almost unchanged at 2.961 Å, and the Ti environment is hardly changed. The structure of $\text{Li}_2\text{Ti}_2\text{O}_4$ is very regular, and the Li^+ ions are all tetrahedral while the Ti^{3+} are all octahedral. Cava *et al.* [177] suggest that, the change to the disordered rock-salt structure of LiTiO_2 at 600° is driven by the increased entropy rather than by any reduction in strain.

In LiTiO_2 , the Ti–Ti distance is 2.93 Å between those at the centres of edge-sharing octahedra. We conclude, following Cava *et al.* [177] that Ti–Ti bonding is possible in all these Li_xTiO_2 phases. One difference between LiTiO_2 and NaTiO_2 is that the TiO_6 unit in LiTiO_2 is an undistorted octahedron, and so there will not be splitting of the t_{2g} band as there is in NaTiO_2 .

4.8.2 Magnetic properties of LiTiO_2

DC susceptibility measurements

The magnetic susceptibility of LiTiO_2 prepared by both the reaction between Li and TiO_2 at 1000° and the stepwise lithiation of anatase at lower temperatures were measured. In the following discussion the two compounds will be labelled as $\text{LiTiO}_2(1000)$ and $\text{LiTiO}_2(\text{BuLi})$. The DC susceptibility was measured using the Cryogenic Limited SQUID susceptometer at the ICL, Oxford or the Quantum Design MPMS₂ magnetometer at the University of Edinburgh. The operation of these instruments is described in Section 3.6.

Measurement of the magnetic moment of the two materials as a function of field

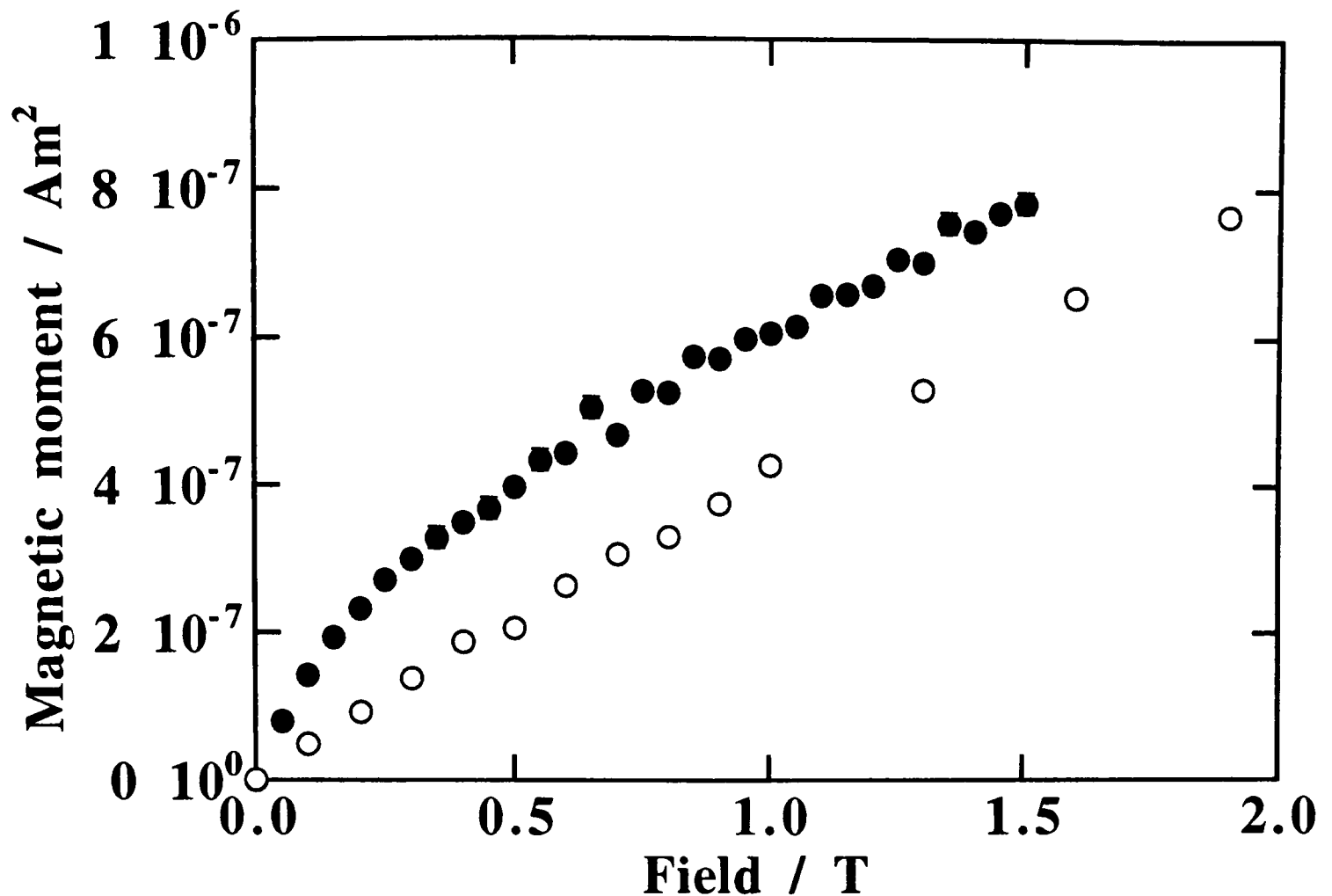


Figure 4.32: The non-linearity of the magnetisation of LiTiO_2 samples measured as a function of field is due to small amounts of iron or nickel impurity.

at room temperature usually indicated non-linearity at fields of up to 1 T as shown in Figure 4.32. The departure from linearity is usually much more pronounced in $\text{LiTiO}_2(1000)$ indicating that it probably contains significant impurities which were not detected by X-ray diffraction and which could arise from the iron preparation vessel or from the presence of small amounts of other Li-Ti-O phases. One would expect the $\text{LiTiO}_2(\text{BuLi})$ sample to contain fewer external impurities although one cannot rule out the possibility of inclusions of some of the intermediate phases due to incomplete conversion at some stage during the synthesis. A sample of $\text{LiTiO}_2(1000)$ containing a negligible amount of ferromagnetic impurity was prepared by lining the Fe ampoule with Mo foil and exercising extreme care in opening the ampoule.

The susceptibility of $\text{LiTiO}_2(1000)$ containing no ferromagnetic contamination measured in a field of 0.1 T as a function of temperature is shown in Figure 4.33. A magnetic transition occurs at 12 K. This transition is absent when the measurement is performed in a field of 1.0 T or larger (Figure 4.34). The transition is believed

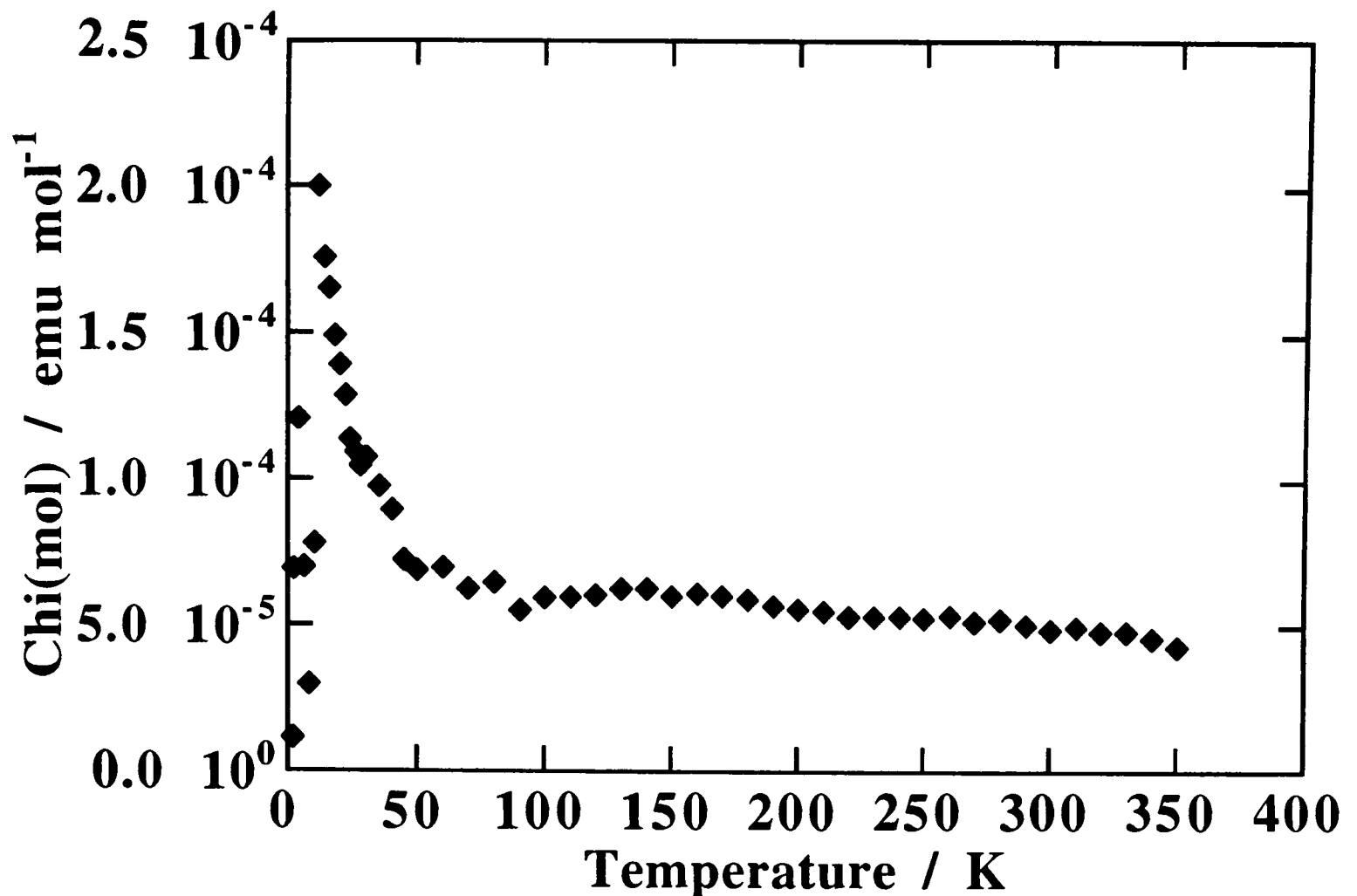


Figure 4.33: The low temperature transition in LiTiO_2 when measured at low field is due to a small amount of the superconducting phase LiTi_2O_4 .

to be due to a small amount of LiTi_2O_4 present in the sample. As has been well documented [176], this compound undergoes a transition to a superconducting phase at 12 K and indeed was the first oxide superconductor to be investigated in detail. Superconductivity cannot be supported in this material at fields as high as 2.0 T (ie. 2.0 T is greater than the upper critical field, H_{c2}) and so the transition is not observed.

The molar susceptibility, χ_{mol} , of the non-contaminated sample of $\text{LiTiO}_2(1000)$ was determined by measuring the magnetic moment at 1.0 T. χ_{mol} and its inverse are plotted in Figure 4.34. This sample does not appear to display Curie-Weiss like behaviour, although a good fit can be made to the form

$$\chi_{mol} = A + C/T \quad (4.29)$$

with $C=0.0023(1)\text{ emuK}^{-1}\text{ mol}^{-1}$ and $A=5.3(6)\times 10^{-5}\text{ emu mol}^{-1}$. The value of C is about one fifth of the value found for NaTiO_2 , which indicates that here the susceptibility is *very* much lower than expected for a magnetic insulator. A , the temperature independent term is much smaller than in NaTiO_2 . The values of the constants A

Sample	$10^5 \times A/\text{emu mol}^{-1}$	$10^3 \times C/\text{emuK}^{-1}\text{mol}^{-1}$
LiTiO ₂ (1000)A	5.35(6)	2.30(3)
LiTiO ₂ (1000)B	5.13(4)	1.98(1)
LiTiO ₂ (BuLi)	4.90(6)	2.33(1)

Table 4.11: The sample dependence of the parameters used to fit the susceptibility of LiTiO₂. LiTiO₂(1000)B contained some ferromagnetic impurity, while LiTiO₂(1000)A did not.

and C for the different LiTiO₂ samples are tabulated in Table 4.11.

The magnetisation of LiTiO₂(BuLi) does not display the transition at 12 K when measured in a field of 0.05 T indicating that the lithiation of LiTi₂O₄ during the synthesis was complete. χ_{mol} was obtained from the difference in magnetic moments measured in the linear region of the M vs H graph at 0.5 T and 1.5 T. This was also fitted well by Equation 4.29 with similar values of C and A . χ_{mol} and its inverse are also plotted in Figure 4.34.

Possibility of spin-glass like behaviour

One would expect that if LiTiO₂ was an insulating magnet, that it would show some characteristics of a spin-glass, because there is disorder between the two metal ion sites and the FCC lattice has frustration which is not relieved by the disorder present in LiTiO₂. Measurements of the uncontaminated sample of LiTiO₂(1000) were carried out in which the sample was cooled in zero field and the susceptibility was measured in a field of 0.1 T during heating. Then the sample was cooled in this field and measured again on warming in the same field. Finally the sample was cooled in 3.0 T field, and the 0.1 T field was then applied and a third measurement was made on warming. There was no measurable difference between the three susceptibility curves which indicates that LiTiO₂ does not show spin-glass like behaviour, and is not a localised electron system. This should be compared with LiNiO₂ [125], a localised electron system with a small amount of disorder which, when coupled with the frustration inherent to the triangular lattice, produces spin glass behaviour.

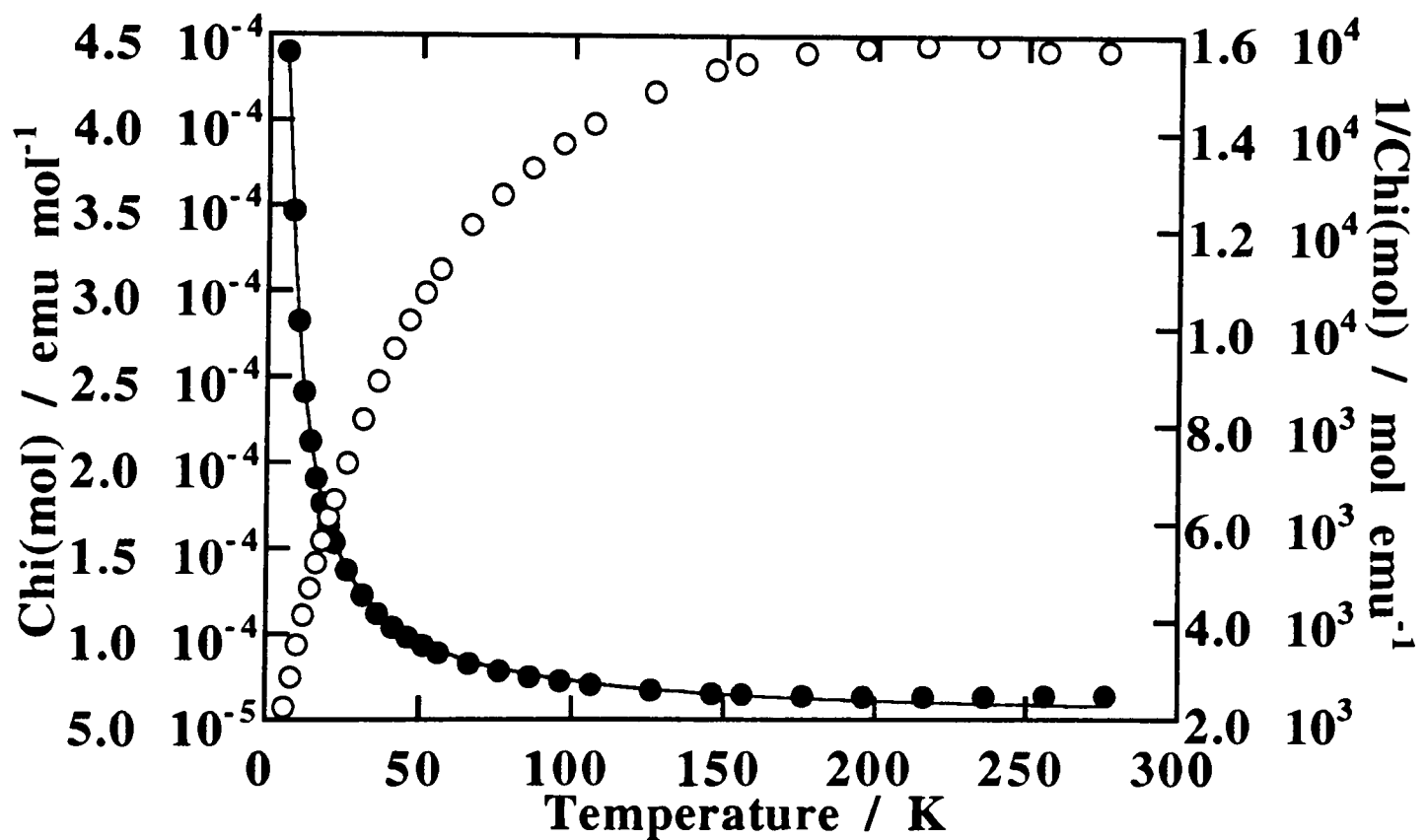
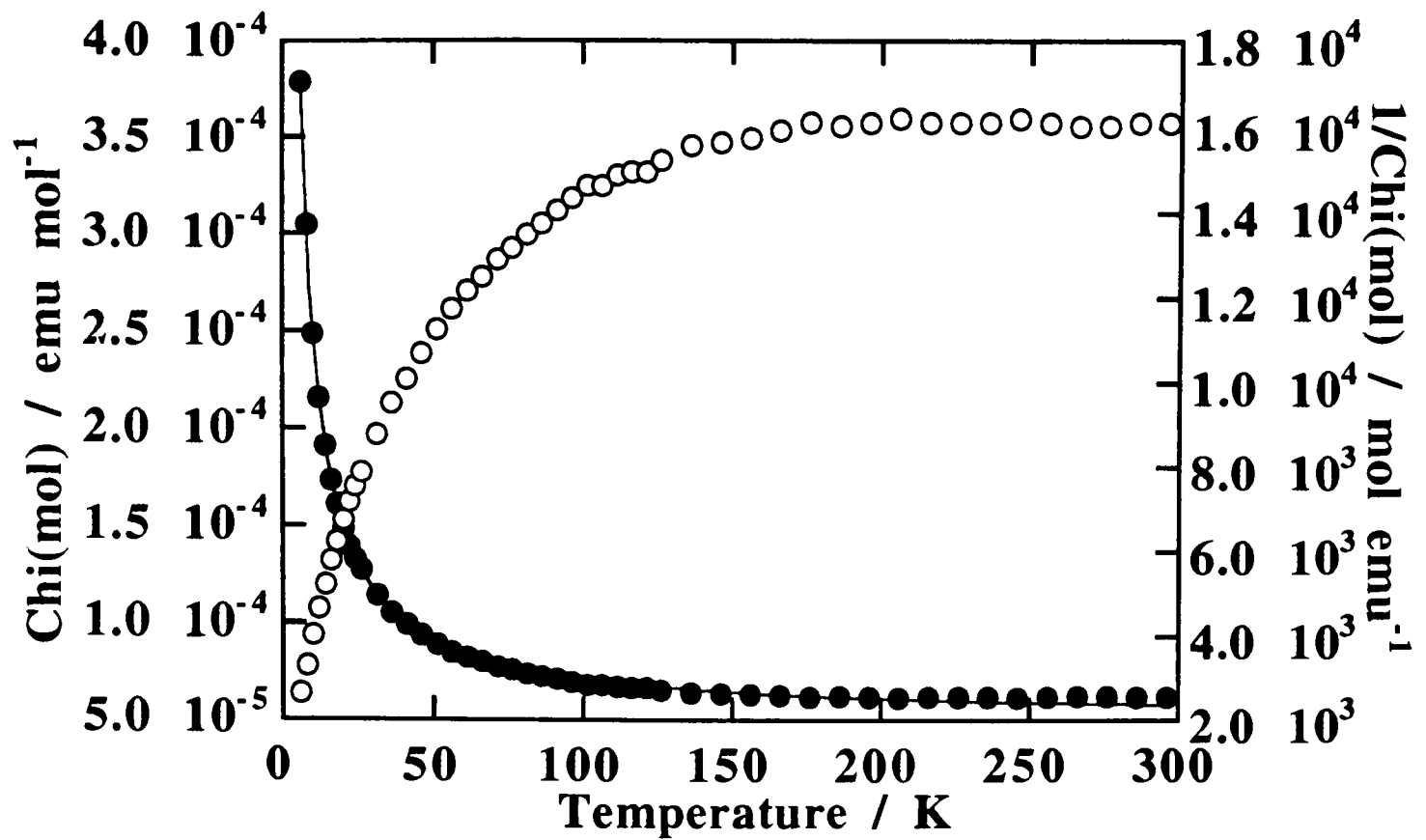


Figure 4.34: The magnetic susceptibility (filled circles) and its inverse (open circles) as a function of temperature for $\text{LiTiO}_2(1000)\text{B}$ (upper) and $\text{LiTiO}_2(\text{BuLi})$ (lower). The susceptibility has been corrected for core diamagnetism [141]. The solid lines are fits to $\chi_{\text{mol}} = A + C/T$ using the values in Table 4.11.

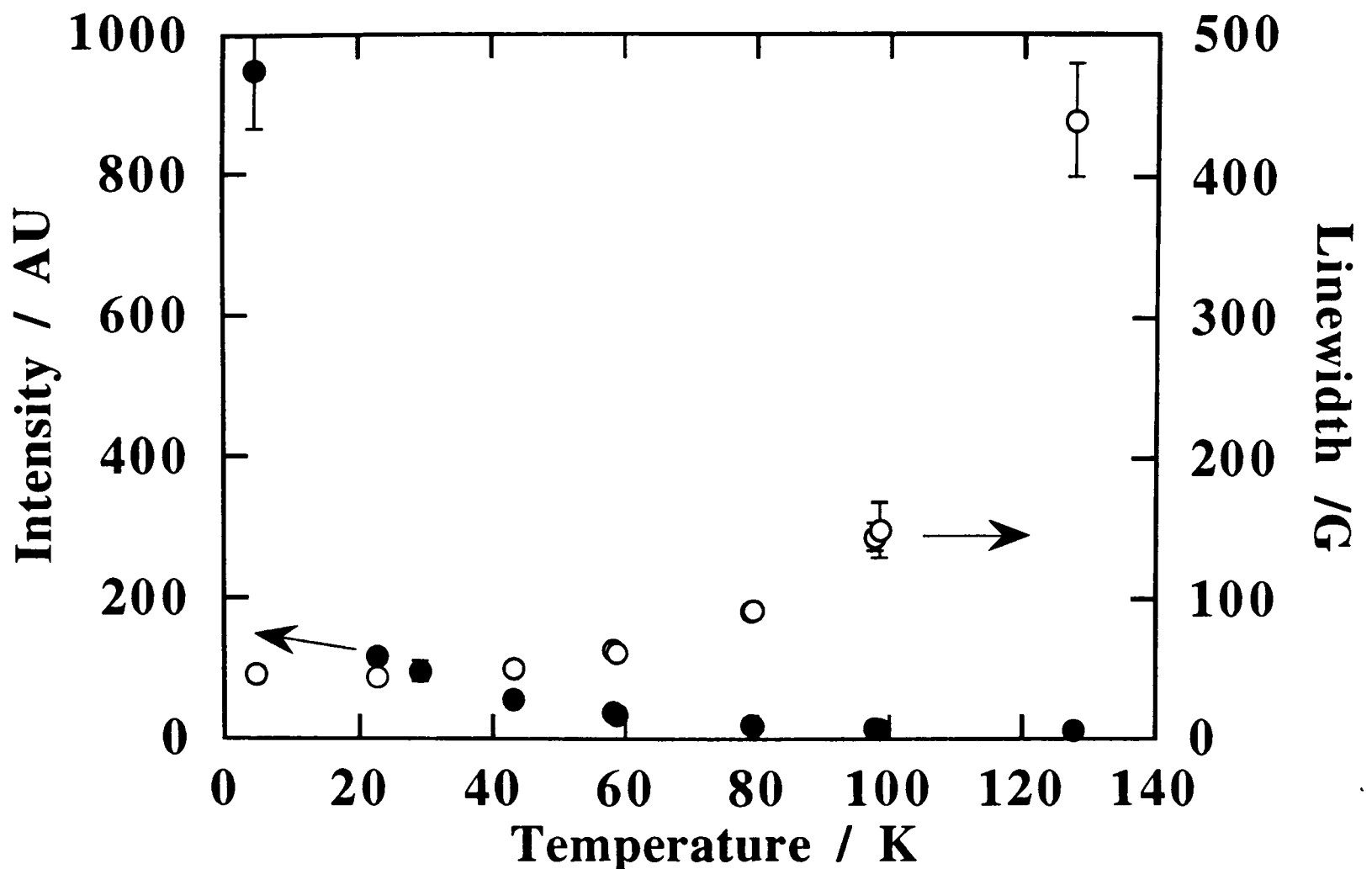


Figure 4.35: The variation of the ESR signal intensity (filled circles) and the measured linewidth (open circles) of $\text{LiTiO}_2(\text{BuLi})$.

ESR measurements

The procedure used for measuring the ESR signal of NaTiO_2 was followed. The sample $\text{LiTiO}_2(\text{BuLi})$ was used since the samples of $\text{LiTiO}_2(1000)$ all contained a small amount of LiTi_2O_4 which becomes superconducting below 12 K and prevents tuning of the spectrometer. As in NaTiO_2 , there is no observable resonance at room temperature, but just below 150 K, a broad resonance is visible which becomes narrow at low temperatures and has a width of about 40 G at 5 K. The linewidth and the intensity of the resonance are shown as a function of temperature in Figure 4.35. The behaviour of both quantities is very similar to the behaviour on NaTiO_2 . The intensities of the LiTiO_2 and NaTiO_2 resonances scale according to the size of the susceptibilities of the two compounds measured using a SQUID magnetometer.

4.8.3 Discussion

There are a number of factors which lead one to conclude that LiTiO_2 , although different in structure, has some of the delocalised electron properties shown by NaTiO_2 and other early transition metal oxides.

- The magnetic susceptibility measured by both DC magnetometry and ESR spectroscopy is small and corresponds to only about 1% of the $S=\frac{1}{2}$ Ti^{3+} moments which would be present in a magnetic insulator.
- There is no difference between zero-field cooled, field cooled and high-field cooled susceptibilities. If the material were insulating, one might expect some difference due to the frustrated and disordered nature of the Ti^{3+} sublattice c.f. LiNiO_2 [125].
- The separation between nearest-neighbour Ti^{3+} ions which are at the centres of edge-sharing octahedra is $2.93 \text{ \AA}$ which is less than the separation between similar units in NaTiO_2 . This suggests that there may be metallic bonding. Although Ti^{3+} only occupies half of the metal ions sites, the connectivity of the lattice is so high, that the network is well above the percolation threshold of about 0.2 (Section 3.1), and so metallic conductivity is possible in principle.

$n(E_F)$ for LiTiO_2 is 0.62 orbital states eV^{-1} per Ti at room temperature. This is almost an order of magnitude less than in NaTiO_2 and three orders of magnitude less than the value in LaTiO_3 . The values of $n(E_F)$ either above a transition or at room temperature for a number of A-Ti-O phases which are thought to be metallic are tabulated in Table 4.12 along with the Ti-Ti distances in each case. The information is presented graphically in Figure 4.36. There is an almost linear dependence of $n(E_F)$ on $r(\text{Ti-Ti})$. Thus a description of all the Ti^{3+} -containing oxides as metallic leads to a sensible correlation between $n(E_F)$ and $r(\text{Ti-Ti})$. As overlap increases, so does the bandwidth, causing the density of states to decrease.

Material	Ti oxidation	$r(\text{Ti-Ti})/\text{\AA}$	$n(E_F)/\text{eV}^{-1}$ per Ti
$\text{Li}_{0.5}\text{TiO}_2$	+3.5	2.88	0.34
LiTiO_2	+3	2.93	0.6
$\text{Li}_2\text{Ti}_2\text{O}_4$	+3	2.96	1.2
LiTi_2O_4	+3.5	2.97	1.6
Ti_2O_3	+3	2.99	1.5
NaTiO_2	+3	3.04	4.6
TiOCl	+3	3.10	7.5
LaTiO_3	+3	3.95	12.4

Table 4.12: A table showing the density of states at the Fermi energy against separation of Ti ions in the centres of edge sharing octahedra for a number of Ti^{3+} containing oxides. The density of states is the number of orbital states per eV^{-1} per Ti. Note that LaTiO_3 is not edge-sharing.

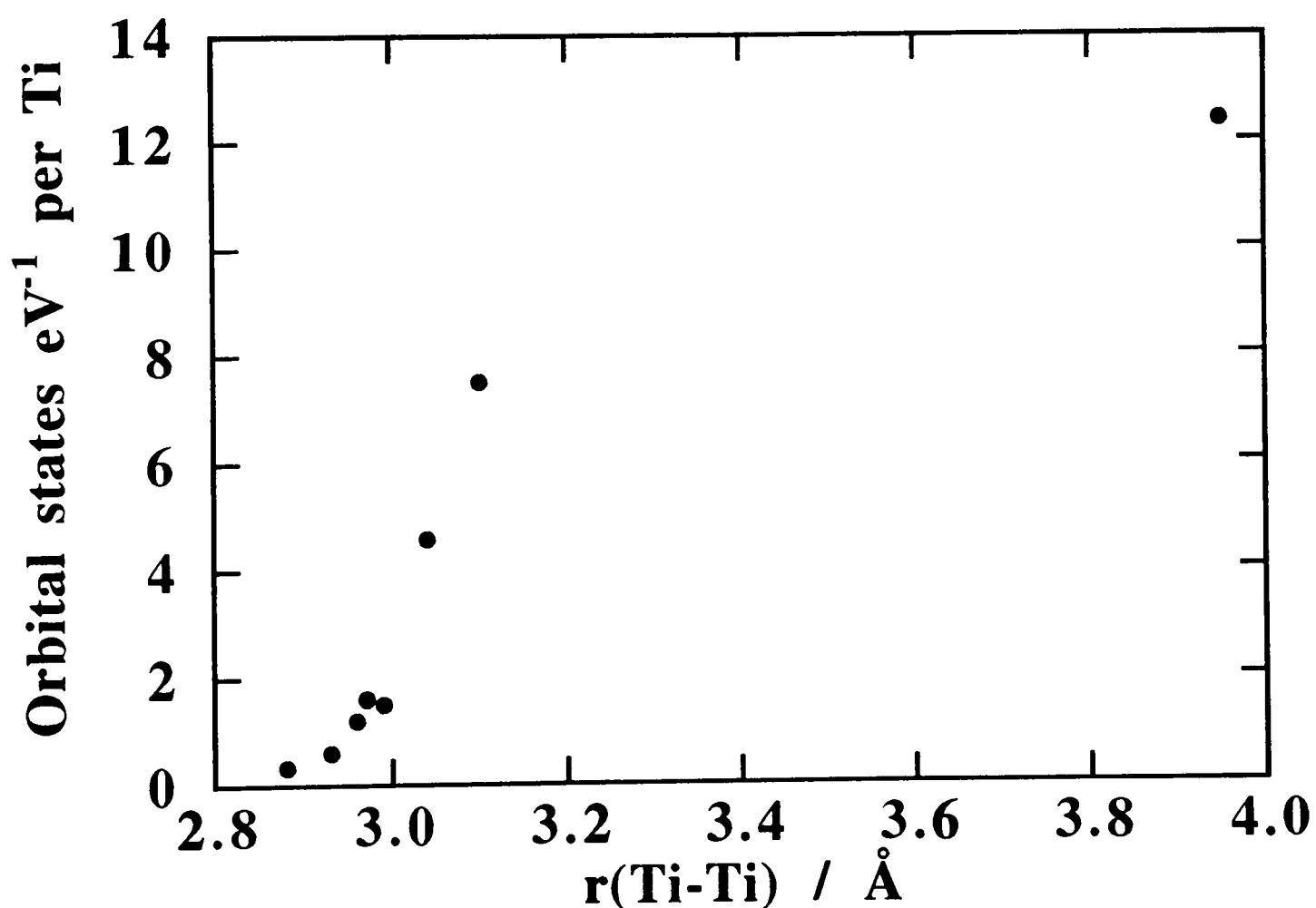


Figure 4.36: A graph showing the variation of the density of states at the Fermi energy $n(E_F)$ against Ti-Ti separation for a number of Ti^{3+} containing oxides.

4.8.4 Summary

The magnetic susceptibility of LiTiO_2 is very small, being one order of magnitude less than that of NaTiO_2 . When a sample which was free of Fe or Ni impurities was prepared — as demonstrated by the linear dependence of the magnetic moment on the applied field — there was found to be no difference in the zero-field cooled, field cooled or high-field cooled behaviour. By analogy with NaTiO_2 and the other titanium and vanadium oxides, it seems likely that LiTiO_2 shows similar metallic behaviour which would account for the low value of the susceptibility and the fact that the Curie-Weiss law is not obeyed. Because of the regular nature of the octahedral coordination in this material, and because the Ti-Ti distance is shorter than in most of the other compounds, it seems less likely that there will be a phase transition of the type observed in the layered materials. No transition is observed in the susceptibility at temperatures up to 350 K, but measurements should be carried out to higher temperatures to confirm this view.

Conductivity measurements would confirm whether the conductivity of the Li_xTiO_2 phases is metallic. In the case of LiTiO_2 , it is possible that, although the Ti sublattice percolates that there may be sufficient disorder to localise the electrons in the manner proposed by Anderson [179], and inhibit the transport, and hence the conductivity.

4.9 Conclusions

Our work on NaTiO_2 has cast doubt on the popular notion [119, 120, 142] that NaTiO_2 is a triangular lattice antiferromagnet and a candidate for having an RVB ground state. We propose that the magnetic behaviour in NaTiO_2 is consistent with a metal to metal transition involving a change of the details of the band structure arising from a change in the TiO_6 geometry. The driving force for the transition is probably increased in-plane Ti-Ti bonding at low temperatures.

Comparison of NaTiO_2 with other materials containing Ti^{3+} , particularly those also containing Li^+ , has allowed us to show that the magnetic susceptibility decreases as the separation of the Ti^{3+} ions in the centres of edge-sharing octahedra decreases.

This suggests that all these materials may be metallic. Metallic behaviour has been confirmed for Ti_2O_3 , LiTi_2O_4 and LaTiO_3 , and on the assumption that all the others are too, one can convert the magnetic susceptibility into the density of states at the Fermi energy and produce a roughly linear correlation with Ti–Ti separation. The correlation is consistent with the view that decreasing the separation affords greater orbital overlap and broadens the bands resulting in a lowering of the density of states at the Fermi energy.

It is necessary to perform further experiments on NaTiO_2 to confirm that it is a metal and to confirm whether the transition is between two metallic states.

Appendix A

Additional experiments performed on NaTiO_2

A.1 Muon spin relaxation measurements

A.1.1 Introduction

Muon spin relaxation, μSR , is a valuable technique for determining magnetic properties. The review by Cox [180] is a summary of the current muon techniques. The abbreviation μSR is also applied to muon spin rotation and muon spin resonance. In this section, it will be used exclusively to refer to muon spin relaxation.

The muon (μ^+) is a heavy relation of the positron, but in these experiments carried out at low energies, it is more instructive to think of it as a light version of the proton ($m_\mu=0.11m_p$). Muons are produced when high energy protons strike a target to produce pions. These decay with a half life of 26 ns producing a muon and a muon neutrino. The muons are all polarised in the same sense following this decay. They then decay with a half life of $2.2\mu\text{s}$ producing a positron which travels preferentially in the direction in which the muon was polarised when it decayed (this is especially true of the highest energy positrons).

In the experiment considered below, all the muons have a polarisation opposed to the beam direction, ie. *full* asymmetry. They implant in electronegative sites within the sample in the same way that a proton would. In NaTiO_2 , the most likely implantation site is a tetrahedral interstitial surrounded by four O^{2-} ions since all the octahedral interstices are filled. When implanted in the sample, fluctuations in

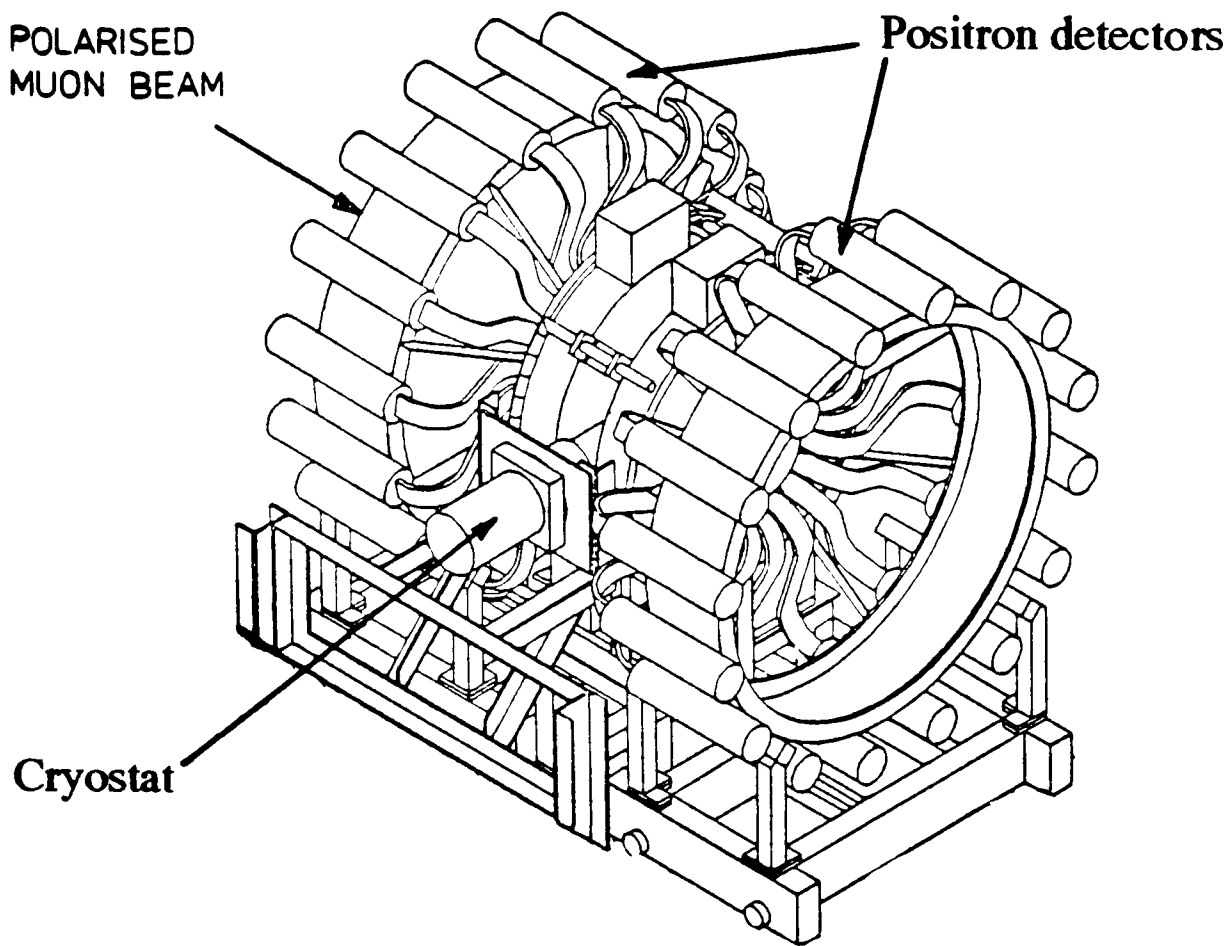


Figure A.1: The μ SR spectrometer MuSR at ISIS.

the internal magnetic fields cause a precession of a muon during its short lifetime, and the asymmetry in the polarisation decays with time.

In the decay process, the positron is emitted in the direction of the muon polarisation, and the time dependence of the detected positrons around the sample gives information on the magnetic fluctuations in the material. Note that the positrons gain sufficient kinetic energy from the decay process (Equation A.1) that they leave the sample before being affected by the magnetic fluctuations.

$$\mu^+ \rightarrow e^+ + \bar{\nu}_e + \nu_\mu \quad (\tau_{\frac{1}{2}} = 2.2 \mu s) \quad (\text{A.1})$$

A.1.2 Experimental

μ SR measurements were carried out using the muon spectrometer MuSR at the Rutherford Appleton Laboratory (RAL). The instrument was employed in longitudinal mode with positron detectors behind the sample and in front of the sample, these directions being defined by the direction of the incident beam. The spectrometer is shown in Figure A.1.

These experiments were carried out at a stage in the research when relatively

little had been done to assess the effect of sample preparation on the magnetic properties. Unfortunately, the samples used in these experiments did not have pronounced magnetic anomalies at 250 K.

Approximately 2 g of sample was packed into a circular depression 30 mm in diameter and 2 mm deep in a silver sample holder. The sample was covered with a piece of 12 μm thick Ag foil which was fairly air-tight and would allow muons to pass through.

The positrons produced by the decay of the depolarised muons were counted using an array of 8 pairs of detectors behind the sample and a further 8 pairs in front. The detected positron produces a photon which travels along a perspex guide and into a photomultiplier. The ratio of the number of positrons detected as a function of time at the forward detector to that detected at the back detector is related to the rate of depolarisation of the muons which depends on the frequency of magnetic fluctuations in the material. A μSR experiment is able to detect much slower fluctuations than would give rise to motional narrowing in an NMR experiment. If the experiment is carried out as a function of temperature, one may identify critical phenomena. If carried out as a function of applied longitudinal field, the frequency spectrum of the fluctuations can be established.

The first experiment was carried out in zero longitudinal field at a series of temperatures between 10 and 270 K and is reported in reference [72]. For a dense spin system, the asymmetry between the forward and back detectors $G_z(t)$ should show a recovery at long times to one third of its initial value as shown in Figure A.2. If the fluctuations are fast, the recovery is suppressed and $G_z(t)$ decays exponentially with time. We fitted $G_z(t)$ to a one-component exponential form,

$$G_z(t) = a_0 \exp(-\lambda t) \quad (\text{A.2})$$

This will also be characteristic of rapidly hopping muons in a metal. A plot of the muon depolarisation parameter, λ , against temperature is shown in Figure A.3. This plot shows no discontinuity at 250 K which either indicates that the muon is an insensitive probe of the changes taking place at the transition, or that the size of the

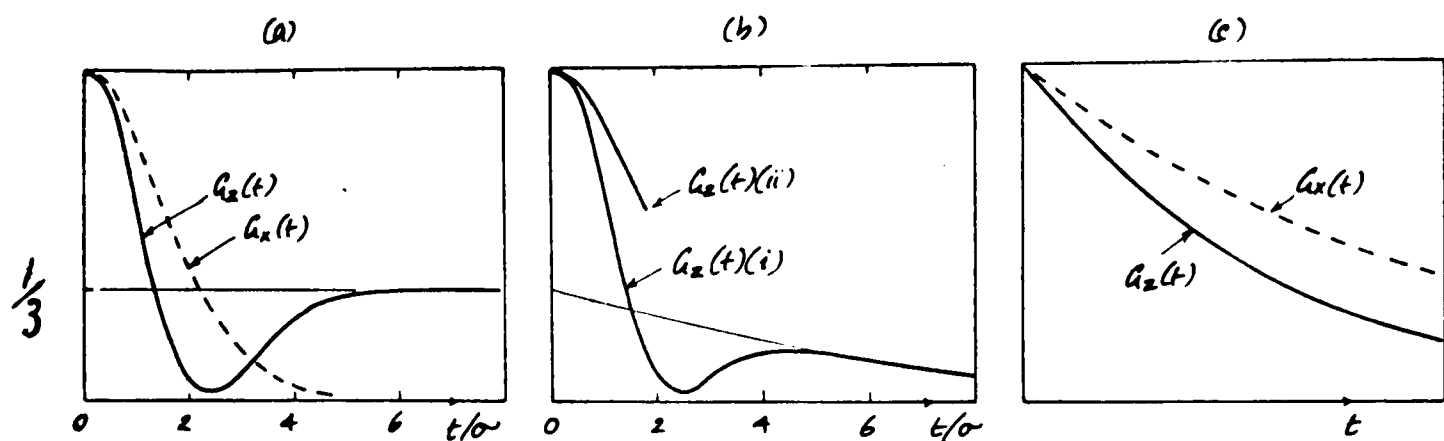


Figure A.2: The expected temporal behaviour of a dense spin system. (a.) Static case with recovery to one-third of the initial value. (b.) Slow fluctuations inhibit the recovery. (c.) Fast fluctuations.

transition was too small to be observed outside the error bars of the experiment.

SQUID magnetometry was not carried out at temperatures below 1.7 K. A second μ SR experiment similar to the one above was carried out at temperatures as low as 0.05 K with the aid of a $^4\text{He}/^3\text{He}$ dilution fridge placed in a ^4He bath cryostat. The depolarisation was measured at temperatures of between 0.05 and 4.0 K in zero applied field, and at 0.05 K and 4.4 K at a series of longitudinal fields of between 5 and 2000 G.

$G_z(t)$ was fitted reasonably well by Equation A.2, but the variation of λ with temperature was not indicative of any magnetic transition below 2 K.

A.2 Nuclear magnetic resonance measurements

The ^{23}Na NMR spectrum of NaTiO_2 was measured with the aim of seeing whether this technique could give any further information on the magnetic phase transition observed at about 250 K in the magnetometry measurements. The spectrum was recorded using a Bruker Spectrospin Ltd MSL 200 spectrometer and an Oxford Instruments 4.7 T cryomagnet. The spectrometer was calibrated using 1.0 M NaCl solution as the standard. The lengths of the 90° and 180° pulses were determined

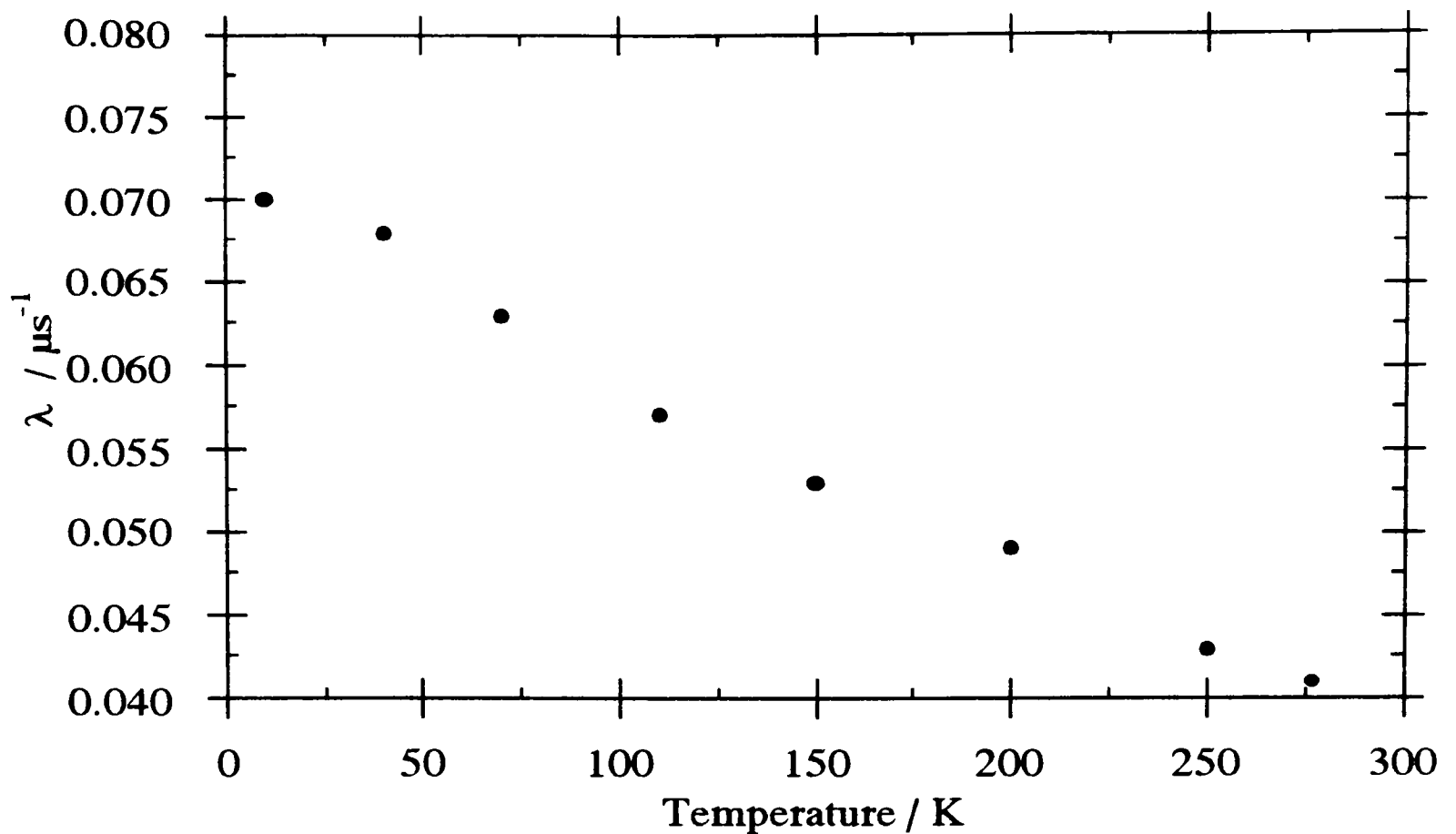


Figure A.3: The variation of muon depolarisation rate as a function of temperature for NaTiO_2 . The magnetic anomaly is not visible, but was small in this sample.

using the NaCl standard.

1 g of NaTiO_{2-2} was loaded into a cylindrical PTFE sample holder in a He-filled dry box and glued shut immediately after removal from the box using Bostik super-glue.

Measurements indicated one resonance with a chemical shift of -18 ppm relative to the NaCl standard. The spectrum, shown in Figure A.4, is broad and asymmetric due to the quadrupolar nature of the ^{23}Na nucleus. Measurements of the static signal at temperatures between 160 K and 300 K failed to reveal the presence of the magnetic transition, even though this is quite pronounced in NaTiO_{2-2} .

Magic angle spinning measurements on NaTiO_{2-1} narrowed the resonance, but were unable to give any further information at this frequency. A higher frequency spectrometer was not available.

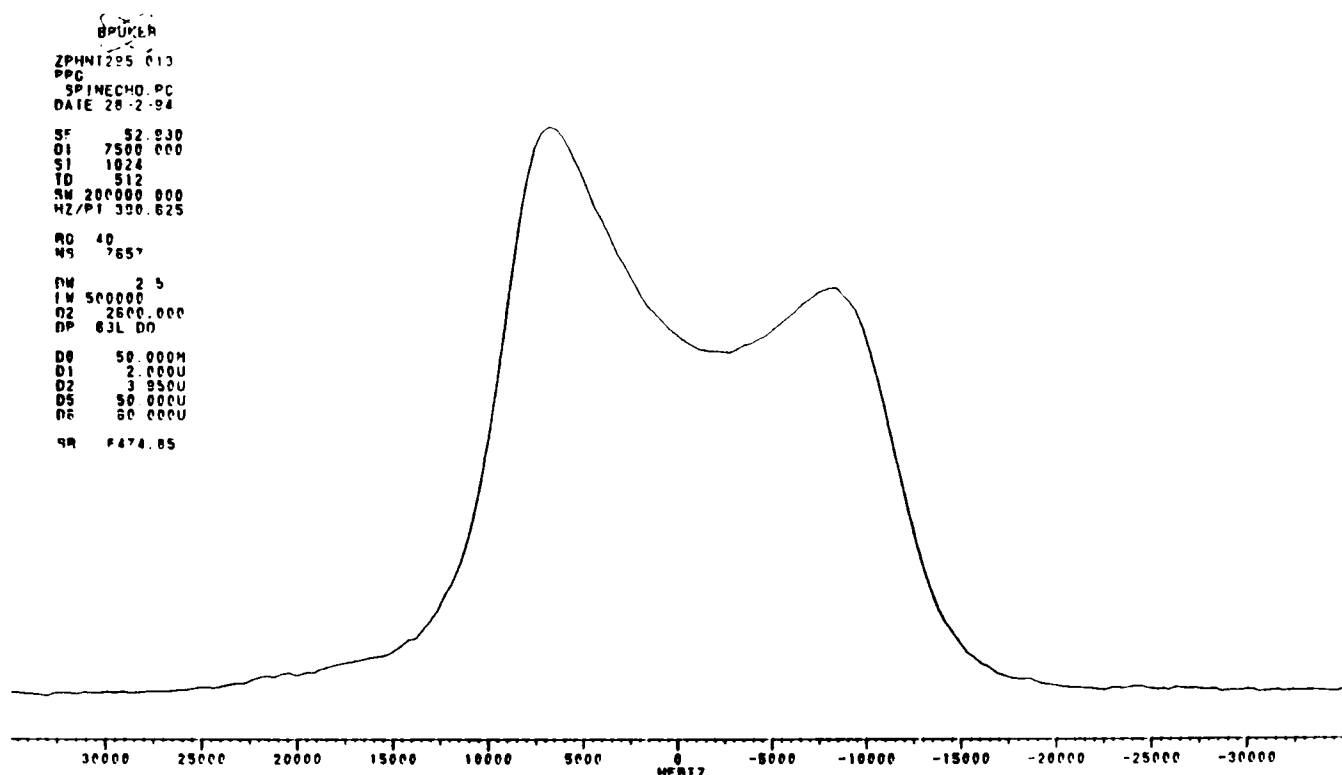


Figure A.4: The static NMR spectrum of $\text{NaTiO}_2\text{-2}$ at room temperature consists of one resonance. This is demonstrated using a spin-echo technique (b.) which detects the central portion of the peak by using the whole of the free induction decay.

A.3 Attempts at single crystal growth of NaTiO_2

A.3.1 Melting and slow cooling

A 25 mm diameter tantalum rod (99+% from Heraeus) was made into an ampoule similar in dimensions to the iron one described in Section 4.3. About 2 g of NaTiO_2 powder was loaded into the ampoule in a nitrogen dry box. Tungsten Inert Gas welding is not capable of welding Ta without oxidation, so electron-beam welding was carried out at The Welding Institute near Cambridge.

The sealed ampoule was heated in a Crystallox STF 16/50 tube furnace in a flow of argon to avoid degradation of the Ta. Previous experiments [181] indicated that a temperature in excess of 1500°C would be required to melt NaTiO_2 . When the Ta ampoule had been heated to approximately 1580°C , the weld failed and a plume of powder escaped from the container. Cooling revealed that the lid had bowed out considerably before a pinhole failure had developed in the weld, indicating a high vapour pressure inside the ampoule before failure.

The apparent difficulty in growing NaTiO_2 from the melt led us to attempt growth using more gentle methods.

A.3.2 Flux Growth

The technique of flux growth involves dissolving the target material in another material to form a melt which is either slowly cooled or from which the flux is evaporated. There are substantial parallels with growth from aqueous solution. The technique has been reviewed by Wanklyn [182]. Reduced oxides of Ti as well as rutile crystals have been grown by flux growth from sodium borate fluxes ($\text{Na}_2\text{B}_4\text{O}_7\text{--B}_2\text{O}_3$) [183, 184]. This flux was used in an attempt to grow crystals of NaTiO_2 . $\text{Na}_2\text{B}_4\text{O}_7$ and B_2O_3 were dried under vacuum and then mixed in stoichiometric proportions to make the flux. This was then ground intimately with NaTiO_2 powder and the mixture was placed in a boat made from 0.15 mm thick Mo foil and the boat was placed in a Carbolite 16/50 tube furnace with a dry Ar flow. Slow cooling and flux evaporation techniques were used. Slow cooling from 1300 to 900°C at 1.0°C min⁻¹ produced shiny black needle-like crystals typically 2×0.1×0.1 mm in size. Flux evaporation was carried out with the Mo boat inside a short mullite tube which was designed to absorb the evaporated flux and prevent damage to the main furnace tube. Growth at 1300°C for 48 hours evaporated all the flux and crystals of similar appearance and dimensions to those grown by slow cooling were obtained.

A small clean crystal was mounted in a 0.5 mm glass capillary and this was mounted on the CAD4 diffractometer in the Chemical Crystallography Laboratory. Indexing from 19 reflections indicated that the material grown was rutile TiO_2 . This indicated that the Ti^{3+} had been oxidised, probably by the flux. NaTiO_2 was found to be insoluble in a less-oxidising NaCl/NaI flux.

A.3.3 Chemical Vapour Transport

Chemical vapour transport is a versatile technique for crystal growth in which powdered material is transported along a temperature gradient using a suitable transport

agent which reacts reversibly with the material of interest. The technique is reviewed by Corbett [185] and in more detail by Schäfer [186].

A quartz tube of length 120 mm and internal diameter 7 mm containing 0.1 g NaTiO_2 and 10 mg I_2 (99.999% from Johnson Matthey) was sealed under vacuum. This was placed in a Crystalox 16/50 tube furnace with the sample at 900° and the other end at 700° ; the gradient was approximately linear. After a few hours, the NaTiO_2 had turned white and the excess I_2 had been transported to the cooler end of the tube. This indicates that I_2 is too oxidising a transport agent. Similarly HCl (99% from Aldrich) and TeCl_4 (99.995% from Aldrich), both commonly used as transport agents were found to be too oxidising.

Appendix B

Units in magnetism

Magnetic units are generally a source of confusion, and errors can be made if quantities such as the magnetic field strength (H) and the magnetic flux density (B) are confused or if the magnetisation (M) and the magnetic moment (m) are used interchangeably. This is particularly true when the SI system of units is used, and accounts for the fact that the c.g.s. system which includes the electromagnetic unit used in this thesis is often favoured.

Unfortunately, many books [144, 187] do not present the discussion of units in a helpful way, often because they pay too much attention to the origin of the magnetism and do not discuss the units of susceptibility in an accessible way. In the following discussion, the units of a quantity will be expressed in square brackets after the name of the quantity. The absence of brackets indicates a dimensionless quantity.

In the SI system, the *volume magnetic susceptibility* of a material at a particular temperature is *defined* by

$$\kappa(\text{SI}) = \frac{M[\text{Am}^{-1}]}{H[\text{Am}^{-1}]}.$$
 (B.1)

This quantity is dimensionless.

In a magnetometer, one talks of ‘applying a field’ of so many Tesla. In fact, one applies a *flux density* (B_0), and this is related to H by

$$H[\text{Am}^{-1}] = \frac{B_0[\text{T}]}{\mu_0[\text{TmA}^{-1}]}$$
 (B.2)

where μ_0 is called the *vacuum permeability* and has the value $4\pi \times 10^{-7} \text{ TmA}^{-1}$. Thus

$$\kappa(\text{SI}) = \frac{M[\text{Am}^{-1}]\mu_0[\text{TmA}^{-1}]}{B_0[\text{T}]} \quad (\text{B.3})$$

In a SQUID magnetometer, one does not measure the magnetisation, but rather the *magnetic moment*, m . The magnetisation is the magnetic dipole moment per unit volume (ie. the magnetisation is an intensive quantity, while the moment is an extensive quantity). By substituting the moment for the magnetisation in the last equation, we define a new susceptibility measured in the units of volume.

$$\chi(\text{SI})[\text{m}^3] = \frac{m[\text{Am}^2]\mu_0[\text{TmA}^{-1}]}{B_0[\text{T}]} \quad (\text{B.4})$$

This is the susceptibility of the *actual sample* placed inside the magnetometer. It is usual to convert this to a molar susceptibility which is measured in $\text{m}^3 \text{mol}^{-1}$.

$$\chi_{\text{mol}}(\text{SI})[\text{m}^3 \text{mol}^{-1}] = \frac{m[\text{Am}^2]\mu_0[\text{TmA}^{-1}]}{B_0[\text{T}]n[\text{mol}]} \quad (\text{B.5})$$

where n is the number of moles constituting the sample. One could also convert this into a susceptibility per unit mass.

It is often more convenient to work in c.g.s. units. In this case $\mu_0 = 1$ and the dimensions are such that one measures the magnetisation, the moment and the susceptibility in electromagnetic units, emu. The molar susceptibility in c.g.s. units is

$$\chi_{\text{mol}}(\text{cgs})[\text{emu mol}^{-1}] = \frac{m[\text{emu}]}{B_0[\text{G}]n[\text{mol}]} \quad (\text{B.6})$$

The units of emu mol^{-1} are equivalent to $\text{cm}^3 \text{mol}^{-1}$, so the conversion between $\chi_{\text{mol}}(\text{SI})$ and $\chi_{\text{mol}}(\text{cgs})$ is

$$\chi_{\text{mol}}(\text{SI})[\text{m}^3 \text{mol}^{-1}] = \chi_{\text{mol}}(\text{cgs})[\text{cm}^3 \text{mol}^{-1}] \times 4\pi \times 10^{-6}. \quad (\text{B.7})$$

Notice that the SI value of μ_0 has returned.

$$\chi_{\text{mol}}(\text{SI})[\text{m}^3 \text{mol}^{-1}] = 10 \times \chi_{\text{mol}}(\text{cgs})[\text{cm}^3 \text{mol}^{-1}] \times \mu_0(\text{SI}). \quad (\text{B.8})$$

The Curie constant, C , is

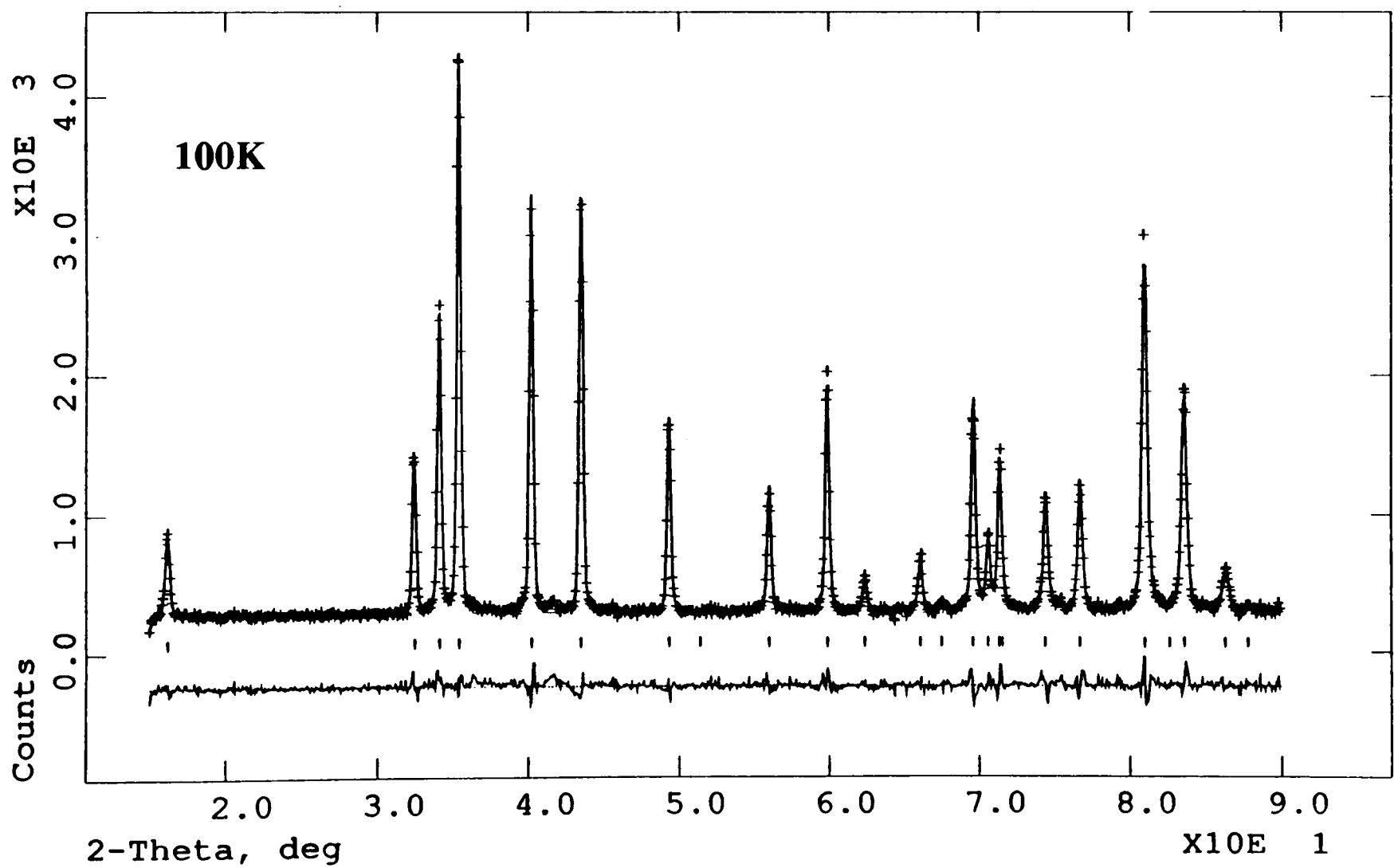
$$C = \frac{N_A \mu_0 \mu_B^2 g^2 S(S+1)}{3k_B}. \quad (\text{B.9})$$

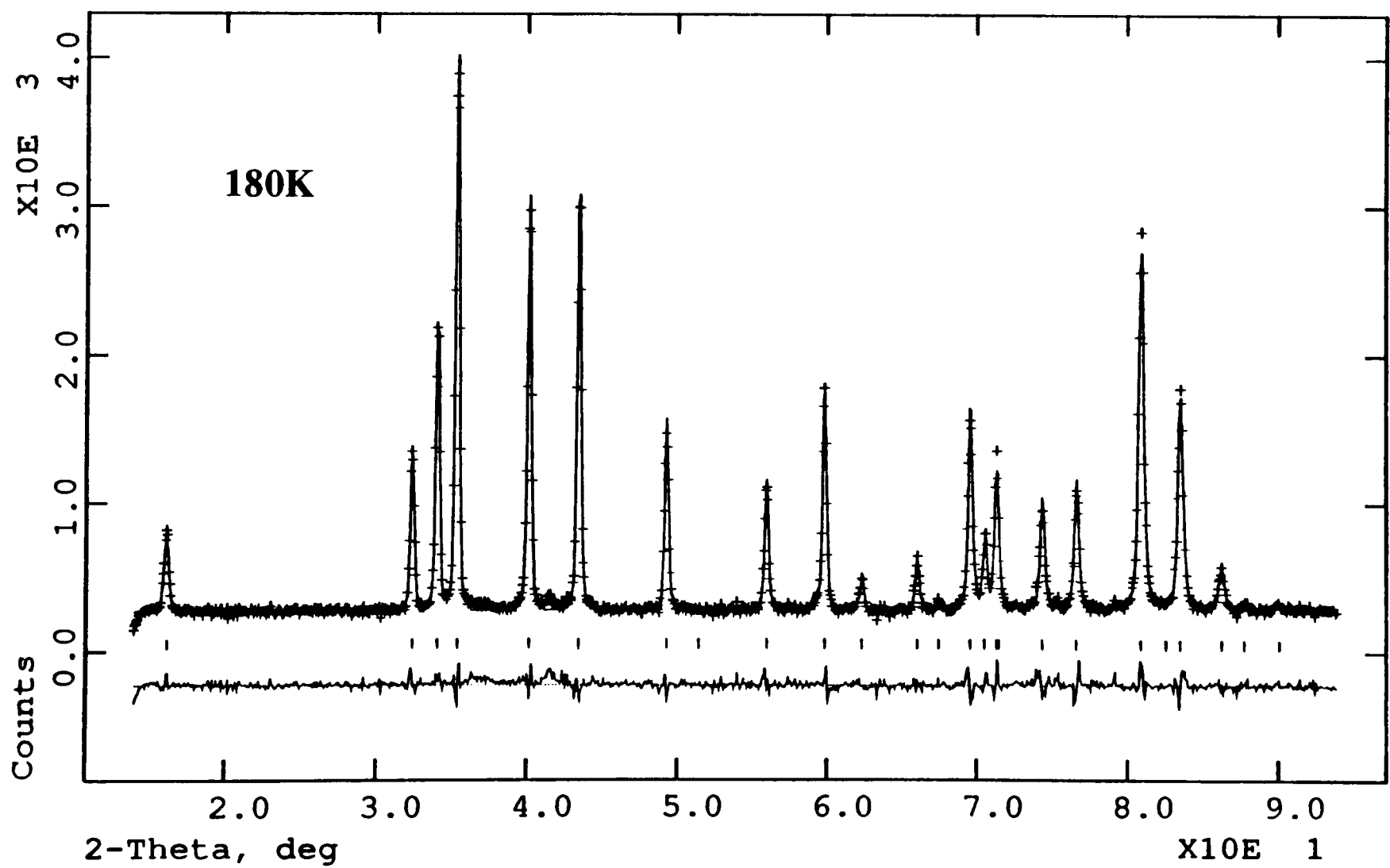
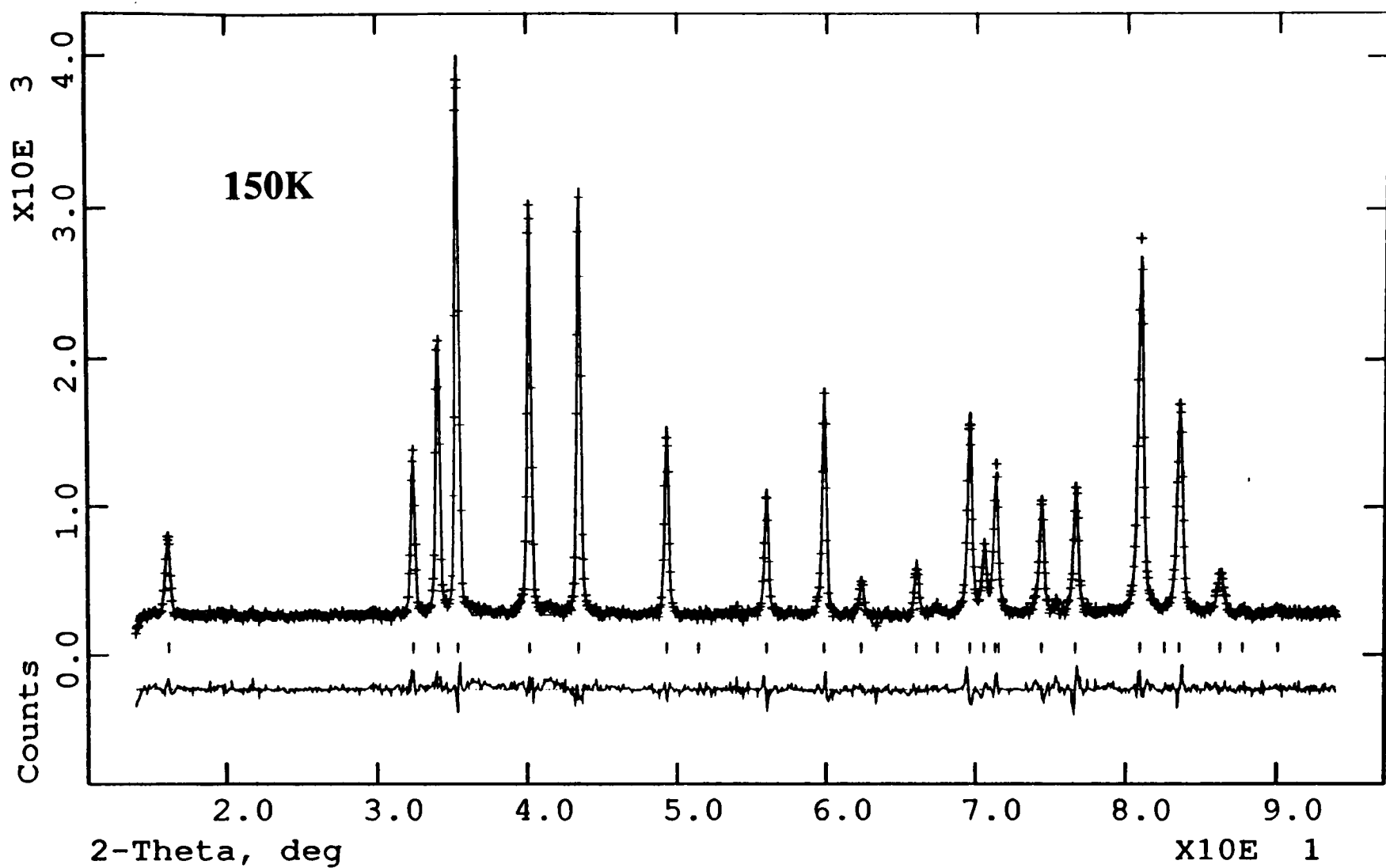
The factor of μ_0 means that $C(\text{SI}) = 10 \times C(\text{cgs})$. This factor of 10 also appears in the calculation of the density of states at the Fermi energy (Equation 4.16).

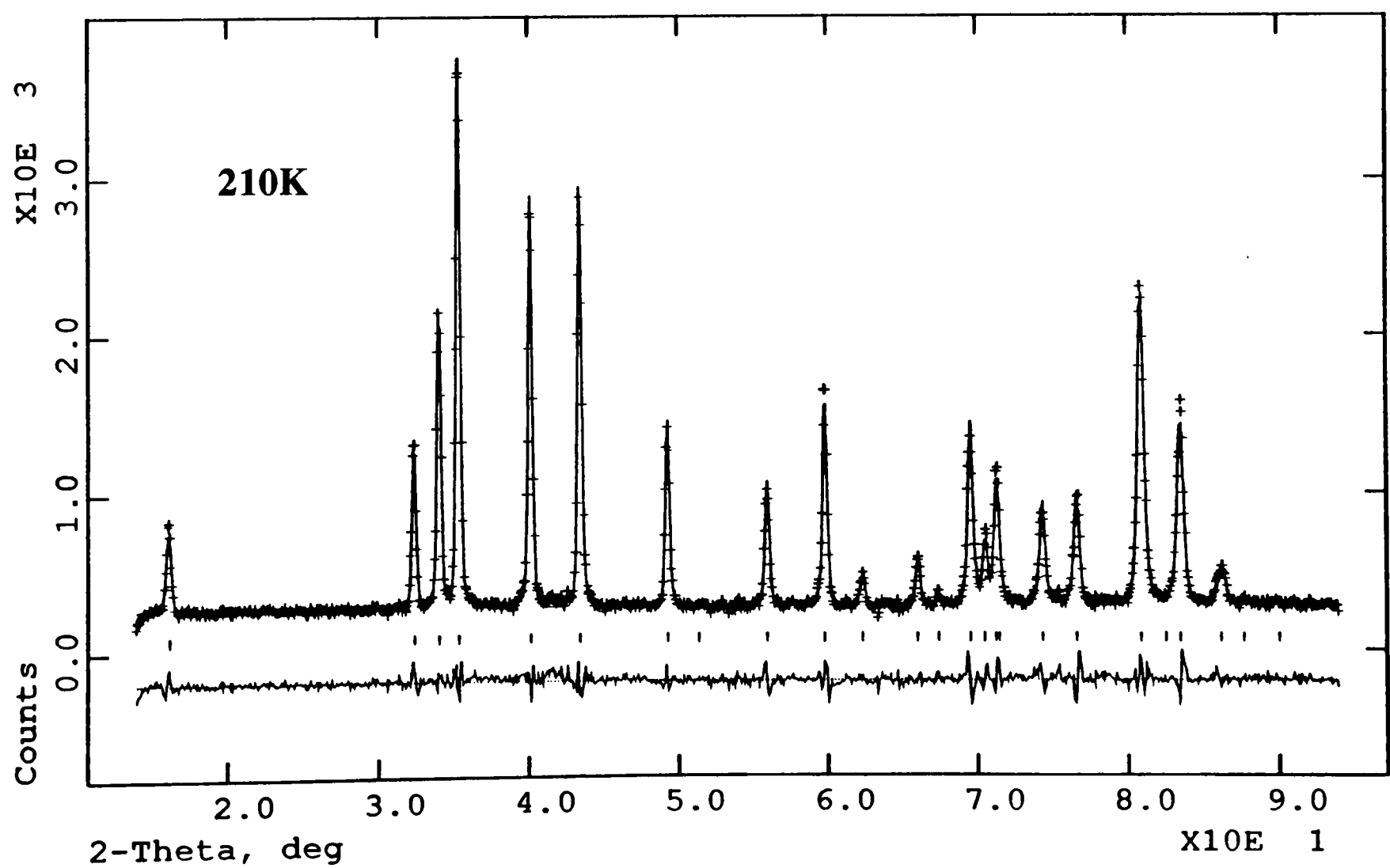
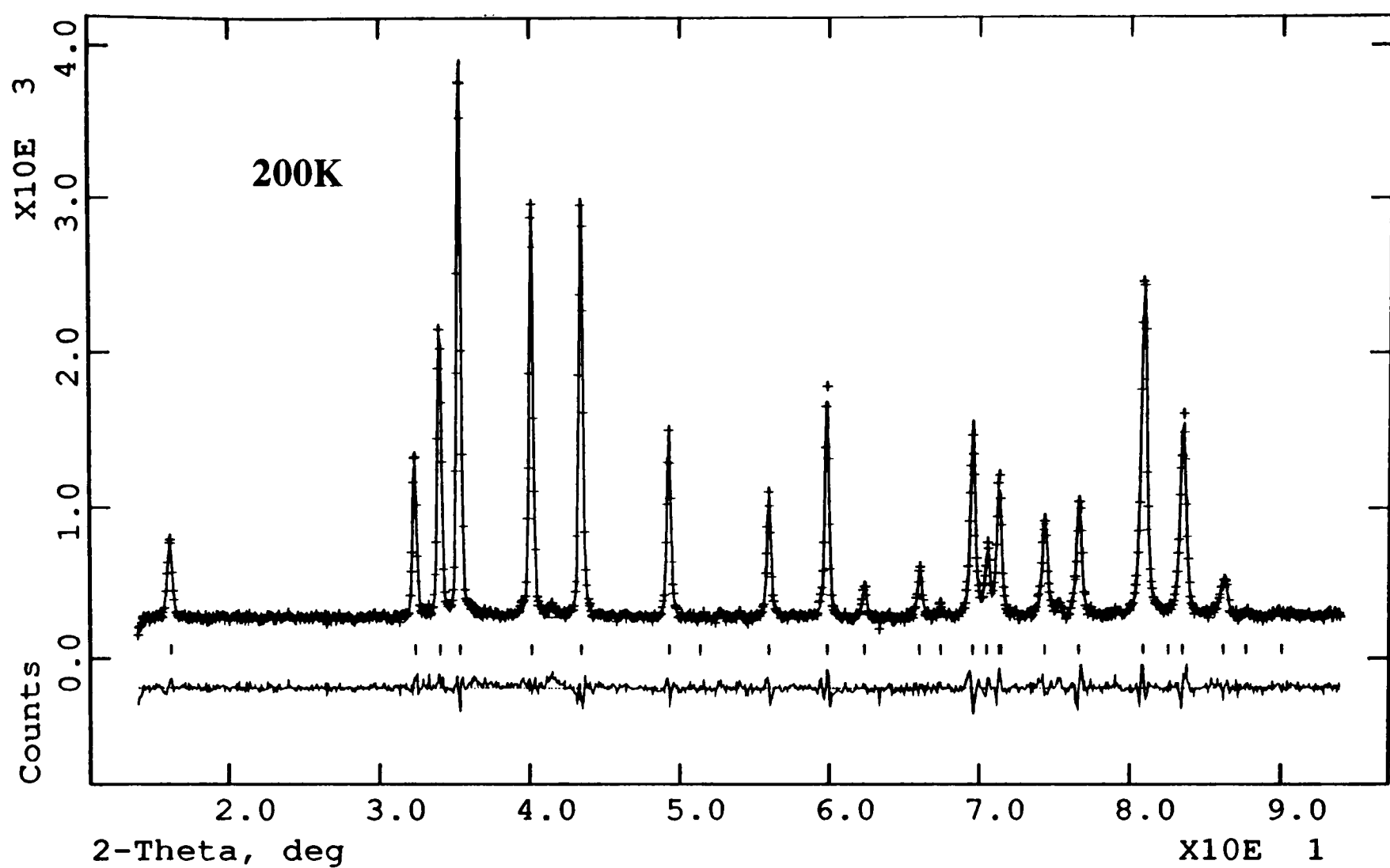
Appendix C

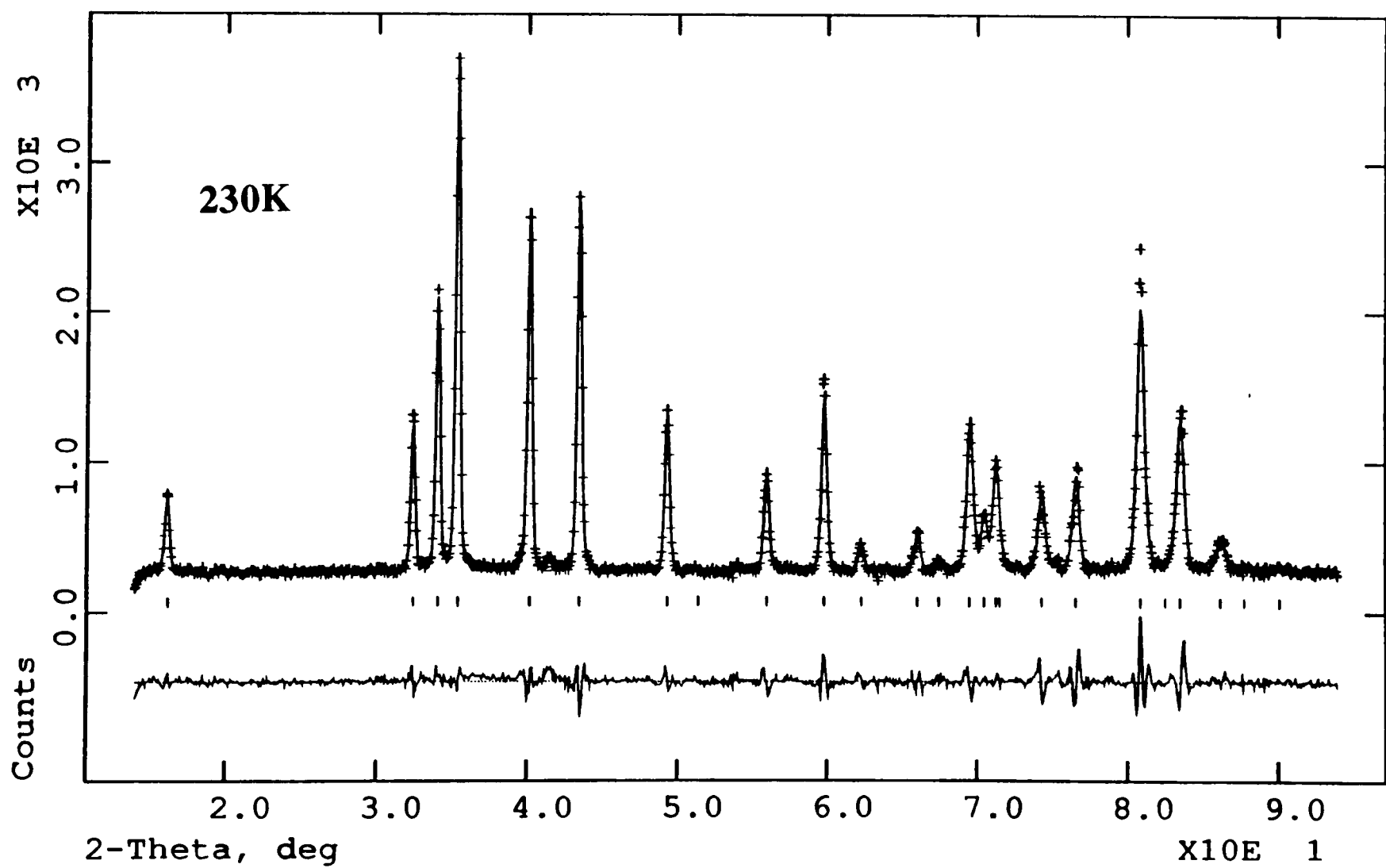
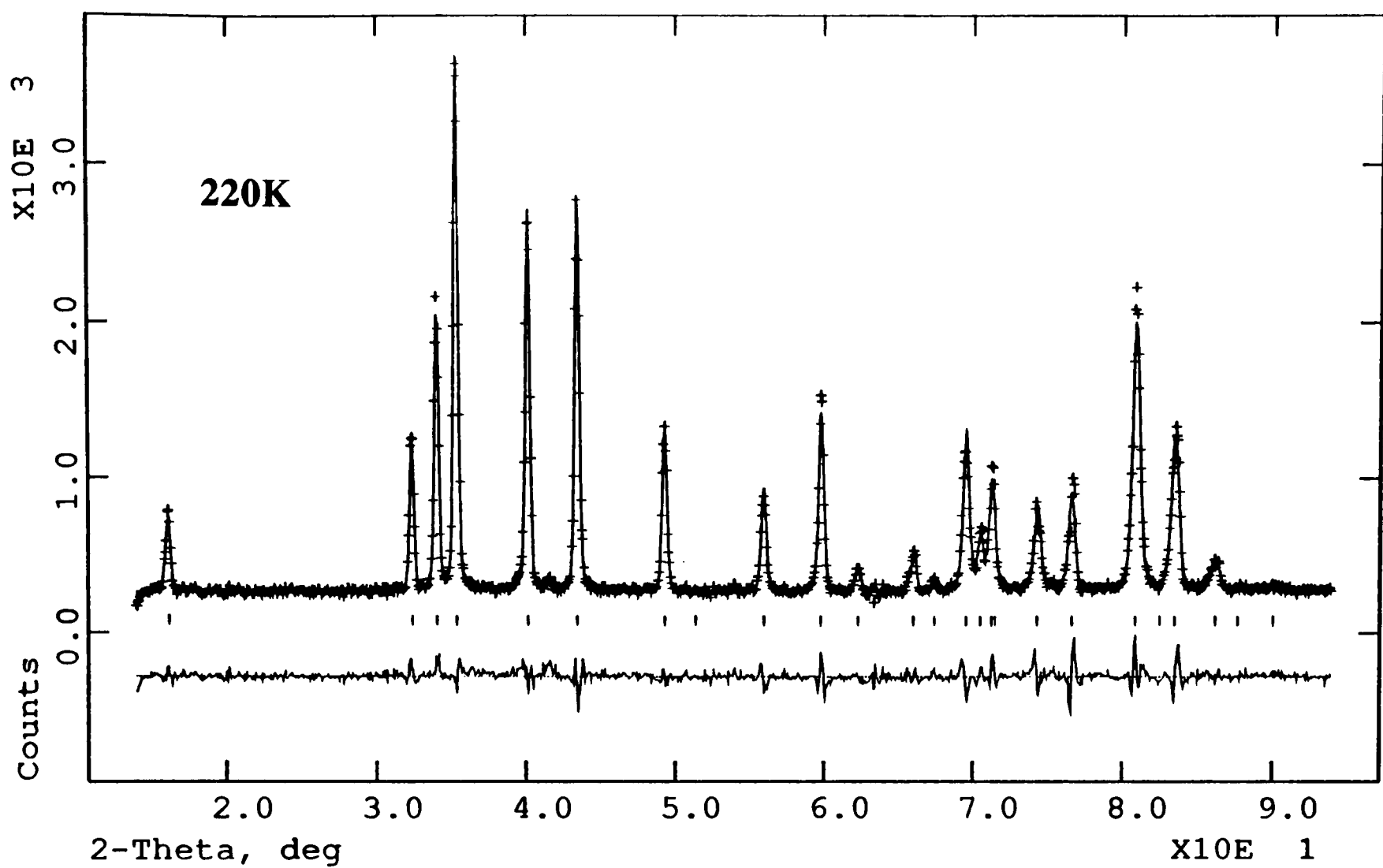
Rietveld refinement of neutron diffraction data of NaTiO₂

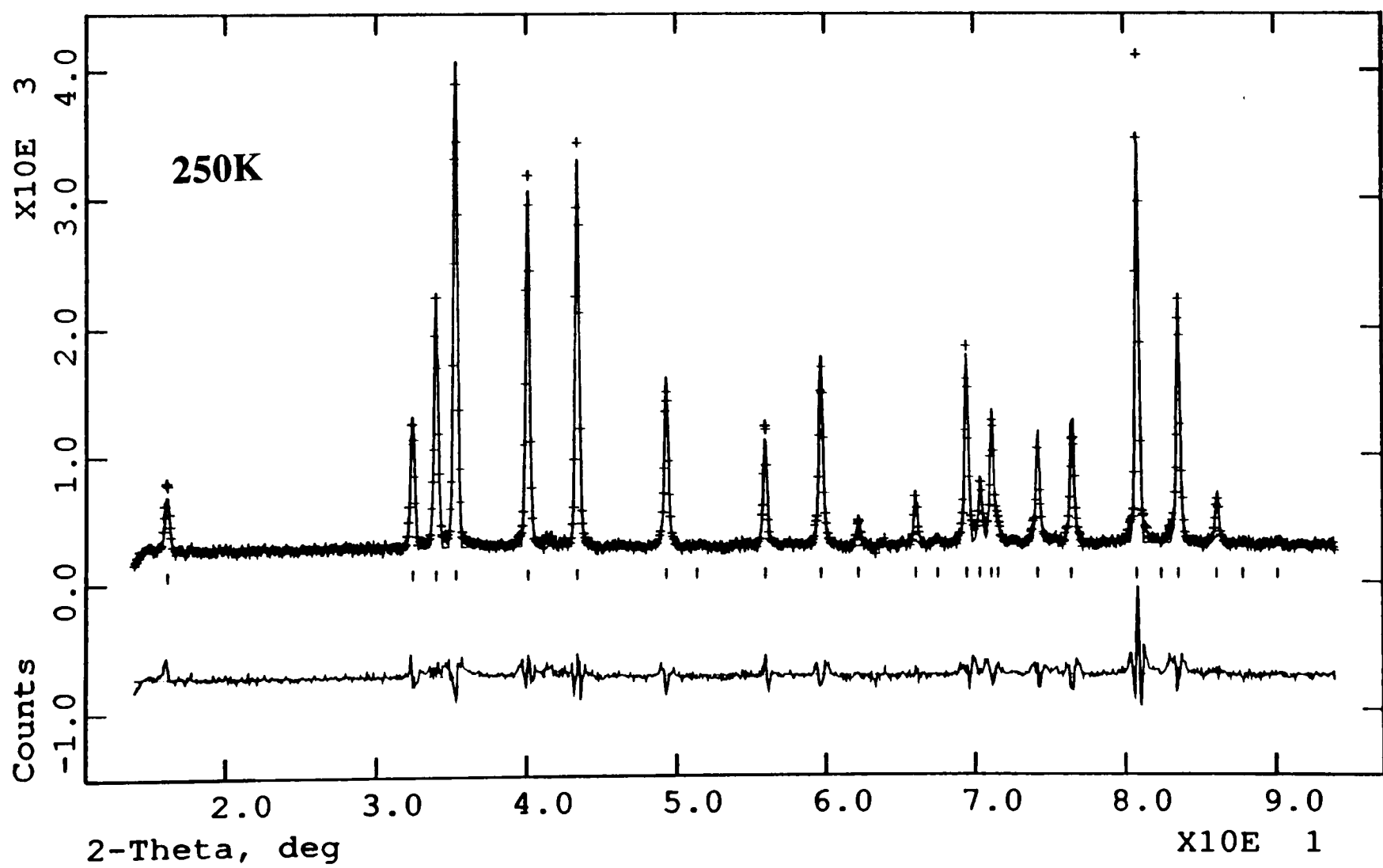
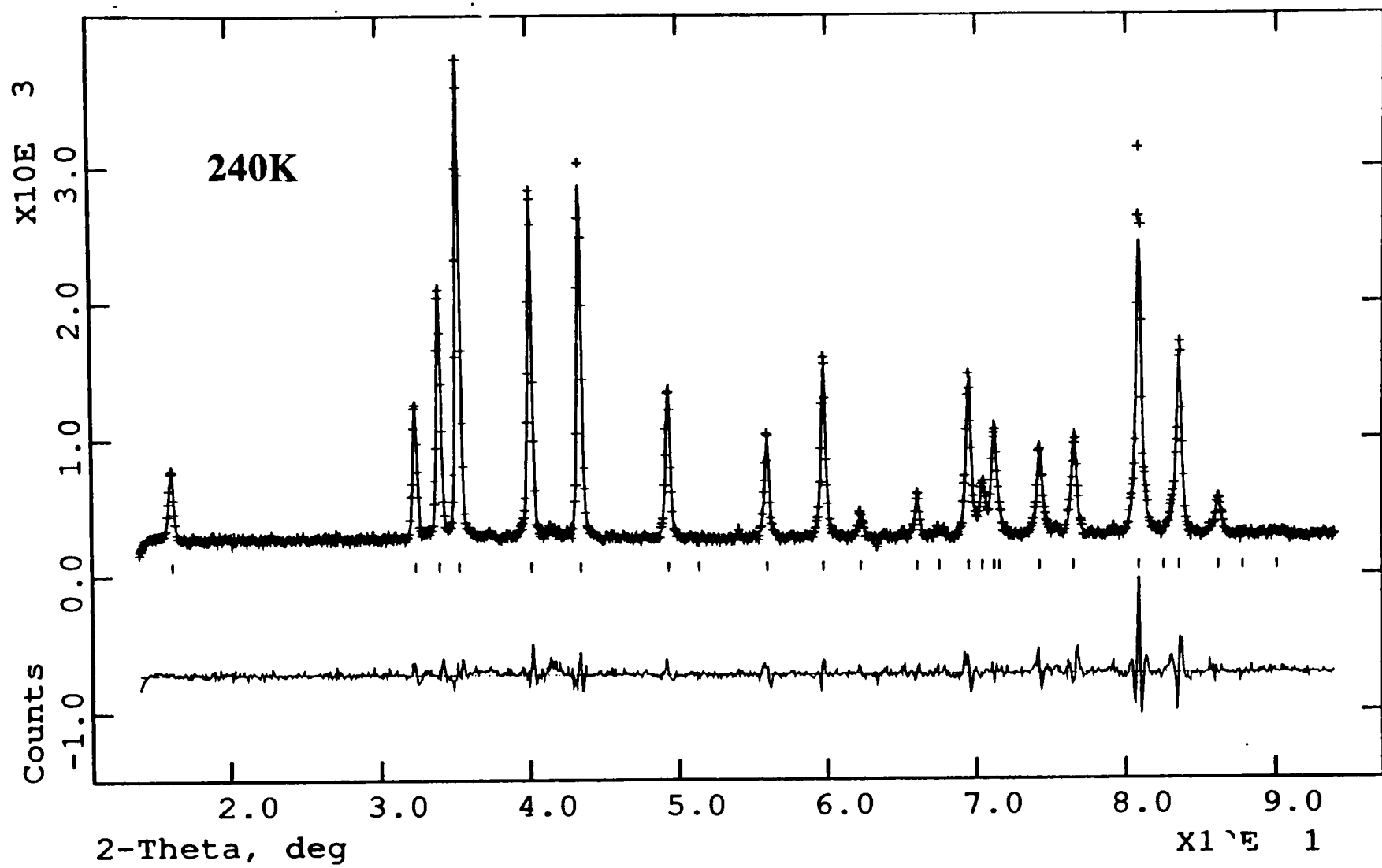
The Rietveld refinements of the neutron diffraction data collected on the diffractometer C2 at Chalk River Laboratories were all carried out using the refinement package GSAS [138]. The fits are shown below. The refined parameters are listed in Table 4.7.

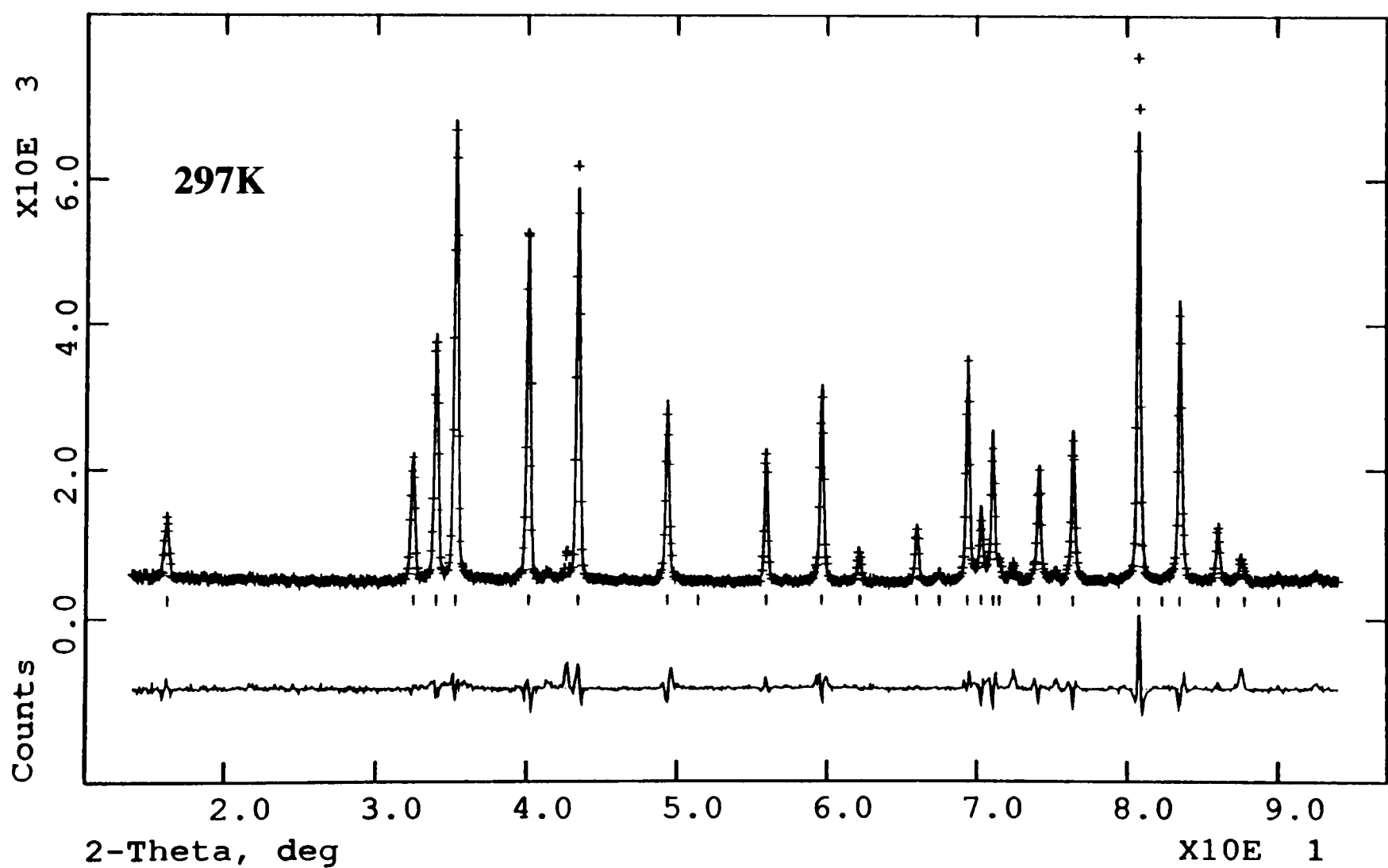
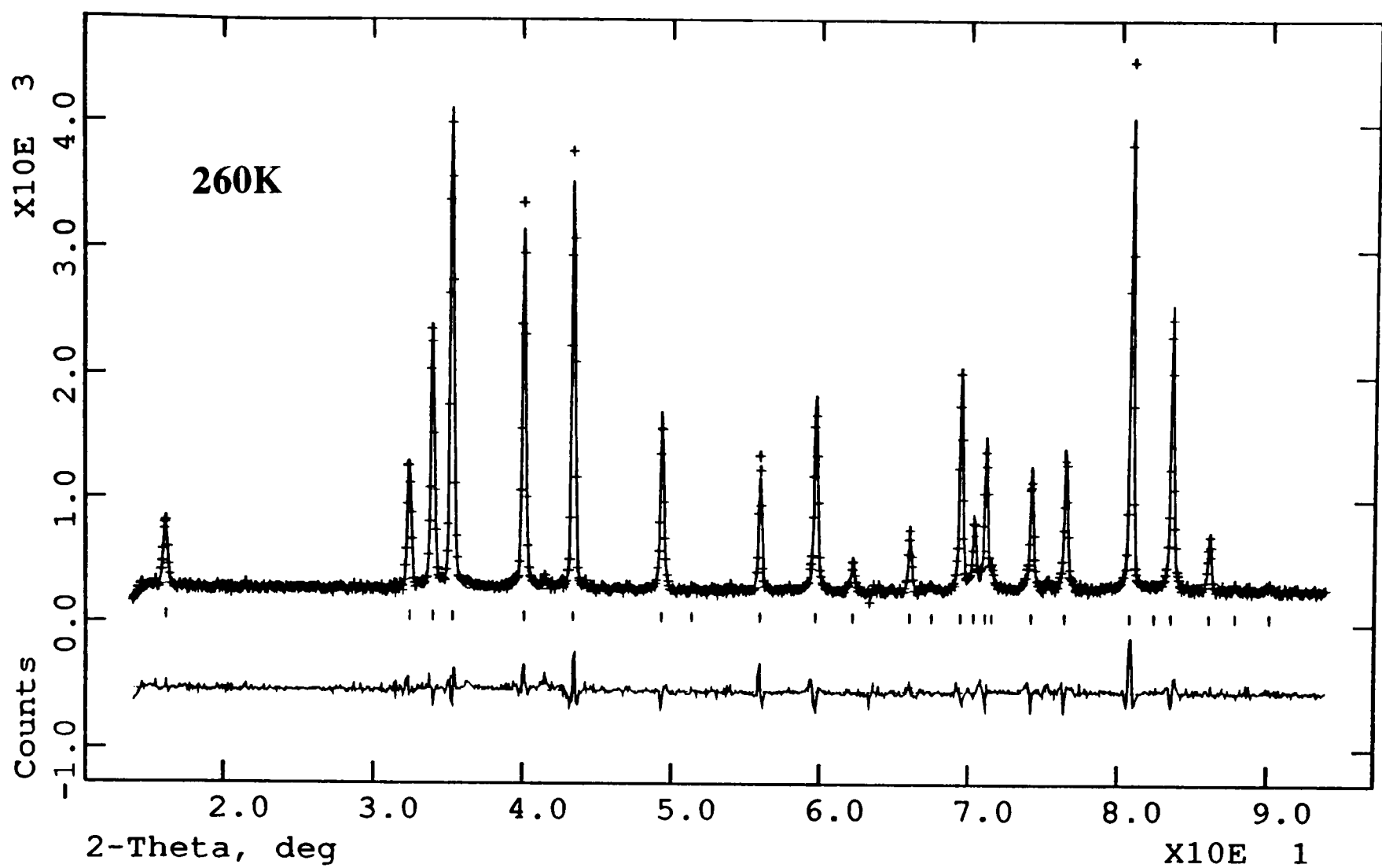












Bibliography

- [1] H.E. Stanley, *Introduction to phase transitions and critical phenomena*, Oxford University Press, Oxford (1971)
- [2] L.P. Kadanoff in *Phase transitions and critical phenomena 5A*, editors C. Domb and M.S. Green, Academic Press, London (1976)
- [3] F.D.M. Haldane, *Phys. Rev. Lett.* **50**, 1153 (1983)
- [4] R.J. Birgeneau, *Am. J. Phys.* **58**, 28 (1990)
- [5] K.P. Sinha and N. Kumar, *Interactions of magnetically ordered solids*, Oxford University Press, Oxford (1980)
- [6] I. Dzyaloshinsky, *J. Phys. Chem. Sol.* **4**, 241 (1958)
- [7] T. Moriya, *Phys. Rev.* **120**, 91 (1960)
- [8] J.B. Goodenough, *Phys. Rev.* **100**, 564 (1955) and J.B. Goodenough, *J. Phys. Chem. Solids* **6**, 287 (1958)
- [9] J. Kanamori, *J. Phys. Chem. Solids* **10**, 87 (1959).
- [10] P.W. Anderson, *Phys. Rev.* **79**, 350 (1950)
- [11] H. Kramers, *Physica* **1**, 182 (1934)
- [12] W. Marshall, *Proc. Roy. Soc. London, Ser. A* **232**, 48 (1955)
- [13] P.W. Anderson, *Phys. Rev.* **86**, 694 (1952)
- [14] P.W. Anderson, *Mat. Res. Bull.* **8**, 153 (1973)
- [15] J. Als-Nielsen in *Phase transitions and critical phenomena 5A*, editors C. Domb and M.S. Green, Academic Press, London (1976)
- [16] L.J. de Jongh *Magnetic Properties of Layered Transition Metal Compounds*, Kluwer Academic Publishers, Dordrecht (1990)
- [17] L. Onsager, *Phys. Rev.* **65**, 117 (1944)
- [18] J. Skalyo, G. Shirane, R.J. Birgeneau and H.J. Guggenheim, *Phys. Rev. Lett.* **23**, 1394 (1969)
- [19] R.J. Birgeneau, J. Skalyo and G. Shirane, *Phys. Rev.* **B3**, 1736 (1971)
- [20] N.B. Mermin and H. Wagner, *Phys. Rev. Lett.* **17**, 1133 (1966)

- [21] H.E. Stanley and T.A. Kaplan, *Phys. Rev. Lett.* **17**, 913 (1966); *J. Appl. Phys.* **38**, 975 (1967)
- [22] V.L. Berezinskii, *Sov. Phys. JETP* **32**, 493 (1971)
- [23] J.M. Kosterlitz and D.J. Thouless, *J. Phys.* **C6**, 1181 (1973)
- [24] S.T. Bramwell and P.C.W. Holdsworth, *J. Appl. Phys.* **73**, 6096 (1993)
- [25] S.T. Bramwell and P.C.W. Holdsworth, *Phys. Rev.* **B49**, 8811 (1994)
- [26] S.T. Bramwell and P.C.W. Holdsworth, *J. Phys.: Condens. Mat.* **5**, L53 (1993)
- [27] J.G. Bednorz and K.A. Müller, *Z. Phys.* **B64**, 189 (1986) and *Rev. Mod. Phys.* **60**, 585 (1988)
- [28] M.K. Wu, J.R. Ashburn, C.J. Torng, P.H. Hor, R.L. Meng, L. Gav, Z.J. Huang, Y.Q. Wang and C.W. Chu, *Phys. Rev. Lett.* **58**, 908 (1987)
- [29] C.W. Chu, *Proceedings of the International Conference on Magnetism 1994, Warsaw*, To be published in *J. Magn. Magn. Mat.*
- [30] C.W. Chu, *J. Supercond.* **7**, 1 (1994)
- [31] E. Manousakis, *Rev. Mod. Phys.* **63**, 1 (1991)
- [32] P. Fazekas and P.W. Anderson, *Philos. Mag.* **30**, 432 (1974)
- [33] G. Shirane, Y. Endoh, R.J. Birgeneau, M.A. Kastner, Y. Hikada, M. Oda, M. Suzuki and T. Murakami, *Phys. Rev. Lett.* **59**, 1613 (1987)
- [34] Y. Endoh, K. Yamada, J.M. Tranquada, G. Shirane, Y. Hikada, M. Oda, Y. Enomoto, M. Suzuki and T. Murakami, *Phys. Rev.* **B37**, 7443 (1987)
- [35] P.W. Anderson, *Science* **235**, 1196 (1987)
- [36] G. Baskaran, Z. Zou and P.W. Anderson, *Solid State Commun.* **63**, 973 (1987)
- [37] M. Greven, R.J. Birgeneau, Y. Endoh, M.A. Kastner, B. Keimer, M. Matsuda, G. Shirane and T.R. Thurston, *Phys. Rev. Lett.* **72**, 1096 (1994)
- [38] S. Chakravarty, B.I. Halperin and D.R. Nelson, *Phys. Rev. Lett.* **60**, 1057 (1988) and *Phys. Rev.* **B39**, 2344 (1989)
- [39] H. Kawamura, *J. Phys. Soc. Jpn.* **54**, 3226 (1985)
- [40] P. Azaria *et al.* *J. Appl. Cryst.* **69**, 6170 (1991); *Phys. Rev. Lett.* **68**, 1762 (1992); *Phys. Rev. Lett.* **64**, 3175 (1990); *Phys. Rev.* **B44**, 2369 (1990)
- [41] A.P. Ramirez, G.P. Espinosa and A.S. Cooper, *Phys. Rev.* **B45**, 2505 (1992)
- [42] C. Broholm, G. Aeppli, G.P. Espinosa and A.S. Cooper, *Phys. Rev. Lett.* **65**, 3173 (1990)
- [43] D. Visser, *Proceedings of the International Conference on Magnetism 1994, Warsaw*, to be published in *J. Magn. Magn. Mat.*

- [44] For discussion of the Kagomé lattice see *Proceedings of the International Conference on Magnetism 1994, Warsaw*, to be published in *J. Magn. Magn. Mat.*
- [45] B.D. Gaulin, J.N. Reimers, T.E. Mason, J.E. Greedan and Z. Tun, *Phys. Rev. Lett* **69**, 3244 (1992); J.E. Greedan, M. Sato and Xu Yan, *Solid State Comm.* **59**, 895 (1986); M. Sato and J.E. Greedan, *J. Solid State Chem.* **67**, 248 (1987); J.N. Reimers, J.E. Greedan, C.V. Stager, M. Bjorgvinnsen and M.A. Subramanian, *Phys. Rev.* **B43**, 5692 (1991); J.N. Reimers, A.J. Berlinsky and A-C. Shi, *Phys. Rev.* **B43** 865 (1991); J.E. Greedan, J.N. Reimers, C.V. Stager and S.L. Penny, *Phys. Rev.* **B43**, 5682 (1991)
- [46] D.A. Huse and V. Elser, *Phys. Rev. Lett.* **60**, 2531 (1988)
- [47] H. Yokoyama and H. Shiba, *J. Phys. Soc. Jpn* **56**, 3570 (1987)
- [48] C. Gros, R. Joynt and T.M. Rice, *Z. Phys.* **B68**, 425 (1987)
- [49] S. Sachdev, *Phys. Rev.* **B45**, 12377 (1992)
- [50] R. Kiriyaama, H. Ibamoto and K. Matsuo, *Acta. Cryst.* **7**, 482 (1954)
- [51] K. Okada, M.I. Kay, D.T. Cromer and I. Almodovar, *J. Chem. Phys.* **44**, 1648 (1966)
- [52] G. Soda and T. Chiba, *J. Phys. Soc. Jpn.* **26**, 249 (1969)
- [53] N. Burger and H. Fuess, *Ferroelectrics* **22**, 847 (1979)
- [54] K. Okada, *Phys. Rev. Lett.* **15**, 252 (1965) and *Phys. Rev.* **164**, 683 (1967)
- [55] M.I. Kay and R. Kleinberg, *Ferroelectrics* **4**, 147 (1972)
- [56] M.J. Bird and T.R. Lomer, *Acta Cryst.* **B27**, 859 (1971)
- [57] K.C. Turberfield, *Sol. Stat. Comm.* **5**, 887 (1967)
- [58] H. Kiriyaama, *Bull. Chem. Soc. Jpn.* **35**, 1199 (1962)
- [59] R.L. Martin and H. Waterman, *J. Chem. Soc.* **1959**, 1359 (1959)
- [60] H. Kobayashi and T. Haseda, *J. Phys. Soc. Jpn.* **18**, 541 (1963)
- [61] R.B. Flippen and S.A. Friedberg, *J. Chem. Phys.* **38**, 2652 (1962)
- [62] M.S. Seehra, *Physics Letters* **28A**, 754 (1969)
- [63] P. van der Leeden, P.A. van Dalen and W.J.M. de Jonge, *Physica* **33**, 202 (1967)
- [64] T. Thio, T.R. Thurston, N.W. Preyer, P.J. Picone, M.A. Kastner, H.P. Jenssen, D.R. Gabbe, C.Y. Chen, R.J. Birgeneau and A. Aharony, *Phys. Rev.* **B38**, 905 (1988)
- [65] K. Yamada, K. Kakurai, Y. Endoh, T.R. Thurston, M.A. Kastner, R.J. Birgeneau G. Shirane, Y. Hidaka and T. Murakami, *Phys. Rev.* **B40**, 4557 (1989)
- [66] N. Burger, H. Fuess and P. Burlet, *Solid State Comm.* **34**, 883 (1980)
- [67] M.S. Seehra and T.G. Castner, *Phys. Rev.* **B4**, 38 (1971)

- [68] S.W. Lovesey, *Theory of Neutron Scattering from Condensed Matter Vols. 1 and 2*, Clarendon Press, Oxford (1984)
- [69] M. F. Collins, *Magnetic Critical Scattering*, Oxford University Press, Oxford (1989)
- [70] M.J. Cooper and R. Nathans, *Acta Cryst.* **A24**, 481 (1968)
- [71] M. Nielsen and H.B. Møller, *Acta Cryst.* **A25**, 547 (1969)
- [72] S.J. Clarke, *Part II Thesis*, University of Oxford (1991)
- [73] S.J. Clarke, A. Harrison, T.E. Mason, G.J. McIntyre and D. Visser, *J. Phys.: Condens. Mat.* **4**, L71 (1992)
- [74] K. Koyama, H. Nobumasa and M. Matsuura, *J. Phys. Soc. Jpn.* **56**, 1553 (1987)
- [75] T. Oguchi, *Phys. Rev.* **117**, 117 (1960)
- [76] S.H. Shenker and J. Tobochnik, *Phys. Rev. B* **22**, 4462 (1980)
- [77] J.D. Reger and A.P. Young, *Phys. Rev. B* **37**, 5978 (1988)
- [78] D.A. Huse, *Phys. Rev. B* **37**, 2380 (1988)
- [79] R. Kubo, *Phys. Rev.* **87**, 568 (1952)
- [80] R.B. Stinchcombe, *J. Phys. C* **4**, L79 (1971)
- [81] R.E. Walstedt, H.W. de Wijn and H.J. Guggenheim, *Phys. Rev. Lett.* **25**, 1119 (1970)
- [82] H.W. de Wijn, R.E. Walstedt, L.R. Walker and H.J. Guggenheim, *Phys. Rev. Lett* **24**, 832 (1970)
- [83] R.J. Birgeneau, J. Skalyo and G. Shirane, *Phys. Rev.* **B8**, 304 (1973)
- [84] T.E. Mason, RESCONV, a FORTRAN program to deconvolve an intrinsic quasielastic peak from the resolution function.
- [85] S. Tyč, B.I. Halperin and S. Chakravarty, *Phys. Rev. Lett.* **62**, 835 (1989)
- [86] S.M. Hayden, G. Aeppli, R. Osborn, A.D. Taylor, T.G. Perring, S.-W. Cheong and Z. Fisk, *Phys. Rev. Lett.* **67**, 3622 (1991); S.M. Hayden, G. Aeppli, H.A. Mook, S-W. Cheong and Z. Fisk, *Phys. Rev.* **B42**, 10220 (1990)
- [87] G. Aeppli, S.M. Hayden, H.A. Mook, Z. Fisk, S-W. Cheong, D. Rytz, J.P. Remeika, G.P. Espinosa and A.S. Cooper, *Phys. Rev. Lett.* **62**, 2052 (1989)
- [88] K.B. Lyons, P.A. Fleury, J.P. Remeika, A.S. Cooper, T.J. Negran, *Phys. Rev.* **B37**, 2353 (1988)
- [89] A. Harrison, S.J. Clarke, T.E. Mason and D. Visser *J. Magn. Magn. Mat.* **104-107**, 557 (1992) (Proceedings of the 1991 International Conference on Magnetism)
- [90] S.J. Clarke, A. Harrison, T.E. Mason and D. Visser, *J. Phys.: Condens. Mat.*, accepted for publication (1994)

- [91] M.S. Seehra and T.G. Castner, *Phys. Rev. B* **1**, 2289 (1970) and *J. Appl. Phys.* **40**, 1240 (1969)
- [92] W.H. Press, S.A. Teukolsky, W.T. Vetterling and B.P. Flannery, *Numerical Recipes in Fortran*, Cambridge University Press, Cambridge, (1992)
- [93] T.E. Mason, FIT3AX, a FORTRAN program to deconvolve the resolution function from an inelastic spin-wave spectrum using Monte-Carlo integration
- [94] C.J. Peters, R.J. Birgeneau, M.A. Kastner, H. Yoshizawa, Y. Endoh, J. Tranquada, G. Shirane, Y. Hidaka, M. Oda, M. Suzuki and T. Murakami, *Phys. Rev. B* **37**, 9761 (1988)
- [95] J. Song and J.F. Annett, *Phys. Rev. B* **42**, 4208 (1990)
- [96] S.J. Clarke and A. Harrison, 1992 *J. Phys. Condens. Mat.* **4** 6217
- [97] S. Tyč and B.I. Halperin, *Phys. Rev. B* **42**, 2096 (1990)
- [98] D.R. Grempel, *Phys. Rev. Lett.* **61**, 1041 (1988)
- [99] P. Kopietz, *Phys. Rev. B* **41**, 9228 (1990)
- [100] A. Chakraborty, A.J. Epstein, M. Jarrell and E.M. McCarron, *Phys. Rev. B* **40**, 5296 (1989)
- [101] S.-W. Cheong, A.S. Cooper, L.W. Rupp Jr., B. Batlogg, J.D. Thompson and Z. Fisk, *Phys. Rev. B* **44**, 1991 (1991)
- [102] T. Idogaki, N. Uryū, *J. Phys. Soc. Japan* **43**, 845 (1977)
- [103] R.B. Stinchcombe *J. Phys. C* **12**, 4533 (1979)
- [104] D.P. Landau *Phys. Rev. B* **22**, 2450 (1980)
- [105] D.J. Breed, K. Gilijamse, J.W.E. Sterkenburg and A.R. Miedema, *Physica* **68**, 303 (1973) and *J. Appl. Phys.* **41**, 1267 (1970)
- [106] M.S. Seehra and T.G. Castner *Phys. Kondens. Mat.* **7**, 185 (1968)
- [107] J. Shimada, H. Abe and K. Ôno, *J. Phys. Soc. Jpn.* **11**, 137 (1955)
- [108] H. Benner and J.P. Boucher, in *Magnetic Properties of Layered Transition Metal Compounds*, editor L J de Jongh, Kluwer Academic Publishers, Dordrecht (1990)
- [109] A. Bencini and D. Gatteschi, *EPR of exchange coupled systems*, Springer-Verlag, Berlin (1990)
- [110] M.S. Seehra and T.G. Castner, *Phys. Rev. B* **47**, 578 (1993)
- [111] N.M. Atherton *Electron spin resonance, theory and applications*, Ellis Horwood, Chichester (1973)
- [112] G.E. Pake and T.L. Estle, *The physical principles of electron paramagnetic resonance*, Benjamin, Reading, Mass. (1973)

- [113] P.M. Richards and M.B. Salamon, *Phys. Rev.* **B9**, 32 (1974)
- [114] S. Chakravarty and R. Orbach, *Phys. Rev. Lett.* **64**, 224 (1990)
- [115] A.V. Lazuta, *Physica C* **181**, 127 (1991)
- [116] P. Ganguly, K. Sreedhar, G. Demazeau and P. Hagenmuller, *J. Phys.: Condens. Mat.* **1**, 213 (1989)
- [117] T. Idogaki and N. Uryû, *J. Phys. Soc. Jpn.* **45**, 1498 (1978)
- [118] J. Clarke, *Sci. Am.* **271**, 36 (1994)
- [119] A.P. Ramirez *Annu. Rev. Mater. Sci.* **24** 453 (1994)
- [120] K. Hirakawa, H. Kadowaki and K. Ubukoshi, *J. Phys. Soc. Jpn.* **54**, 3526 (1985)
- [121] T.A. Hewston and B.L. Chamberland, *J. Phys. Chem. Sol.* **48**, 97 (1987)
- [122] H. Yoshizawa, H. Mori, K. Hirota and M. Ishikawa, *J. Phys. Soc. Japan* **59**, 2631 (1990)
- [123] K. Hirakawa and H. Kadowaki, *Physica* **B136**, 335 (1986)
- [124] K. Hirakawa, R. Osborn, A.D. Taylor and K. Takeda, *J. Phys. Soc. Japan* **59**, 3081 (1990)
- [125] J.N. Reimers, J.R. Dahn, J.E. Greedan, C.V. Stager, G. Liu, I. Davidson and U. Vonsachen, *J. Solid State Chem.* **102**, 542 (1993)
- [126] P. Hagenmuller, A. Lecerf and M. Onillon, *C. R. Acad. Sci.* **255**, 928 (1962)
- [127] A. Maazaz and C. Delmas, *C. R. Acad. Sci.* **295**, 759 (1982)
- [128] C. Delmas, J.-J. Braconnier, A. Maazaz and P. Hagenmuller, *Rev. Chim. Miner.* **19**, 343 (1982)
- [129] A L Wayda and J L Dye *J. Chem. Educ.* **6** 356 (1985)
- [130] H.P. Klug and L.E. Alexander, *X-ray diffraction procedures for polycrystalline and amorphous materials*, John Wiley & sons, New York (1974)
- [131] J.K. Cockcroft, A suite of programs for use in structure determination by powder diffraction: REFCEL (refinement of lattice parameters from powder data); BONDLA (Bond length and angle determination); DRAGON (calculation of diffraction peaks for a particular space group and unit cell)
- [132] H.M. Rietveld, *Acta. Cryst.* **20**, 508 (1966)
- [133] H.M. Rietveld, *Acta Cryst.* **22**, 151 (1967)
- [134] H.M. Rietveld, *J. Appl. Cryst.* **2**, 65 (1969)
- [135] C.J. Howard, *J. Appl. Cryst.* **15**, 615 (1982)
- [136] *The Rietveld Method*, editor R.A. Young, International Union of Crystallography, Oxford University Press, Oxford (1993)

- [137] S.J. Clarke, J.K. Cockcroft and A.N. Fitch, *Z. Kryst.* **206**, 87 (1993)
- [138] A.C. Larsen and R.B. Von Dreele, *The General Structure Analysis System* (GSAS), a suite of programs for determining crystal structures from single crystal data and from powder data using the Rietveld method. (1985, 1990)
- [139] J.K. Cockcroft, PROFIL A program for Rietveld profile refinement.
- [140] Manual for GSAS, obtainable from the authors at LANSCE, MS-H805, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA.
- [141] Corrections for core electron diamagnetism were taken from *Landolt-Bornstein New Series II/10: Magnetic properties of transition metal compounds, supplement 2*, Springer-Verlag, Berlin (1979)
- [142] K. Takeda, K. Miyake, K. Takeda and K. Hirakawa, *J. Phys. Soc. Japan* **61**, 2156 (1992)
- [143] A. Harrison and M.A. MacWhannell, *Private Communication*, (1994)
- [144] R.L. Carlin *Magnetochemistry*, Springer-Verlag, Berlin (1986)
- [145] I. Yamada, K. Ubukoshi and K. Hirakawa, *J. Phys. Soc. Japan* **54**, 3571 (1985)
- [146] A. Tuel, J. Drab, P. Gelin, M. Dufaux, J-F. Dubel and Y.B. Taant, *J. mol. cat.* **63**, 95 (1990)
- [147] H.M. Gladney and J.D. Swalen, *J. Chem. Phys.* **42**, 1999 (1965)
- [148] R.L. Greene, H. Maletta, T.S. Plaskett, J.G. Bednorz and K.A. Müller, *Solid State Commun.* **63**, 379 (1987)
- [149] D. Vaknin, S.K. Sinha, C. Stassis, L.L. Miller and D.C. Johnston, *Phys. Rev.* **B41**, 1926 (1990)
- [150] S. Senoussi, M. Oussena, M. Ribault and G. Collin, *Phys. Rev.* **B36**, 4007 (1987)
- [151] H. Tang, G. Xiao, A. Sing, Z. Tesanonc, C.L. Chien and J.C. Walker, *Phys. Rev. Lett.* **62**, 957 (1989)
- [152] T.A. Hewston and B.L. Chamberland, *J. Solid State Chem.* **65**, 100 (1986)
- [153] N.F. Mott, *J. de Physique* **42**, 277 (1981)
- [154] D.A. MacLean and J.E. Greedan, *Inorganic Chemistry* **20**, 1025 (1981)
- [155] N.F. Mott *Metal insulator transitions*, Taylor and Francis, London (1990)
- [156] N.W. Ashcroft and N.D. Mermin, *Solid State Physics*, Saunders College, Philadelphia (1976)
- [157] P.K. Misra and L.M. Roth, *Phys. Rev.* **177**, 1089 (1969)
- [158] P.A. Cox, *Transition metal oxides: An introduction to their electronic structure and properties*, Clarendon Press, Oxford (1992)

- [159] H.J. Zeiger, *Phys. Rev.* **B11**, 5132 (1975)
- [160] J. Ashkenazi, M.G. Vincent, K. Yvon and J.M. Honig, *J. Phys.* **C14**, 353 (1981)
- [161] C.E. Rice and W.R. Robinson, *Mat. Res. Bull.* **11**, 1355 (1976)
- [162] L.L. Van Zandt, J.M. Honig and J.B. Goodenough, *J. Appl. Phys.* **39**, 594 (1968)
- [163] H.J. Zeiger, T.A. Kaplan and P.M. Raccach, *Phys. Rev. Lett.* **26**, 1328 (1971)
- [164] S.H. Shin, G.V. Chandrashekar, R.E. Loehman and J.M. Honig, *Phys. Rev.* **B8**, 1364 (1973)
- [165] S. Ogawa, *J. Phys. Soc. Japan* **15**, 1901 (1960)
- [166] K. Tsutsumi, H. Okomoto, C. Hama and Y. Ishihara, *J. Magn. Magn. Mat.* **90-1**, 181 (1990)
- [167] L.P. Cardoso, D.E. Cox, T.A. Hewston and B.L. Chamberland, *J. Solid State Chem.* **72**, 234 (1988)
- [168] D.A. MacLean, H.-N. Ng and J.E. Greedan, *J. Solid State Chem.* **30**, 35 (1979)
- [169] D.A. Crandles, T. Timusk and J.E. Greedan, *Phys. Rev.* **B44**, 13250 (1991)
- [170] R.J. Beynon and J.A. Wilson, *J. Phys.: Condens. Mat.* **5**, 1983 (1993)
- [171] J.B. Goodenough, *Prog. Solid State Chem.* **5**, editor H. Reiss, Pergamon Press, Oxford (1971)
- [172] L.C. Jackson, *Phil. Mag.* **4**, 269 (1989)
- [173] D.B. McWhan, J.P. Remeika, T.M. Rice, W.F. Brinkman, J.P. Maita and A. Menth, *Phys. Rev. Lett.* **27**, 941 (1971)
- [174] R.G. Egdell, *Private Communication*, (1994)
- [175] N. Tsuda, K. Nasu, A. Yanase and K. Siratori, *Electronic Conduction in Oxides*, Springer-Verlag, Berlin (1983)
- [176] D.W. Murphy, M. Greenblatt, S.M. Zahurak, R.J. Cava, J.V. Waszczak, G.W. Hull and R.S. Hutton, *Rev. Chim. Miner.* **19**, 441 (1982)
- [177] R.J. Cava, D.W. Murphy, S.M. Zahurak, A. Santoro and R.S. Roth, *J. Solid State Chem.* **53**, 64 (1984)
- [178] A. Lecerf, *Ann. Chim.* **7**, 513 (1962)
- [179] P.W. Anderson, *Phys. Rev.* **109**, 1492 (1958)
- [180] S.F.J. Cox, *J. Phys.* **C20**, 3187 (1987)
- [181] A. Harrison and J.D. Garrett *Private Communication* 1990
- [182] B. Wanklyn in *Crystal Growth* editor B.R. Pamplin, Pergamon Press, Oxford (1975)

- [183] R F Bartholemew and W B White *J. Cryst. Growth* **6** 249 (1970)
- [184] J S Berkes, W B White and R Roy *J Appl. Phys.* **36** 3276 (1965)
- [185] J.D. Corbett in *Solid state chemistry: techniques*, editors A.K. Cheetham and P. Day, Clarendon Press, Oxford (1987)
- [186] H. Schäfer *Angew. Chem.* **10** 43 (1971); *Chemical transport reactions*, Academic Press, New York (1964); *Preparative methods in solid state chemistry*, editor P. Hagenmüller, Academic Press, New York (1972); *Angew. Chem.* **15** 713 (1976).
- [187] J. Crangle, *Solid State Magnetism* Edward Arnold, London (1991)