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ABSTRACT

Paramagnetic resonance (p.r.) at low temperatures has been investigated in a number of substances in the solid state. Paramagnetic ions in the solid state are subjected to strong crystalline electric fields which profoundly modify the magnetic properties of the free ion. The orbital momentum of the free ion is completely or partially "quenched", leaving the spin momentum unaffected, except to a small extent due to spin-orbit coupling. The ground state consists of a number of levels, generally singlets or doublets. The separations of these levels may be varied by the application of an external magnetic field.

If two levels have energies w_1 and w_2 and an external r.f. magnetic field, of frequency ν such that $h\nu = w_1 - w_2$, is applied, transitions can be excited between the levels, within the limitations of certain selection rules. As the population of the two levels depends upon the Boltzman distribution there is a nett absorption of energy from the r.f. field when transitions occur. If this energy is lost to the crystal lattice quickly enough it is not reradiated. In practice a fixed frequency is chosen and the separation of the energy levels is adjusted by applying an external magnetic field so that the above condition is satisfied.

By studying the fields at which the absorption occurs the position of the energy levels in zero field can be inferred.

The energies of the levels may be expressed concisely in the form of a "spin hamiltonian" which involves a number of parameters which have to be found experimentally. The general spin hamiltonian for an ion in a field of rhombic symmetry is:

$$\mathcal{H} = \beta(g_x H_x S_x + g_y H_y S_y + g_z H_z S_z) + D \left[S_z^2 - \frac{1}{3}S(S+1) \right] \\ + E(S_x^2 - S_y^2) + A_x S_x I_x + A_y S_y I_y + A_z S_z I_z$$

S is the effective spin chosen so that the multiplicity of the ground state is $2S + 1$, β is the Bohr magneton, the g 's are spectroscopic splitting factors along the axes of the crystal field. D represents the effect of the axial component of the field along the z axis and E represents the rhombic component of the crystal field. The transitions between the levels defined by these parameters give rise to the so-called fine structure lines. I is the nuclear spin and the terms in A , S and I represent the interaction between the magnetic moments of the electron and of the nucleus. This interaction splits each fine structure line into $2I + 1$ equally intense, equally spaced hyperfine lines. Thus

the number of hyperfine lines defines the nuclear spin unambiguously. Also the separation between the lines is proportional to the nuclear magnetic moment so that in certain cases this can be estimated.

The specimens used have usually consisted of single crystals of a diamagnetic salt containing about 1% of an isomorphous paramagnetic salt. This dilution separates the paramagnetic ions and reduces the line width caused by their mutual interaction.

The experimental arrangement is of the standard type used in Oxford. Some refinements of technique have been used for particular experiments which needed them. Experiments have been performed at wavelengths between 10 cm and 0.8 mm. A klystron oscillator, run from a stabilised power pack, feeds power to a half wave resonant cavity which contains the sample placed in a position where the r.f. magnetic field is strong. This cavity can be placed in a dewar vessel of refrigerant and between the poles of an electromagnet. A wavemeter measures the wavelength and a crystal detector rectifies the power coupled out of the resonant cavity. The external field has a small 50 c/s modulation superimposed on it so that an absorption signal is swept through 100 times a second. The signal from the detector may then

be amplified in a video-amplifier. If the amplified signal is fed to the Y-plates of an oscilloscope, which has a correctly phased 50 c/s time base, the trace displays a graph of absorption against magnetic field within the region covered by the field modulation. This technique enables a spectrum to be analysed very rapidly.

Complex Cyanides

The p.r. spectra of two complex cyanides of divalent ions, $K_4V(CN)_6 \cdot 3H_2O$ and $K_4Mn(CN)_6 \cdot 3H_2O$, have been studied.

The orbital momentum of the vanadous ion is completely quenched so that it is in an $S = 3/2$ state and its behaviour resembles that of the same ion in ionic crystals. The g-value, 1.992, is closer to the free spin value and the crystal field parameters, $D = -0.0264 \pm 0.0004 \text{ cm}^{-1}$ and $E = -0.0072 \pm 0.0004 \text{ cm}^{-1}$, are smaller showing that the effect of higher levels is less than in the ionic salts. The hyperfine structure constant $A = -0.00555 \pm 0.00003 \text{ cm}^{-1}$ is only 36% smaller than in the ionic salts, showing that the configurational interaction which produces the hyperfine structure is not greatly modified by the covalent bonding.

In the manganous ion the cubic field does not completely lift the orbital degeneracy of the ground state. The lowest triplet is split into a singlet and

a higher doublet by the rhombic component of the crystal field so that the g-values differ widely from the free spin value. The ion behaves with effective spin $S = 1/2$ and has g-values $g_x = 2.624 \pm 0.008$, $g_y = 2.182 \pm 0.008$ and $g_z = 0.72 \pm 0.05$. The hyperfine structure is also anisotropic and the hyperfine structure constants are $A_x = 0.00845 \pm 0.00005 \text{ cm}^{-1}$, $A_y = 0.00465 \pm 0.00005 \text{ cm}^{-1}$ and $A_z = 0.0083 \pm 0.0013 \text{ cm}^{-1}$. The manganous ion in this type of compound resembles the titanous ion in ionic compounds and an attempt has been made to fit the parameters with the titanium theory of Abragam and Pryce (1951). This gives reasonable values for the configurational interaction constant and the mean value of the radius of the electron orbit.

Nuclear spins

The nuclear spin and magnetic moment of vanadium ^{50}V has been measured in a crystal of $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ containing a few milligrams of vanadium enhanced to contain $\sim 20\%$ ^{50}V . The spin was found to be six and the ratio of the nuclear gyromagnetic ratios of $^{50}\text{V}/^{51}\text{V}$, 0.380, agrees well with the value measured by nuclear resonance of 0.3792. The spin and nuclear gyromagnetic ratio (0.557) fit well with the values calculated by Hitchcock (1952) using a j-j spin-orbit coupling model of the nucleus and

assuming a δ -function potential.

The nuclear spin and magnetic moment of radioactive cobalt 57 have been measured in a crystal of $K_2Zn(SO_4)_2 \cdot 6H_2O$ containing > 0.5 μ grams of ^{57}Co . The crystal also contains some stable ^{59}Co up to 2.4 μ grams total cobalt content. Only one set of hyperfine structure lines is resolved so that the spin and magnetic moment of ^{57}Co are the same as ^{59}Co ; i.e. the spin is $7/2$ and the magnetic moment is 4.6 ± 0.2 nuclear magnetons.

Chromic methylamine alum

Paramagnetic resonance measurements on crystals of $Cr(CH_3NH_3)(SO_4)_2 \cdot 12H_2O$ show that the crystals undergo a change in structure at $157 \pm 3^\circ K$. Above this temperature the crystal symmetry is cubic and the Cr^{+++} ions are in a crystal field which has a small trigonal component superimposed on the cubic component. Below this temperature there is an additional rhombic component in the crystal field and the crystal symmetry is lower, probably tetragonal. At both $90^\circ K$ and $20^\circ K$ the parameters in the spin hamiltonian are $g = 1.975 \pm 0.010$, $D = 0.0071 \pm 0.0007 \text{ cm}^{-1}$ and $E = 0.0092 \pm 0.0008 \text{ cm}^{-1}$. These values give a Stark splitting in zero field of $0.177 \pm 0.002 \text{ cm}^{-1}$ which disagrees with the value of $0.188 \pm 0.007 \text{ cm}^{-1}$ calculated by Kurti and Gardner (1954)

from adiabatic demagnetisation measurements. Measurements at frequencies near the Stark splitting give results which lie between the two values so that it is not possible to say whether this discrepancy is real. Measurements of nearest neighbour lines and of line widths indicate that there is extremely little exchange interaction between neighbouring Cr^{+++} ions.

The transition is possibly due to a freezing out of a random rotary motion of the methylamine radical as the substance is cooled through the transition temperature. This temperature is the same as that found by Griffiths and Powell (1952) at which there is a discontinuity in the value of the dielectric constant.

Interactions between neighbouring ions

The p.r. spectrum of two adjacent paramagnetic ions consists of a series of lines, corresponding to the various orientations of the spins with respect to one another, which occur as satellites to the lines produced by isolated ions. The number of and separation between these satellites depends upon the size and nature of the interaction between them. The magnetic interaction may be calculated if the distance between the ions is known, so that if allowance is made for this, the size and nature of exchange interaction may be inferred from the

positions of the satellite lines. Investigations of this sort have been done in crystals containing about 10% paramagnetic salt in an isomorphous diamagnetic one, so that there is considerable chance of having two ions adjacent.

A study of lanthanum ethyl sulphate containing up to 30% neodymium shows that there is a small anisotropic exchange interaction with the two nearest neighbours and undetectable exchange interaction with the six next nearest. There is however no exchange with the next nearest neighbours in concentrated neodymium ethyl sulphate. This discrepancy is not explained.

A study of nearest neighbour satellites was made in $\text{KCr}(\text{SeO}_4)_2 \cdot 12\text{H}_2\text{O}$. The problem is complicated by there being four ions in the unit cell all of which have different crystal field axes. It has not been possible to make an unambiguous interpretation of the results and the best interpretation does not agree with the results of adiabatic demagnetisation experiments of Kurti and Gardner (unpublished).

The results of this type of investigation are rather discouraging and seem to indicate that one can hope to obtain satisfactory results only in particular substances.

Rare earth ethyl sulphates

Paramagnetic resonance has been observed in terbium ethyl sulphate using the yttrium salt as a dilutant. The spectrum may be explained using the hamiltonian postulated for the praseodymium salt (Bleaney and Scovil, 1952):

$$\mathcal{H} = g_{\parallel} \beta H_z S_z + A S_z I_z + \Delta S_x$$

where $g_{\parallel} = 17.72 \pm 0.02$, $S = 1/2$, $I = 3/2$,

$A = 0.209 \pm 0.002 \text{ cm}^{-1}$ and $\Delta = 0.387 \pm 0.001 \text{ cm}^{-1}$. The

lowest level is a doublet $J_z = \pm 6$ which is admixed with

$J_z = 0$ by the crystal field. This admixes the +6 and -6

levels and $\Delta M = 0$ transitions are obtained if the r.f.

magnetic field is placed parallel to the external field.

The nuclear spin of terbium 159 is estimated to be

1.5 ± 0.4 nuclear magnetons.

The work of Bleaney and Scovil (1952) on praseodymium ethyl sulphate has been extended using yttrium ethyl sulphate as a dilutant. The asymmetrical line shape is explained as being the result of the splitting Δ in the above hamiltonian not having a single value but a Gaussian distribution of values. The nuclear magnetic moment of praseodymium 141 is estimated to be 4.5 ± 1.1 nuclear magnetons.

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The results of the investigation of the properties of the compounds of the rare earths and of the actinides are presented in the following chapters.

All paragraphs are numbered consecutively, which will facilitate finding the place of any particular paragraph. In the case of the rare earths and actinides, the numbering is given in the following order: first the element, then the compound, and finally the paragraph. Thus, for example, the first paragraph on the properties of the rare earths is numbered 1.1.1. The numbering of the paragraphs is given in the following order: first the element, then the compound, and finally the paragraph. Thus, for example, the first paragraph on the properties of the rare earths is numbered 1.1.1. The numbering of the paragraphs is given in the following order: first the element, then the compound, and finally the paragraph. Thus, for example, the first paragraph on the properties of the rare earths is numbered 1.1.1.

INTRODUCTION

The magnetic properties of paramagnetic substances have been widely studied in all phases. Their study in the solid state is particularly interesting because of the modification of the properties of the free ion by the crystalline electric field, produced by the surrounding charged ions.

All paramagnetic substances contain ions, which are small magnetic dipoles, to which they owe their magnetic properties. In the ion the orbital and spin momentum of each electron have an associated magnetic moment, and only ions with an unfilled electron shell have a resultant magnetic moment. As the valency electrons, which are usually the outermost ones in the atom, are lost when the atom forms a compound, only the electrons in d- and f-electron shells produce paramagnetism in the solid state. This limits paramagnetism to certain regions of the periodic table known as the transition groups, which occur when the following sub-shells are partially filled: 3d (the iron group), 4d (palladium group), 4f (rare earth group), 5d (platinum group), 5f (uranium group). Of these the iron and rare earth groups have been most fully investigated, and it is with these that this thesis is concerned.

At low temperatures co-operative phenomena such as ferromagnetism and antiferromagnetism often occur. As these phenomena do not occur in the substances studied, in the temperature ranges used, they will not be discussed further. In a normal paramagnetic substance the dipoles are practically independent of one another, the interactions being small and making only slight modifications to their magnetic properties. Most of this thesis is concerned with ions in which these interactions have been reduced or eliminated, and only chapter 6 is concerned with the study of the interactions.

Information about paramagnetic ions can be found in several ways. Susceptibility, paramagnetic relaxation, paramagnetic resonance (afterwards abbreviated to p.r.) and specific heat measurements all contribute information of a slightly different nature. In the solid state there are often several ions in the unit cell which are situated in different crystal fields; this may lead to their having different magnetic properties; or, if the crystal field produces anisotropy, to their having different magnetic axes. As susceptibility, relaxation and specific heat measurements involve only properties averaged over the bulk of material they are incapable of distinguishing these magnetically distinct ions. As p.r. measurements produce a different spectrum for each type of ion the technique

is very suited to investigation of the solid state, and can contribute information much more detailed than that found by other methods. Also, small quantities of impurities do not affect the results.

THE RESONANCE PRINCIPLE

The principles of resonance have been often discussed (see e.g. Purcell, Torrey and Pound, 1946; Bloch, Hansen and Packard, 1946). A free ion with total angular momentum quantum number J will precess about an external magnetic field such that the projection of the momentum vector in the direction of the field is M , where M can have values $J, J - 1, \dots, -J$. Associated with this precession is an energy $g\beta HM$, where g is the spectroscopic splitting factor, β the Bohr magneton and H the magnetic field. If a sinusoidally varying magnetic field is introduced in a plane perpendicular to that of the steady field, with such a frequency that its quantum is $h\nu = g\beta H$, it may induce transitions between these possible energy levels. The selection rules limit transitions to those in which $\Delta M = \pm 1$. If the oscillating field has a component parallel to the steady field $\Delta M = 0$ transitions are allowed also. Between any two adjacent levels, therefore, transitions are induced in both directions. However, as the upper level is less populated than the lower one, corresponding to the Boltzmann factor, there are more

transitions from the lower level to the upper level than in the opposite direction, and there is a nett absorption of energy from the oscillating field. It is with the detection and explanation of this absorption that p.r. is concerned. Using a conveniently available field of about 8 Kgauss. this absorption for a free electron spin occurs when microwaves of 1.25 cm. wavelength are used to provide the oscillating field. Wavelengths between 10 cm. and 8 mm. are usually used for this work. It is general practice to work at constant frequency and to measure the absorption as a function of magnetic field, as this is much easier than measuring the absorption as a function of frequency.

If the nucleus of the paramagnetic ion has a magnetic moment this will produce a hyperfine structure (sometimes abbreviated to h.f.s.). In strong magnetic fields the nuclear moment will precess about the magnetic field produced by the surrounding electrons. The projection of the nuclear momentum vector m on the latter field may have values $I, I - 1, \dots - I$. This splits the energy levels corresponding to M into $2I + 1$ equally spaced levels. The selection rules require that when a transition occurs $\Delta m = 0$, because the r.f. field has little interaction with the small magnetic moment of the nucleus. Taking for simplicity a case when $J = 1/2$ and $I = 3/2$

the energy levels as a function of external magnetic field have been drawn in diagram 0.1. The transitions which obey the transition rules are shown, the vertical line of constant length representing the fixed quantum of energy, and it is seen that a nuclear spin I gives rise to a hyperfine structure of $2I + 1$ equally spaced lines.

In a weak external field, when it is comparable to the field due to the nuclear moment, the electron must be regarded as being in a composite field. The levels no longer vary linearly with external field so that the hyperfine lines are no longer equally spaced. Also states of different m are admixed so that, as transitions are allowed between levels which contain components with the same value of m , transitions may occur between levels for which transitions were forbidden at high fields. In very low fields the total electronic moment and the nuclear moment vectors must be added to give a new momentum vector $\vec{F} = \vec{J} + \vec{I}$.

If the nucleus has a quadrupole moment there is interaction between it and the gradient of the electric field at the nucleus due to the surrounding electrons. To a first approximation this interaction changes the energy levels by an amount proportional to m^2 , so that the positions of the hyperfine lines is unchanged. If the external magnetic field is not parallel to the gradient of

$$S = \frac{1}{2}$$

$$I = \frac{3}{2}$$

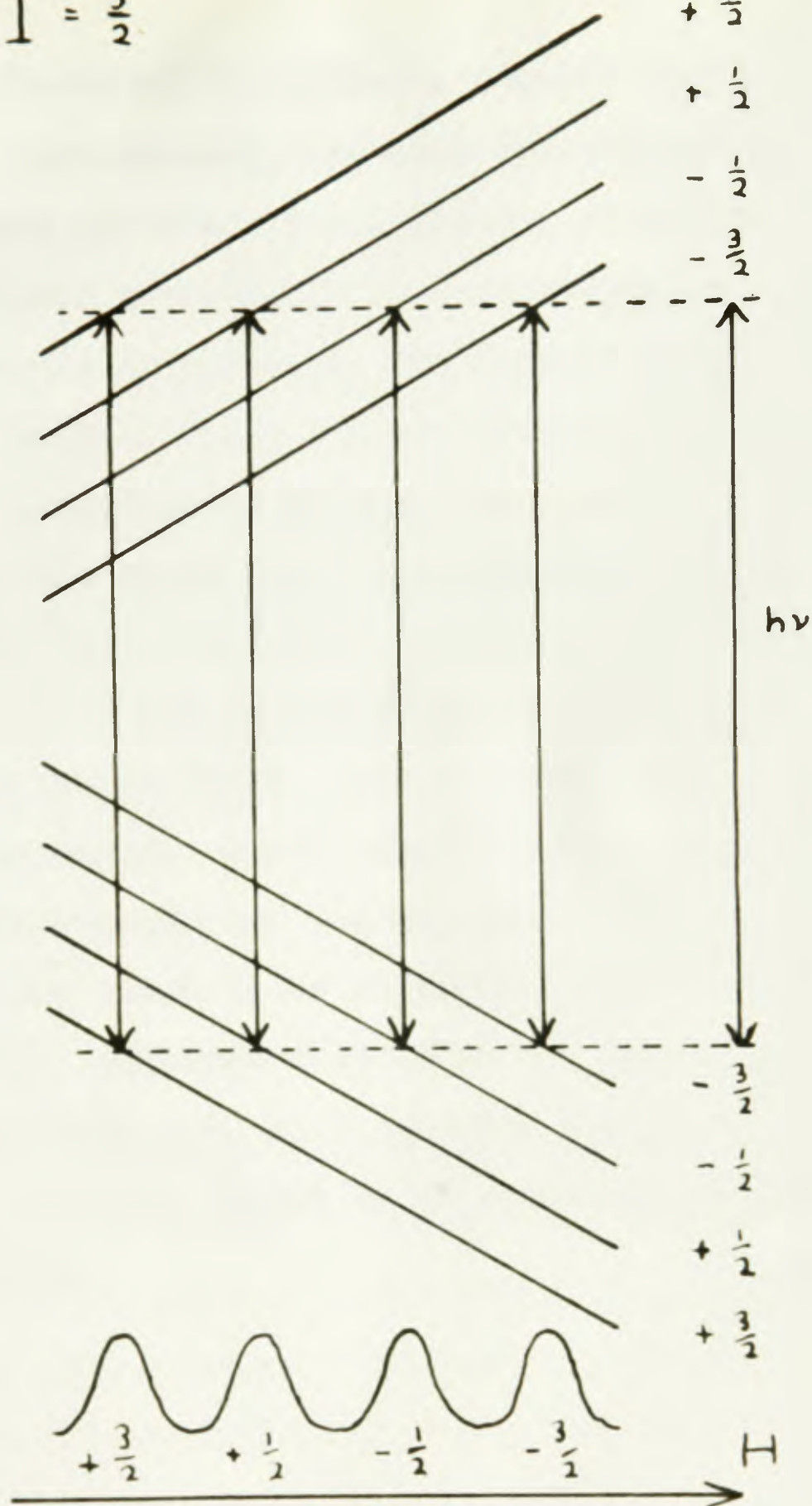
$$I_m$$

$$+\frac{3}{2}$$

$$+\frac{1}{2}$$

$$-\frac{1}{2}$$

$$-\frac{3}{2}$$



Energy level diagram for $S = \frac{1}{2}$, $I = \frac{3}{2}$ in strong magnetic field showing the allowed transitions.

Diagram 0.1

the electric field at the nucleus, various states of different m are admixed, and some previously forbidden transitions are allowed. The intensity of the lines produced by these transitions is proportional to the square of the quadrupole interaction, and depends on the angle between the magnetic field and the electric field gradient. In most ions investigated by p.r. the quadrupole moment is too small to make these lines sufficiently intense.

When the ion is subjected to strong crystalline field in the solid state its energy levels are considerably modified, and levels which would be degenerate in the free ion become separated. Their behaviour in a magnetic field may become anisotropic and the separation of levels split by the field may cease to be a linear function of the field in weak fields. Although this makes the system of energy levels complicated, p.r. is a powerful method for analysing such complex systems, though it is generally restricted to the ground state.

CHAPTER 1

THEORETICAL CONSIDERATIONS

1.1 THE HAMILTONIAN OF THE FREE ION

The terms of the hamiltonian of the free ion have been fully discussed in various literature and are summarised by Bleaney and Stevens (1953). A brief account of them is given here; they are enumerated in order of decreasing magnitude, as perturbation methods are used to find the eigenvalues and therefore they are dealt with in this order.

The coulomb interaction of the electrons with the nucleus and with each other introduces:

$$W_1 = \sum_k \left(\frac{p_k^2}{2m} - \frac{ze^2}{r_k} \right) + \sum_{j < k} \frac{e^2}{r_{jk}}$$

The first term represents the kinetic energy of the electrons. This expression is treated using the self consistent field method (see Condon and Shortley, 1951), which assumes that the electrons move independently around a fixed nucleus, but restricted by the requirements of the Pauli exclusion principle. The eigenstates specify individual electronic orbits and are in fact 'configurations'. As the separation between them is $\sim 10^5 \text{ cm.}^{-1}$ and at room temperature only levels up to a few hundred cm.^{-1} are populated, only the

lowest configuration need generally be considered.

The magnetic interaction between electron spins and orbits (Van Vleck, 1932) introduces:

$$W_2 = \sum (a_{jk} \bar{l}_j \cdot \bar{s}_k + b_{jk} \bar{l}_j \cdot \bar{l}_k + c_{jk} \bar{s}_j \cdot \bar{s}_k)$$

If the spin-spin and orbit-orbit components of W_2 are included with W_1 and the eigenvalues are found by a more refined method than the self consistent field method, the configurations are found to be split up into a number of terms specified by total orbital and total spin momentum vectors $\bar{L}$ and $\bar{S}$. The lowest term in the configuration is given by Hund's rule. The interaction of each spin with its own orbit is much stronger than that with other orbits so its contribution may be written $a_{jj} \bar{l}_j \cdot \bar{s}_j$, and if only the lowest spectral term is considered it can be written $\bar{L} \cdot \bar{S}$. This splits each term into a number of multiplets characterised by a total angular momentum vector J , the separation between multiplets being $\sim 10^3 \text{ cm.}^{-1}$

The interaction of orbits and spins with the external field introduces:

$$W_3 = \beta (\bar{L} + 2\bar{S}) \cdot \bar{H}$$

where β is the Bohr magneton. This gives rise to energy levels separated by $\sim 1 \text{ cm.}^{-1}$ in readily available fields.

The magnetic field due to the electrons interacts with the magnetic moment of the nucleus introducing (Fermi, 1930):

$$W_4 = 2\gamma\beta_N \sum_k \left[\left(\frac{(\vec{l}_k \cdot \vec{s}_k) \cdot \vec{I}}{r_k^3} + \frac{3(\vec{r}_k \cdot \vec{s}_k)(\vec{r}_k \cdot \vec{I})}{r_k^5} \right) + \frac{8}{3}\pi\delta(r_k)\vec{s}_k \cdot \vec{I} \right]$$

where γ is the gyromagnetic ratio of the nucleus and β_N the nuclear magneton. The δ -function term is zero except for s-electrons. Most of the electrons contributing to paramagnetism in the solid state are in d or f configurations, but in order to explain observed hyperfine structures it is necessary to postulate that, for part of the time, one of the electrons of an inner s-shell is promoted to an outer s-shell. For example, in the iron group the usual configuration is $3d^n$, and it is postulated that a small amount of configuration $3s^1 3d^{n-1} 4s^1$ is introduced. These s-electrons make a large contribution to the h.f.s., so that a very small amount of this configurational interaction is needed to account for the observed h.f.s.; the amount is insufficient greatly to modify the fine structure of the spectrum. This configurational interaction is introduced by the Coulomb repulsion between the electrons, which is the last term in the expression W_1 . The term W_4 has magnitude $\sim 10^{-2} \text{ cm}^{-1}$.

The interaction between the electric quadrupole moment of the nucleus (if $I > 1/2$) and the electric field

gradient due to the electrons has been shown to introduce (see Bleaney and Stevens, 1953):

$$W_5 = \frac{e^2 Q}{2I(2I - 1)} \sum_j \left(\frac{I(I + 1)}{r_j^3} - \frac{3(r_j \cdot I)^2}{r_j^5} \right)$$

The quadrupole moment Q is as defined by Mack (1950).

This is a very small term, $\sim 10^{-4} \text{cm}^{-1}$.

Direct interaction between the external field and the magnetic moment of the nucleus introduces a small term ($\sim 10^{-4} \text{cm}^{-1}$):

$$W_6 = -\gamma \mu_N \bar{I} \cdot \bar{H}$$

1.2 THE CRYSTALLINE ELECTRIC FIELD

In the solid state each paramagnetic ion is surrounded by a regular array of ions, most of which are diamagnetic. As they are all electrostatically charged they set up a considerable electric field around the paramagnetic ion. The symmetry of the potential energy V due to this field depends upon the positions of the neighbouring ions; to calculate the magnitude of this energy accurately is difficult, so this is usually estimated from the splitting of the energy levels it produces. It is important, as perturbation theory is used, to add this term to the hamiltonian in the correct order. Three distinct cases

arise which will be discussed separately.

Case 1. In the iron group (3d shell) the effect of the crystal field is smaller than W_1 but larger than W_2 , and is usually added in the calculation before the spin-orbit coupling. It lifts the $2L + 1$ fold degeneracy of the terms to an extent depending upon the symmetry of the field; Bethe (1929) has used group theory methods to calculate to what extent this degeneracy is lifted in fields of different symmetry. In the iron group the paramagnetic ion is usually surrounded by an octahedron of water molecules so it is assumed that the field comprises a large cubic component together with a smaller component of lower symmetry. The separation of the orbital levels is $\sim 10^4 \text{ cm.}^{-1}$ so that it can be estimated by measuring absorption in the optical and infra red regions, and the magnitude of the crystal field calculated from the size of these separations.

If the crystal field leaves a singlet orbital level lowest the spin-orbit coupling and second order effects of the crystal field lift the $2S + 1$ fold degeneracy of the lowest orbital level, separating the levels by a few cm.^{-1} . If the lowest level is not an orbital singlet then these effects produce much larger splittings.

In the case when the lowest term has $L = 0$ the crystal field can have no direct effect on the levels and is only

able to split them by high order effects through spin orbit coupling. This thesis however is not concerned with this case so it will not be discussed.

The theorem of Jahn and Teller (1937) states that for polyatomic non linear molecules a degenerate state is never stable since the molecule will automatically be distorted to give an asymmetry sufficient to remove the degeneracy. This theorem is also applicable to a paramagnetic ion in a crystal field, so that the crystal field distorts itself so as to remove any ~~orbital~~ degeneracy which may remain. There is however a rule due to Kramers (1930) which states that in a system containing an odd number of electrons the degeneracy of each level must be at least twofold in the absence of an external magnetic field. Generally, therefore, in ions with an odd electron resonance should be observed, as the lowest level is a spin doublet. In ions with an even number of electrons, there are not Kramer's doublets so that resonance may not be possible.

Case 2. In the rare earth group (4f) the effect of the crystal field is smaller than W_2 but larger than W_3 . The fact that this is so much smaller than in the iron group may be explained by the facts that the mean radius for electronic orbits is smaller than for 3d-electrons, and that the 4f-electrons are deep inside the ion and are shielded from the field by the surrounding electron shells.

In this case therefore the crystal field lifts the $2J + 1$ fold degeneracy of each component of the multiplets.

Most work on the rare earth ions has been done in the ethyl sulphates which have D_{3h} symmetry, where the ion is in a field of hexagonal symmetry whose potential is represented by (Elliott and Stevens, 1951)

$$V = A_2^0(3z^2 - r^2) + A_4^0(35z^4 - 30r^2z^2 + 3r^4) \\ + A_6^0(231z^6 - 315r^2z^4 + 105r^4z^2 - 5r^6) \\ + A_6^6(x^6 - 15x^4y^2 + 15x^2y^4 - y^6)$$

The first three terms of this split the J level into doublets characterised by $\pm J_g$, and (if J is integral) a singlet $J_g = 0$. The term in A_6^6 however admixes states which differ by ± 6 in J_g . This will split some of the doublets if J is integral, and will give allowed transitions within some of the doublets if J is half integral.

Gadolinium is in an S state as $L = 0$ and in this case the crystal field is only able to split up the spin multiplet through high order interactions.

Case 3. This case occurs when the ion may be said to be covalently bonded to its neighbours. The complex cyanides, in which the ion is covalently bonded to six (CN) groups, which are at the corners of a surrounding octahedron, are the examples of this case which are discussed in this

thesis.

The electric field of the diamagnetic neighbours is of the same order as the electrostatic field between the electrons though still smaller than the coulomb field of the nucleus. The theory has been developed by Van Vleck (1935), Howard (1935), Kotani (1949) and Stevens (1953). The complex, which is of the form XY_6 , is treated by a Hartree self-consistent field method assuming that the electrons move in a field of octahedral symmetry. This produces the result that the d-electron configuration is split into an orbital triplet and an orbital doublet some 10^5 cm^{-1} higher. It is assumed that the 3d electrons go into the lower six levels obeying a modified Hund's rule such that the value of S is a maximum. There is considerable evidence that this is justified from measurements on the 4d and 5d transition groups as well as on the 3d group. Thus with three d-electrons the spin should be $3/2$, with four 1, with five $2/2$ and with six 0. This explains the fact that potassium ferrocyanide and potassium cobalticyanide, which have six 3d electrons, are diamagnetic.

A distortion of the octahedral symmetry of the crystal field is expected from the Jahn-Teller principle. In fact the crystals have low symmetries and the magnetic properties generally show rhombic symmetry, but as this case is complex to treat theoretically the modification produced by a

tetragonal field has been investigated by Stevens (1953). This will of course be a poor prediction of the magnetic properties if the symmetry is rhombic but will be a better approximation than assuming a pure octahedral field. This tetragonal field together with spin-orbit coupling will raise the degeneracy of the lowest level.

1.3 THE SPIN HAMILTONIAN

Pryce (1950) has shown how a much simpler hamiltonian can be derived from the full hamiltonian whose eigenstates are the lowest eigenstates of the full hamiltonian. This hamiltonian, the spin hamiltonian as it is called, describes the energy levels close to the ground state in terms of relatively few parameters. This gives a natural division between experiment and theory; the former seeks to discover a spin hamiltonian which will explain the spectrum observed, and the latter seeks to explain the spin hamiltonian in terms of a model. Abragam and Pryce (1951)^a show how the spin hamiltonian may be derived using operator equivalents and obtain:

$$\mathcal{H} = \bar{S} \cdot \bar{D} \cdot \bar{S} + \bar{H} \cdot \bar{g} \cdot \bar{S} + \bar{S} \cdot \bar{T} \cdot \bar{L} + \bar{L} \cdot \bar{P} \cdot \bar{L} - \gamma \beta_H \bar{H} \cdot \bar{I} - \beta^2 \bar{H} \cdot \bar{\Lambda} \cdot \bar{H}$$

$\bar{S}$ is the effective spin of the ground state defined such that the ground state consists of $2\bar{S} + 1$ levels. The last term is usually omitted as it is independent of $\bar{S}$ and $\bar{I}$ and does not modify the resonance spectrum: it gives rise

to temperature independent paramagnetism. The terms due to the quadrupole interaction ($\bar{I} \cdot \nabla \cdot \bar{I}$) and direct interaction between the nucleus and the external field ($\gamma \beta_N \bar{H} \cdot \bar{I}$) are very small and will be neglected as this thesis is not concerned with cases in which they are important.

The above hamiltonian is more usefully expressed in terms of components along a system of axes defined by the crystal field, z being reserved for the axis of any axial component.

$$\mathcal{H} = D \left(S_z^2 - \frac{1}{3} S(S+1) \right) + E (S_x^2 - S_y^2) \\ + \beta (g_z H_z S_z + g_x H_x S_x + g_y H_y S_y) + A_z I_z S_z + A_x I_x S_x + A_y I_y S_y$$

The terms in D and E come from the second order effects of the crystal field together with spin-orbit coupling and spin-spin coupling; they give a splitting of the levels of different S_z in zero external field. When the crystal field has no rhombic component the term in E is not present.

The values of g_x , g_y and g_z are affected by the higher levels of the ion. In the iron group if the crystal field leaves an orbital singlet lowest and well separated from higher levels the magnetism comes entirely from the spin. The spin-orbit coupling admixes other orbital levels with the ground level but the effect is small so that the anisotropy in the g -values will be small and they will all

be close to the free spin value. If the lowest level is not a singlet, or is a singlet with other orbital levels close to it, the orbital magnetism is only partially quenched and, as it is tied to the crystal field, the g -values are very anisotropic. In the rare earth group the g -values of a doublet $\pm J_z$ will be $g_{||} = 2\Lambda J_z$ and $g_{\perp} = 0$, where Λ is the Lande g factor. Admixture of other states will modify both of these g -values. If the symmetry is axial g_z can be replaced by $g_{||}$, and g_x and g_y by $g_{\perp}$.

The terms A_z , A_x and A_y are the components of the hyperfine structure term T which is derived from W_4 and has the form $2\gamma\beta\beta_N\left(\frac{1}{r^3}\right)\left[K + \text{other terms}\right]$ where K is the contribution from s -electrons and the other terms from non s -electrons (see 1.1). When the symmetry is axial A_x and A_y are usually replaced by B .

Bleaney (1951) has quoted expressions for the allowed transitions between the levels described by the spin hamiltonian for the case of high fields. There are several features of the spectrum which are generally true and which are useful for analysis of the spectrum.

If the g -values and h.f.s. are anisotropic with axes x , y and z , and have values g_x , g_y , g_z , A_x , A_y , and A_z , then in any direction lmn the g -value and h.f.s. constant K are given by:

$$g^2 = g_x^2 l^2 + g_y^2 m^2 + g_z^2 n^2$$

$$K^2 g^2 = g_x^2 A_x^2 l^2 + g_y^2 A_y^2 m^2 + g_z^2 A_z^2 n^2$$

This gives relations for any plane in which the extreme g -values and h.f.s. constants are g_p and g_q , and A_p and A_q

$$g^2 = g_p^2 \cos^2 \theta + g_q^2 \sin^2 \theta$$

$$K^2 g^2 = g_p^2 A_p^2 \cos^2 \theta + g_q^2 A_q^2 \sin^2 \theta$$

where θ is the angle with the p axis.

Following the usual method the results described in this thesis will be fitted to a spin hamiltonian and an explanation of the values of the various parameters will be attempted.

1.4 LINE WIDTHS

The width of the spectral lines obtained in (p.r.) do not depend on the apparatus used but on other factors.

When quanta are absorbed by transitions between two levels the population of the two levels tends to become equal so that absorption disappears. The spins are, however, coupled to the crystal lattice by some mechanism so that they can transfer energy to it, and thus thermal equilibrium is maintained with the lattice. The time which

it takes for a spin to exchange energy with the lattice is a characteristic of the system, described by the relaxation time, τ , which is the time constant of the equation of approach of the system to equilibrium. It is thus a measure of the lifetime of a spin in the excited state. If τ is very large ($\tau > 10^{-4}$ sec) the two levels become equally populated in a very short time and absorption is greatly reduced or disappears; this effect is known as saturation. If τ is small the lifetime of a spin in the excited state is small, and therefore the indeterminacy in the energy is large. This will produce a broadening of the absorption line which may be so large that the line cannot be detected ($\tau < 10^{-10}$ sec). Applying the Heisenberg uncertainty principle it is found that to produce a line width of one gauss the relaxation time must be $\sim 10^{-7}$ sec. Thus it is important that the relaxation time is within a small range of values.

These relaxation processes take place because the thermal vibrations of the lattice cause a modulation of the crystal field which can interact with the electron spins through the spin-orbit coupling. Two mechanisms have been postulated for this interaction. The one assumes that a quantum of energy is exchanged directly with the lattice; this is a first order process but requires lattice

quanta of energy equal to the separation of the two levels. The second process is a scattering of lattice quanta, analogous to the Raman effect; this is a second order process but all the lattice quanta can participate. The relaxation time due to the former process is theoretically proportional to T^{-1} (where T is the absolute temperature) and that of the latter process is proportional to $T^{-7}(T < \Theta)$ or T ($T > \Theta$) (see Van Vleck, 1940); so that a combination of these two effects should have a temperature dependence T^{-n} where n lies between 1 and 7. This is generally found to be true, the value of n varying with temperature. Thus the spin-lattice relaxation time may be adjusted to be in the required range by using a suitable temperature. For this reason experiments are often performed at 90°K, 20°K or lower. The value of τ also depends on the separation between the ground state and the next orbital level which is coupled to the ground state by spin-orbit coupling, τ being long if the separation is large and short if the separation is small. In the salts investigated there should therefore be a correlation between the relaxation time and the position of the lower orbital levels.

Contribution to the line width comes from neighbouring ions which have a magnetic moment. Each ion slightly modifies the magnetic field at its neighbour, and as the

effect is to a certain extent random averaged over all the ions it produces an increased width of the line. The size of the line width produced depends upon the field produced by the neighbours, which is proportional to their magnetic moment and to the inverse cube of their distance away.

Neighbouring paramagnetic ions produce by far the biggest contribution to line width. Both magnetic dipole-dipole and exchange interaction produce effects. Van Vleck (1948) calculated the area, the second moment and the fourth moment of an absorption line assuming that the ions behaved as free spins. Pryce and Stevens (1950) calculated the area and second moment making no assumptions about the ions. It is found that the second moment is a sum of the form $\sum (W_{ij})^2$ where W_{ij} is the interaction between ions i and j . Thus the problem becomes a succession of two ion components; the contributions from each ion being added together to give the total second moment. Interactions between pairs of ions are considered briefly at the end of this chapter and more fully in chapter 6.

The size of the contribution to line width depends upon whether the ions precess about the same axis. When similar ions precess about parallel axes there is no contribution to the second moment from exchange. Van Vleck found, however, that there is a contribution to the fourth moment so that the line becomes more peaked; this

phenomenon is known as exchange narrowing. Also, due to a resonance effect, the dipole-dipole interaction produces a larger width in this case than it does when the ions are dissimilar. The similar ions precess with the same frequency about the same axis, so that, in addition to the steady field, each produces a rotating field at the other which is of the resonant frequency. This reduces its lifetime and therefore broadens the line. Van Vleck's formula for the mean square width of a line for the case of dipole-dipole interaction between free spins is:

$$h^2(\Delta\nu^2)_{av} = \frac{3}{4} S(S+1)g^4\beta^4 \sum_{jk} \left(\frac{1 - 3\cos^2\theta}{r^3} \right)^2_{jk} + \frac{1}{3} S'(S'+1)g^2g'^2\beta^4 \sum_{jk'} \left(\frac{1 - 3\cos^2\theta}{r^3} \right)^2_{jk'}$$

where j and k are similar ions and k' are dissimilar ones. Dashed parameters refer to k' ions and undashed to ions k and j . The contribution to r.m.s. line width from similar ions is seen to be $3/2$ of that from dissimilar ions.

Isotropic exchange between dissimilar ions also contributes to the second moment of the line. Anisotropic exchange always contributes to the second moment.

As the dipole-dipole interaction falls off as the

inverse cube, and exchange either as the inverse of a higher power or as the inverse exponential, of the distance between the ions, line width from this cause may be reduced by using salts in which the paramagnetic ions are well separated. Such salts require many ions per molecule so that the paramagnetic ion is surrounded by diamagnetic ions; typical salts used are $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $\text{CoK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. Further separation of the paramagnetic ions may be achieved by diluting the paramagnetic salt with an isomorphous diamagnetic salt. Mixed crystals containing 1% of the paramagnetic ion usually exhibit lines in which this contribution to line width is negligible.

The magnetic moments of the nuclei of neighbouring diamagnetic ions will contribute to the line width. In ionic compounds the paramagnetic ion is often surrounded by waters of crystallization. The protons in these molecules produce a line width of about 6 gauss (Bleaney and Ingram, 1951)^a. (Line widths will always be quoted as the half width of the line at the half power points). The deuteron has a magnetic moment one third of that of the proton, so that if the water of crystallisation is replaced by heavy water this width is reduced to 2 gauss. In potassium chromicyanide, which crystallises without waters of crystallisation, Bowers (1952) obtained a width of 1 gauss.

Chapter 6 deals with interactions between pairs of adjacent ions. A hamiltonian can be set up by adding the spin hamiltonian for each ion together with a term to represent their interaction, and then treating the pair as a unit in which only one spin is involved in a transition.

Magnetic interaction adds to the hamiltonian a term:

$$\frac{\beta^2}{hcr^3} \left[g\bar{S} \cdot g\bar{T} - \frac{3(g\bar{S} \cdot \bar{r})(g\bar{T} \cdot \bar{r})}{r^3} \right]$$

where $\bar{S}$ and $\bar{T}$ are the two spins and $\bar{r}$ the distance between them. This is axially symmetrical about the line joining the spins and may be written:

$$aS_xT_x + \beta S_yT_y + \gamma S_zT_z$$

where z is the direction of the line joining the spins and $\alpha = \beta = -\frac{1}{2}\gamma$.

Exchange may be isotropic, adding a term $-J\bar{S} \cdot \bar{T}$, where $\bar{S}$ and $\bar{T}$ are the actual spins of the ions concerned (Van Vleck, 1947), or it may be anisotropic adding a term of the form

$$(a + j)S_xT_x + (b + j)S_yT_y + (c + j)S_zT_z$$

where it has been split into an isotropic component j and an anisotropic component a , b and c such that $a + b + c = 0$. This purely arbitrary definition of isotropic and anisotropic exchange is used, as the anisotropic exchange does not then contribute to the Curie-Weiss Δ (see Appendix 1). In many cases arguments can be advanced

to show that it is reasonable that the line joining the two spins is one of the axes of the anisotropic exchange. In this case the exchange and magnetic interactions can be combined linearly to give an interaction of the form:

$$AS_xT_x + BS_yT_y + CS_zT_z$$

where $A = (a + a + j)$, $B = (\beta + b + j)$ and $C = (\gamma + c + j)$ and z is the direction of the line joining the spins, and the x and y axes are determined by the rhombic components of the anisotropic exchange. If the anisotropic exchange has axial symmetry about the z axis the term in the hamiltonian reduces to a form:

$$\rho S_zT_z + \sigma(S_xT_x + S_yT_y)$$

In either case the values of the parameters concerned may be measurable by studying nearest neighbour lines (chapter 6), and if the size of the magnetic interaction is known it may be possible to draw conclusions about the size and nature of the exchange.

CHAPTER 2

EXPERIMENTAL DETAILS

2.1 PREPARATION OF CRYSTALS

Ions in the solid state are situated in a crystal field which often makes the spectrum anisotropic, so it is desirable to work on single crystals. Even for use at the longest wavelengths the crystals need not be bigger than a five mm. cube. Crystals of this size are usually easy to grow. All the crystals used for the work described in this thesis have been grown from aqueous solution.

Good crystals have been obtained by allowing a warm saturated solution to cool, or by evaporating a solution in a vacuum desiccator; but to obtain best results it is necessary to put a small seed crystal in a saturated solution at room temperature, and to evaporate it slowly. The evaporation may be done in a desiccator or in the open air. Good temperature control is necessary, especially if the solubility varies considerably with temperature. Crystals which are grown too rapidly are often twinned, or contain parallel growths. A twinned crystal has two or more parts whose crystallographic axes are in different directions, which would make an anisotropic spectrum very complicated to interpret. A crystal exhibiting parallel growth is one which consists of several crystals which have

grown together with parallel axes. If these axes are not quite parallel the lines in an anisotropic spectrum will be broadened to an extent which may obscure their structure.

Sometimes it is necessary to grow crystals from a very small quantity of solution or from heavy water solution (1.1). For this a special apparatus is used (diagram 2.1) which comprises: a detachable pot which contains the solution; and a tube which has a limb which can be immersed in liquid oxygen, and a tap through which the whole apparatus can be evacuated. The pot has a cross section of 1 sq. cm. and a length of 5 cm., and it has a flat bottom on which the crystal grows. It is connected to the other part of the apparatus by a vacuum tight cone and socket joint. When the other limb is put in liquid oxygen, water vapour condenses in this limb and water evaporates from the solution. The rate of diffusion from one limb to the other, and therefore the rate of evaporation from the solution, is controlled by the pressure of air in the apparatus. Crystals have been grown with and without a seed, but better results are obtained if one is used.

Two methods have been used to make heavy water solutions free from light water:- the solute has been dehydrated and dissolved in heavy water; light water crystals of the solute have been dissolved in heavy water

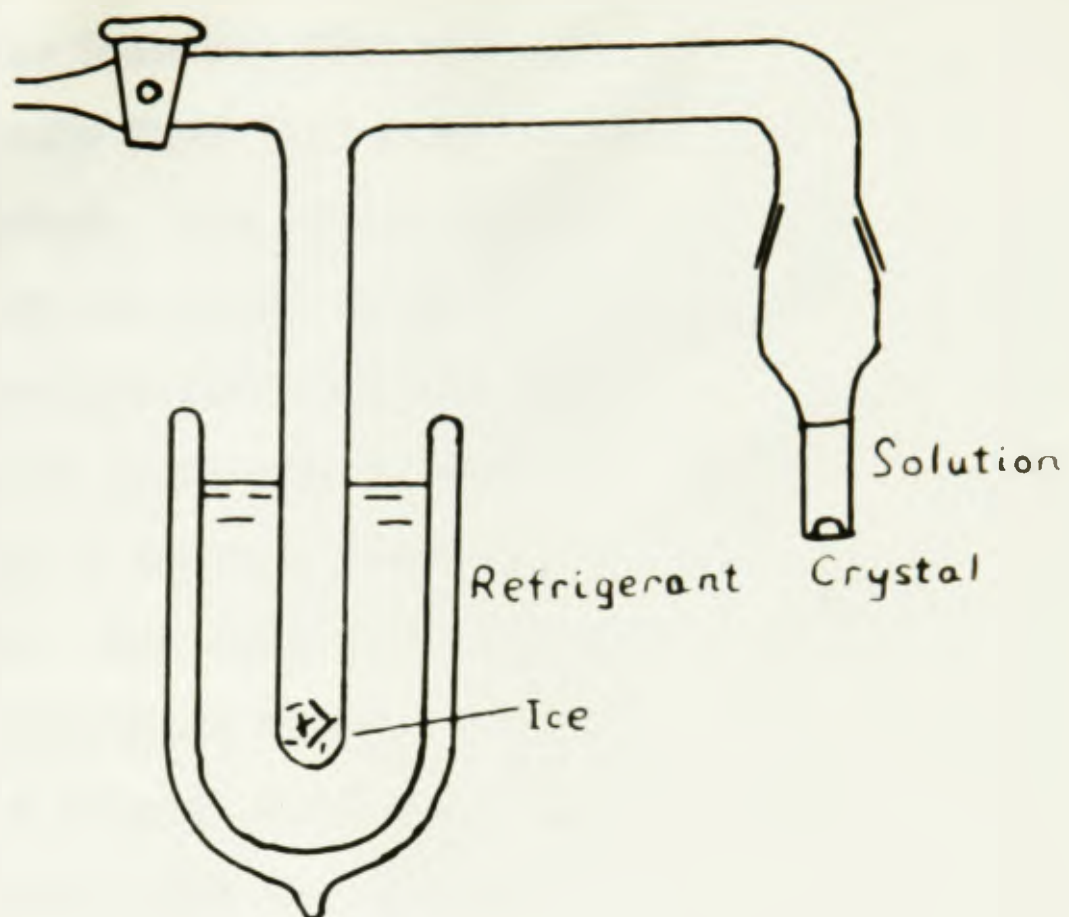


Diagram 2.1

and crystals from this solution redissolved in heavy water, and crystals from this solution dissolved in further heavy water. The latter technique gives a solution in which the heavy water is 99% pure, which is sufficient to produce deuteron linewidth.

It is usually necessary to mount the crystal in the resonator so that a certain plane is parallel to the wall of the resonator. For this to be possible the crystal must have well developed faces. When the desired face coincides with a crystal face this face is simply stuck on to the resonator with tap grease (tap grease is found to be better than Durofix, sometimes used, as it does not tend to crack the crystal when it is cooled). If the plane does not coincide with a crystal face the crystal may be ground with fine sandpaper so that it does have such a face. As this cannot be done more accurately than a few degrees a better method is to mount a well formed crystal face on a distrene wedge, which can be cut at an angle accurate to $1/4^\circ$. Unfortunately this pushes the crystal into the centre of the resonator where the r.f. magnetic field is smaller so that the sensitivity is reduced. As the reduction is only by a factor of about three this technique is usually used. The wedge material has a dielectric constant of about 2.5 which means that it considerably increases the apparent size of the cavity;

but this can be allowed for by tuning the klystron.

2.2 PRINCIPLES OF DETECTION

The method used is that developed by Bleaney (Bleaney and Stevens, 1953). The crystal is placed in a resonant cavity at a place where the r.f. magnetic field is strongest. When absorption occurs in the crystal the "Q" of the cavity is lowered, and this effect has to be detected.

The following treatment is a summary of the account in Bleaney and Stevens (1953). The power absorbed by the sample in an oscillating magnetic field $H_1 \cos \omega t$ is $\frac{1}{2} \omega \chi'' H_1^2$ where χ'' is the imaginary part of the susceptibility. The power absorbed in the resonant cavity may be written:

$$\frac{1}{Q_0} \omega \frac{H_1^2}{8\pi} V$$

where Q_0 is the quality factor of the unloaded cavity, and V is the effective volume of the cavity, given by

$\int H^2 dv = H_1^2 V$. The fractional change in resistance of the cavity when absorption takes place is the ratio of the power absorbed in the sample to that absorbed in the unloaded cavity or $4\pi \chi'' Q_0 / V$

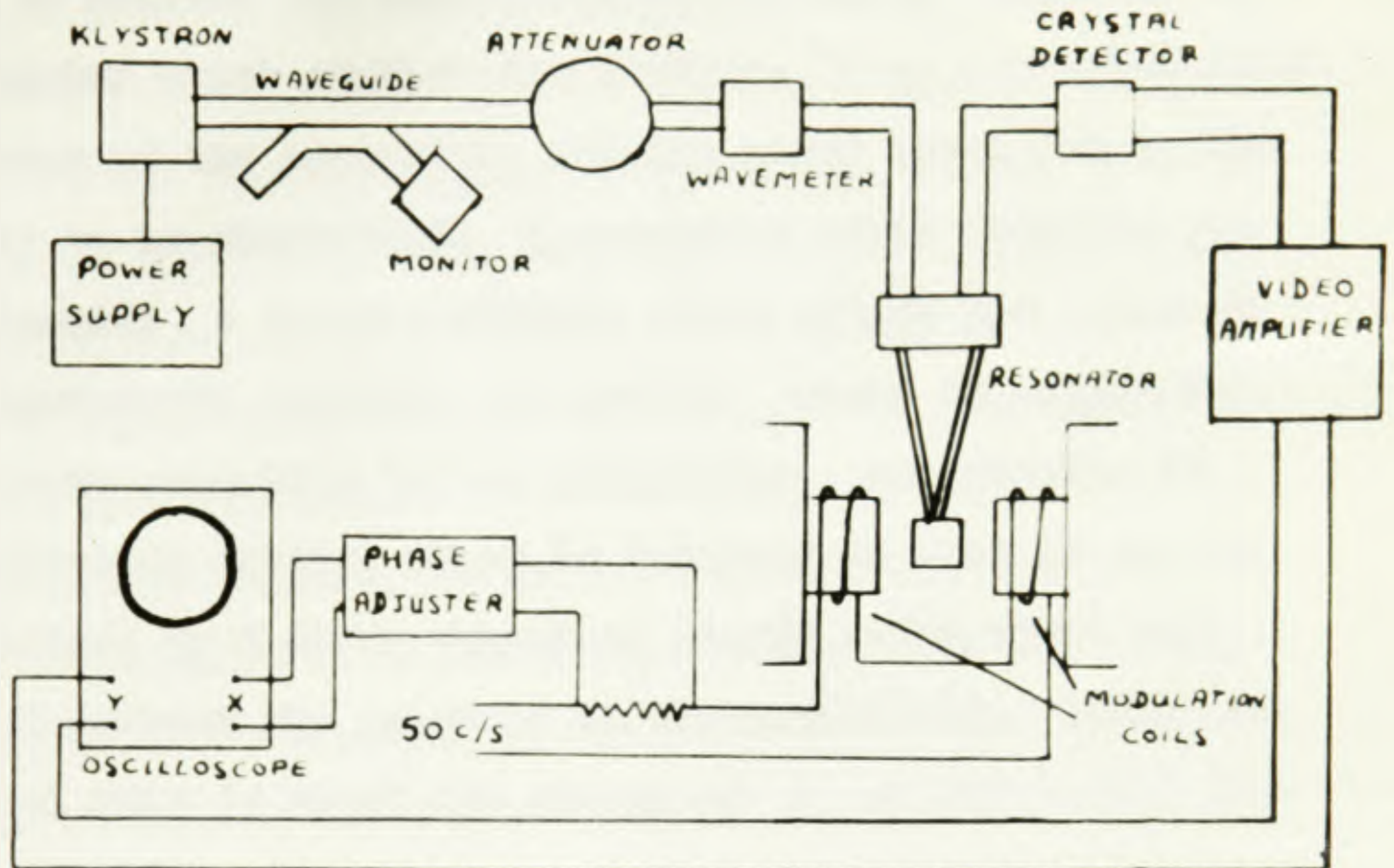
If the cavity is represented by a tuned circuit, coupled to an oscillator of constant power by a mutual

inductance, it can be shown that the maximum sensitivity at the receiver is obtained when the loaded Q of the cavity is half of the unloaded Q . If a receiver with noise factor N and bandwidth df is used the minimum signal which can be detected corresponds to a susceptibility:

$$\chi''_{\min} = \frac{V}{\pi Q_0} \left(\frac{N k T df}{P} \right)^{1/2}$$

where P is the input power from the oscillator, k is the Boltzmann constant and T the absolute temperature. With a 3 cm. cavity $Q_0 \sim 5000$, $V \sim 3 \text{ cm}^3$, say $N = 10$ and $P = 40$ milliwatts the value of χ'' is 10^{-13} . For an ion with $S = 1/2$, $g = 2$ and gram-ionic mass 100, if the line width as a fraction of frequency is 10^{-3} at 20°K , the minimum quantity which is theoretically detectable is about 10^{-12} grammes. The equations quoted above show which factors influence the sensitivity of the method of detection.

The apparatus used at all wavelengths is essentially the same; the slight differences will be described in the more detailed sections. The block diagram 2.2 illustrates the arrangement of this apparatus. A reflex klystron oscillator generates microwave power which is fed through a rectangular H_{01} waveguide to various components: a directive feed which extracts about 1% of the power to be rectified by a crystal detector and



Video detection apparatus

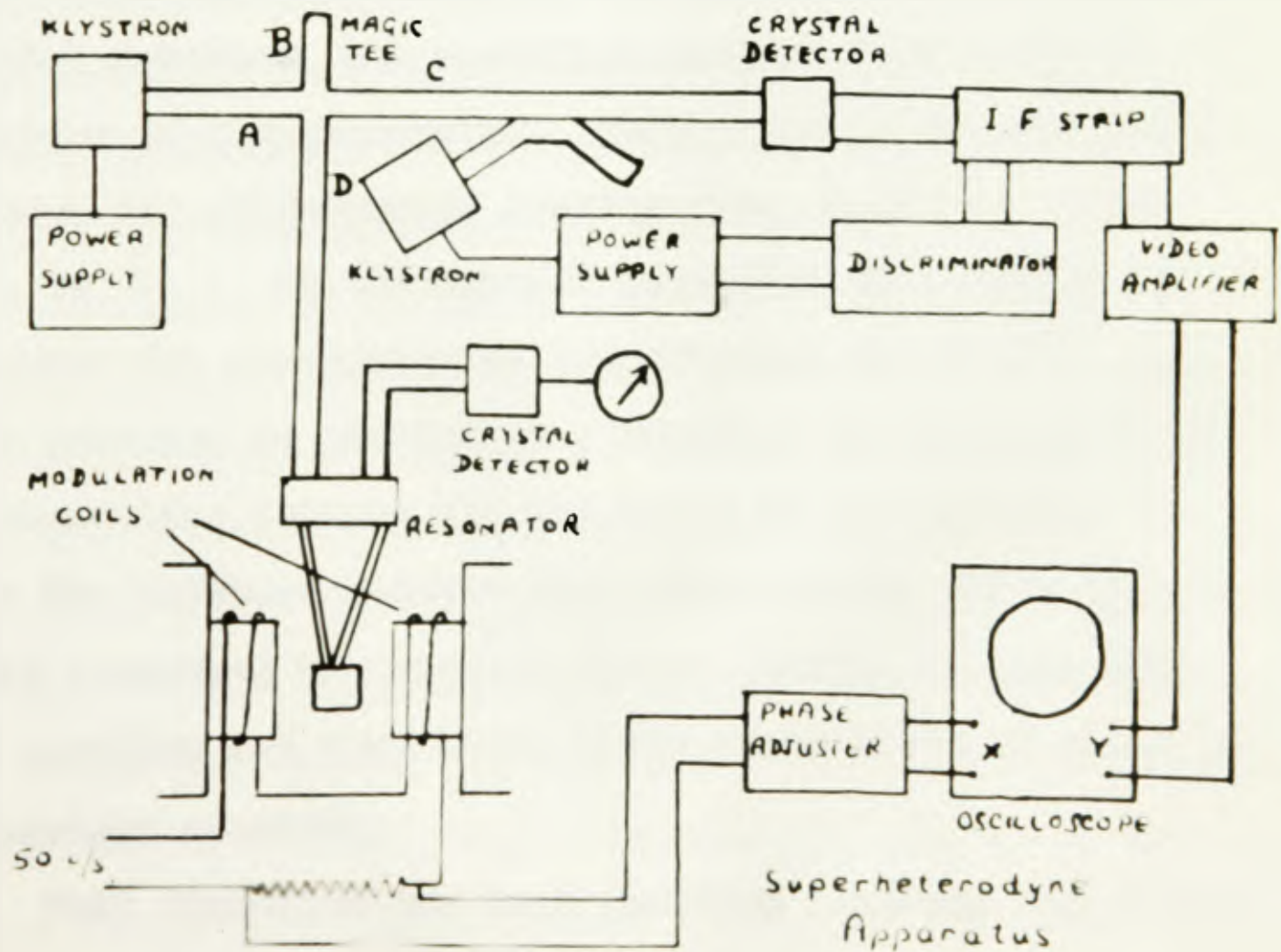


Diagram 2.2

used to monitor the oscillator's output; a variable attenuator which enables the klystron to be decoupled from the rest of the apparatus, and the power level fed to the cavity to be controlled; a wavemeter which measures the wavelength; a line-lengthener which alters the phase of the microwaves reaching the cavity; stubs to adjust the impedance presented to the oscillator; and finally to the resonant cavity, which is designed so that it can be surrounded by a dewar vessel of liquid refrigerant and placed between the poles of an electro-magnet. There are several ways in which the change of Q of the cavity may be detected.

Power may be coupled out of the cavity and fed to a crystal detector, the rectified current from which is measured by a galvanometer. Absorption in the resonator reduces the galvanometer reading from its normal level

θ_0 to θ . As the crystal rectifier is a square law detector the absorption is proportional to $(\theta_0/\theta)^{1/2} - 1$. This quantity is plotted as a function of magnetic field. As absorption detunes the resonator it is necessary to tune the klystron between each measurement. This method, first described by Bagguley et al. (1948), is only used for plotting out very broad lines whose width or shape is accurately required.

This technique has been modified (Bleaney and Ingram,

1949). A small 50 c/s. modulation is superimposed on the magnetic field, so that any absorption which occurs within the range of field swept, is swept through twice in each $1/50$ th of a second. Thus the signal reaching the detector crystal is modulated at an audio frequency, and may be amplified by an amplifier, so gaining much greater sensitivity. The amplified signal is fed to the Y-plates of an oscilloscope whose X-plates are fed with the voltage developed across a resistance in series with the current supplying the sinusoidal field. A conventional phase-shift network in the X-plate supply enables the spectrum to be displayed as a curve of absorption against magnetic field which is nearly linear in field (linear to about 2%). This method is both more sensitive and quicker than the galvanometer method and is the one which has been used for most of the work described in this thesis.

The signal from the detector crystal is fed by coaxial cable to a step up transformer which matches it to the noise resistance of the following amplifier. This provides the detector crystal with a low d.c. impedance while the a.c. impedance remains high. This reduces the d.c. bias on the detector and thereby reduces the noise produced in it, the actual gain in signal/noise ratio is about five. The first valve of the amplifier is a low noise, low hum, pentode; both this and the

transformer are shielded from stray magnetic fields by mu-metal screens. The remainder of the amplifier uses conventional R-C coupling. This amplifier suffers from the disadvantage that there is a phase shift of the low frequency components of the signal relative to the high frequency ones, the former leading the latter in phase. This causes a depression of the base line after the signal, the amount of depression depending on the length of the signal. This is troublesome when an accurate line shape is required or when looking for small lines in the presence of large ones.

Mr. L.J. Arundel has designed an amplifier which is free from this disadvantage. The ideal is an amplifier which has zero phase shift from 50 c/s. up to 5 Kc/s. To achieve this by making the time constants of the circuit sufficiently long is impracticable. There are two other possible ways: to have a few stages each compensated individually, or to have many stages with heavy negative feed back suitably adjusted. The latter technique is used in two separate two stage amplifiers in cascade (circuit diagram 2.3). A cathode follower is used in the first feed back line to reduce hum pick up in the first valve; the cathode follower amplifies the feed back signal so that it can be fed across a smaller cathode resistor, so that only a small fraction of the cathode resistor need be not

A.F. WAVEFORM AMPLIFIER

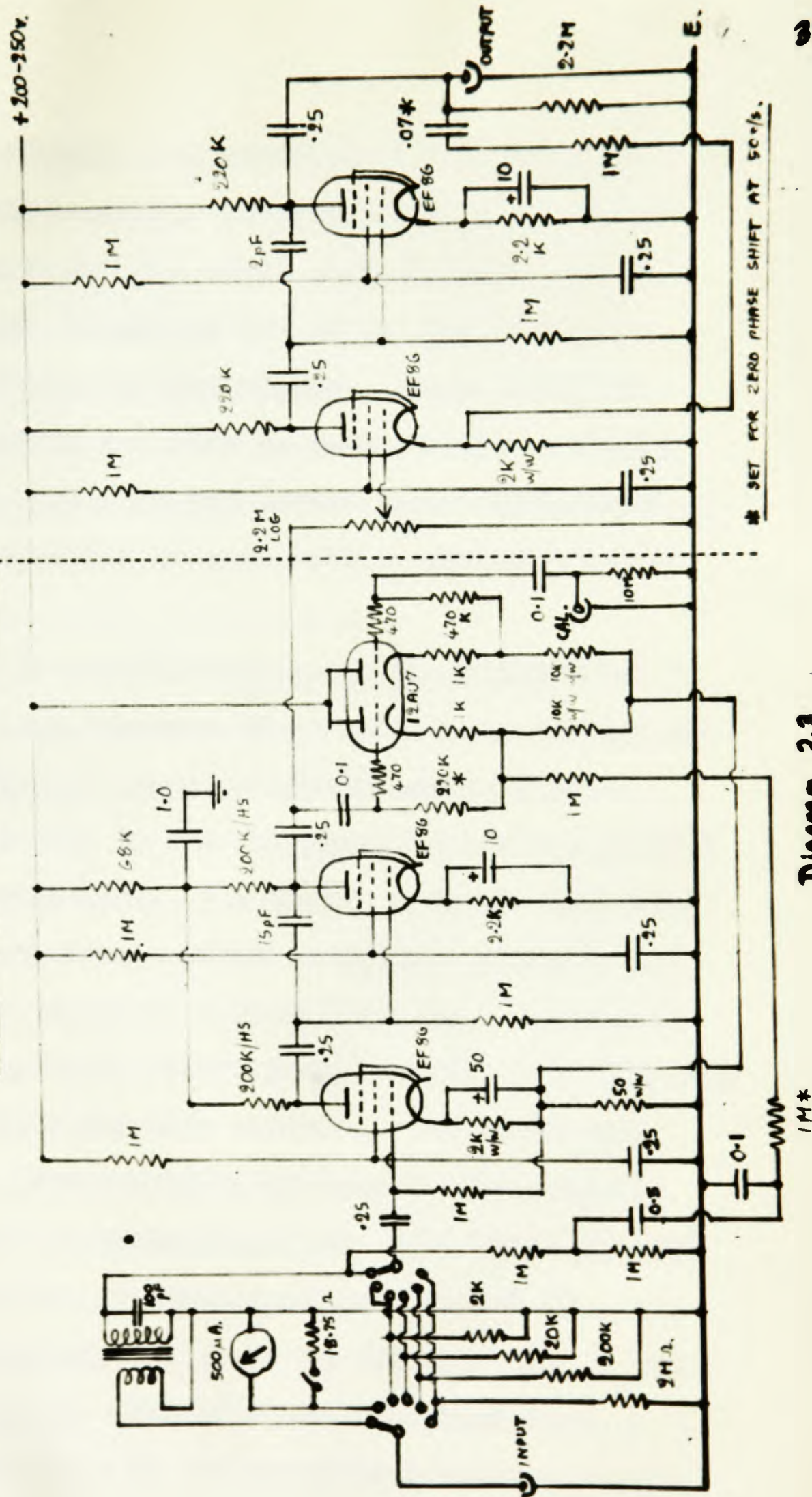


Diagram 2.3

decoupled. The starred components can be adjusted so that phase shift in the amplifier is zero at 50 c/s. Under these conditions there is a small rise in gain at the lowest frequencies (about 0.1 db. at 50 c/s.) but this has negligible effect on line shapes. Phase shift in the input transformer can also be reduced by a suitable feedback network, but when the lowest phase distortion is desired the amplifier is used with a resistive input load.

An increase in signal/noise ratio is obtained by detecting at 45 Mc/s. instead of at audio frequencies, as the noise in silicon-tungsten detector crystals is inversely proportional to the frequency at low frequencies (e.g. Torrey and Whitmer). The signal from the resonator is mixed with power from a local oscillator tuned to a frequency 45 Mc/s. from the main oscillator. The signal is amplified at 45 Mc/s. before video detection. Following the usual convention for this method of detection the reflected signal from a critically coupled resonator is used, rather than the transmitted one. The block diagram (2.2) illustrates the principles of this method of detection. Main oscillator power is fed into arm A of the hybrid ring and is divided equally between arms B and D. That reflected in D is divided between A, in which it is attenuated before returning to the valve and

so pulls it very little, and C, where it is mixed with the local oscillator power. The resonator alone is not perfectly reflectionless so that matching stubs are used to improve the match. If the frequency of the local oscillator is to be controlled electronically a small amount of reflected power is necessary to keep the local oscillator locked on frequency; the noise level increases as this quantity of reflected power is increased as it introduces more main oscillator noise.

A circuit diagram of an automatic frequency control system which is used is given (diagram 2.4). The detected power is fed to a modified ^{Foster - Seeley} ~~Seeley-Jordan~~ discriminator tuned to 45 Mc/s. The out of balance component is fed to the reflector of the local oscillator which pulls it back on frequency when it tends to wander. Automatic gain control keeps the signal level constant when the input power to the system is reduced as the match of the resonator is improved.

This system gives a factor of 10 improvement in signal/noise over audio frequency detection at room temperature and less at 90°K, probably because noise due to microphonics becomes more serious when the Q of the resonator is greater.

As the noise introduced by the amplifier is proportional to the square root of its bandwidth an improvement in

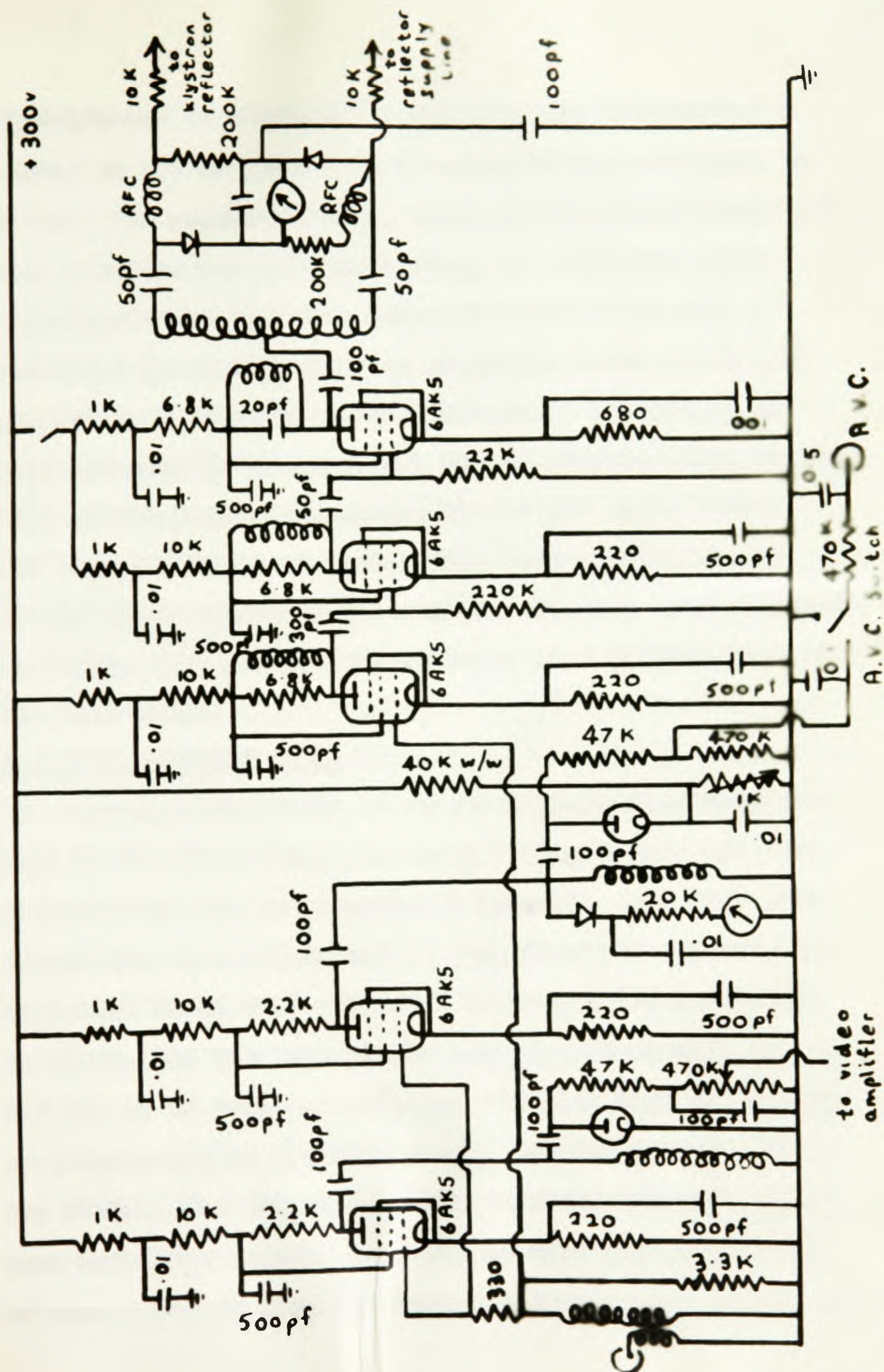


Diagram 24

signal/noise is obtained by reducing its bandwidth. A factor of 100 is gained by reducing it from 20 Kc/s. to 2 c/s. The magnetic field, which must be very steady for this purpose, has a 80 c/s. sweep of about one gauss superimposed on it. The detected signal from the resonator is amplified by an amplifier tuned to 80 c/s. and fed to a phase sensitive detector. The output of this detector is proportional to the average slope of the part of the spectrum included in the one gauss sweep. The magnetic field is slowly increased and the output of the phase sensitive detector is recorded as a function of field, thus giving a curve which is a differential of the line shape.

2.3 THE MAGNETIC FIELD

The magnetic field is supplied by an electro-magnet made by Tickford Ltd.; it has a U-shaped yoke and pole pieces which may be adjusted or removed. For work with X-band the pole pieces are 10 cms. diameter and are separated by 42 mm.; for work at K-band the separation is 24 mm. and the pole pieces are tapered from 10 cm. to 6.3 cm. at an angle of 45° , and the flat face has a small projecting rim at the edge to improve the homogeneity of the field. The two coils which surround the pole pieces each have 3000 turns. They can be used carrying up to 10 amps., but as they get very hot they cannot be run at

this level for very long; at this current the K-band pole pieces give 12.5 Kgauss. and the X-band ones give 7.5 Kgauss. The iron begins to saturate well below these fields so that the calibration curves of field against current are far from linear. With no pole pieces the field is linear with current with a small remanence of 20 gauss and reaching 1.5 Kgauss. at 10 amps.

The power pack which supplies the magnet operates by rectifying the mains. Mains power is fed through an isolating transformer to a variac which controls the field. The output of the variac is rectified by a selenium rectifier bridge, the output of which is fed to the magnet coils through a choke-condenser smoothing network. The high inductance of the magnet coils greatly improves the smoothing. The current to the magnet is read on an Ernest Turner sub-standard meter.

Two small coils of 400 turns, to provide the alternating sweeping field, are bolted to the main coils. They are fed with 50 c/s. currents up to 2 amps. from a variac: they give sweeps of up to 400 gauss from peak to peak.

For some low field work a solenoid has been used. This has 2000 turns and will carry up to 15 amps giving up to 1.4 Kgauss. in a cylindrical space 22 cms. long and 5 cms. in diameter. The sweep is superimposed on the

d.c. current by means of a 24 volt transformer whose secondary is put in series with the d.c. supply.

MEASUREMENT OF MAGNETIC FIELD

The field is calibrated using proton resonance, the principles of which are discussed in Bloembergen (1948). A coil which is situated in the field is connected by a length of rigid coaxial line to an oscillator head which contains a 6AK5 pentode which acts both as the oscillator and as a mixer, to mix in a calibration signal from a BC221 crystal calibrated variable frequency oscillator. The frequency of the resonance oscillator is adjusted by means of a variable condenser in the oscillator head, which together with the coil forms the oscillator's tuned circuit, until proton resonance is detected by a fall in the Q of the tuned circuit. As the field is swept the signal is modulated at 50 c/s., and may be amplified and displayed on the oscilloscope as a small pip, whose intensity and sharpness improve as the coil is moved to a more homogeneous part of the field. The frequency of the oscillator is measured by adjusting the BC221 to give zero beat; the field H is related to the frequency f by:

$$H = 234.86 \times 10^{-6} f$$

The coils are of two types. One comprises a coil, 1/4" diameter, wound in a distrene former, containing liquid paraffin as a proton source, the whole of which is

surrounded by a screening can. This type is for use at room temperature. The other type is to be used at low temperatures immersed in the refrigerant, and is used inside a metal tube which acts as its screening can. The distrene formers are similar to the other type but they are hollow, so that at 20°K liquid hydrogen is the source of protons; for work at 90°K a piece of distrene suffices. A special coil for measuring fields down to 500 gauss has been built. This uses liquid hydrogen as its proton source, and, as it has to be bigger than the other coils, it can only be used in a dewar vessel of 28 mm. internal diameter, which means that it can only be used for calibrating a field in terms of current. With the X-band resonator the low temperature type of coil is used, and with K-band it is possible to place the p.r. and the proton resonance apparatus in the field side by side.

A plot of field against current is made; the magnetic field is always turned up to a maximum to saturate it, and then turned down to zero before a measurement is made, to ensure that the results are repeatable. This calibration is used for all but the most accurate work as it is reliable to about 1/3%. For more accurate measurement of the position of a p.r. line it is necessary to display both the proton pip and the p.r.

line simultaneously, and to adjust the proton pip to coincide with the p.r. line. This can be done either by using a double beam oscilloscope, one beam for each signal; or by feeding the p.r. signal on to the grid, and the proton resonance signal on to the screen, of the first valve of the amplifier. The former method is more satisfactory when both signals are very weak.

The sweep is calibrated by adjusting the field so that a narrow p.r. line is at one end of the trace and adjusting the proton pip to be at the other end. The field at which the proton signal occurs is measured and then the field at which the p.r. line occurs, and the difference is the sweep.

A useful method of quick calibration is to put a little diphenyl trinitro-phenyl-hydrazyl in the resonator. This is an organic free radical giving a very sharp line with a g-value of 2.0038 ± 0.0002 . (Holden et al. (1950) and Townes and Turkevitch (1950)). g-values near 2 can be measured very accurately by measuring the distance in field from the p.r. signal to this line with a calibrated sweep.

2.4 AUXILIARY ELECTRONIC EQUIPMENT

The Calibrator: (Scovill, 1951). In this apparatus a short pulse is obtained from the 50 c/s. mains by squaring the waveform, differentiating the square wave

and clipping it. The phase of the pulse is adjusted by a standard phase shift network which precedes the device. The pulse is fed to a potentiometer so that a fraction of it, calibrated to 1%, may be fed on to the screen of the first valve of the amplifier. This gives a signal which can be adjusted to be the same height as the p.r. signal. Thus the relative heights of several p.r. signals may be compared.

The Clipper. This device is used when observing small lines in the presence of large ones which saturate the amplifiers of the oscilloscope. The clipper enables any amount of the top of a large line to be clipped off so that saturation can be avoided.

Photography. It is sometimes desirable to photograph a spectrum. For this purpose a Cossor Oscilloscope with a camera is used. It is often convenient to use an electronic switch which blacks out the signal for alternate 1/100th sec. so that only one trace appears on the screen.

2.5 TEMPERATURE CONTROL

The resonator is usually surrounded by a dewar vessel containing refrigerant. The most used refrigerants are liquid oxygen (90°K), liquid hydrogen (20°K) and solid CO_2 (195°K); it is, however, possible to obtain temperatures down to 13°K by pumping out the space over the liquid hydrogen to a few mm. Hg. pressure.

2.6 DETAILS OF MICROWAVE APPARATUS

1.25 CM. APPARATUS Q-BAND

A high voltage reflex klystron 2K33 is used as a source of microwave power. Typical operating conditions are: anode at earth, cathode - 1800 volts, grid - 1900 volts, reflector - 2000 volts, current 10 milliamps. The voltages are supplied by an electronically stabilised power pack which has a ripple of less than 10 millivolts in 2000 volts. A small diode between the reflector and the cathode prevents the reflector from going positive with respect to the cathode. The klystron heater is supplied by lead accumulators, because when it is supplied by a.c. it produces hum on the output of the valve. There is provision for a small 50 c/s. voltage to be superimposed on the reflector voltage through a condenser. This causes the output of the klystron to vary sinusoidally over a small range of frequencies. This facilitates tuning the cavity as its whole mode can be swept through and its tuning curve displayed on the oscilloscope with a sinusoidal time base.

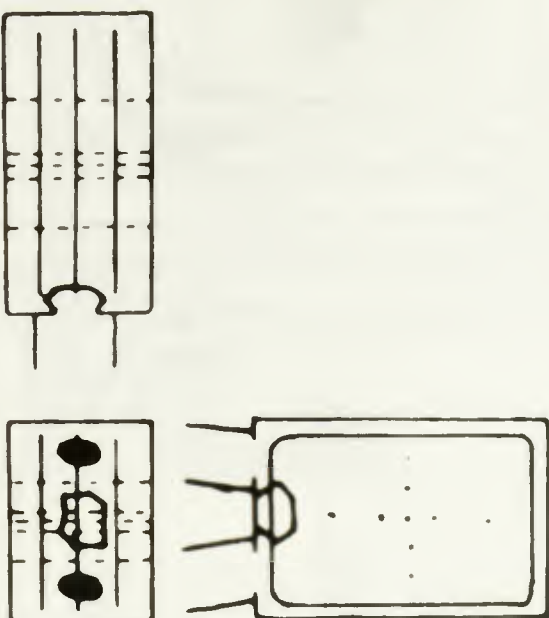
The wavemeter is an H_{01} cavity type with a 3 cm. barrel coupled to the waveguide so as to reduce absorption by it at other modes. (Bleaney, Loubater and Penrose, 1947). It may be used either by detecting the reduction of power to the resonator, or by a small amount of power coupled out

of it when it is on tune. The adjustable plunger is screwed out to two or three adjacent positions of resonance and the distance between each of them is a half wavelength in the wavemeter.

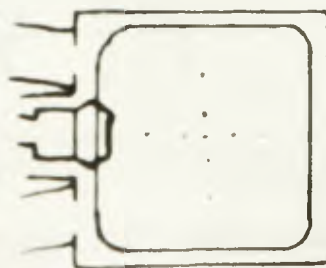
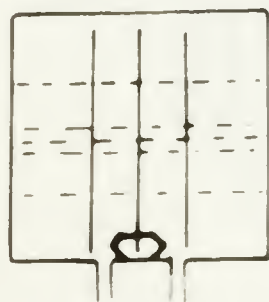
The crystal detectors used are 1N26 shielded silicon-tungsten crystal rectifiers which are mounted coupled to a probe across the waveguide. Best results are obtained when they give a rectified current of between 200 and 1000 microamps.

Two types of resonant cavity have been used, one operating on the H_{111} cylindrical mode and one on the H_{011} rectangular mode.

The first type has been described by Scovil (1951). The distribution of r.f. field in it is shown in diagram 2.5, which shows that for maximum filling factor the sample has to be mounted at the centre of one end of the resonator; the diagram also shows how power is coupled in and out of the resonator through two symmetrically placed holes in the top of the cavity, which couple to the end of two waveguides. The coupling holes should define the direction of the r.f. field, but the sample often pulls it into a different direction so that the angle between the d.c. and r.f. fields is not accurately known. Diagram 2.6 shows a sketch of the resonator. The waveguides which feed the cavity are made of german silver,



H₀₁₁ rectangular mode
used at 125 and 3 cm



H₁₁₁ cylindrical mode
used at 125 cm

coupling holes, blacked in

— lines of magnetic flux
- - - lines of electric flux

Diagram 2.5

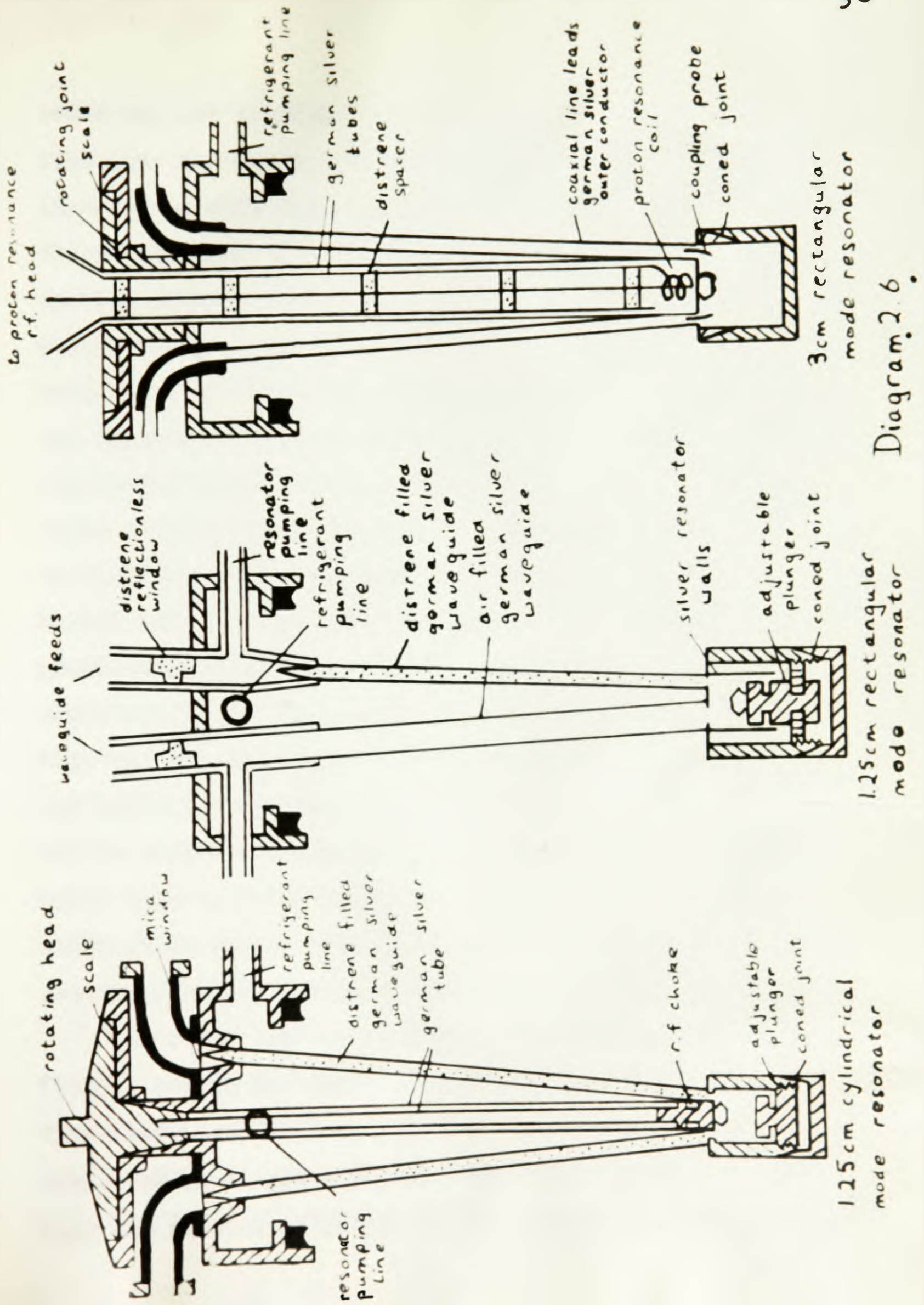


Diagram 2.6.

which has low thermal conductivity, to reduce the heat flow into the resonator; they are also filled with distrene so that they are smaller than if they were air filled, and thus enable the apparatus to be fitted in the gap between the pole pieces of the magnet. These waveguides are secured at their upper ends to a brass resonator head which also has a housing for the top of the dewar vessel which surrounds the whole apparatus. The sample is mounted on a small brass disc which fits flush with the top wall of the resonator through a hole in this top wall. The disc is mounted on a german silver tube the other end of which is attached to a graduated rotatable head, which fits into the brass headpiece of the apparatus making a vacuum tight joint. This enables the crystal to be rotated in a plane to any desired direction. The bottom of the resonator may be screwed in and out for coarse tuning adjustments, and a thin slightly coned cap fits over the bottom to which it is sealed with glycerine, which freezes without cracking, making a vacuum tight joint at low temperatures.

The other type of resonator is described by Bowers (1953), and is for use with a rotatable magnet. The distribution of r.f. fields and a sketch of the resonator are given in diagrams 2.5 and 2.6 respectively. In this case the crystal is placed on the bottom of the resonator

and it cannot pull the polarisation of the r.f. field in it, as this is rigidly defined by the rectangular shape. As the resonator was designed for detection using the reflected wave the input waveguide is air filled and is critically coupled to the cavity; a low reflection window in this guide makes a vacuum seal for low temperature work. The other details of the design are similar to the other type of resonator and will therefore not be discussed.

As the absorption is proportional to the sine of the angle between the d.c. and r.f. magnetic fields, the magnet can only usefully be rotated to an orientation about 60° from the place where they are perpendicular, as beyond this the spectrum becomes too faint. The former resonator has the advantage that the crystal may be rotated through 360° with unvarying signal intensity; however it often has to be retuned on rotation and the latter type does not have to be retuned.

6 MM. APPARATUS Q-BAND

A high voltage reflex klystron type VX357 was borrowed from R.R.E., Malvern. Typical operating conditions are: anode at earth, cathode - 2400 volts, grid - 2500 volts, reflector - 2800 volts, current 15 milliamps. The same power supply is used as for K-band. Usually the valve is cooled by blowing air over it; however as this introduced

a good deal of microphonics it is run for short periods without being cooled for very precise work. The valve is very sensitive to the impedance presented to it so it has to be used with attenuation to decouple it from the other components and matching stubs to obtain optimum output.

An H01 cavity wavemeter of 14 mm. diameter is used. The main detector crystal is of the type which is placed across the waveguide, which is mounted in a holder made by Hilger and Watts after a design by R.R.E., Malvern. K-band crystals are used wherever other detectors are necessary, such as for monitoring.

For the few experiments done at Q-band the K-band resonators were found to be perfectly satisfactory. A good p.r. signal is obtained from the mode which gives most current at the detector crystal, so this is used; probably for this mode the resonator is a whole wavelength long. No attempt is made to match the Q-band waveguide to the K-band resonator feeds as it does not appear to be necessary.

3 CM. APPARATUS K-BAND

For this wavelength high voltage reflex klystrons, type CV129 are used with the same high voltage power pack as previously described. Typical operating conditions are: anode at earth, cathode -1300 volts, grid - 1400

volts, reflector - 1500 volts, current 8 milliamps.

Two types of wavemeter have been used, and H₀₁ cavity wavemeter and a coaxial wavemeter, the latter having the advantage that it gives the wavelength in air directly. The VX4077 silicon-tungsten crystal rectifier is used in a holder similar to the K-band one. These crystals work best at about 2 milliamps. rectified current.

The resonator used is described by Bowers (1953). It is a rectangular H₀₁₁ type and has a tube immediately above it for a proton resonance coil (2.3). The distribution of r.f. fields and a sketch of the resonator are shown in diagrams 2.5 and 2.6 respectively. The power is fed to the cavity by coaxial lines with probe coupling, the outer conductors being german silver tube to reduce heat inflow, and inside each is the dielectric and centre conductor of Uniradio 32 coaxial cable. The resonator is made in two halves, the join being half way along its length. The outer wall of the upper half is cylindrical and slightly coned so that the bottom, which has a matching cone, fits on to it making a vacuum tight seal when the cone is lubricated with glycerine. The crystal may be placed on the top or bottom of the resonator, but for work with proton resonance the top is better, so that the sample and the proton coil are as nearly as possible in the same field. The coaxial lines from the resonator are

connected to the waveguide by short lengths of flexible coaxial line, which couple into the waveguide with probes matched by backing plungers. The whole unit is mounted so that it can be rotated about a vertical axis, and like the 1.25 cm. H_{011} resonator it only gives a spectrum of suitable intensity over an angle of 120° .

OTHER WAVELENGTHS

Some measurements have been made at wavelengths between 4.5 and 10 cm using an apparatus borrowed from Mr. P.M. Llewellyn. The valves are of the type which use an externally tunable resonator to make them easily tunable over a large range. For the shorter wavelengths a 3 cm resonator was loaded by filling it with benzene and for the longer ones a series of coaxial line resonators were used. The wavelength was measured with a coaxial line wavemeter.

CHAPTER 3

COMPLEX CYANIDES

3.1 INTRODUCTION

Bowers (1952) has studied p.r. in $K_3Cr(CN)_6$ diluted with isomorphous diamagnetic $K_3Co(CN)_6$ and has obtained very narrow lines (1 gauss width) because the crystals contain no waters of crystallisation. Although the other group of cyanides, isomorphous with $K_4Fe(CN)_6 \cdot 3H_2O$, has waters of crystallisation, the Fe^{++} ion is surrounded by CN groups so that the water molecules, which are outside these CN groups, contribute little to the line width. Because narrow lines were expected $K_4V(CN)_6 \cdot 3H_2O$ was studied to see if it was a suitable substance for measuring the nuclear spin of ^{50}V (see chapter 4). Other members of this isomorphous group were studied because of the interest in the spectra of the XY_6 complexes.

Except for the ferrous complex, which is diamagnetic and is therefore used as a dilutant for the other compounds, the divalent complexes are very unstable. They oxidise in acid solution, and even in water if it contains dissolved air. For this reason they have to be prepared and kept in an atmosphere of carbon dioxide, and in order to grow crystals they have to be dissolved in air free water with excess KCN, and the solution evaporated rapidly in a vacuum desiccator in which the residual gas is inert. It was not

possible to grow crystals of the concentrated salts as the oxidation was so rapid. Even diluted with the ferrous salt, so much of the paramagnetic salt oxidised that it was impossible to control or know the concentration of the paramagnetic ion. As the crystals are so difficult to prepare only the ions with Kramers degeneracy have been studied as they are more likely to exhibit resonance. These are V^{++} ($3d^3$) and Mn^{++} ($3d^5$); no $3d^1$ complex exists.

3.2 CRYSTALLOGRAPHY

The complex cyanides of form $M'_4M''(CN)_6 \cdot 3H_2O$, where M' is a monovalent cation which can be K^+ and M'' is a divalent cation V^{++} , Cr^{++} , Mn^{++} or Fe^{++} , form an isomorphous series.

The crystallography of this series is given by Groth (1906) and in Structure Reports (1947-8). There are two types of crystal; one is monoclinic, pseudo tetragonal, with lattice constants a and $c = 9.34\text{\AA}$, $b = 16.86\text{\AA}$ and $\beta = 90^\circ \pm 5'$, having four ions in the unit cell and space group C_{2h}^6 ; the other is tetragonal with lattice constants $a = 37\text{\AA}$ and $c = 33.69\text{\AA}$, having eight ions in the unit cell and space group C_{4h}^6 . In both types the M'' ion is surrounded by an almost regular octahedron of CN groups, two of which point along the b axis and the other four of which are in the ac -plane pointing in directions 18° to the a and c

axes. In the *ac*-plane there is a layer structure formed by the M'' ions with their four CN groups and the M' ions; in the tetragonal type alternate layers are turned through 90° , thus the unit cell is almost twice the size as for the monoclinic type. The monoclinic type shows a tendency to twin in the *ac*-plane one part of the crystal being rotated through 90° with respect to the other part. The crystals obtained which are not twinned exhibit two magnetically distinct ions in the unit cell while those which are obviously twinned have four. The crystals grown must therefore be of the monoclinic variety. The tendency to twinning is accentuated so much by the fact that crystals have to be grown in a few hours that few untwinned crystals have been grown. Most of the work described here has been done on the untwinned crystals obtained.

The crystals grow in flat rectangular plates parallel to the *ac*-plane, thus having well developed 010 faces. The other principle faces are the 110 and 011 faces which form the edges of the plates, so that there is no way of distinguishing between the *a* and *c* axes by visual inspection.

Powell and Bartindale (1945) measured the Fe-C distance as 1.85Å and the C-H distance as 1.18Å, they also found that the Fe-C-H bonds were linear.

3.3 POTASSIUM VANADOCYANIDE

The free vanadous ion ($3d^3$) is in a ${}^4F_{3/2}$ state. In ionic compounds the cubic component of the crystal field splits the orbital term into a singlet, which is lowest, and two triplets, the lowest of which is $\sim 10^4 \text{ cm}^{-1}$ above the singlet. The lowest orbital level is split into two spin doublets by the components of the crystal field lower than cubic. This is also the case for the isoelectronic Cr^{+++} ion. In the KV_6 complex the vanadous ion is also expected to be in a pseudo S state with $S = 3/2$. In this case also the lowest level is split into two spin doublets by the interaction with the upper levels through spin-orbit coupling. Thus the situation in the complex salt is very similar to that in the ionic one. As the crystal field leaves an orbital singlet lowest and well separated from other orbital levels the g-value is expected to be close to 2 and isotropic, so that the fine structure should be interpreted using a hamiltonian:

$$\mathcal{H} = g\beta\bar{H}\cdot\bar{S} + D\left[S_z^2 - \frac{1}{3}S(S+1)\right] + E(S_x^2 + S_y^2)$$

As in $\text{V}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Bleaney and Ingram^{and Scovil} 1951)^b and in $\text{K}_3\text{Cr}(\text{CN})_6$ a hyperfine structure is observed. The electron distribution in the ground state produces no magnetic field at the nucleus, so that this hyperfine structure is explained by configurational interaction (chapter 1.1) which gives

rise to an isotropic h.f.s. adding a term $A\bar{S}\cdot\bar{I}$ to the hamiltonian.

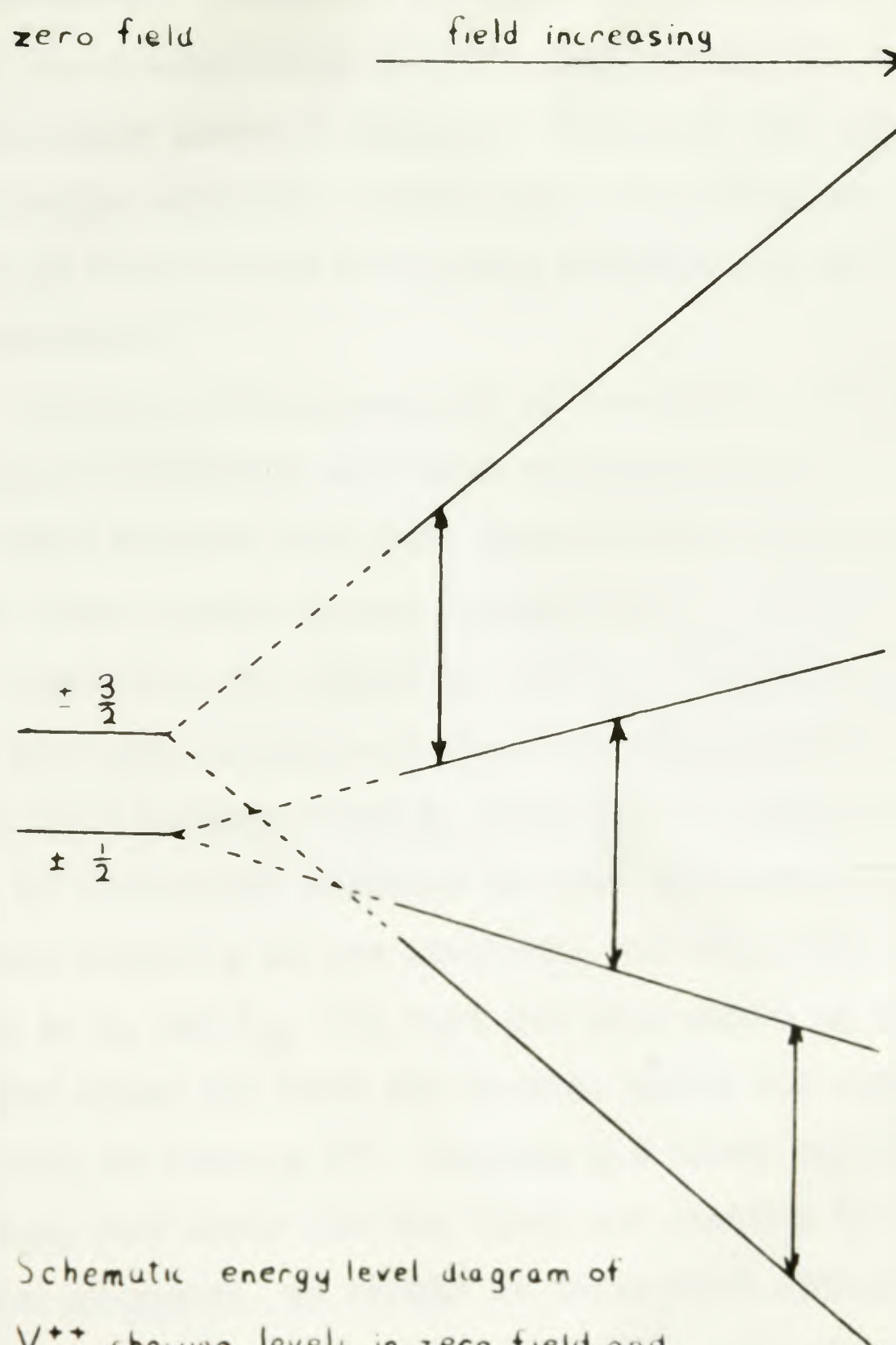
FINE STRUCTURE

Diagram 3.1 shows the energy levels in zero field and their variation with field at high fields; it also shows that there are three transitions. The technique used for investigating the fine structure is similar to that described by Bleaney et al (1949). As the magnetic field is varied from being parallel to one magnetic axis to being parallel to another the $M = \pm 3/2$ to $\pm 1/2$ lines move considerably, their separations having extreme values along the magnetic axes. If second order effects are neglected and the separation of these lines along the three axes x, y and z are X, Y and Z the separation along any line l,m,n will be

$$\Delta = Xl^2 + Ym^2 + Zn^2$$

The $M = 1/2$ to $-1/2$ line moves only a little due to second order effects when the angular orientation of the magnetic field is altered.

To find the position of the magnetic axes the spectrum which is observed at 90°K is plotted out as a function of angle in the ac-plane, as in this plane the spectra of the two ions are coincident. In this plane the two mutually perpendicular directions where the outer ($M = \pm 3/2$ to $\pm 1/2$) lines reach extremes were found to be at $45^\circ \pm 3^\circ$ to the



Schematic energy level diagram of V^{++} showing levels in zero field and high fields and the allowed transitions between them.

Diagram 3.1

crystal axes. These two directions are called K_1 and K_2 axes, the former being the one along which the separation of the outer lines is largest. There is also fortuitously a direction where all three lines are collapsed, a fact which is very useful for making measurements on b.f.s. separations.

There is little movement of the lines in the K_2b -plane (various directions are shown in diagram 3.2). In the K_1b -plane however both ions show maximum separations of the outer lines nearly midway between the K_1 and b axes, these two directions are called K_4 and K_5 . Investigation in the K_4K_2 and K_5K_2 planes show that the separation of the outer lines is a maximum along K_4 and K_5 and a minimum along K_2 . This is sufficient evidence to show that both ions have an axis along K_2 in the ac -plane, and the other two axes close to K_4 and K_5 . In fact one axis makes an angle 43° and the other 47° with the b -axis, where the angles are accurate to about $\pm 3^\circ$. Diagram 3.2 shows the axes for only one ion, but those for the other are derived by reflection in the ac -plane; it should be noted that although the axes for the two ions almost coincide, only along K_2 is it the same axis for each ion.

The separation of the outer lines along the axes are:
 z axis (chosen as it is the largest) 1145 gauss, x axis

Diagram 3.2
Directions of axes
 $K_4V(CN)_6 \cdot 3H_2O$

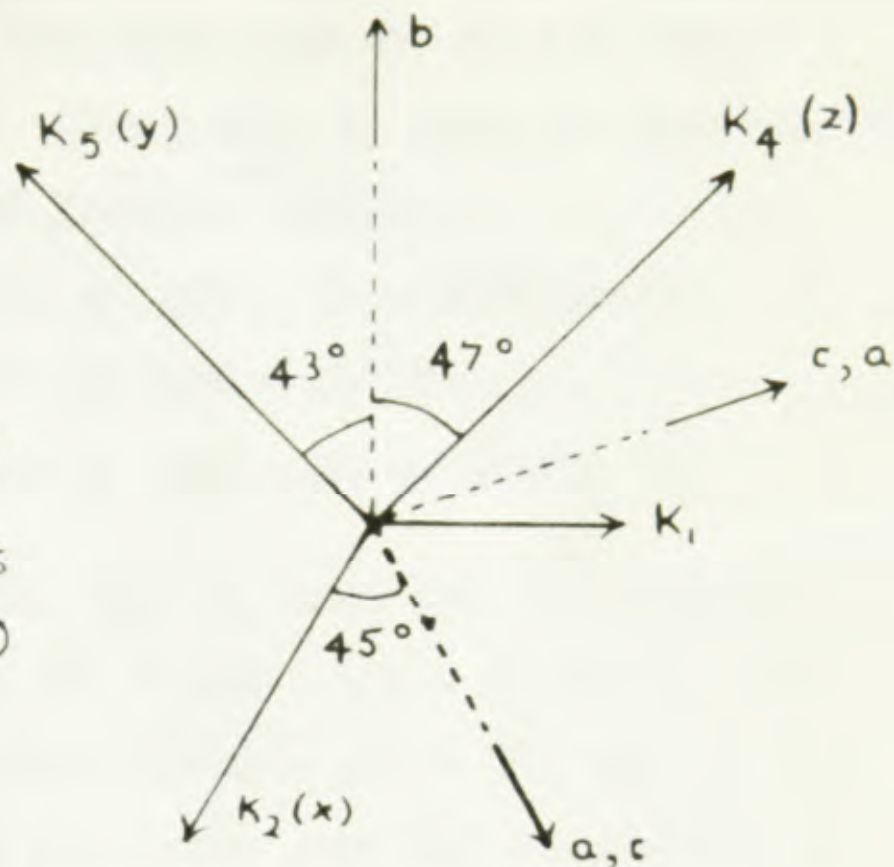
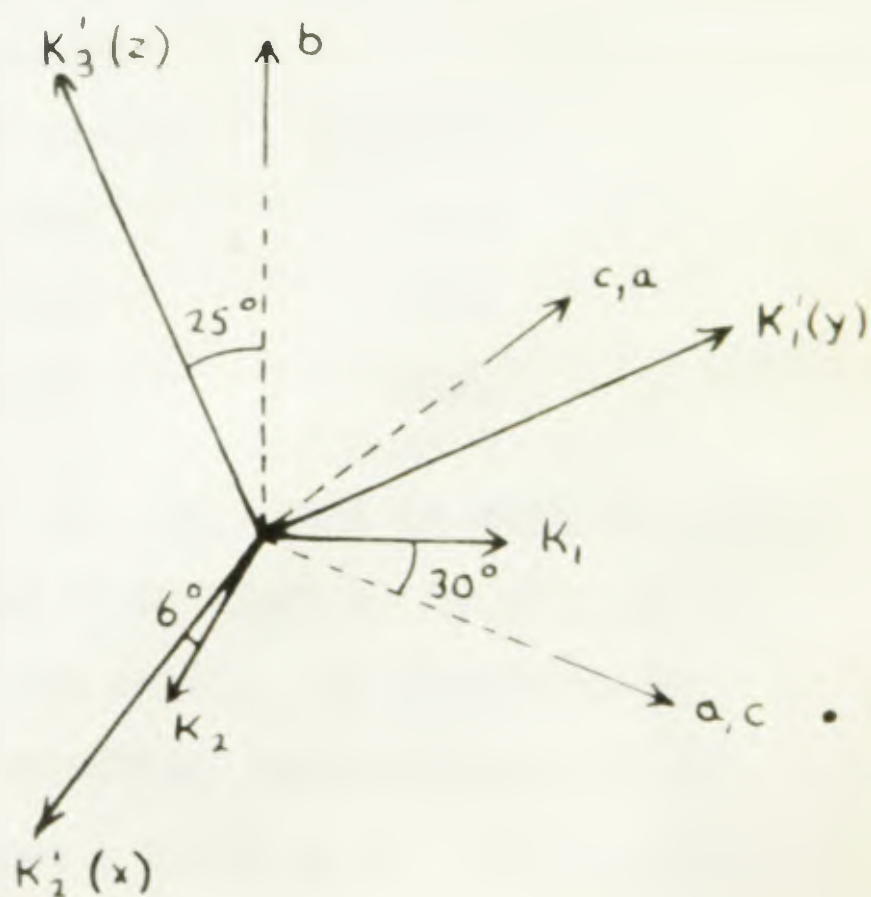


Diagram 3.3
Directions of axes
 $K_4Mn(CN)_6 \cdot 3H_2O$



(chosen so that E has the same sign as D) 102 gauss, and y axis 1030 gauss. Along the z axis the transitions are given by (Bleaney and Ingram, ^{and Scovil,} 1951):

$$+ 3/2 \text{ to } + 1/2 \quad h\nu = g\beta H + 2D - 3E^2 D / (h\nu)^2$$

$$+ 1/2 \text{ to } - 1/2 \quad h\nu = g\beta H + 3E^2 / h\nu$$

$$- 1/2 \text{ to } - 3/2 \quad h\nu = g\beta H - 2D - 3E^2 D / (h\nu)^2$$

The transitions along the x axis are obtained by substituting $-\frac{1}{2}(D - 3E)$ for D and $-\frac{1}{2}(E + D)$ for E , and along the y axis by substituting $-\frac{1}{2}(D + 3E)$ for D and $-\frac{1}{2}(E - D)$ for E . These relations give the separation of the $\pm 3/2$ to $\pm 1/2$ lines along the various axes to be: z , $4D$; x , $-(2D - 6E)$; y , $-(2D + 6E)$. The best fit to the experimental results is given by $D = 264$ gauss and $E = 77.5$ gauss which give values:

	calculated	observed
z axis	1140	1145
x axis	105	101
y axis	1035	1031

The mean of the positions of the two lines in each direction gives the value of H in the expression $h\nu = g\beta H$, as the $3E^2 D / (h\nu)^2$ terms are negligibly small. If allowance is made for the second order correction the position of the $+ 1/2$ to $- 1/2$ line also gives a value of H . Experimentally the distance between this field and the signal due to

diphenyl-trinitro phenyl hydrazyl was measured on a calibrated sweep. If g is written $(g_0 + \Delta g)$ and H as $(H_0 + \Delta H)$ where g_0 and H_0 are the values appropriate to the free radical, the quantity measured is ΔH which is $-\Delta g H_0 / g_0$. The values of ΔH expressed in gauss were: from $\pm 3/2$ to $\pm 1/2$ lines 46 ± 3 ; from $1/2$ to $-1/2$ lines, z axis 46 , x axis 46 , y axis 44 , which give a mean of 46 ± 2 gauss. This is the mean position of the centre of the h.f.s. which is 3.6 gauss lower in field than the field corresponding to $I = 0$ due to a second order shift which is explained in the next section. Correcting for this shift $\Delta g = -0.0118 \pm 0.0006$ which gives $g = 1.9920 \pm 0.0006$, and values of $D = 0.0264 \pm 0.0004 \text{ cm}^{-1}$. and $E = 0.0072 \pm 0.0004 \text{ cm}^{-1}$.

The $M = \pm 3/2$ to $\pm 1/2$ lines are broader than the $1/2$ to $-1/2$ lines, being broadest when the separation between them is greatest. Bowers (1953) also found this in potassium chromicyanide; it also occurs in the vanadous Tutton salt and the chromic alum and is probably due to a variation in crystal field parameters over the volume of the crystal. A crystal containing probably less than 1% V^{++} has a linewidth of 3.5 gauss in the central line and about 12 gauss in the outer lines at their greatest separation.

Near the position of collapse in the xy -plane the line width in the outer transitions is nearly the same as in the central one so that the lines have good intensity. Each fine structure line is split into eight equally intense hyperfine lines. The relative intensity of one hyperfine line in each outer transition was measured, using a signal from the calibrator (chapter 2.4) at 90°K , 20°K and about 13°K . At 90° the intensities are equal, and at 20° and 13° the ratios of intensity are 0.91 and 0.90 respectively. As the energy levels corresponding to $M = 3/2$ and $1/2$ are higher than those corresponding to $-3/2$ and $-1/2$ the line due to transitions between the former two will be less intense than that between the latter two. Thus the relative intensity measurements enable the transitions to be identified. Following the $3/2$ to $1/2$ transition until the field is along the z axis the transition is found to be on the high field side of the central transition, so that D is negative.

HYPERFINE STRUCTURE

The nuclear spin of ^{51}V is $7/2$ so that each fine structure line is split into eight hyperfine lines. These can be allowed for in the equations for the energy of the (M, m) to $(M - 1, m)$ transitions ^{by adding a} term:

$$- A_m - A^2(I(I + 1) - m^2)/2h \gg - A^2m(2M - 1)/2h \gg$$

The last term is zero for the central line and the second term equal for values of m , so that A may be measured by measuring the overall separation of the h.f.s. in the central $M = 1/2$ to $-1/2$ transition, which gives $7A$. Proton resonance measurements on the $m = \pm 7/2$ lines give a value of $A = 59.8 \pm 0.3$ gauss or 0.00555 ± 0.00003 cm⁻¹. For $m = \pm 1/2$ the second term is 3.6 gauss so that these two hyperfine lines in the central transition are shifted to lower fields by this amount. This is the correction allowed for in the g value calculation in the last section.

The value of $A^2/2h$ is 0.22 gauss, so that if A is positive the overall h.f.s. separation in the $M = 3/2$ to $1/2$ transition is 3 gauss bigger, and in the $-1/2$ to $-3/2$ transition is 3 gauss smaller than it is in the $1/2$ to $-1/2$ transition; if A is negative the case in the two transitions is reversed. Along the x axis the $3/2$ to $1/2$ transition has an overall h.f.s. 3 gauss smaller than the central transition. Along the direction which is the y axis for one ion and the z axis for the other the $3/2$ to $1/2$ transition has an overall h.f.s. 4 gauss smaller than the $-1/2$ to $-3/2$ transition. This difference of relative overall h.f.s. is also confirmed in the direction in the ac -plane where all three transitions are superimposed and the differences therefore are more obvious. Thus the sign of A is negative.

3.4 POTASSIUM MANGANOCYANIDE

The free manganous ion ($3d^5$) is in a $6S_{5/2}$ state. In the KY_6 complex, however, the five $3d$ electrons fill all but one of the levels in the lower orbital triplet so that the ion is in an $S = 1/2$, $L = 1$ state. A tetragonal distortion of the crystal field splits the orbital triplet into a singlet and a higher doublet (Stevens, 1953). This makes the problem similar to titanium (Ti^{+++} , $3d^1$, $2D_{3/2}$) in which the cubic field leaves an orbital triplet lowest and a tetragonal field splits this into a singlet and an upper doublet. In fact the field is rhombic rather than tetragonal, and it splits up the upper doublet also giving rhombic g-values, so that the hamiltonian is:

$$\mathcal{H} = \beta(g_x^H S_x + g_y^H S_y + g_z^H S_z)$$

The nuclear spin of manganese 55, $I = 5/2$, gives rise to a hyperfine structure which is also anisotropic and is represented in the hamiltonian by a term:

$$A_x^S S_x I_x + A_y^S S_y I_y + A_z^S S_z I_z$$

This contrasts with the h.f.s. in the Mn^{++} ion in ionic crystals where it is isotropic and is entirely due to promotion of a $3s$ electron to a $4s$ level.

THE SPECTRUM

At 20°K the spectrum consists of two broad lines, which are resolved into six hyperfine lines when the

temperature is reduced to about 14°K. At 14°K the lines are 13 gauss wide in a crystal which probably contains about 1% Mn^{++} , though exact estimation of the concentration is impossible.

The spectrum is analysed in the same way as the potassium vanadocyanide spectrum. The two directions of extreme g-value in the ac-plane (K_1 and K_2) are found to make angles of 30° and 60° with the crystal axes; the angles are accurate to about three degrees. As the a and c axes cannot be distinguished, the direction of the K_1 and K_2 axes have to be found for each crystal separately. Diagram 3.3 shows the directions of the various axes. In the K_2b plane the direction, K'_2 , of extreme g-value was only $6^\circ \pm 3^\circ$ from the ac plane, so that this direction is very close to an axis. In the K_1b plane the extreme direction K'_1 is $25^\circ \pm 3^\circ$ from the ac plane. A wedge was made so that the crystal could be rotated in the $K'_1K'_2$ plane. The two directions K'_1 and K'_2 , and the perpendicular to them K'_3 , are close to the axes of extreme g-value and the closeness to these axes can be estimated by the correlation of the results in different planes. Measurements in the $K'_1K'_3$ and $K'_2K'_3$ planes were made at 3 cm., as the g-value along K'_3 is low and a lower g-value can be measured than at 1 cm.

The low g -value direction, K_3' , has been chosen as the z axis, and the K_1' and K_2' axes have been called respectively y and x . The g -values in the directions K_1' and K_2' are respectively $g_y = 2.182 \pm 0.008$ and $g_x = 2.624 \pm 0.008$. The actual g -value along K_3' could not be measured because the spectrum moved to higher fields than could be obtained, but the variation of g -value with angle was plotted to within 20° of K_3' , so that the g -value could be fairly accurately extrapolated. A plot of g^2 against $\cos^2\theta$ was made for two mutually perpendicular planes perpendicular to $K_1'K_2'$, the intercept on the K_3' axis giving g_z^2 (see chapter 1.3). The agreement of the values found in the two planes is a measure of how close K_3' is to the axis. The two graphs are shown in diagram 3.4. The value of g_z is 0.72 ± 0.05 .

The line width along K_1' is about 25 gauss and is slightly bigger along K_2' . As the K_3' axis is approached the lines become much broader and fainter. Their actual width is difficult to assess because of the hyperfine structure.

Measurements of the h.f.s. separations in the x and y directions give the values of A_x and A_y directly as:

$$A_x = 67.0 \pm 0.5 \text{ gauss} = 0.00845 \pm 0.00005 \text{ cm}^{-1}.$$

$$A_y = 49.5 \pm 0.5 \text{ gauss} = 0.00465 \pm 0.00005 \text{ cm}^{-1}.$$

The value of A_z was obtained by extrapolation. If the h.f.s. constants are expressed in gauss the value of the

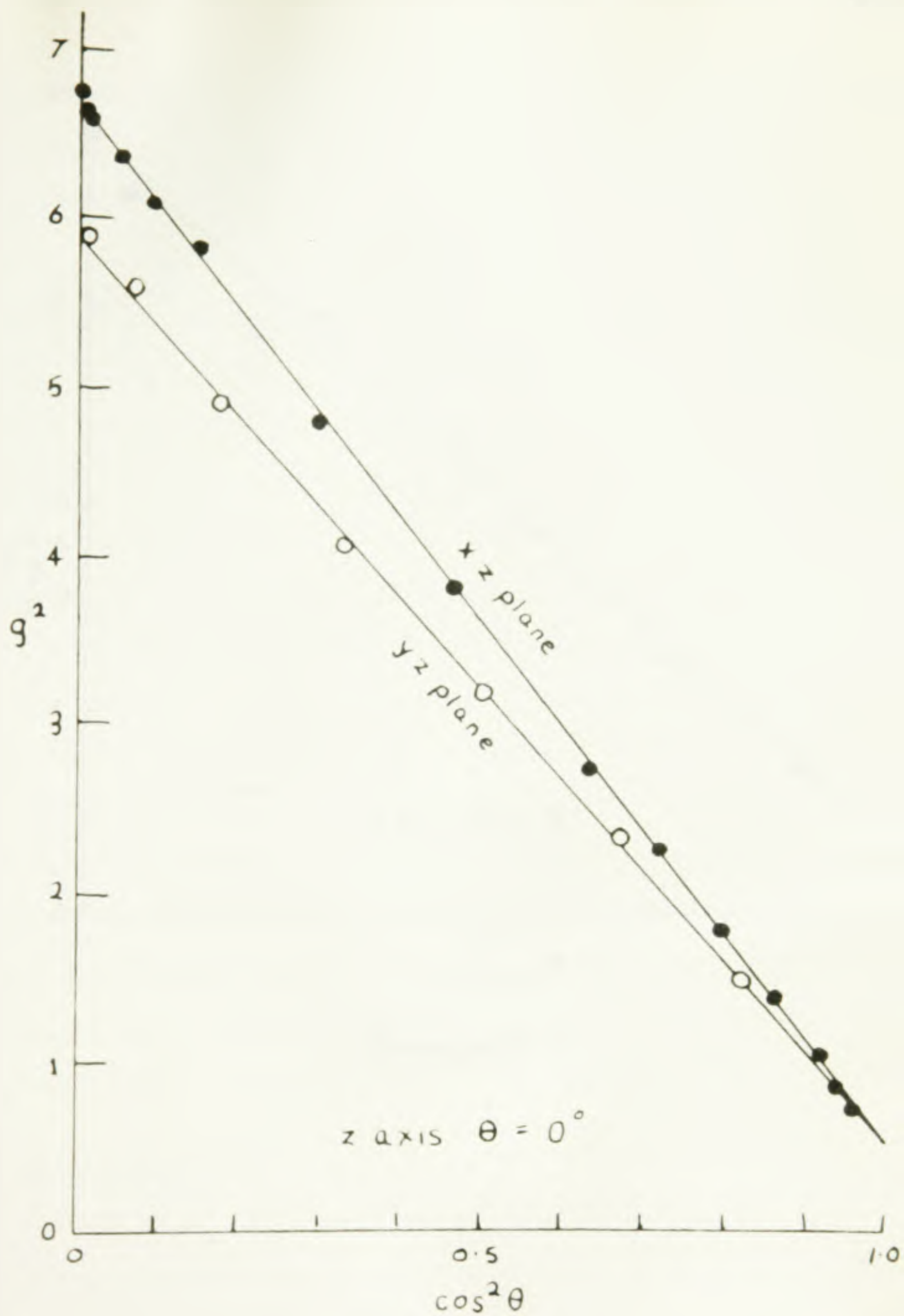


Diagram 3.4

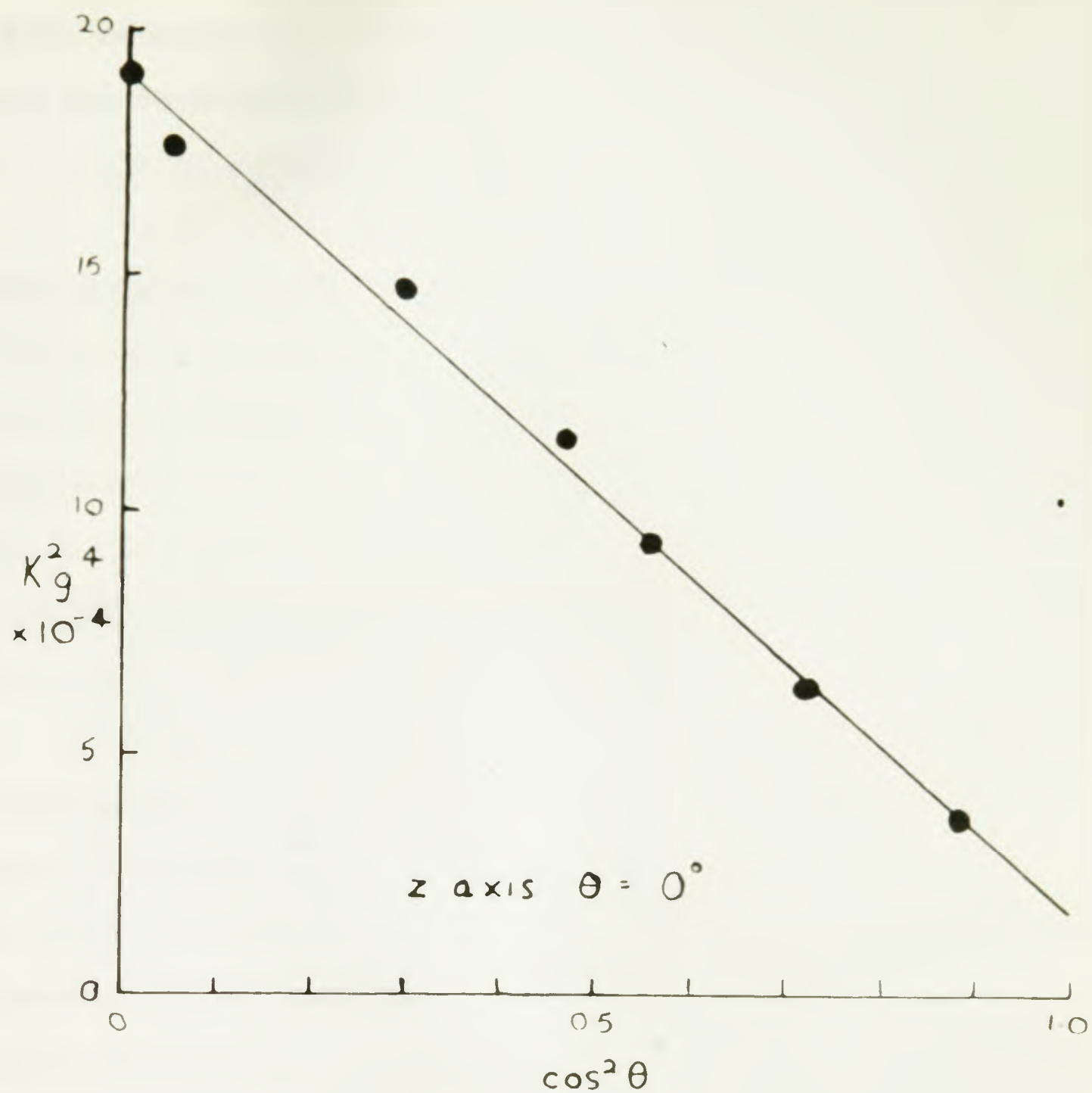


Diagram 3.5

h.f.s. constant K in an arbitrary direction is calculated from the expression quoted in chapter 1.3 to be:

$$K^2 g^4 = A_p^2 g_p^4 \cos^2 \theta + A_q^2 g_q^4 \sin^2 \theta$$

where θ is the angle to the q axis. Thus a plot of $K^2 g^4$ against $\cos^2 \theta$, in a plane containing the z axis, gives an intercept of $A_z^2 g_z^4$, from which A_z can be calculated as g_z is known. Diagram 3.5 shows a plot in one of the planes in which the measurements for the g -value extrapolation were made. This gives the value of $A_z = 250 \pm 40$ gauss $= 0.0083 \pm 0.0013$ cm.

There is no sign of any small lines in between the large hyperfine lines, which enables an upper limit to be put on the quadrupole interaction. As crystal growing was so difficult it was not possible to grow a crystal with narrower lines, in order to get a better chance of seeing quadrupole lines. The resolution obtained was such that had there been quadrupole lines 1/100th the intensity of the main lines they would have been detected.

3.5 DISCUSSION

There is little relation between the magnetic axes of either of these salts and the directions of the bonds to the surrounding CN groups; nor is there much resemblance between the directions in the two salts.

Miss M. O'Brien has attempted to calculate a theory to take into account the rhombic symmetry in the manganous salt. Several possible sets of values for the parameters fit the results with only fair accuracy, but no one set is outstandingly better than any other. As this is the case a crude analysis will be given assuming that the symmetry in the manganous salt is tetragonal. As it has already been pointed out, the vanadous salt is very similar to an ionic salt and no special theory need be developed.

Table 3.1 shows the g-values of the V^{++} and Cr^{+++} ions in ionic and complex compounds.

TABLE 3.1

ion	ionic compound	complex compound
Cr^{+++}	1.976 ± 0.002	1.992 ± 0.002
V^{++}	1.951 ± 0.002	1.992 ± 0.002

These values show that the effect of higher levels is smaller in the complex salts as their departure from the free spin value is smaller. This is consistent with the fact that the crystal field parameters are also much smaller in the complex salts.

If Δ is the separation between the lowest singlet and the next multiplet and λ is the spin-orbit coupling coefficient then: (for the ionic case)

$$g = 2(1.0012 - 4\lambda/\Delta)$$

If we assume that this is true for the complex salt the above g-values indicate that Δ is 2.5 times bigger in the complex salt than in the ionic one. This may be compared with the value of 2.7 found by Bowers (1953) for this ratio for the Cr^{+++} ion. Laporte (1928) gives for the free ion $\lambda = 55 \text{ cm}^{-1}$ so that for the vanadocyanide $\Delta = 1.1 \times 10^4 \text{ cm}^{-1}$. As there is some evidence for the spin orbit coupling coefficient being smaller in the solid state than in the free ion this value may be large. This corresponds to an absorption in the near infra red which is not very consistent with the reddish brown colour of the salt.

In the case of covalent bonding where the crystal field is of the same strength as the Coulomb repulsion between the electrons one might expect a considerable change in the amount of configurational interaction as this is produced by the Coulomb repulsion. This ought greatly to modify the hyperfine structure. In fact the value of A is only 36% smaller in the cyanide than in the ionic salt, and in chromic compounds A is only 25% smaller in the complex salt (Bowers, 1953).

For the case of five d-electrons Bleaney (unpublished) assumes the following states for the ground doublet:

$$\begin{aligned} \alpha |A+\rangle &+ \beta |B-\rangle &+ \gamma |C-\rangle \\ \alpha |A-\rangle &- \beta |B+\rangle &- \gamma |C+\rangle \end{aligned}$$

which give g-values:

$$g_x/2 = a^2 - \sqrt{2}ka\beta + 2\gamma(ak - \sqrt{2}\beta)$$

$$g_y/2 = a^2 - \sqrt{2}ka\beta - 2\gamma(ak - \sqrt{2}\beta)$$

$$g_z/2 = a^2 - (1 + k)\beta^2 + (k - 1)\gamma^2$$

k is a factor which is unity for an electron which spends all its time in an orbit around one nucleus, and any departure from unity represents the fact that a proportion of the time is spent on other nuclei. There will be a departure from unity in this case because the electron spends some time on the surrounding CN groups. Taking parameters $k = 0.96$, $a^2 = 0.535$, $\beta^2 = 0.456$, $\gamma^2 = 0.009$ the g-values are $g_z = 0.72$, $g_x = 2.63$ and $g_y = 2.19$ which are very close to the experimental values. The above theory assumes that k is the same for all axes which may not be true; but as there is no way of finding the ratio of the values of k along the different axes it is the only reasonable assumption to make.

The g-values of the isoelectronic Fe^{++} ion in potassium ferricyanide (Bowers, unpublished) may be explained assuming parameters $k = 0.89$, $a^2 = 0.494$, $\beta^2 = 0.503$ and $\gamma^2 = 0.003$ which give $g_z = 0.91$, $g_x = 2.37$ and $g_y = 2.11$ which are close to the experimental values. The value of k is very sensitive to the value of g_z which is, for both ions, the least accurate

g-value, so that the difference between its values for the two ions may not be as large as the above calculations show. A ^{smaller} ~~larger~~ value of k might be expected in the trivalent ion as the additional positive charge may cause the bonding of the CN groups to be stronger which is equivalent to the electron spending more time on the CN groups.

If A_z is taken to be $A_{||}$, and the average of A_x and A_y is taken to be $A_{\perp}$, an attempt can be made to fit the experimental results on the hyperfine structure to the theoretical formulae for Ti^{++} in a tetragonal field. If Δ is the splitting between the lower orbital singlet and the next orbital doublet and λ is the spin-orbit coupling coefficient, the parameters in the spin hamiltonian are given by (Abragam and Pryce, 1951)^b:

$$g_{||} = -1 + 3(\Delta + \lambda/2)/S, \quad g_{\perp} = 1 + (\Delta - 3\lambda/2)/S$$

where $S = [(\Delta + \lambda/2)^2 + 2\lambda^2]^{1/2}$ and $P = 2\gamma\beta\beta_N/r^3$

and the equations for the hyperfine structure constants may be reduced to:

$$A_{||} = P \left[(g_{||} + 3g_{\perp} - 12)/7 - (g_{||} + 1)/3 \right]$$

$$A_{\perp} = P \left[(-3g_{||} + 11g_{\perp} - 12)/14 - (g_{||} + 4)/6 \right]$$

Allowance may be made for the time spent by the electron on other nuclei by taking the states necessary to explain the g-values and calculating new g-values assuming that $k = 1$. If these values are substituted in the above equations the hyperfine structure is explained by values

of $\kappa = 1.1$, $P = 110 \times 10^{-4}$ which is comparable with the value of 92×10^{-4} found in ionic compounds of Mn^{++} . The value of $1/r^3$ is 2.44 atomic units which is probably somewhat smaller than in ionic crystals. This is reasonable as the electron spends more of its time on the surrounding nuclei, which effectively increases r .

Using the above value of $1/r^3$ and calculating the intensity of the lines produced by a quadrupole moment $Q = 0.5 \times 10^{-24} \text{ cm}^2$ they are about 0.1% of the hyperfine lines and therefore could not have been observed experimentally.

It was shown that the parameter T is related to the asymmetry ratio of the nucleus γ by

$$T = \left(\frac{1}{2}\right) 2 \pi \beta \mu_N \left\{ \gamma - \frac{1}{2} \right\}$$

The term involving $\gamma - \frac{1}{2}$, which is isotropic, is due to configuration interaction, where $\gamma - \frac{1}{2}$ is the nuclear factor representing the admixture of the configuration with an unpaired s -electron. The "other term" is the contribution to the interaction due to the orbital moment of the electron, and the spin moment of the s -electron. These depend on the distribution of energy levels near the ground state, and will generally be anisotropic.

CHAPTER 4

NUCLEAR SPIN

4.1 INTRODUCTION

In chapter one (1.3) it was shown that if the paramagnetic ion has a nuclear spin I , the magnetic interaction between the associated nuclear magnetic moment and the moment due to the electrons surrounding it introduced a term into the spin hamiltonian:

$$\bar{S} \cdot T \cdot \bar{I}$$

It was also shown that this splits each fine structure line into $(2I + 1)$ hyperfine lines. The nuclear spin of an ion, which exhibits p.r. , can therefore be measured at once merely by counting the number of lines into which each fine structure line is split.

It was shown that the parameter T is related to the gyromagnetic ratio of the nucleus γ by:

$$T = \left(\frac{1}{r^3} \right) 2 \gamma \beta \beta_N \left\{ \kappa + \text{other terms} \right\}$$

The term involving " κ ", which is isotropic, is due to configurational interaction, where " κ " is the numerical factor representing the admixture of the configuration with an unpaired s-electron. The "other terms" are the contribution to the interaction due to the orbital moments of the electrons, and the spin moments of the non s-electrons. These depend on the distribution of energy levels near the ground state, and will generally be anisotropic.

In the first transition group of the periodic table the hyperfine structures of V^{++} ($4F_{3/2}$) and Mn^{++} ($6S_{5/2}$) are almost entirely due to configurational interaction, so that a value of $\left\{ \left(\frac{1}{r^3} \right) \kappa \right\}$ may be calculated, using values of γ from nuclear resonance. The structures of Co^{++} ($4F_{9/2}$) and Cu^{++} ($2D_{5/2}$) both contain anisotropic contributions from the "other terms" which can be separated from the isotropic contribution from κ . Knowing the energy level distribution the "other terms" may be calculated, thus allowing an estimate of $\left(\frac{1}{r^3} \right)$; so that in this case κ and $\left(\frac{1}{r^3} \right)$ may be estimated independently. Bleaney pointed out that in many compounds of these ions the values of $\left\{ \left(\frac{1}{r^3} \right) \kappa \right\}$ did not vary by more than 20% from ion to ion, so that one may use the value of $\left\{ \left(\frac{1}{r^3} \right) \kappa \right\}$ to estimate values of γ in other ions when T is known. In the case of rare earth ethyl sulphates Gd ($8S_{7/2}$) has no hyperfine structure so that, as the "other terms" are zero, we may assume that $\kappa = 0$.* For other ions, if the distribution of energy levels near the ground state can be found, the "other terms" can be calculated and a value of γ estimated.

T , which is a measure of the magnetic field due to the electrons at the nucleus, depends only upon the system of electrons surrounding the nucleus and not upon nuclear properties. The ratio of the values of T for two isotopes

* See note at the end of the chapter

is thus accurately equal to the ratio of the values of γ .

With p.r. it is therefore possible to estimate accurately the ratio of γ for two isotopes, and to estimate an absolute value for γ to $\sim 20\%$. These measurements may be done on very small quantities of material. Only one tenth of a microgram of the ion is needed to be detected by the simple video-frequency method, and presumably as little as one hundredth of a microgram would be sufficient if lock-in detection were used. There are however several drawbacks to this method for measuring nuclear parameters.

In principle it does not matter if the isotope whose nuclear spin we require is mixed with other isotopes, as each will produce its own distinct hyperfine structure. However, as the total intensity in the spectrum is proportional to the number of ions producing it, the spectrum of an abundant isotope may completely swamp those of less abundant isotopes. As it is very difficult to observe small lines in the presence of very large ones, the spectrum of the less abundant isotopes may not be seen at all. Generally not more than a few times as much of an unwanted isotope can be tolerated, so that the substance used must be fairly isotopically pure.

The substance must also be chemically pure, having less than the quantity of specimen ion of any impurity whose spectrum coincides with that of the specimen. Also

to obtain sufficient resolution to measure hyperfine structure it is often necessary to mix the specimen with much larger quantities of a diamagnetic ion.

Several nuclear spins have been measured by p.r. Table 4.1 is a list of these together with the reference to the published reports. Trenam (1953a)* working on iron enhanced in ^{57}Fe was not able to observe any hyperfine structure outside the line due to even isotopes; this enabled him to put an upper limit on the magnetic moment of the ^{57}Fe nucleus of 0.05 nuclear magnetons, but the nuclear spin could not be measured.

Stable isotopes whose nuclear spins ought to be measurable by p.r. are ^{50}V and ^{61}Ni ; there are also several artificially produced radioactive isotopes with lifetimes sufficiently long to make measurements possible. In this thesis measurements on ^{50}V and ^{57}Co are described.

4.2 VANADIUM 50

Naturally occurring vanadium contains 99.8% of isotope mass 51 and 0.2% isotope mass 50. ^{51}V has a nuclear spin $I = 7/2$ so that each fine structure line is split into eight hyperfine lines. Walchli, Leyshon and Schoitlin (1952) have measured the ratio of the gyromagnetic ratios of $^{50}\text{V}/^{2p}$, by nuclear resonance, as 0.649527 ± 0.00007 , and Knight and Cohen (1949) have measured the ratio of the

* see also ~~Trenam (1954)~~ Bleaney and Trenam (1954)

Table 4.1

Ion	Spin	Reference
^{53}Cr	$3/2$	Bleaney and Bowers, 1951
147, 149 Sm	$7/2, 7/2$	Bogle and Scovil, 1952
143, 145 Nd	$7/2, 7/2$	Bleaney and Scovil, 1950
167 Er	$7/2$	Bleaney and Scovil, 1951
91, 101 Ru	$5/2, 5/2$	Griffiths and Owen, 1952
239, 241 Pu	$1/2, 5/2$	Bleaney et al., 1954a,b
237 Np	$5/2$	Bleaney et al., 1954c

gyromagnetic ratios of $^{51}\text{V}/^1\text{H}$ as 0.26290, also by nuclear resonance. This gives the ratio of gyromagnetic ratios of $^{50}\text{V}/^{51}\text{V}$ to be 0.3792. The ^{51}V gives rise to a spectrum of eight equally spaced lines separated by Δ between each of them, and ^{50}V gives rise to $(2I + 1)$ lines separation 0.3792Δ between each of them. Diagram 4.1 shows the positions of these two spectra, not allowing for second order shifts. The nuclear spin of ^{50}V must be integral as the nucleus has an odd number of protons and an odd number of neutrons, so that there is a hyperfine line in the centre of the spectrum corresponding to $^{50}\text{m} = 0$. In natural vanadium the lines due to ^{50}V are so faint as to be invisible within the much stronger spectrum of ^{51}V .

36 milligrams of V_2O_5 , enriched to contain $\sim 20\%$ ^{50}V , were obtained from the Electromagnetic Separator Group at A.E.R.E., Harwell. This gives intensities such that there would be a reasonable chance of resolving the two spectra if a suitable chemical compound could be found.

Bleaney, Ingram and Scovill (1951) made measurements on $\text{V}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ diluted to about 1% in $2\text{Zn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, and obtained a spectrum of eight hyperfine lines of width 12 gauss and separation 96 gauss in the $M = 1/2$ to $M = -1/2$ transition. This was not thought to be sufficiently good resolution so an attempt was made to reduce the line width by growing crystals from

heavy water. The V^{++} ion is so unstable in solution that growing crystals from natural water is very difficult, the additional difficulties involved using heavy water make it quite impossible. The tendency to oxidize in solution is probably why no success was obtained with $V SiF_6 \cdot 6H_2O$. As described in chapter 3 (3.3) $K_4V(CN)_6 \cdot 5H_2O$ is found to give lines 3.5 gauss broad separated by 60 gauss, when diluted to about 1% with the isomorphous ferrous salt. This is the salt used for the work described here. It is interesting that Kikuchi, Sirvets and Cohen (1952) were able to do similar measurements on $V (NH_4)_2(SO_4)_2 \cdot 6H_2O$ diluted to 1.5% in the isomorphous zinc salt. Their results are in good agreement with those described here.

NUCLEAR SPIN

Measurements were made with the magnetic field along the axis of the crystalline field for one ion where the $M = 3/2 \leftrightarrow 1/2$ and $M = -3/2 \leftrightarrow -1/2$ transitions lie completely outside the $M = 1/2 \leftrightarrow -1/2$ transition, and also the $M = 1/2 \leftrightarrow -1/2$ transitions for both ions are superimposed. This direction and the corresponding one for the other ion, are the only two where one obtains a simple eight line spectrum for the $M = 1/2 \leftrightarrow -1/2$ transition free from overlap by other transitions. Lines of about one seventh the intensity of those due to ^{51}V are observed

in the positions predicted by diagram 4.1, the lines which are observed are also shown on the diagram. A difficulty at once arises as it is not obvious whether the spin is 6 or 7. There are definitely no lines corresponding to $50_m = \pm 8$, and there are definitely lines corresponding to $50_m = \pm 6$, but although no $50_m = \pm 7$ lines are visible it could be because they are not resolved from the $51_m = \pm 5/2$ lines of $51V$. Diagram 4.2 shows a photograph of the part of the spectrum which is important. The $51_m = +3/2$ and $+5/2$ lines are marked and $50_m = 4, 5$ and 6 . There is no evidence whatever for a line $50_m = 7$, so that, if it can be shown that were it there it would be resolved, the spin of $50V$ is 6.

To account for the hyperfine structure in the $M = 1/2 \leftrightarrow -1/2$ transition a term:

$$- A_m - \frac{A^2}{2h\nu} \left\{ I(I+1) - m^2 \right\}$$

Diagram 4.2

is added to the expression for the energy change in a transition. The first term produces the equally spaced hyperfine lines while the second smaller term shifts them all to slightly lower fields, the shift being smaller the bigger m . Table 4.2 shows the positions of the hyperfine lines for $50V$ and $51V$ measuring from the place where the line would be were there no hyperfine structure ($I = 0$),

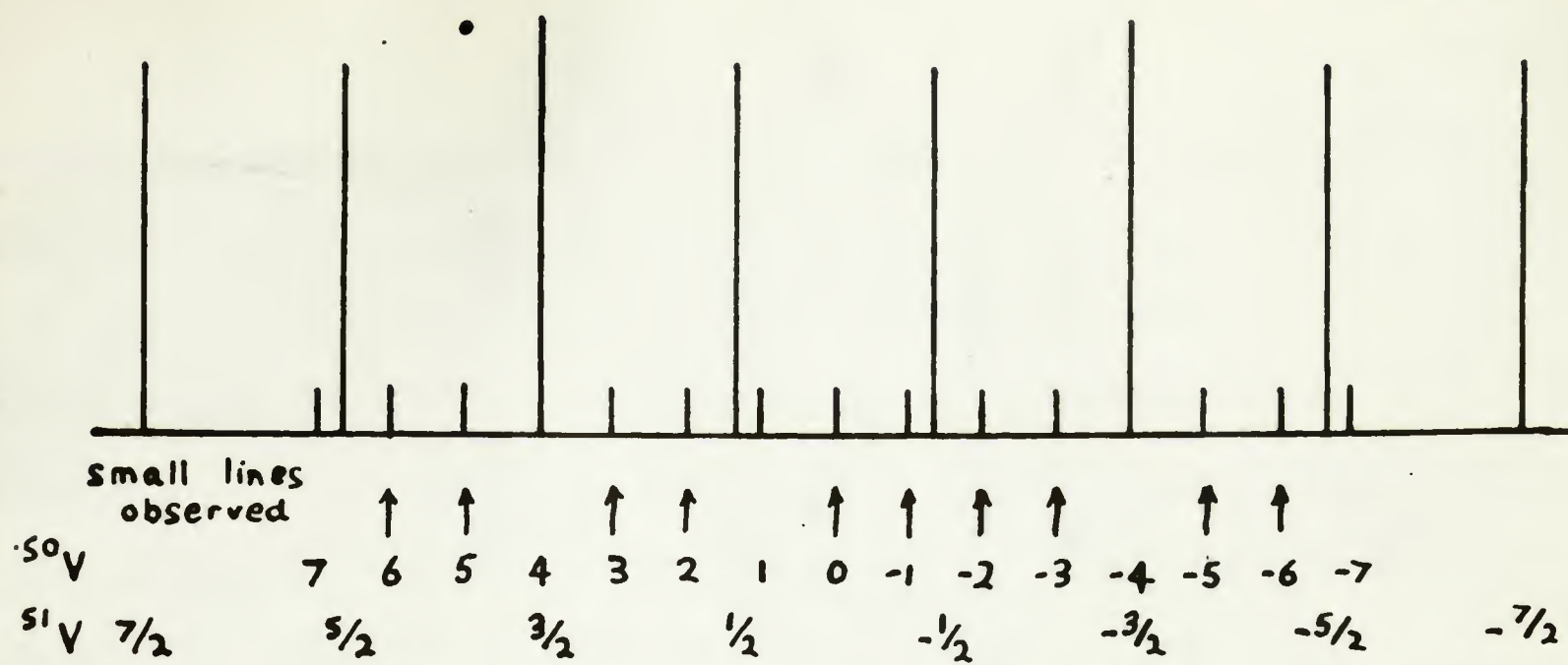


Diagram 4.1

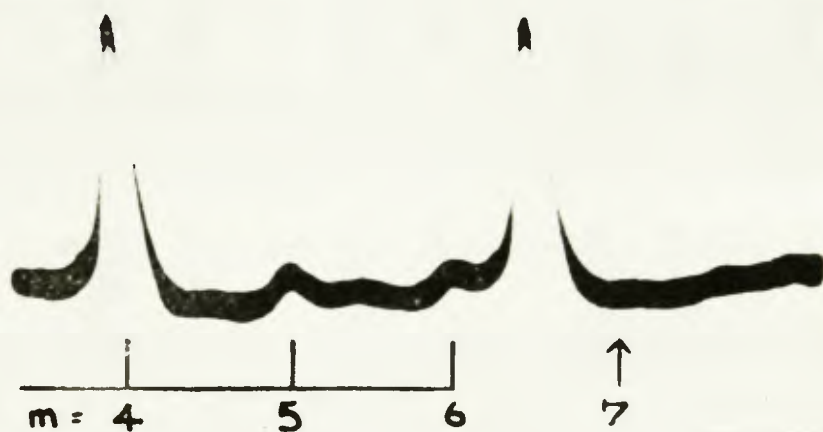


Diagram 4.2

Table 4.2

51_m	- 7/2	- 5/2	- 3/2	- 1/2	+ 1/2	+ 3/2	+ 5/2	+ 7/2
	- 210.8	-151.6	- 93.0	-33.3	+ 26.5	+ 87.0	+ 147.4	+ 209.2
50_m	- 7	- 6	- 5	- 4	- 3	- 2	- 1	0
	- 159.0	- 136.6	- 114.3	- 92.0	- 69.5	- 47.0	- 24.4	- 1.8
50_m	+ 1	+ 2	+ 3	+ 4	+ 5	+ 6	+ 7	
	21.0	43.8	66.5	89.4	112.3	135.4	158.6	

Values in Gauss

calculated assuming $51_A = -59.9$ gauss, $50_A = -22.7$ gauss and $h\nu = 8.16$ K gauss.

On the low field side the separation between $51_m = -5/2$ and $50_m = -7$ is only 7.4 gauss so it is unlikely to be resolved. On the high field side however the separation $51_m = +5/2$ to $50_m = +7$ is 11.2 gauss, which is only 7% less than the separation $51_m = +5/2$ to $50_m = +6$ which is 12.0 gauss. The latter line is clearly resolved so that it is almost certain that there is no $50_m = +7$ line. Evidence is added by the fact that the $50_m = -1$ can be seen in the wings of the $51_m = -1/2$ line and the separation between them is only 9.2 gauss (this figure is calculated assuming $50_I = 6$).

An experiment was performed superimposing a proton pip on the spectrum and putting it near the place where the $50_m = 7$ line would be, to see what resolution could be obtained. The height of the pip was adjusted to be the same as the $50_m = 6$ line but, as it was narrower by a factor of three, better resolution was obtained in this experiment than if there were a $50_m = 7$ line; however this gives an indication of the possible resolution. The $50_m = 7$ line is predicted to be 23.2 gauss higher in field than $50_m = 6$. The proton pip was just resolved when it was 17.2 gauss higher, and easily resolved when 20.9 gauss higher. Even allowing for the line width one would therefore

expect the $50_m = 7$ line to be resolved.

The nuclear spin of ^{50}V is therefore found to be 6, the largest nuclear spin so far discovered.

GYROMAGNETIC RATIOS

The separations between lines were measured by setting the proton pip to be in coincidence with each line in turn. The value of 51_A was found by measuring the separation between the $51_m = 7/2$ and $51_m = -7/2$ lines and dividing by 7, the number of spaces between them. Two experiments were done to find 50_A , one measuring the separation between $50_m = 5$ and $50_m = -5$, and one using $50_m = -5$ and $50_m = +6$. The $50_m = \pm 5$ lines were well resolved so setting a proton pip to coincide with the line was easier than setting it to coincide with the $50_m = \pm 6$ lines which were not so well resolved. $50_m = +6$ was better resolved than $50_m = -6$ so that a measurement was made using -5 and $+6$, but it is not quite as reliable as the one using ± 5 . A line in the wings of a larger line always appears closer to the large line so that the $50_m = -5$ to $50_m = +6$ separation is expected to be large, this may account for the slightly higher value of $50_A/51_A$. This ratio is the ratio $50_\gamma/51_\gamma$ which may be compared with 0.372 quoted earlier. Results are quoted in Table 4.3.

Table 4.3

Lines used	Separation between them in gauge (Average of 5 readings)	Value of λ Gauss	$50\text{\AA}/51\text{\AA}$
$50m = -5, +6$	249.5 ± 1.5	22.65 ± 0.15	0.3805 ± 0.001
$51m = -7/2, +7/2$	417 ± 1	59.6 ± 0.15	
$50m = -5, +5$	228 ± 1.5	22.80 ± 0.15	
$51m = -7/2, +7/2$	421 ± 1	60.1 ± 0.15	0.3795 ± 0.001

4.3 COBALT 57

A target of spectrographically standardised iron was bombarded with 18 MeV deuterons in the cyclotron at Birmingham University, producing about 10 millicuries of ^{57}Co (by $d - n$ reaction on ^{56}Fe), and smaller quantities of ^{58}Co ($d - 2n$ on ^{56}Fe) and ^{54}Mn ($d - \alpha$ on ^{56}Fe). There was a little more than one microgram of ^{57}Co and about one tenth of a microgram of ^{58}Co and ^{54}Mn . These quantities should all be easily detectable by p.r., so an attempt was made to measure the spins of these three radioactive isotopes. The half lives of the isotopes are sufficiently long for each operation to be done carefully (^{57}Co is 270 days, ^{58}Co is 80 days, ^{54}Mn is 310 days).

A piece of iron was carefully soldered to one of the standard copper cyclotron targets for bombardment. To use the beam efficiently it had to be about 20 mm. by 5 mm. by 3 mm. thick, which is about one gram of iron. If the spectra of the radioactive isotopes were to be seen this had to contain less than one microgram of Co and Mn, requiring iron free from these impurities to $1 : 10^6$. Commercial spectrographic analyses only quote Cobalt and Manganese impurities to about $5 : 10^6$ so that there was risk of there being too much stable Mn and Co present to make the experiment successful. In fact the crystal finally prepared contained too much stable Mn, so that no ^{54}Mn

spectrum was seen; it also contained so much stable Co that only the more abundant ^{57}Co could be examined, there being no sign of a spectrum due to ^{56}Co . It ought to be possible to resolve the spectra of ^{56}Co and ^{54}Mn if a further bombardment of specially purified iron is done. The difficulties of making a sufficiently pure iron target have not yet been overcome.

PREPARATION OF THE CRYSTAL

The copper and solder on the cyclotron target were waxed over, leaving only the bombarded iron surface exposed. The bulk of the iron was then dissolved in concentrated hydrochloric acid, taking care that the iron did not anywhere dissolve away right down to the solder. The bulk of the iron was removed by two extractions of the FeCl_3 with ether. The remaining aqueous layer was evaporated to a small volume and painted in a narrow band across a strip of Whatman's No. 1 filter paper, which had been previously washed with 2 N. hydrochloric acid. The elements present in this residue were separated using a conventional paper-chromatographic technique (e.g. Burstall et al. 1950), employing ethyl methyl ketone containing 8% by volume of concentrated hydrochloric acid as the solvent. The positions of the ^{54}Mn and $^{56,57}\text{Co}$ bands were determined by measuring their radioactivity. The paper containing them

was cut out and washed with dilute hydrochloric acid. To facilitate the chemistry a little cobalt and manganese free zinc sulphate was added to act as a carrier for the radioactive materials. The zinc sulphate made up into crystals of $\text{Zn K}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ gave no p.r. spectrum, showing it to be sufficiently pure for this purpose. The solution containing the radioactive samples was evaporated to dryness and ignited to remove ammonium salts and particles of filter paper; it was then dissolved in sulphuric acid, evaporated to dryness, and dissolved in heavy water containing about 1/10 gram of $\text{Zn K}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. Great care was taken in all these operations that no impurity was introduced; 'Analar' reagents, twice distilled in all glass apparatus, were used. Dr. F.P.D. Shaw kindly carried out all the chemistry described above.

The apparatus described previously (2.1) was used for growing a crystal from about 1 ml. of heavy water solution. A single crystal of mass ~ 30 milligrams was grown. Comparison of the radioactivity of the crystal with that of the various residues showed that the crystal contained about 60% of the total activity.

The spectrum of Co^{++} in $\text{Zn K}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ has been studied by Bleaney and Ingram (1951)². $\text{Zn K}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ grows in monoclinic crystals with two magnetically distinct ions in the unit cell, one being derived from the other by

reflection in the crystallographic ac-plane. Each Co^{++} ion in $\text{Co K}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ is in a crystal field of predominantly cubic symmetry with a small tetragonal field superimposed. The hyperfine structure is best resolved when the external magnetic field is parallel to the tetragonal axis. Here the separation between the hyperfine lines is 80 gauss. Bleaney and Ingram obtained lines six gauss broad in very dilute crystals grown from H_2O , so that this could be reduced to two gauss using D_2O . This should give a good chance of resolving the ^{57}Co from any ^{59}Co present in the radioactive crystal.

THE SPECTRUM

Most of the work on the radioactive crystal was done at 20°K and ~ 1.25 cms. wavelength. The crystal was mounted in the resonator on its ab-face as this was well developed. A spectrum of two sets of eight, equally intense, nearly equally spaced, lines was obtained, corresponding presumably to the two different types of ion. The spectra of the two ions coincided well along the b-axis. The spectra in this region are very anisotropic, so that the external field must subtend the same angle to the crystal field axis of each ion, to about $.25^\circ$. This can only be the case along the b-axis* (diagram 4.3). Measurements of the g-value along the b-axis and the a-axis were made, using proton resonance to measure the field at the centre of the spectrum.

* because the crystal field has a small rhombic component.

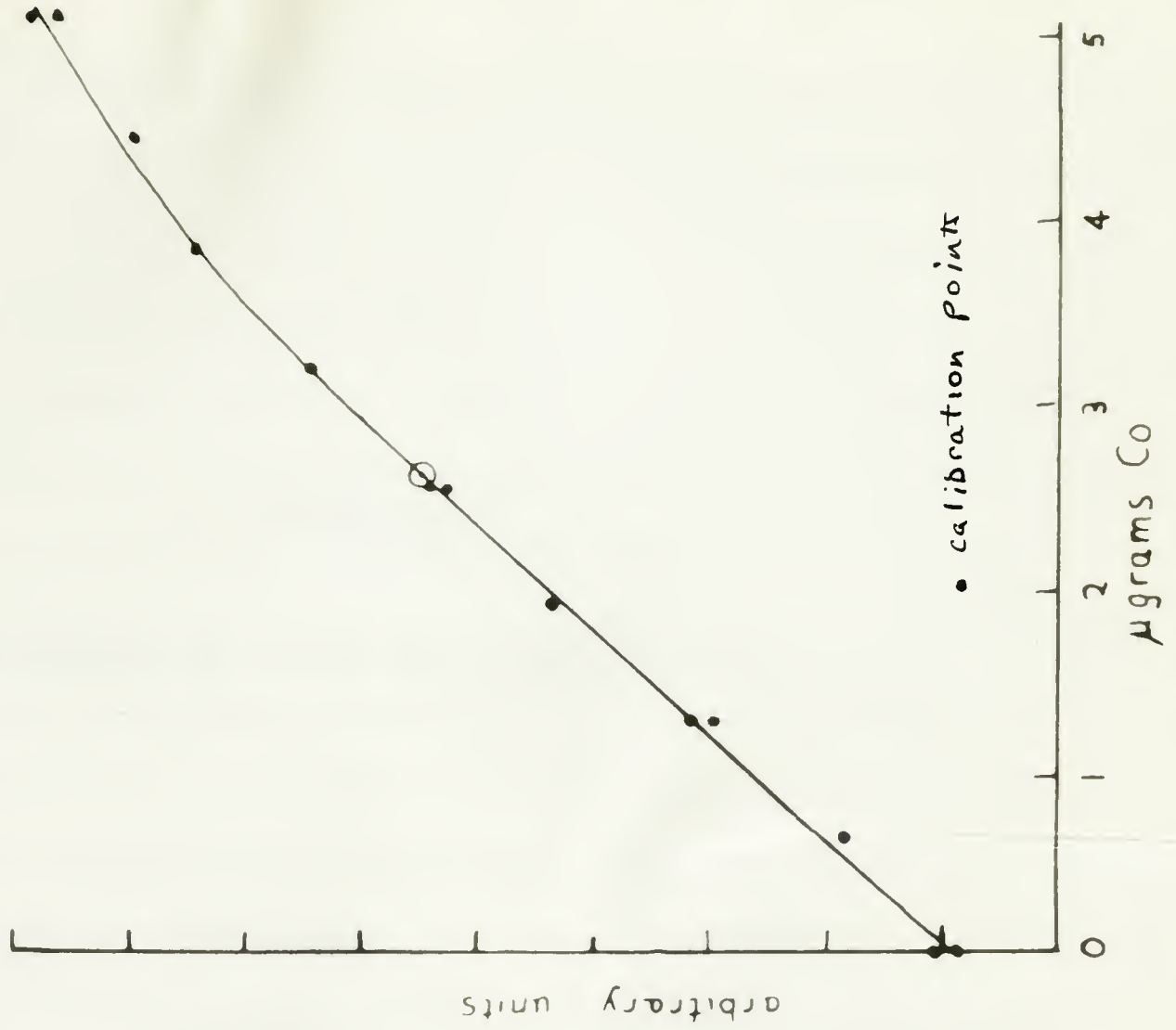


Diagram 4.4

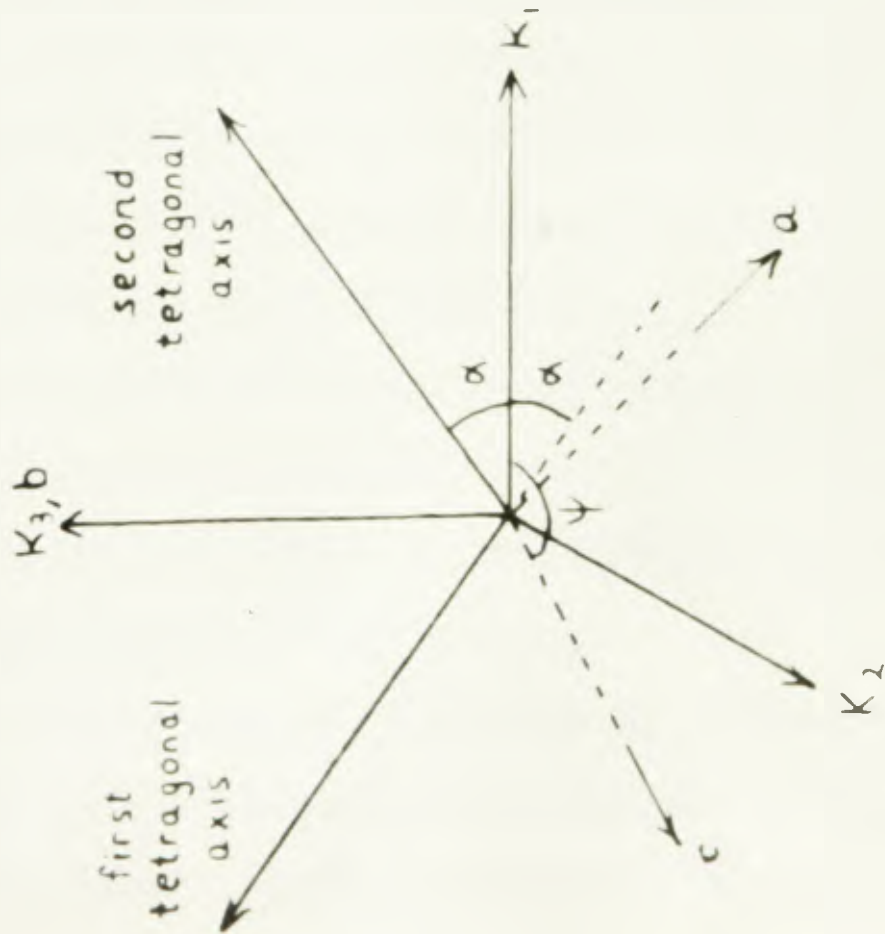


Diagram 4.3

Axes in $\text{CoK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$

Measurements were also made at a magnetic field along the z-axis. These measurements, however, were not g-values of ^{59}Co alone but were measured by comparing the signal, and summarized in Table 4.4.

The results for the measurements are given in the characteristic column of the following summary in the direction perpendicular to the magnetic field. The

Table 4.4

g values of Co in $\text{Zn K}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$

^{59}Co value also shows that the ^{59}Co signal is a nuclear spin of $3/2$. The spectrum of ^{59}Co was also plotted as an example where the lines are separated into a doublet of $3/2$. The b-axis is also at a value of 4.33. The a-axis is also at a value of 4.11 $\pm$.01. The ^{57}Co value is 4.34 $\pm$.01. The a-axis is also at a value of 4.12 $\pm$.01. The signal-to-noise ratio is 100%, the signal is a doublet of only eight lines of equal intensity.

This analysis leads to some general conclusions:

- The observed spectrum is due to ^{59}Co and not to ^{57}Co and is not a result of the ^{59}Co signal.
- The spectrum is due to ^{59}Co and is not a result of the ^{57}Co signal.

Measurements were also made on a crystal containing ^{59}Co along the a-axis. These measurements, together with the g-value of ^{59}Co along the b-axis measured by Bleaney and Ingram, are summarised in table 4.5.

The spectrum in the radioactive crystal showed the characteristic collapse of the hyperfine structure in the direction perpendicular to the tetragonal axis. The separation of the hyperfine lines is the same as it is in ^{59}Co , which also shows eight lines corresponding to a nuclear spin of $7/2$. The spectrum at 1.25 cms. was displayed on an oscilloscope where the lines had signal/noise ratio of 20/1. There was no sign of any other lines in the spectrum; nor any sign of the lines being asymmetrical or slightly double, as if two nearly identical spectra were overlapping. A measurement was made at 3 cms. using lock-in detection by Mr. R.S. Trenam, who obtained a signal/noise ratio of 100/1, but still obtained a spectrum of only eight lines of equal intensity.

This evidence leads to three possible conclusions:

- (a) The spectrum observed was due to ^{59}Co which was present in such large quantities as to obscure the spectrum due to ^{57}Co .
- (b) The spectrum was in fact due to ^{57}Co , which therefore has a nuclear spin of $7/2$ and a magnetic moment very nearly equal to that of ^{59}Co .

(c) ^{59}Co and ^{57}Co were present in comparable quantities, but have the same spin and almost the same magnetic moment. If the spins of the two isotopes are different the central lines would be more intense than the outer ones, because only the former would be due to both isotopes.

Two independent measurements were made of the radioactivity of the crystal. Both measurements were done by a scintillation counter method measuring the intensity of characteristic γ -rays. Dr. M.A. Grace measured the relative intensity of γ -radiation from ^{57}Co and ^{56}Co giving a ratio of 2 : 1. He also concluded that the crystal contained five millicuries of ^{57}Co . Dr. J.R. Prescott estimated that the minimum possible quantity of ^{57}Co was five millicuries, and was possibly nearer ten. Neither of these estimations allows for internal conversion of the γ -rays (capturing of the quantum by a K-electron), which may reduce the γ -ray intensity actually leaving the crystal by a considerable factor. The actual factor is unknown. One millicurie of ^{57}Co corresponds to about 0.11 micrograms, so that the crystal contains at least $1/2$ microgram of ^{57}Co and probably more.

A crystal of $\text{Zn K}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ was grown containing 2.6 micrograms of stable ^{59}Co (the quantity was estimated by photometric analysis described later). The intensity

of its spectrum was compared with that of the radioactive crystal when they were put side by side in the resonator, each mounted on the ab-face in such a position that the strength of the r.f. field in each was the same. The magnetic field was oriented so that the spectra of one ion in each of the crystals nearly coincided. The lines due to the active crystal were about $3/5$ the intensity of those due to the other one. As the cobalt spectrum is so anisotropic, it is not really reliable to estimate the quantity of cobalt in the active crystal by saying that the ratio of the intensities of the spectra is the same as the ratio of the quantities of cobalt in the two crystals; but it gives an indication that the quantity in the active crystal was about 1.5 micrograms.

As the evidence did not favour any particular one of the possibilities the crystal was redissolved in its original mother-liquor, and $1/2$ microgram of natural ^{59}Co added. The crystal grown from this solution contained $2/3$ of the total activity so that in addition to its initial content the crystal now contained 0.3 micrograms of ^{59}Co . Once again only a single spectrum was observed. An intensity comparison, similar to the one described in the last paragraph, indicated that the crystal contained ~ 1.5 micrograms of cobalt. As the intensity of the active crystals spectrum had 20 : 1 signal/noise ratio the

spectrum of the added ^{59}Co should have been 4 : 1, and would have been seen easily if it had been resolved. This eliminates the possibility that the spectrum is entirely due to ^{57}Co with a greatly different moment and spin. The quantity of cobalt contained in the active crystal was estimated, using nitroso-R salt as an indicator and a colorimetric method with a spekker photometer. Diagram 4.4 shows the series of calibration points and the point given by the radioactive solution. This gave the total cobalt content of the crystal to be 2.4 ± 0.1 micrograms. The ratio of ^{57}Co : ^{59}Co was at least 0.5 : 1.9, which eliminates possibility (a). If all the cobalt in the first crystal had been ^{57}Co then, as 0.3 micrograms of ^{59}Co had been added, the ratio of ^{57}Co : ^{59}Co in the crystal would be 2.1 : 0.3. In both of these extreme cases there was sufficient of each isotope to make its spectrum visible if it were resolved. As they were not resolved a limit can be put on the difference of the magnetic moments. A slight difference of magnetic moment slightly alters the separation of the lines, so that it would be most noticeable on the outermost lines. A very careful experiment was done by Mr. R.B. Treeman using the lock-in detector at 3 cms. The width of the outermost lines in the spectrum was the same as the inner ones, measuring to an accuracy of about 10%. There is no sign of doubling of

the outer lines; diagram 4.5 shows the lock-in detector traces of the lines at either end of the spectrum (the curve is a differential of the line shape and shows no trace of irregular changes of slope).

Assuming the least favourable concentration of ^{57}Co : ^{59}Co of 0.5 : 1.9 a reconstruction of the outermost line of the spectrum was made to see how far the two lines could be separated before they were resolved. Diagram 4.6 shows this reconstruction; the smaller line is clearly visible when the two lines are separated by 1.1 of the line width. As the line width is 12.5 gauss the maximum possible separation of the lines is ~ 14 gauss. Therefore the maximum possible difference between the magnetic moments is 5%.

Thus the nuclear spin of ^{57}Co is $7/2$ and the magnetic moment is 4.6 ± 0.2 nuclear magnetons (the magnetic moment of ^{59}Co is 4.6 nuclear magnetons).

The line width in the radioactive crystal, 12.5 gauss, is considerably larger than the 2 gauss expected. This is possibly due to the intense γ -ray bombardment to which the crystal is being subjected. If the position of the ions is seriously disturbed by this bombardment the crystal field at the cobalt ions may become randomly distorted: in such an anisotropic spectrum this distortion would produce considerable line width. The broadening might be less

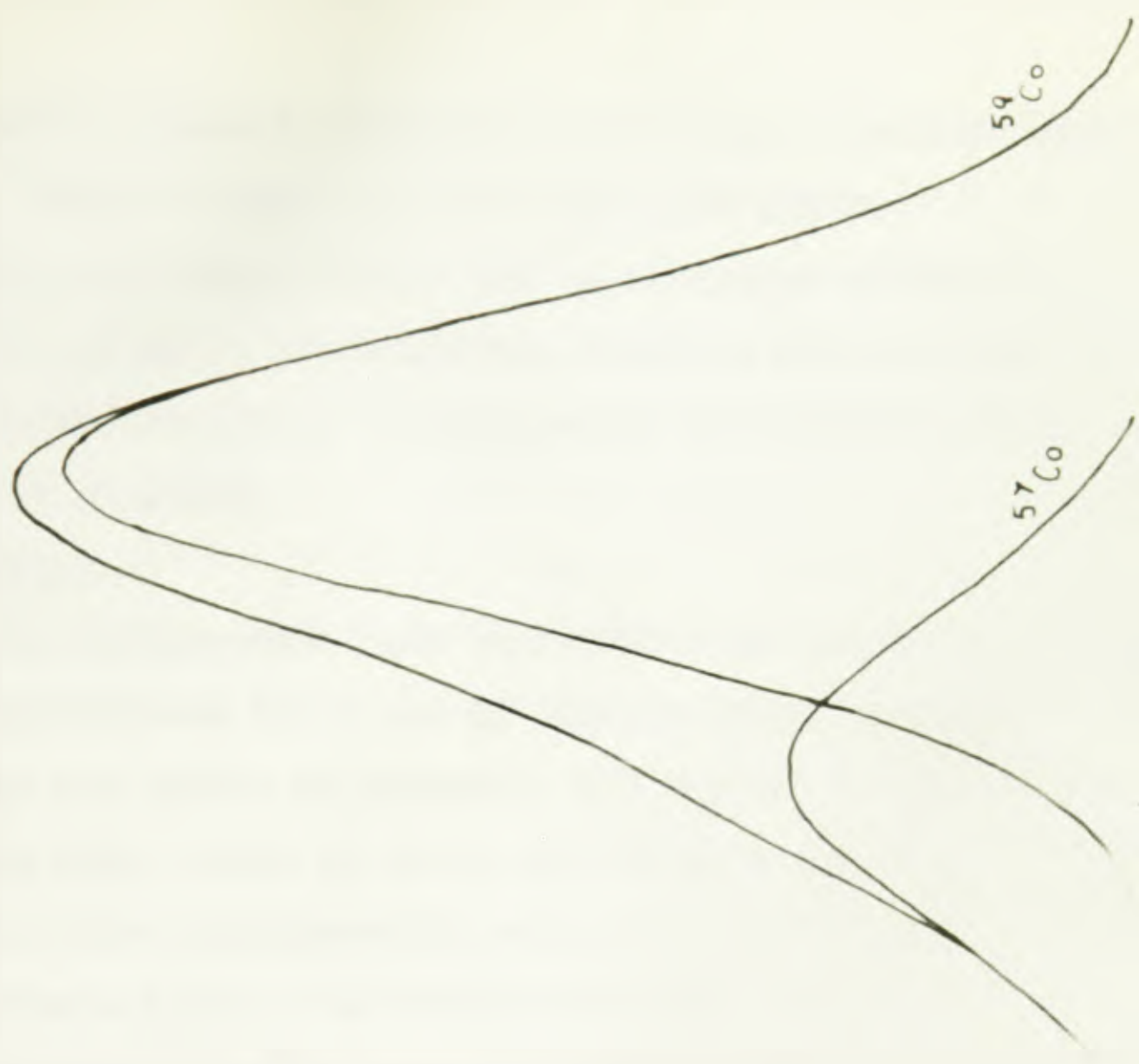


Diagram 4.6



Diagram 4.5

serious if a cobalt salt with an isotropic spectrum were used. Trenam (1953)^b has found that one ion in $3Co(NO_3)_2 \cdot 2La(NO_3)_3 \cdot 24H_2O$ has an isotropic spectrum. The separation of the hyperfine lines is only 44 gauss but this disadvantage may be compensated if a smaller line width is obtained.

DISCUSSION

The measurements made on vanadium 50 are of particular interest because it is one of the few stable isotopes which have an odd number of neutrons (27) and an odd number of protons (23). Both of these odd nucleons should be in $f_{7/2}$ states. The total possible spin, which is the one predicted by Nordheim (1951), is therefore $I = 7$. The fact that $I = 6$ conforms to the apparent tendency of odd-odd nuclei not to have the extreme value for their spin which the odd particles permit. Excluding cases when both odd nucleons are in $1/2$ states 6Li , ${}^{22}Na$, ${}^{24}Na$, ${}^{36}Cl$, ${}^{40}K$ all have smaller than extreme values while only ${}^{10}B$ and ${}^{86}Rb$ have extreme values (table 2, Klinkenberg 1952). Hitchcock (1952), using the $j-j$ spin orbit model of the nucleus, has worked out the energy levels of the nucleus of ${}^{50}V$ for different types of nuclear potential functions. He found that a level with spin 6 lies lowest if he assumed a δ -function potential; the associated gyromagnetic ratio he calculated to be 0.542 which agrees quite well with the measured

value of 0.557.

Cobalt 57 has 27 protons and 30 neutrons in its nucleus. The odd neutron is in a $4f_{7/2}$ state, which accounts for the nuclear spin. ^{57}Co has two less neutrons than ^{59}Co , which are in $3p_{3/2}$ states, according to Klinkenberg (1952). The fact that the magnetic moment of ^{57}Co is so closely equal to that of ^{59}Co shows that the removal of this pair of neutrons does not disturb the lowest available level of the proton.

κ in the rare earths.

Bleaney and Low (1954) have found a small κ in divalent europium. This however gives a very small contribution to the h.f.s. of the rare earth ions and may be neglected for the cases of terbium and praseodymium which are discussed in chapter 7.

CHAPTER 5

CHROMIC METHYLAMINE ALUM

5.1 INTRODUCTION

The spectrum of chromic methylemine alum $\text{Cr}(\text{NH}_3\text{CH}_3)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ has been investigated by Bagguley and Griffiths (1950) at room temperatures and by Bleaney (1950) at low temperatures. These workers found that the Stark splitting is $0.165 \pm 0.005 \text{ cm}^{-1}$ at room temperatures and $0.170 \pm 0.003 \text{ cm}^{-1}$ at 90°K and 20°K . Gardner and Kurti (1954) obtained a value of $0.188 \pm 0.007 \text{ cm}^{-1}$ by adiabatic demagnetisation methods, and relaxation specific heat measurements by Cooke, Meyer and Wolf (unpublished) confirmed this. In an attempt to explain this discrepancy a thorough investigation of the substance was undertaken.

5.2 CRYSTALLOGRAPHY OF THE ALUMS

The crystallography of the alums, which are an isomorphous series of salts with chemical formula $\text{M}^{+++}\text{M}^+(\text{XO}_4)_2 \cdot 12\text{H}_2\text{O}$, (where M^{+++} is an ion from the first transition group of the periodic table, M^+ is an alkali metal, ammonium or methylemine ion, and X is a sulphur, selenium or tellurium ion) is described by Beavers and Lipsom (1934). They have space group T_h^6 with four ions in the unit cell and are classified in three types α , β and γ . Large monovalent ions like Cs^+ and $(\text{NH}_3\text{CH}_3)^+$

form a β type structure which X-ray evidence shows to have a regular octahedron of water molecules around the M^{+++} ion. In the α type, formed by medium sized monovalent ions, this octahedron has a trigonal distortion about the 111 axis of the unit cell. Magnetic measurements show that the β type also has this trigonal distortion about the 111 axis. The M^{+++} ions form a face centred structure so that the nearest ions to one at 000 are at $\frac{1}{2}\frac{1}{2}0$ etc. Beevers and Lipsom only quote data for aluminium methylamine alum, but this is also assumed to apply to the chromic salt as there is only 0.3% difference in unit cell size between aluminium potassium sulphate and chromium potassium sulphate.

Chromic potassium sulphate is typical of most alums. It has well developed 111 faces and sometimes has small 100 and 110 faces. Chromic methylamine alum, however, (Lipsom, 1935) in addition to well developed 111 faces has large 210 faces and it often has small 100 faces. This makes the crystal faces in the methylamine alum slightly more difficult to recognise but measurements of the angle between faces resolves any ambiguity.

5.3 THE SPECTRUM OF THE CHROMIC ION

The ground state of the free chromic ion is $4F_{3/2}$. The cubic field in the alums splits the configuration into a singlet and two higher triplets, and the trigonal field splits the spin quadruplet into two doublets. The

energy levels are described by the hamiltonian:

$$\mathcal{H} = g\mu_B \bar{H} \cdot \bar{S} + D \left[S_z^2 - \frac{1}{3} S(S+1) \right]$$

Each of the four types of ion has its own trigonal axis along one of the four body diagonals of the unit cell.

There are certain directions and planes in which the alums are conveniently studied. From the above hamiltonian the separation of the lines due to the $S_z = 3/2$ to $1/2$ and $-1/2$ to $-3/2$ transitions is seen to be $2D(1 - 3\cos^2\theta)$, where θ is the angle between the direction of the external field and the trigonal axis. Along the 100 directions all ions are equivalent with zero separation of the $\pm 3/2$ to $\pm 1/2$ lines, and in the 100 plane the ions are equivalent in pairs. Along the 110 direction one pair has separation of the outer transitions of $2D$ and the other pair has separation $-2D$. Along the 111 direction one ion has separation $4D$ (as this direction is parallel to its axis) and the other three are equivalent with separation $-2D/3$. In the plane perpendicular to the 111 direction one ion has separation $-D$ (as the plane is always perpendicular to its axis) and the other ions have equivalent spectra about axes at 120° to one another.

Most of the work described here has been done in two planes, the 111 and the 110. The former is obtained by mounting the crystal on a 111 face and the latter by

using a wedge. A crystal of $\text{KCr}(\text{SeO}_4)_2 \cdot 12\text{H}_2\text{O}$ was mounted in these two planes, and its behaviour is consistent with the above hamiltonian. Diagram 5.1 shows how closely the spectrum follows the predictions of the last paragraph; this diagram also shows that the crystals can be mounted fairly accurately in the desired plane, because inaccuracies of mounting would cause a departure from this predicted behaviour.

5.4 DILUTE CRYSTALS

The angular dependence of the spectrum of a crystal of aluminium methylenamine alum containing 1% Cr^{+++} in the 111 and 110 planes is shown in diagrams 5.2 and 5.3. The type of spectrum obtained in the 110 plane depends upon the plane investigated. Experiments done on a crystal in planes 110, 011 and 101 in turn showed that two planes gave spectra of type 5.3a and one gave one of type 5.3b. However, it was possible in other samples to change the type of spectrum from a crystal mounted on the same face by allowing it to warm up and cooling it down again. These spectra may be explained if it is assumed that there is a rhombic distortion of the trigonal field. This modifies the hamiltonian to:

$$\mathcal{H} = g\beta\mathbf{H} \cdot \mathbf{S} + D \left[S_z^2 - \frac{1}{3}S(S+1) \right] + E(S_x^2 - S_y^2)$$

In order to keep the overall cubic symmetry it is necessary to postulate more than four ions in the unit cell. As the spectra show that there are only four ions it is supposed that the crystal has tetragonal symmetry. The rhombic axes of the four ions are supposed to be in directions:

z axis	y axis	x axis
separation $4D$	separation $2D + 6E$	separation $2D - 6E$
111	$1\bar{1}0$	$11\bar{2}$
$11\bar{1}$	$1\bar{1}0$	112
$1\bar{1}1$	110	$\bar{1}12$
$\bar{1}11$	110	$1\bar{1}2$

The separation quoted is that of the $\pm 3/2$ to $\pm 1/2$ lines. The spectrum 5.3b is in the plane 110 which passes through the trigonal axis of one ion, giving a value of $4D$. In fact the diagram shows that the direction is not quite along 111 but makes an angle of 60° with the cube edge. In the 111 plane the external field is always perpendicular to one ion which is marked with a ^{thick} dashed line in diagram 5.2. The two axes of extreme separation in this plane therefore give approximate values of $2D + 6E$ and $2D - 6E$. Thus the value of E is about 10% that of D . The $2D - 6E$ axis is crossed in the 110 plane, also in this plane is the $2D + 6E$ axis for one pair of ions in the 110 direction.

Thus accurate values of D and E may be measured in this plane. The mean of several values give $4D = 4.15 \pm 0.07$ Kgauss, $2D - 6E = 1.50 \pm 0.05$ Kgauss and $2D + 6E = 2.71 \pm 0.07$ Kgauss. These give $D = 1.04 \pm 0.02$ Kgauss and $E = 0.10 \pm 0.01$ Kgauss.

Several other features of the spectrum may be fitted to this model. The separation for the other pair of ions in the 110 direction is $5D/2 + 3E/2$ which is just a little larger than $2D + 6E$; this is seen to be so in diagram 5.3b. In the planes 101 and 011 (diagram 5.3a) the $4D$ separation should be most nearly approached at an angle 53° from the cube edge; the separation along the face diagonal should be D for one pair of ions and $\sim 0.8D$ for the other pair. Both of these predictions are verified. At 37° from the cube edge is the direction almost perpendicular to the axis of one ion, and the separation here should be $1.15D$. The measured separation, averaged over a number of determinations, is $1.14D$.

The observed spectrum therefore fits well with the postulation that the structure of the alums becomes tetragonal at low temperatures. Each ion is in a rhombic crystal field such that D and E have the values quoted above, and the directions of the axes are as stated above with a 5° rotation about the y axis away from the cube edge. The tetragonal axis need not be in the same direction

in different parts of the crystal, or in the same part of the crystal under different cooling conditions. The direction probably depends upon internal strains, which in turn depend upon how the crystal is secured in the resonator and how far strains have been removed by cracking. Several crystals have exhibited more than four lines in the unit cell, and these crystals are often found to be cracked when they are removed from the resonator, which suggests that different parts of the crystal may have assumed different tetragonal axes depending upon the local strains in the cracked fragments.

5.5 CONCENTRATED CRYSTALS

Diagrams 5.4 and 5.5 show the results of similar measurements in the 111 and 110 planes of a concentrated crystal of chromic methyamine alum. The lines are much more difficult to follow as they are much broader but the behaviour is similar to that in the dilute crystal. The crystal field parameters however have different values. Measurements were made at both 90°K and 20°K and the fields at which lines occurred were found using proton resonance. Table 5.1 shows the average of several values for different axes; 4D is always measured in the 111 direction, but $2D \pm 6E$ are measured in both planes.

TABLE 5.1

Temperature	z axis separation in kgauss $4D$	x axis separation in kgauss $2D + 6E$	y axis separation in kgauss $2D - 6E$
90°K	3.77 ± 0.03	2.40	1.22
20°K	3.80 ± 0.03	2.44	1.26

These give a mean value of $D = 0.945 \pm 0.008$ kgauss and $E = 0.10 \pm 0.01$ kgauss.

The g-value was measured at 90°K and 20°K by finding the position of the $1/2$ to $-1/2$ line and the mean position of the other two lines in the 111 direction. The value obtained, $g = 1.975 \pm 0.01$, agrees well with the g-values found in other chromic alums. This figure enables D and E to be expressed in cm^{-1} giving $D = 0.0671 \pm 0.0007 \text{ cm}^{-1}$ and $E = 0.0092 \pm 0.0008 \text{ cm}^{-1}$.

In zero magnetic field the splitting between the $\pm 1/2$ and the $\pm 3/2$ levels, due to the crystal field, is $2\sqrt{D^2 + 3E^2}$. This gives a value of $0.177 \pm 0.002 \text{ cm}^{-1}$, which is larger than the value found by Bleaney assuming no rhombic component, but is considerably smaller than the value of Kurti and Gardner.

5.6 EXCHANGE EFFECTS

The remaining discrepancy between the results of p.r. and adiabatic demagnetisation measurements might be explained if there were considerable exchange between the

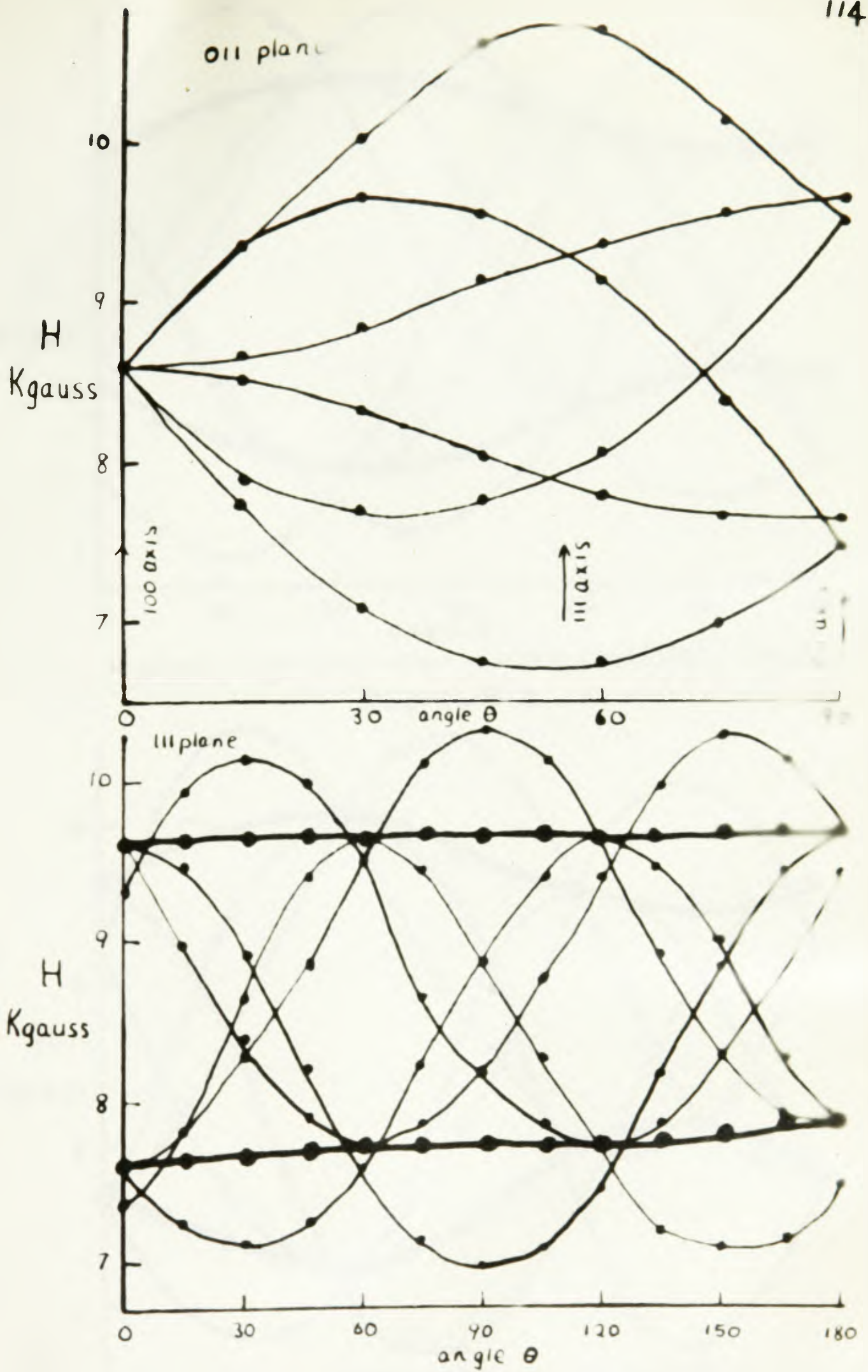
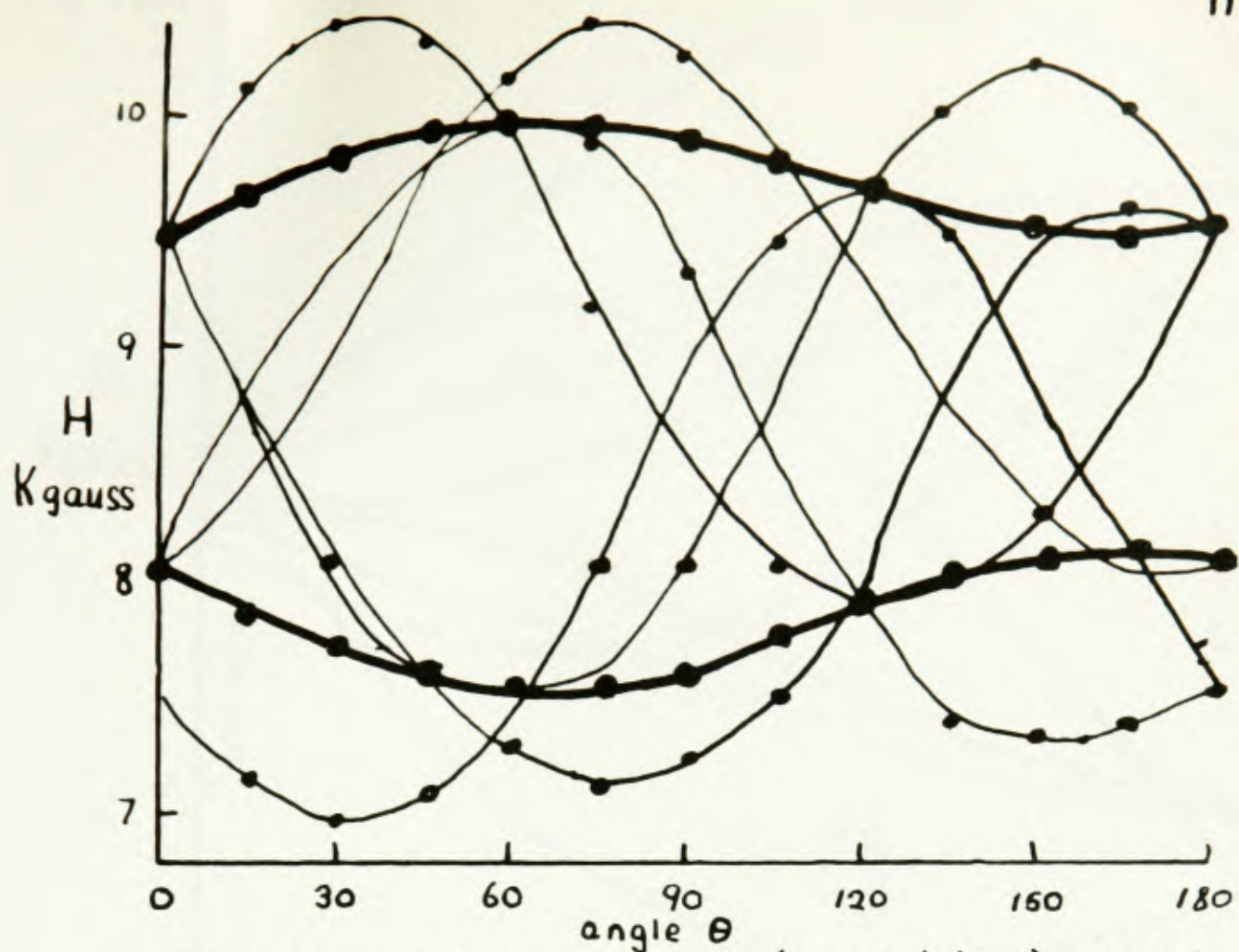
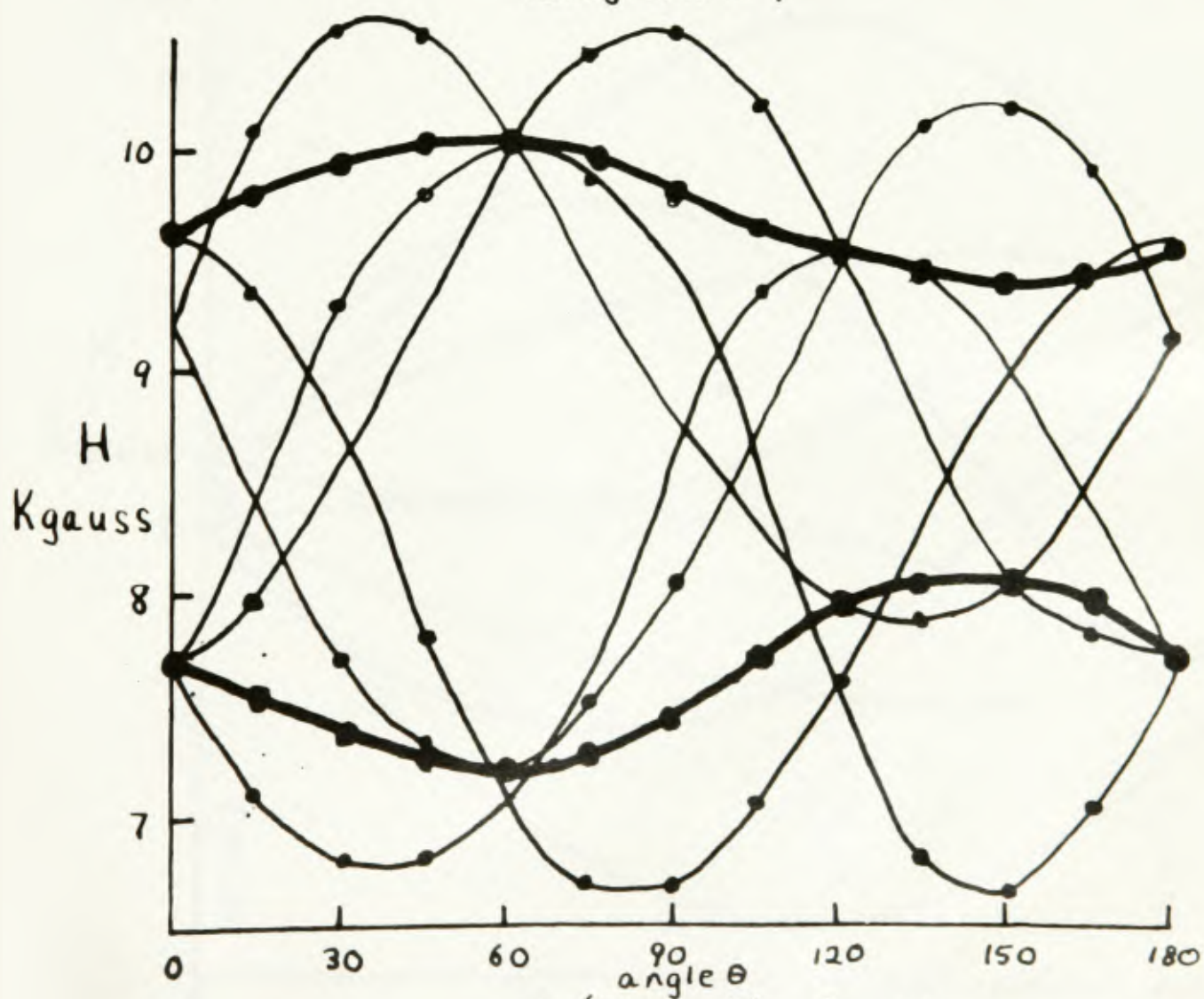


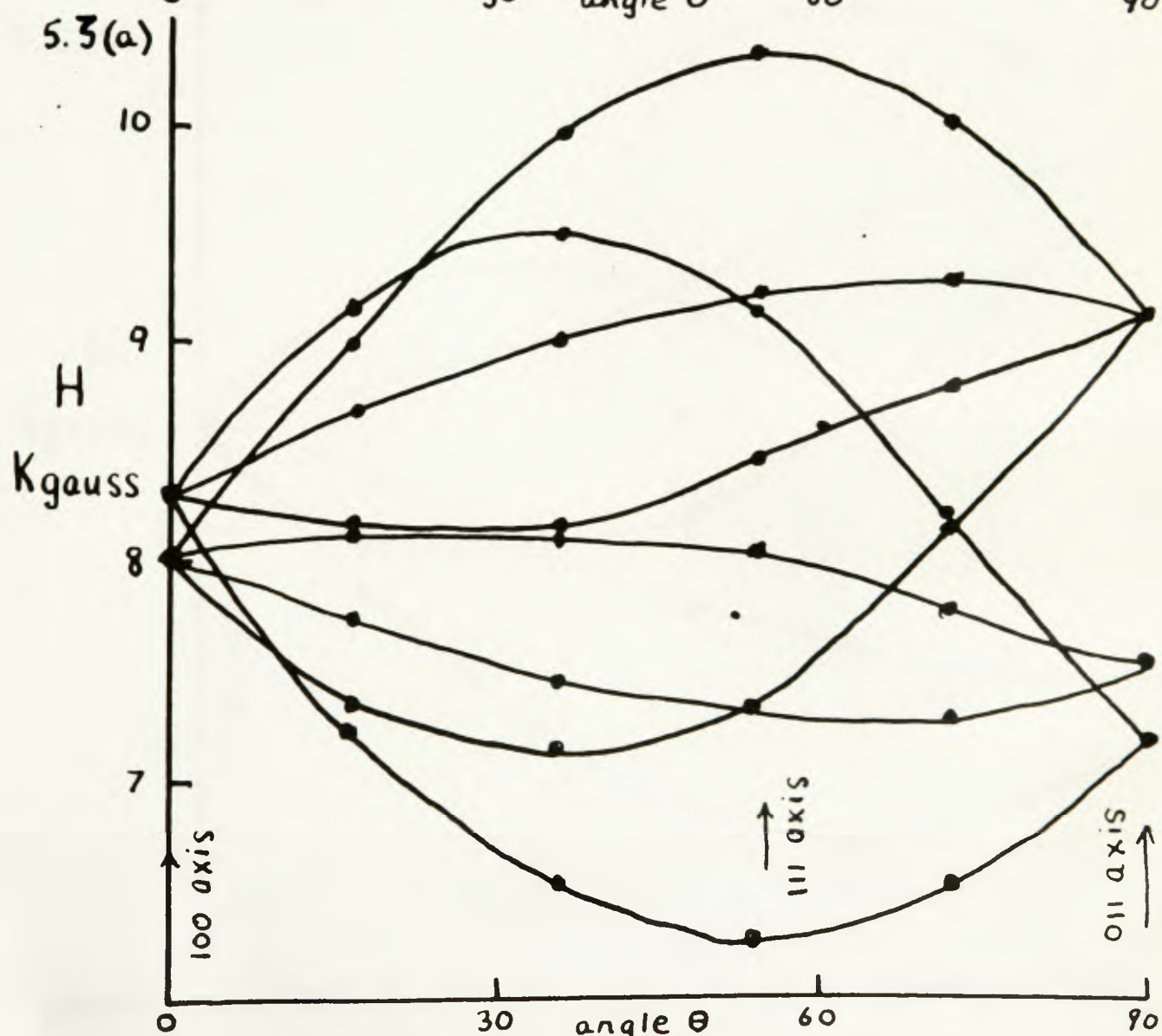
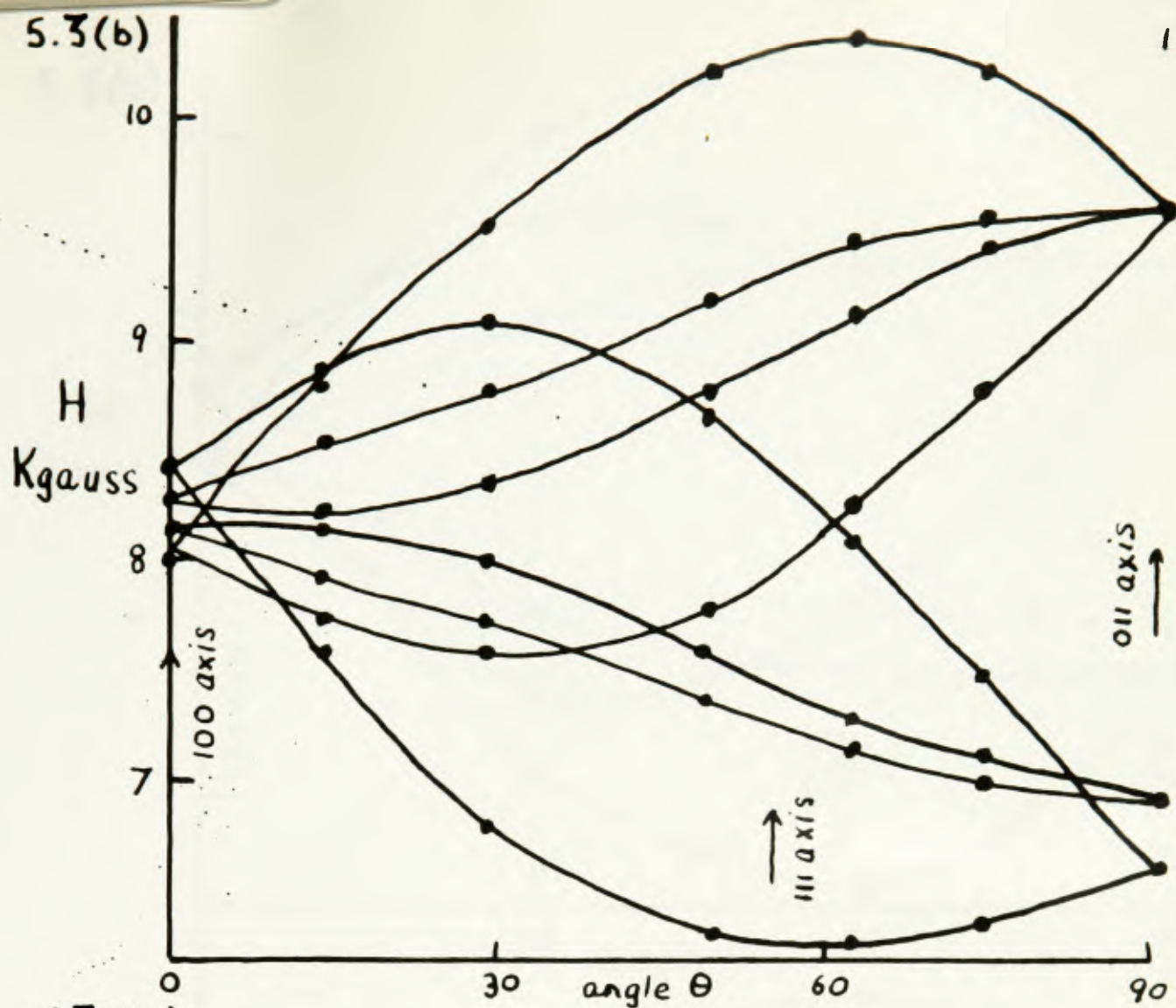
Diagram 5.1



III plane : concentrated $\text{Cr}(\text{NH}_3\text{CH}_3)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$
Diagram 5.4

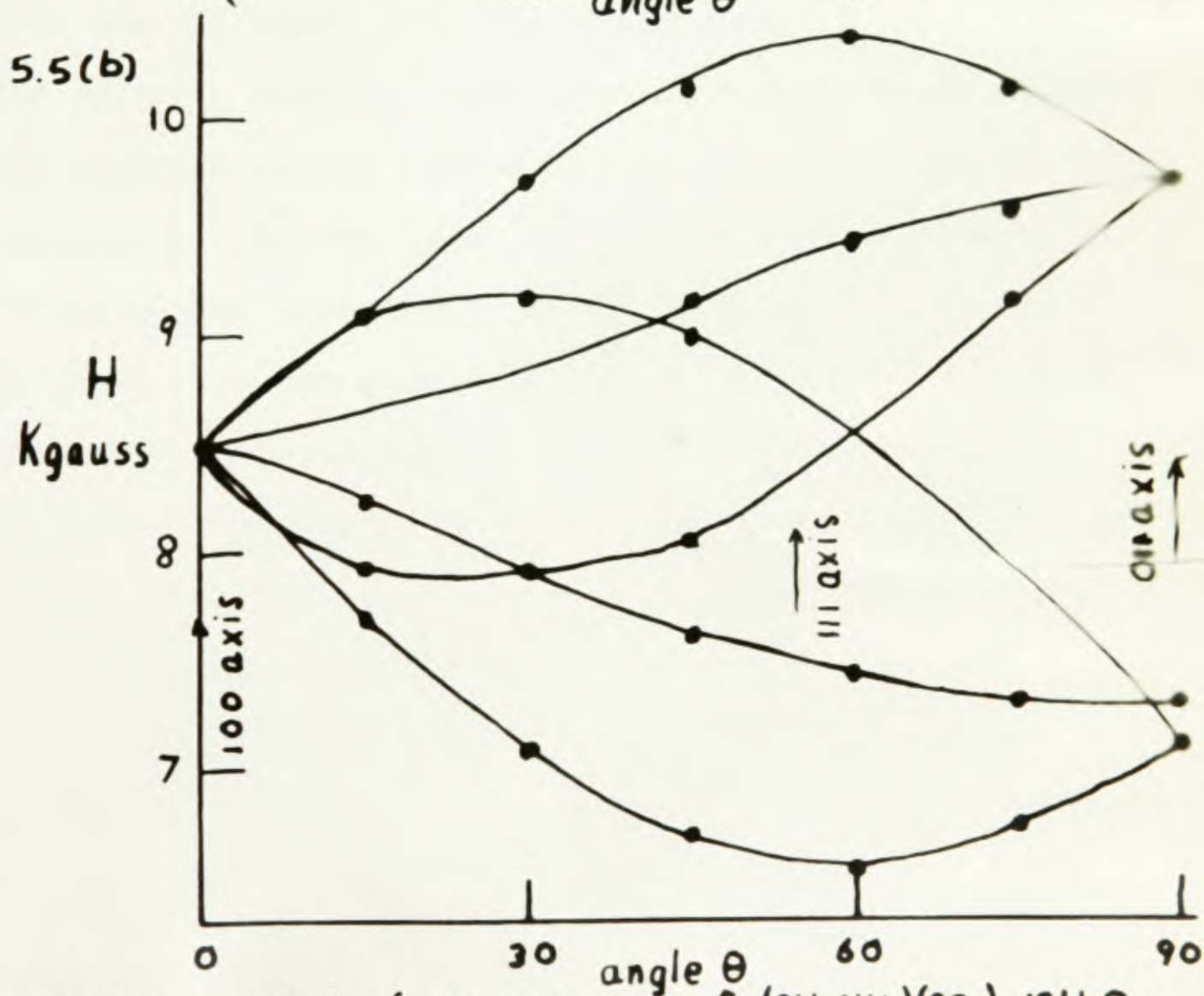
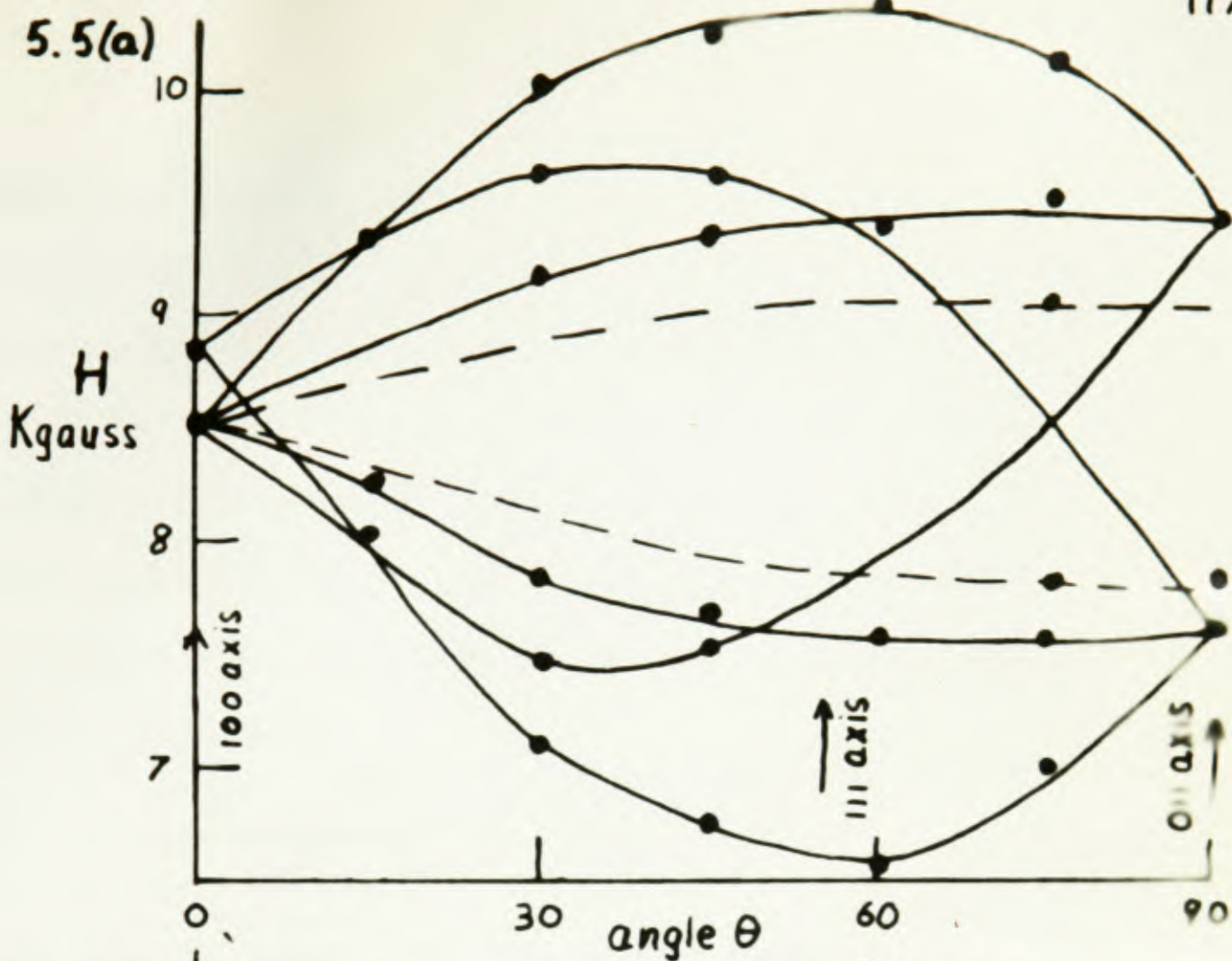


III plane : dilute $\text{Cr}(\text{NH}_3\text{CH}_3)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$
Diagram 5.2



on planes: dilute $\text{Cr}(\text{NH}_3\text{CH}_3)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

Diagram 5.3



001 planes, crystal of concentrated $\text{Cr}(\text{CH}_3\text{NH}_2)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

Diagram 5.5

neighbouring chromic ions.

The theory of Van Vleck (1937) has been developed to calculate the contribution to the specific heat and Curie-Weiss constant for a spherical sample when there is interaction between neighbours, adding a term to the hamiltonian of the form $AS_xT_x + BS_yT_y + CS_zT_z$ (see chapter 1.4). The contribution to the specific heat is given by (Appendix 1):

$$\frac{C_T^2}{R} = \frac{J^2(J+1)^2}{6k^2} \sum \frac{(A^2 + B^2 + C^2)}{3}$$

where the sum is taken over all neighbours.

The crystal field of each nearest neighbour is derived from the central ion by reflection in the cube face in which it is situated, and the line joining the ions bisects the angle between the directions of the trigonal fields of the ions so that it seems reasonable to take this as one of the axes of anisotropic exchange. In this case the above general form of interaction may be used with the line joining the ions being the z axis (chapter 1.4).

If A , B and C are written $(\alpha + a + j)$, $(\beta + b + j)$ and $(\gamma + c + j)$, (where α , β and γ represent magnetic interaction, a , b and c represent anisotropic exchange, defined such that $a + b + c = 0$, and j represents isotropic exchange), and exchange from all but the nearest neighbours

is neglected, this expression may be reduced to:

$$\frac{C_T^2}{R} = \frac{j^2(J+1)^2}{6k^2} \left[4.8(\alpha^2 + \beta^2 + \gamma^2) + 4(a^2 + b^2 + c^2) + 12j^2 - 24\alpha c \right]$$

The Curie-Weiss Δ is given by (Appendix 1):

$$\Delta = 4 \frac{j(j+1)}{k} j$$

Kurti and Gardner obtain $193 \pm 7 \times 10^{-4} \text{ deg}^2$ as the contribution to the specific heat of chromic methylamine alum from interactions and the Stark splitting. The Stark splitting contributes $D^2 + 3E^2$ which is 161×10^{-4} , and the magnetic interaction contributes 9.6×10^{-4} which leaves a discrepancy of 22×10^{-4} with a total possible error of 11×10^{-4} . Kurti and Gardner also find a Curie-Weiss Δ of $0 \pm 0.02^\circ\text{K}$ which would be given by an isotropic exchange of $j = 9 \times 10^{-4} \text{ cm}^{-1}$. This would give a contribution to the specific heat of $\sim 0.2 \times 10^{-4} \text{ deg}^2$ so that the residual specific heat must be due almost entirely to anisotropic exchange. If the exchange is assumed to have a similar form to magnetic interaction the value of a is $25 \times 10^{-4} \text{ cm}^{-1}$. For comparison the value of a is $27 \times 10^{-4} \text{ cm}^{-1}$. Exchange of this type should be detected by studying the nearest neighbour lines (see chapter 6) in a semi-dilute salt. Exchange of the size suggested would double the separation of the nearest neighbour lines, and

would also double the mean square width of the lines in the concentrated salt (it may be regarded as an effective doubling of the magnetic interaction for the nearest neighbours).

In the 111 direction the spectrum is confused as the rhombic component of the crystal field slightly separates the $1/2$ to $-1/2$ lines of the four ions and makes the satellite lines difficult to observe. However a crystal of aluminium methylvamine alum containing 2% chromium gives very faint satellites about 45 gauss on either side of the main line, and one containing 10% chromium gives clear satellites about 50 gauss from the main line. This corresponds more closely to the 40 gauss expected from magnetic interaction than to the 80 gauss if exchange were included. In the 100 direction the lines are very broad and no satellites are seen. In the 110 direction the 10% crystal gives satellites separated by about 150 gauss which agrees well with the 158 expected from magnetic interaction alone.

In the 111 direction the $3/2$ to $1/2$ line moves to high fields well clear of the other lines in the spectrum, so that it is possible to plot out its shape using no sweep and a galvanometer to measure the detector current. This is in fact the only case of a line which is completely resolved from the rest of the spectrum. Several crystals

were used and measurements were made at 90°K and 20°K. Two crystals gave values of the mean square width which increased by about 25% on cooling to the lower temperature, and one gave a slightly smaller value at 90° which did not change on cooling further. This suggests that the behaviour of the former crystals is spurious, and the increase in width is probably due to crystal distortions or to variation of the direction of the crystal field axis in different parts of the crystal. The value of 110 gauss from the latter crystal is therefore taken as the true value for the mean square width. This agrees well with the value of 120 gauss given by Van Vleck's formula (1.4) if magnetic interaction alone is considered.

Evidence from these measurements thus appears to favour the hypothesis that exchange interaction in this salt is small. This however leaves unexplained the discrepancy between p.r. and adiabatic demagnetisation measurements.

5.7 MEASUREMENTS IN ZERO FIELD

The $3/2$ to $1/2$ transition occurs at:

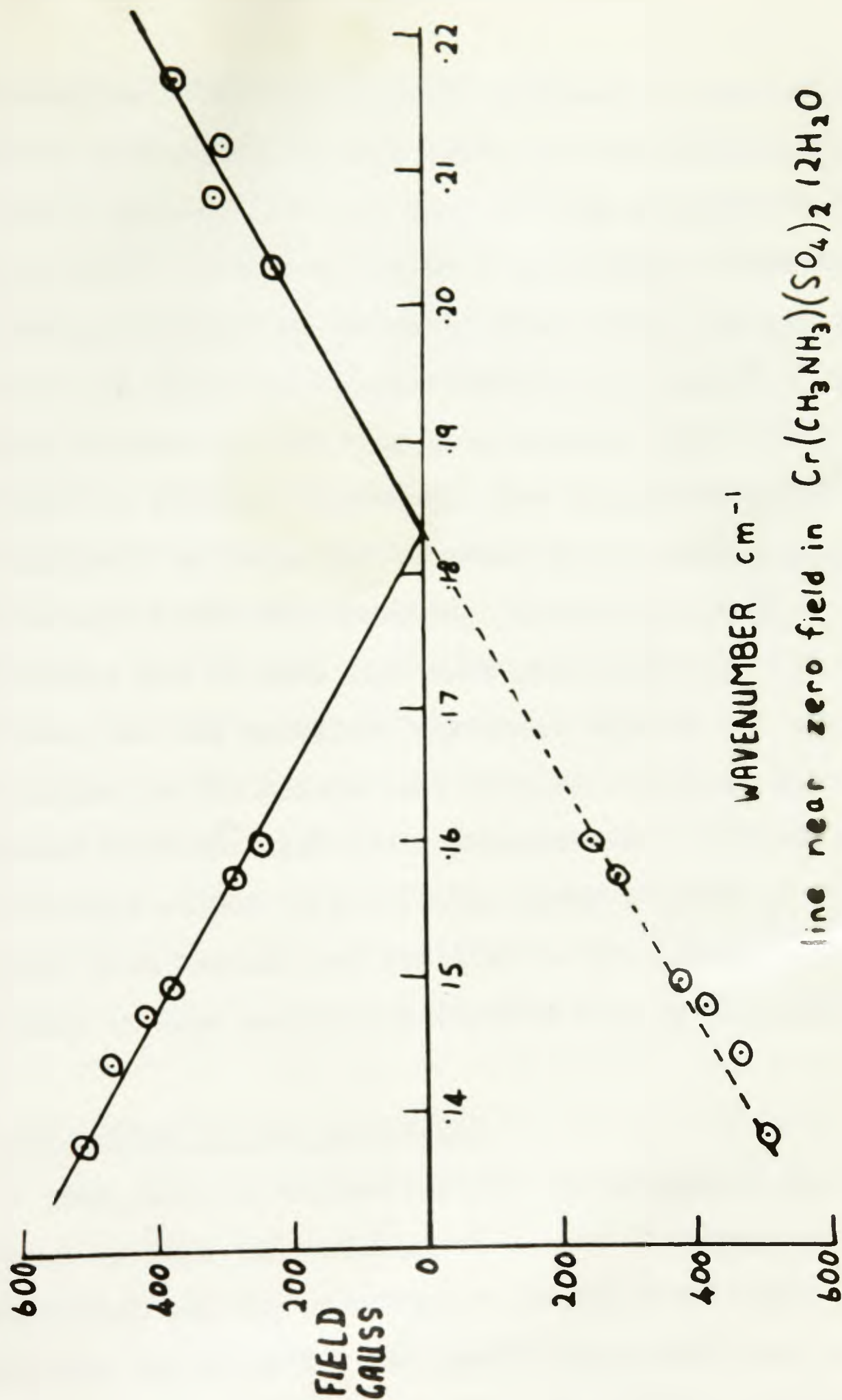
$$h\nu = g\beta H + 2D + 3E^2/(g\beta H + 2D)$$

so that when $H = 0$, $h\nu = 2D + 3E^2/D$ and in small fields the transition occurs at:

$$h\nu = g\beta H(1 - 3E^2/2D^2) + 2D + 3E^2/D.$$

Measurements have been made with the field in the 111 direction at 90°K in the low field region on both dilute

and concentrated crystals. The dilute crystal yields quite high precision results; the line occurs in zero field when $\bar{\nu} = 0.1939 \pm 0.0006 \text{ cm}^{-1}$ which agrees well with the value 0.1944 ± 0.0004 of $2D + 3E^2/D$ calculated from the parameters measured at high fields. Diagram 5.6 shows a plot of the field at which the line occurs against the measuring frequency in the low field region for the concentrated salt. The measurements made between $\bar{\nu} = .13$ and $.16 \text{ cm}^{-1}$ are not very precise as the signal strength is poor; also they tend to be in too high fields as the line is not completely resolved from the larger lines in higher fields, but this error should diminish as the line moves to smaller fields. The points lie remarkably well on a straight line considering that low signal strength, large line width and complications due to additional lines which have zero transition probability in high fields, make the measurements extremely difficult. These measurements give $.183 \text{ cm}^{-1}$ as the Stark splitting with an error of about $.01 \text{ cm}^{-1}$ and the value is inclined to be high because the low frequency points are in too high fields. The slope of the line is a little greater than the theory predicts but correction for this makes only a small reduction in the splitting. Measurements in the region of $\bar{\nu} = .183$ however, show a line in zero field from $.2 \text{ cm}^{-1}$ downward



line near zero field in $\text{Cr}(\text{CH}_3\text{NH}_3)_2(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

Diagram 5.6

in wavenumbers. The line becomes narrower as the wavenumber is reduced because it is more nearly in zero field, but the line is narrower at .176 than at .183 which indicates that the latter is nearer the true splitting. Unfortunately it is not possible, with the oscillators used, to work in the region of just smaller wavenumbers, so that it is not possible to check if the line gets broader again as the wavenumber is further decreased. The disagreement makes it very difficult to judge the accuracy of the deductions from the high field measurements. These high field measurements can be done with more precision than low field ones and the excellent agreement between the two measurements in the dilute salt inspires faith in the deductions from the high field measurements. However as the intercept method in low fields gives a value in fair agreement with Gardner and Kurti it is not possible to say that there is some additional contribution to the specific heat.

5.8 THE NATURE OF THE TRANSITION

A thin plate of dilute crystal was placed in the resonator so that the external field was parallel to the 111 direction and the spectrum was examined at room temperature and at 90°K. The positions of the various lines in the spectrum are given in kilogauss in the table below

(the crystal was not accurately mounted so that there is not exact coincidence of the $\pm 3/2$ to $\pm 1/2$ triplet at room temperature).

room temp.	4.20	5.24d	5.40	6.16	6.20t	6.77	7.13d	9.58
------------	------	-------	------	------	-------	------	-------	------

90°K	4.15	5.19d	5.69	6.22d	6.24d	6.65	7.30d	9.86
------	------	-------	------	-------	-------	------	-------	------

d = doublet t = triplet

If the resonator is allowed to warm up slowly from 90°K, and the klystron is continually tuned to the resonator, one of the doublets of the $1/2$ to $-1/2$ transition splits up, one line moving up field into the other doublet and one a few gauss down field, as the transition temperature is passed. Similar results are found in a concentrated crystal, though they are more difficult to observe as the lines are broader. A copper-constantan thermocouple was screwed into the brass of the resonator so that the temperature at which the transition occurred could be measured. The mean of several determinations gave, for the dilute salt 170°K, and for the concentrated salt 157°K. The error in these may be as much as three degrees and will probably be on the high side as they were taken while the sample warmed up. These temperatures correspond very closely to those found by Griffiths and Powell (1952).^{*} This would suggest that the same mechanism

^{*} temperature of abrupt discontinuity in dielectric constant.

might be responsible for both effects.

The methylamine ion is the only ^{axially} ~~non-spherically~~ symmetrical ion which forms an alum. It is possible that in order to obtain the required spherical symmetry the radical is rotating in a random way to give itself an average spherical form. If at a certain temperature this rotation ceased and the radical set with its axis in a particular direction, the crystal structure would be distorted into a lower symmetry, and tetragonal symmetry is the highest symmetry possible in such a case. Such an effect would probably be cooperative and the direction of the tetragonal axis would be determined by local strains.

A nuclear resonance experiment was done by Rollin and Watson to see if the rotation of the methylamine radical could be detected. The rotating protons should give a sharp line, so that this should be visible at room temperature and at the temperature of solid carbon dioxide and not at 90°K. A sharp line less than 1 gauss broad was visible at room temperature and at 195°K, and only a broad line (~ 30 gauss) at 90°K which is consistent with the theory of a quenched rotation.

* ~~Except for $(\text{NH}_4)^+$ which~~

CHAPTER 6

INTERACTIONS BETWEEN NEIGHBOURING IONS

6.1 INTRODUCTION

Interaction between neighbouring paramagnetic ions broadens the resonance line (chapter 1.4). By studying line width and line shape it might be possible to find out something about the size and nature of the interactions. However, as the line shape has contributions from all the surrounding neighbours, it is a complex, and in many cases impossible task to analyse the measurements.

In a crystal where the paramagnetic substance is diluted with an isomorphous diamagnetic substance, most of the lattice sites which were occupied by paramagnetic ions are occupied by diamagnetic ones. In this case most of the nearby paramagnetic ions surrounding a particular ion are replaced by diamagnetic ones which contribute little to the line width. The probability of finding two adjacent paramagnetic ions is proportional to the concentration of the paramagnetic ions. As explained in chapter 1.4, for groups of two or more adjacent paramagnetic ions, a hamiltonian can be derived by adding the hamiltonians for the individual ions, together with a term to represent the interaction between them. Generally such groups of ions give rise to lines which are slightly displaced from the line due to isolated ions, and they appear as

satellites on either side of this line (see for example Bleaney, Elliott and Scovil, 1951). In very dilute crystals these lines are very faint, and in fairly concentrated crystals the spectrum is complicated by the fact that groups of more than two ions give quite intense lines, and lines due to an isolated pair become faint, as the probability of such pairs is small. As the case of isolated pairs is the least complex to deal with theoretically, most work has been done on crystals containing between 10% and 2% of the paramagnetic ion, where isolated pairs produce lines of good intensity and are not complicated by lines from other groups.

The position of the satellites may be calculated in terms of magnetic and exchange interaction. Provided that the distance between ions is known from crystallographic measurements, the magnetic interaction can be calculated. Thus from the measured interaction the size and nature of the exchange can be found. By studying various compounds it should be possible to discover how exchange varies with the type of, and distance between, the ions between which it operates. There are however two limitations to the method.

The spectrum of many ions can be analysed only at low temperatures, and in order to calculate the magnetic interaction thermal expansion must either be ignored, or

a value for the coefficient of expansion estimated. Measurements of thermal expansion have not been made on any of the substances studied, and as the expansion may even be anisotropic it has been ignored in calculations of magnetic interaction, and the possible effects of expansion are considered when individual cases are discussed later.

Precise measurements can be made only on the dilute crystals, whereas most interest is in concentrated crystals, and, although the order of magnitude of the interactions must be the same in both, no accurate values for concentrated salts can be found.

The substances in which nearest neighbour lines have been studied will be described separately in this chapter.

6.2 NEODYMIUM ETHYL SULPHATE

Scovil (1951) observed nearest neighbour (sometimes abbreviated to n.n.) lines in concentrated neodymium ethyl sulphate when the steady field was parallel to the crystal axis. The lines were not resolved perpendicular to the axis but an estimate of their position could be made. In both directions the separations of the n.n. lines appeared to be that expected, assuming that the interaction between neighbours is purely magnetic. As this case is not complicated by large exchange it was

studied to see how well the observed lines agreed with theory, which in this case is well understood.

To calculate the positions of the n.n. lines a knowledge of the crystallography of the ethyl sulphates and the general features of the spectrum of M^{+++} in the ethyl sulphates are required. Both of these will be briefly discussed.

CRYSTALLOGRAPHY OF THE ETHYL SULPHATES

The ethyl sulphates of form $M^{+++}(C_2H_5SO_4)_3 \cdot 9H_2O$, where the possible M^{+++} ions include Yt⁺⁺⁺ and the rare earths, form an isomorphous series. X-ray examination of Yt and Ce ethyl sulphate has been made by Kotelar (1937) who found that the space group was probably C_{6h}^2 . There are two M^{+++} ions per unit cell and both are surrounded by nine water molecules, whose distribution is shown in diagram 6.1. This distribution has a threefold axis of symmetry which explains the crystal field assumed by Elliott and Stevens (chapter 1.2) for these salts. Diagram 6.2 shows a plan and elevation view of the distribution of neighbouring M^{+++} ions and their distances apart.

The crystals grow in flat hexagonal plates such that the crystal axis lies in the plane of the plate parallel to one pair of edges. The salts sometimes crystallise as needles, but this type of crystal is not used as it is

arrangement of
Neodymium nearest
neighbours in
 $\text{Nd}(\text{CH}_3\text{SO}_3)_3 \cdot 9\text{H}_2\text{O}$

plane perpendicular
to axis

plane containing
axis

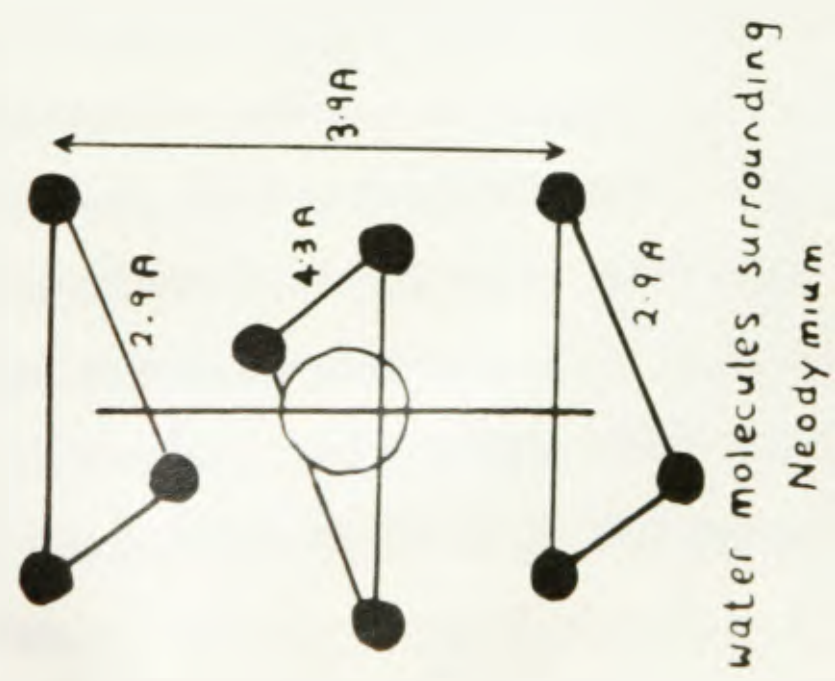
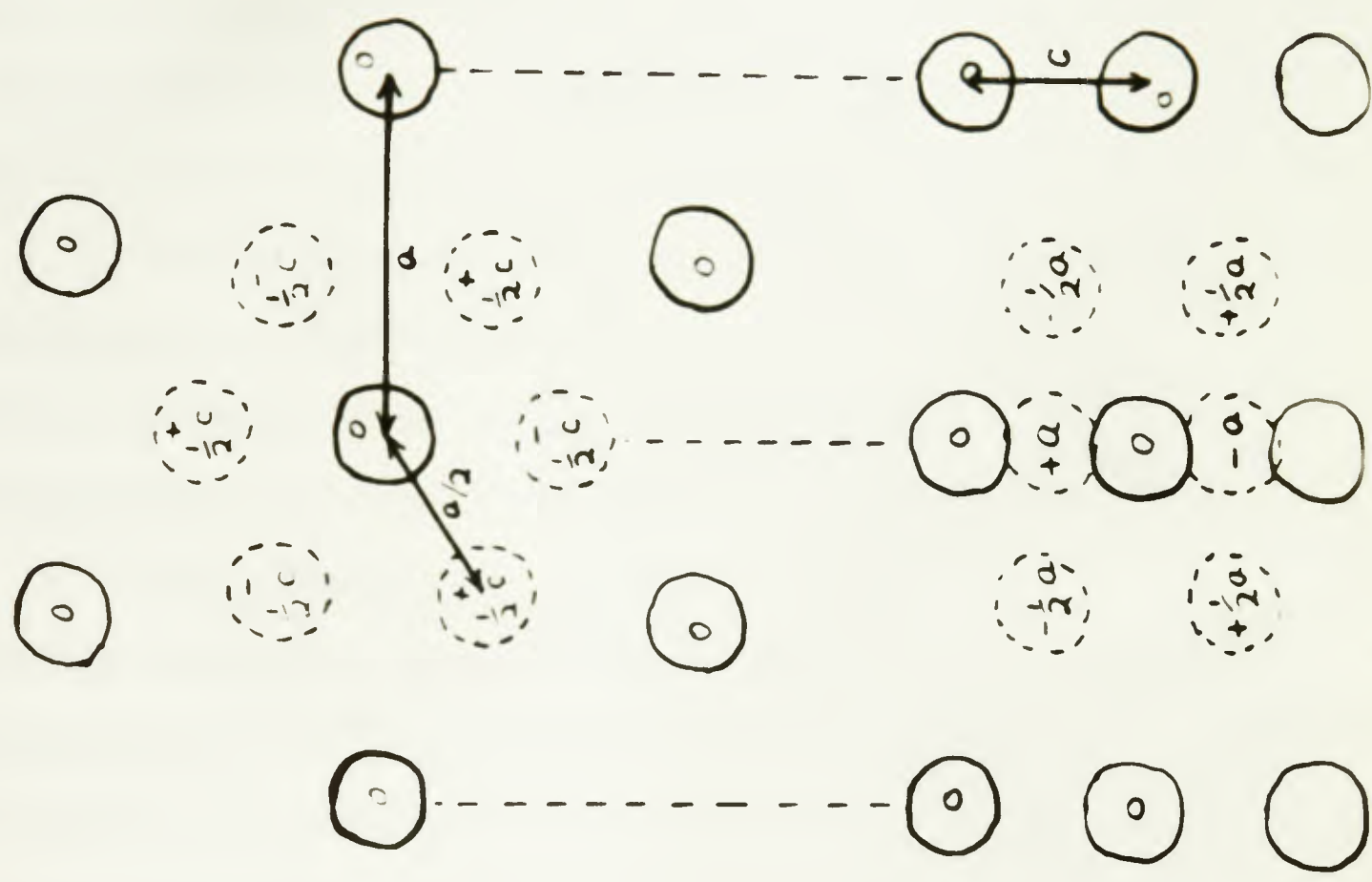


Diagram 6.1

long and thin and therefore contains little material.

THE NEODYMIUM SPECTRUM

This is observed at 20°K and is described in three papers: Bleaney and Scovill (1950), Bleaney, Scovill and Trehan (1952) and the theory in Elliott and Stevens (1951). The free Nd^{++} ion is in a $4f^3$, $^4I_{9/2}$ state and, in the ethyl sulphate has a ground state of the form

$$\cos \theta |J_z = \pm 7/2\rangle + \sin \theta |J_z = \mp 5/2\rangle$$

so that in a magnetic field $\Delta M = 1$ transitions occur between the components of this doublet. The doublet has effective spin $1/2$ and is described by the hamiltonian:

$$\mathcal{H} = g_{\parallel} \beta H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y)$$

Naturally occurring neodymium contains seven isotopes, five of which have even mass number and two of which, 143 (12.2%) and 145 (8.3%), have odd mass number and therefore give rise to hyperfine structure, which for each consists of eight lines (as $I = 7/2$ for both). This adds a term $A S_z I_z + B(S_x I_x + S_y I_y)$ to the hamiltonian. The values of the parameters are $g_{\parallel} = 3.535$, $g_{\perp} = 2.073$, $143A = 0.03803$, $143B = 0.01989 \text{ cm}^{-1}$, $145A = 0.02364 \text{ cm}^{-1}$, $145B = 0.01237 \text{ cm}^{-1}$. Both ions are magnetically equivalent so that the spectrum consists of a central line (due to the even isotopes), and sixteen lines (due to the odd isotopes) which have about 1.5% the intensity of the central one.

THEORY

The two nearest neighbours of any Nd^{+++} ion lie along the crystal axis 7.11Å away. The six nearest lie 8.65Å away along a line 65° from the axis at the corners of two equilateral triangles one above and one below the ion if the axis is vertical. There are six neighbours 14.08Å away at the corners of a regular hexagon in the plane perpendicular to the axis, and two 14.22Å away along the axis.

For cases where there is axial symmetry magnetic interaction and exchange may be written (chapter 1.4):

$$\rho S_z T_z + \sigma (S_x T_x + S_y T_y)$$

but for cases where there is not axial symmetry the interaction is more complex and its form is not easily calculated. The nearest neighbours can be treated using the above form of interaction; but, as the problem is complex and exchange is small, the ions further away will be treated as if only magnetic interaction were present.

The three separate cases which have to be considered are: interaction between isotopes both of even mass number, interaction between isotopes one of which has even and one of which has odd mass number, and interaction between isotopes both of which have odd mass number. Since 80% of the isotopes have even mass number the latter case can be neglected. The hamiltonian for two isotopes

of even mass number is (spine S and T):

$$\mathcal{H} = g_{\parallel} \beta H_z (S_z + T_z) + g_{\perp} [\beta H_x (S_x + T_x) + \beta H_y (S_y + T_y)] \\ + \rho S_z T_z + \sigma (S_x T_x + S_y T_y)$$

and for the case when one isotope has odd mass number a term $A S_z I_z + B (S_x I_x + S_y I_y)$ is added.

For isotopes of even mass number when the external field is parallel to the crystal axis the $|++\rangle$ and $|--\rangle$ states are degenerate so that off diagonal elements admix them. The diagonalized matrix of the hamiltonian is (in the brackets of type $|++\rangle$ describing the states the first sign is the sign of S_z and the second that of T_z in the state.):

$$\begin{array}{l} |++\rangle \\ \frac{1}{\sqrt{2}}(|+-\rangle + |-+\rangle) \\ \frac{1}{\sqrt{2}}(|+-\rangle - |-+\rangle) \\ |--\rangle \end{array} \left| \begin{array}{cccc} g_{\parallel} \beta H + \frac{1}{4} \rho & 0 & 0 & 0 \\ 0 & -\frac{1}{4} \rho + \frac{1}{2} \sigma & 0 & 0 \\ 0 & 0 & -\frac{1}{4} \rho - \frac{1}{2} \sigma & 0 \\ 0 & 0 & 0 & -g_{\parallel} \beta H + \frac{1}{4} \rho \end{array} \right|$$

which gives transitions at:

$$h\nu = g_{\parallel} \beta H + \frac{1}{2} \rho - \frac{1}{2} \sigma$$

$$h\nu = g_{\parallel} \beta H - \frac{1}{2} \rho + \frac{1}{2} \sigma$$

Thus the satellite lines are symmetrically placed on either side of the line due to single ions at $h\nu = g_{\parallel} \beta H$, and they are separated by $\rho - \sigma$.

For one isotope of even and one isotope of odd mass

number when the external field is parallel to the crystal axis the $| + - \rangle$ and $| - + \rangle$ states are not degenerate and off diagonal elements can be treated by perturbation theory. The matrix of the hamiltonian is, assuming that the S ion has the hyperfine structure:

$$\begin{array}{l|cccc} |++\rangle & g_{\parallel} \beta H + \frac{1}{2} A m + \frac{1}{4} \rho & 0 & 0 & 0 \\ |+-\rangle & 0 & \frac{1}{2} A m - \frac{1}{4} \rho & \frac{1}{2} \sigma & 0 \\ |-+\rangle & 0 & \frac{1}{2} \sigma & -\frac{1}{2} A m - \frac{1}{4} \rho & 0 \\ |--\rangle & 0 & 0 & 0 & -g_{\parallel} \beta H - \frac{1}{2} A m + \frac{1}{4} \rho \end{array}$$

which gives transitions at:

$$h\nu = g_{\parallel} \beta H + A m + \frac{1}{2} \rho + \sigma^2/4 A m$$

$$h\nu = g_{\parallel} \beta H + A m - \frac{1}{2} \rho + \sigma^2/4 A m$$

The latter term is only half a gauss for $m = 7/2$ so that it can be neglected and the satellites are symmetrically placed about the hyperfine line of an odd mass number isotope and are separated by ρ .

The cases when the external field is perpendicular to the axes may be similarly calculated and give symmetrically placed satellites with separations $-\frac{1}{2}(\rho - \sigma)$ for isotopes of even mass number, and σ for one of odd and one of even mass number. Thus by measuring the separation of n.n. satellite lines ^{parallel to the axis} on both the main line due to even isotopes and on hyperfine lines, values of ρ and σ may be calculated, and a measurement of the

satellites of the hyperfine line perpendicular to the axis gives a confirmation of these values.

The separation of the satellites due to interaction between even isotopes on the axis is found to be:

$$\delta = g_{\theta}^{-2} \left[g_{\parallel}^2 \cos^2 \theta (\rho - \sigma) - \frac{1}{2} g_{\perp}^2 \sin^2 \theta (\rho - \sigma) \right]$$

The angular dependence of separation of satellites due to interaction of two isotopes of even mass number, the line joining which is not parallel to the axis, has been calculated assuming only magnetic interaction (this result is not affected by isotropic exchange). The calculation has been done for the plane containing the axis and the line joining the two ions, which makes an angle ψ with the axis. The magnetic interaction is of form

$K [g^S \cdot g^T - 3(g^S \cdot r)(g^T \cdot r)/r^2]$ and the separation δ is:

$$\delta = \frac{K}{g_{\theta}^2} \left[(g_{\parallel}^4 \cos^2 \theta + g_{\perp}^4 \sin^2 \theta) - 3(g_{\parallel}^2 \cos \theta \cos \psi + g_{\perp}^2 \sin \theta \sin \psi)^2 \right] \\ - \frac{K}{2g_{\theta}^2} \left[g_{\parallel}^2 g_{\perp}^2 (1 - 3 \sin^2(\theta - \psi)) + g_{\theta}^2 g_{\perp}^2 \right]$$

When the external field is parallel to the axis a row of three ions along the axis gives satellites on the lines, due to transitions of the middle ion, which are separated by 2.05ρ , and on the lines due to transitions of the end ions which are separated by 1.11ρ . The calculation for three adjacent ions which are not all on the axis is much more difficult; it is however expected that the satellites

will have a separation slightly larger than ρ as the additional ion nearly completely destroys the effect of resonance between two adjacent ions on the axis (chapter 1.4). In the concentrated salt the resonance is entirely destroyed and the separation of the satellites should be 2ρ parallel to the axis and 2σ perpendicular to it.

EXPERIMENTAL RESULTS

If a crystal contains less than 4% Nd^{+++} the n.n. lines are less intense than the hyperfine lines and cannot be observed. The lines have therefore been investigated in crystals containing between 4% and 100% Nd^{+++} ion. Usually lanthanum was used as a dilutant but cerium and yttrium have also been used. Cerium can be used, although it is paramagnetic, as it has a very short spin-lattice relaxation time, and so does not broaden the Nd^{+++} resonance line.

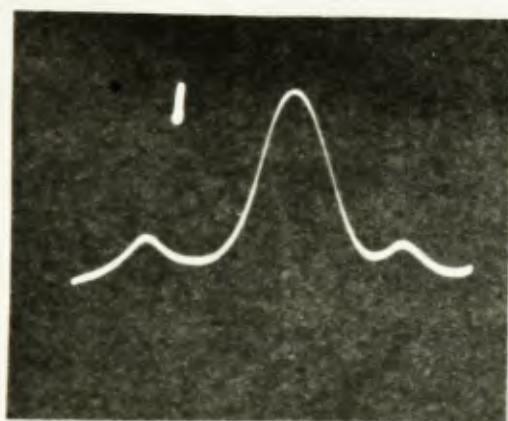
Measurements have been made at 20°K at both 1.25 and 3 cm. wavelength.

In crystals containing less than 10% Nd^{+++} the separation of the satellites, with the external field parallel to the axis, is always the same; but the lines were asymmetrically placed about the line due to single ions (see diagram 6.2), and this asymmetry varies with concentration. The asymmetry is much larger than that

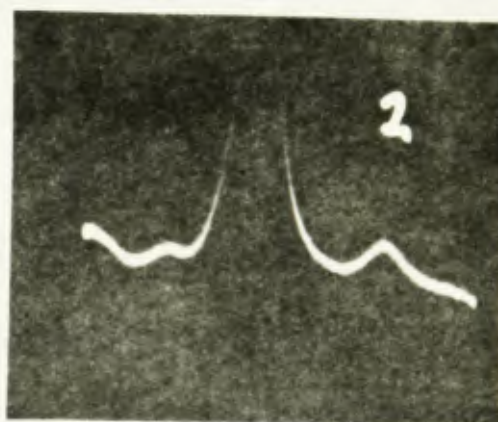


Field perpendicular to crystal axis in 1:10 Nd:La ethyl sulphate, (a) along projection of line joining two ions (b) along bisector of two such directions

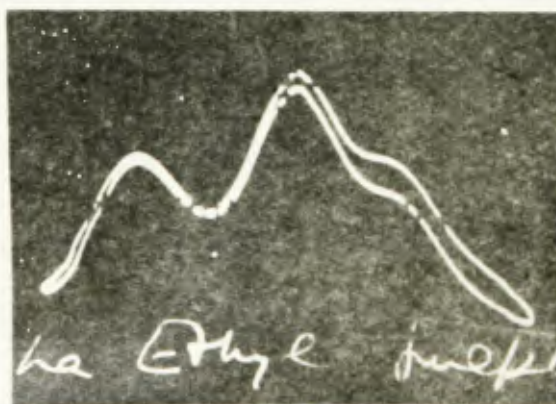
Diagram 6.2



Satellites on line due to even isotopes in 1:10 Nd:La ethyl sulphate



Satellites on line due to odd isotopes in 1:10 Nd:La ethyl sulphate



Satellites on line due to even isotopes in 1:3 Nd:La ethyl sulphate

Diagram 6.3

produced by second order effects. For any crystal the difference between the distance of the two satellites from the main line is about 2.5 times as much at 1.25 cm. wavelength as it is at 3 cm. wavelength. The results on some crystals are shown in table 6.1. A small change in g-value produces a shift in field of: $\Delta H = - (hc/\beta \lambda g^2) \Delta g$, where λ is the wavelength of r.f. radiation used. Thus the effect observed may be due to a change in g-value, possibly due to distortions of the crystal field caused by the introduction of ions of different size into the crystal lattice. A distortion of the crystal field might affect the value of the term in A_6^6 which alters the admixture of $J_z = \pm 7/2$ and $J_z = \pm 5/2$ in the ground state, and so alters the values of $g_{||}$ and $g_{\perp}$. A small change in ϕ (see THE NEODYMIUM SPECTRUM) makes $g_{||}$ and $g_{\perp}$ change by nearly the same amount in opposite directions. This is in fact found to be the case.

The change in g-value in 1:3 Nd:La crystal is about 0.03. Scovil (1951) finds a difference of this order between the g-values of concentrated Nd and 1:200 Nd:La ethyl sulphate, which may be real although it is smaller than the quoted error. Scovil's values are quoted below; the first row is for the dilute crystal and the second for the concentrated one; these values were corrected for an error in wavemeter calibration before they were

TABLE 6.1

crystal	shift of satellites in gauss		ratio
	3 cm.	1 cm.	
1:3 Nd:La	17	41.5	2.4
1:10 Nd:La	16	32	2.0
1:10 Nd:Yt	32	79	2.5
1:10 Nd:Ce	3	13	3

TABLE 6.2

dilutant	shift of satellites in gauss	unit cell constant a in Å units
La	+ 16	14.080
Ce	+ 7	14.048
Nd	0	13.992
Yt	- 40	13.903

published.

<u>$g_{\parallel}$</u>		<u>$g_{\perp}$</u>	
3 cm.	1 cm.	3 cm.	1 cm.
$3.544 \pm .001$	$3.58 \pm .04$	$2.0780 \pm .0002$	$2.09 \pm .02$
$3.58 \pm .06$	$3.61 \pm .06$	$2.06 \pm .06$	$2.05 \pm .06$

The theory that the shift of the satellites is due to a change in g -value is supported by the fact that the mean of the fields at which the satellites occur is shifted by the same amount for both those on the line due to even isotopes and those on the hyperfine lines.

Table 6.1 shows that the change in g -value is much smaller when Ce is used as a dilutant and is of opposite sign when Yt is used, though the separation of the satellites is the same. There is a correlation (see table 6.2) between the g -value shift and the size of the unit cell of the dilutant. This fact also supports the theory that the shift is due to a change of g -value produced by the distortion of the crystal field.

The separation of the satellites in crystals containing between 4% and 10% Nd^{+++} were measured by proton resonance and the results were as follows: parallel to the axis on the line due to even isotopes 196 ± 1 gauss, parallel to the axis on the outer h.f.s.

line 168 ± 1 gauss, perpendicular to the axis on the line due to even isotopes 167 ± 1 gauss, and perpendicular to the axis on the outer h.f.s. line 42 ± 3 gauss. The last measurement had to be done in an indirect way as only one satellite was visible. It is assumed that the mean field of the satellites on both the h.f.s. line and the even isotope line are shifted equally. This shift can be measured on the even isotope line, so that from the measured separation of one satellite from the h.f.s. line, the separation of the two satellites may be calculated. The results parallel to the axis give $\rho = -277 \pm 2 \times 10^{-4} \text{ cm}^{-1}$ and $\sigma = 46 \pm 2 \times 10^{-4} \text{ cm}^{-1}$. The values of the separations perpendicular to the axis calculated from these parameters, 167 ± 1 gauss and 47.5 ± 2 gauss, agree well with the measured values.

The variation of the separation of the satellites, as the angle (which the external field makes with the crystal axis) is varied, is in excellent agreement with the formula quoted in the theoretical part of this section.

Ketelaar (1937) gives the separation of the nearest ion in La ethyl sulphate to be 7.11Å and in Nd ethyl sulphate to be 7.07, whereas Roberts, Sartain and Borie (1953) give 7.12 for the latter value. For calculation of the magnetic interaction the value 7.11Å has been used. If the interaction between the ions were purely magnetic the

values of ρ and σ would be $-307 \times 10^{-4} \text{ cm}^{-1}$ and $53 \times 10^{-4} \text{ cm}^{-1}$ respectively. Thus the contributions to ρ and σ from exchange are $+30$ and -7 respectively (in units of 10^{-4} cm^{-1}). If exchange were all isotropic the contributions to ρ and σ would be proportional to $g_{\parallel}^2$ and $g_{\perp}^2$ respectively; the ratio is about 3 but they both have the same sign. Thus in order to explain the above results some anisotropic exchange must be postulated. The results would also be fitted almost exactly by magnetic interaction alone if the separation of the ions were 3% bigger. Even if the crystal does expand along the axis on cooling to 20°K it is unlikely to do so by 3%, so that it is still probable that there is both isotropic and anisotropic exchange present.

The six next nearest neighbours, which are 8.65Å away along a line making 65° with the axis, produce lines which can be seen in certain directions. Along the axis the satellites which all six produce are superimposed, but they are only 12 gauss from the main line and are not resolved. In the plane perpendicular to the axis there are directions every 60°, which are the projections of the line joining the ion to one of these off axis ions, where the separation of the satellites should be 80 gauss. These should have the same intensity as the satellites due to a pair of neighbours on the axis which are separated

by 167 gauss. In these directions the satellites are resolved and have separation of 81 gauss which is in excellent agreement with the predictions and suggests that there is little exchange interaction from these ions, as would be expected. As the external field is rotated in the perpendicular plane the satellites due to these off axis neighbours move in and out of the main line with a 60° period. At the bisectors of the directions of maximum separation the intensity of the satellites is doubled as these due to two neighbours are superimposed, but they are not resolved. Diagram 6.3 shows photographs of the satellites in these two extreme positions.

The contribution of other ions further away is too small to produce individual lines; neighbours in these positions just produce a broadening of the lines.

Measurements on crystals containing about 30% Nd^{+++} give, in addition to the satellites due to two adjacent neighbours, satellites due to three ions in a row (diagram 6.2). The more intense satellites (due to two adjacent ions) are separated by 183 ± 3 gauss, and the less intense ones (due to three ions) are separated by 360 ± 20 gauss. These figures are in quite good agreement with the predictions of the theoretical part of this section. The separation of the satellites on the hyperfine lines is the same as on the main line, as would

be expected because in neither case are the $| + - \rangle$ and $| - + \rangle$ states degenerate.

In the concentrated crystal the satellites are due to the two neighbours along the axis on either side of the ion undergoing a transition. On both main and hyperfine lines these satellites should be separated by 332 gauss and be symmetrical. They are in fact found to be symmetrical and the same for the main line as the hyperfine lines, but they are separated by 367 gauss, which is very close to the separation of 372 gauss which would be obtained if the interaction were entirely magnetic.

No explanation of this anomaly can be found. It is unlikely that exchange which exists in the dilute crystals disappears in the concentrated crystals. However, specific heat measurements by Roberts, Bartain and Borie (1953) give a value for the interaction specific heat which closely agrees with that which would be expected from magnetic interaction alone. If the exchange measured in the dilute crystals is assumed to be present in the concentrated crystal the specific heat measurements can only be fitted by assuming that the six neighbours 8.65 Å away contribute anisotropic exchange interaction which is 60% of their magnetic interaction. There is no evidence whatsoever that such is the case, in fact measurements on a dilute crystal with the external field along the line

Joining the ion to one of these neighbours show satellites which are just visible and separated by about 90 gauss, which compares well with 88 gauss expected from magnetic interaction alone. In this particular direction the satellites due to on axis neighbours have zero separation so that the lines must be due to the other off axis neighbours. Thus the difference between the dilute and concentrated crystals is unexplained.

Some measurements have also been made in a crystal containing lanthanum, neodymium and gadolinium ethyl sulphates in the ratio of 100:10:1. At 20°K the neodymium produces n.n. satellites on the lines in the gadolinium spectrum. The hamiltonian for a gadolinium ion adjacent to a neodymium ion is set up in the same way as for adjacent neodymium ions.

The Gd^{+++} spectrum consists of seven fine structure lines which can be described by the hamiltonian (Bleaney, Elliott, Scovil and Trenam, 1951, and Elliott and Stevens, 1953):

$$\mathcal{H} = \beta \hbar \cdot g \cdot \vec{S} + A_{2^0 2^0}^0(S_z) + A_{4^0 4^0}^0(S_z) + A_{6^0 6^0}^0(S_z) + A_{6^6 6^6}^6(S)$$

where S is $7/2$ and g is 1.994. The other terms are introduced by the crystal field and are calculated from the separations of the seven lines. $(A_{2^0 2^0}^0(S_z))$ is a shortened way of writing the operator equivalent of the

A_2^0 term in the expression for V in chapter 1.2). There is no hyperfine structure in the spectrum (see chapter 1.2).

With the external field parallel to the axis the satellites on each of the lines were separated by 188 gauss which, as has been explained above, is the separation expected for magnetic interaction alone. Measurements perpendicular to the axis are not precise as the satellites are not completely resolved, but they too suggest that the separation is that expected from magnetic interaction alone. Thus there appears to be little exchange interaction between Nd^{+++} and Gd^{+++} in the ethyl sulphate. The satellites are however unsymmetrically placed about the main line, the asymmetry being different for each line. The displacement on the central line might be explained by a change of g -value of 0.0003. The shift in the satellites on all the other lines can be accounted for by a decrease in all the crystal field parameters A_2^0 , A_4^0 and A_6^0 . All these changes might be produced by the distortion of the lattice produced by the introduction of an ion of different size.

6.3 CHROMIC POTASSIUM SELENATE

Unlike the methylamine alum, chromic potassium selenate alum undergoes no transition above 20°K, and its spectrum can be explained by assuming a crystal field of trigonal symmetry. For this reason it should be easier to study nearest neighbour lines in the selenate. It was expected that the exchange would be small, as none of the chromic alums previously studied has shown large departures from the line widths expected from pure magnetic interaction.

The crystallography of the alums and the spectrum of the Cr^{+++} ion have been described in chapter 5 (5.2 and 5.3).

Measurements of the g-value and crystal field parameter D have been made at 1.25 and 3 cm on a number of crystals containing various percentages of chromium. The mean g-value is 1.977 ± 0.002 and table 6.3 gives the values of D . It is seen that it increases with dilution and also with decrease in temperature. Measurements made at about 15°K detected no further change in the value of D , but they were accurate only to a few percent.

Measurements have been made at 90°K at frequencies near where the low field line occurs in zero field, which is when $h\nu = 2D$. This can be done with considerable precision in crystals containing 1% Cr where the line occurs

in zero field at $\nu = 0.181 \pm 0.001 \text{ cm}^{-1}$ agreeing well with the prediction from high field measurements at $0.182 \pm 0.001 \text{ cm}^{-1}$. In the uniaxial crystal the line occurs in zero field at $\nu = 0.181 \pm 0.001 \text{ cm}^{-1}$ agreeing well with the high field prediction at $0.181 \pm 0.001 \text{ cm}^{-1}$.

TABLE 6.3

The theory is $D = \frac{1}{2} \Delta E_{\text{crystal field}} \left(\frac{1}{2} \right)$

TABLE 6.3

Values of D in cm^{-1} for various concentrations of Cr^{+++} in $\text{AlK}(\text{SeO}_4)_2 \cdot 12\text{H}_2\text{O}$.

Temp.	100% Cr	10% Cr	1% Cr
90°K	$.064 \pm .002$	$.0895 \pm .0010$	$.0900 \pm .0003$
20°K	$.070 \pm .002$	$.0980 \pm .0010$	$.0983 \pm .0003$

in zero field at $\bar{\nu} = 0.181 \pm 0.0006 \text{ cm}^{-1}$ agreeing well with the predictions from high field measurements of $0.180 \pm 0.0006 \text{ cm}^{-1}$. In the concentrated chromium salt the line occurs in zero field at $\bar{\nu} = 0.126 \pm 0.006 \text{ cm}^{-1}$ agreeing well with the high field predictions of $0.128 \pm 0.004 \text{ cm}^{-1}$.

THEORY

The theory is quite complicated because there are four magnetically distinct ions in the unit cell, each ion has twelve equidistant nearest neighbours and the effective spin is $3/2$. If the ion considered lies at the corner of the unit cube the nearest neighbours lie at the centres of the adjacent faces.

It has been shown (5.4) that it is reasonable to express the interaction between two neighbours by adding a term to the hamiltonian of the form $AS_xT_x + BS_yT_y + CS_zT_z$ where z is the line joining the two ions. If the ions are at (000) and $(\frac{1}{2}\frac{1}{2}0)$ the z axis is $1\bar{1}0$. As the 001 face is the reflection face in which one ion is derived from the other it is reasonable that 001 should be one axis, say the y axis, so that $1\bar{1}0$ is the x axis.

In a strong external field which is at an angle θ to the crystal field axis the hamiltonian for a single ion may be written:

$$\begin{aligned} \mathcal{H} = & g\beta HS_z + \frac{1}{2}D \left[S_z^2 - \frac{1}{3}S(S+1) \right] (3\cos^2\theta - 1) \\ & + \frac{(D\cos\theta\sin\theta)^2}{2h\nu} S_z (8S_z + 1 - 4S(S+1)) \\ & + \frac{(D\sin^2\theta)^2}{8h\nu} S_z (2S(S+1) - 2S_z - 1) \end{aligned}$$

In this expression the matrix for $\mathcal{H}$ has been diagonalised using perturbation theory, thus introducing the terms in D^2 . The hamiltonian for two interacting ions can be set up by adding two such expressions and the term to represent the interactions. As the field is strong it is convenient to use it as the direction of quantisation so that the interaction becomes an expression of the form $a_{ij}S_iT_j$ where i and j are the coordinates x, y or z . As the a 's are of the order of 50 gauss matrix elements connecting states with different total spin ($S_z + T_z$) may be neglected, because the perturbation is of order $a^2/h\nu$. The only elements which do not change the total spin are $a_{zz}S_zT_z$ and $(a_{xx} + a_{yy})(S_+T_- + S_-T_+)$. These terms will in future be written as eS_zT_z and $f(S_+T_- + S_-T_+)$. The hamiltonian may be written as a series of matrices each characterised by a value of the total spin, between which there is negligible interaction and within which the terms in f give the only admixture. The general form of this matrix is written overleaf. $D(3\cos^2\theta - 1)$ has been written D_0 , p and q are the second order terms $(D\cos\theta\sin\theta)^2/2h\nu$

s, t

$$\frac{3}{2}, \frac{3}{2} \quad 3G + D\theta_s + D\theta_t + 6p_s + 6p_t + 3q_s + 3q_t + 9e/4.$$

$$\frac{3}{2}, \frac{1}{2} \quad 2G + D\theta_s - D\theta_t + 6p_s - 6p_t + 3q_s + 3q_t + 3e/4. \quad 3f.$$

$$\frac{1}{2}, \frac{3}{2} \quad 3f. \quad 2G - D\theta_s + D\theta_t - 6p_s + 6p_t + 3q_s + 3q_t + 3e/4.$$

$$\frac{3}{2}, -\frac{1}{2} \quad G + D\theta_s - D\theta_t + 6p_s + 6p_t + 3q_s - 3q_t - 3e/4. \quad 2\sqrt{3}f.$$

$$\frac{1}{2}, \frac{1}{2} \quad 2\sqrt{3}f. \quad G - D\theta_s - D\theta_t - 6p_s - 6p_t + 3q_s + 3q_t + e/4. \quad 2\sqrt{3}f.$$

$$-\frac{1}{2}, \frac{3}{2} \quad 2\sqrt{3}f. \quad G - D\theta_s + D\theta_t + 6p_s + 6p_t - 3q_s + 3q_t - 3e/4.$$

$$\frac{3}{2}, -\frac{3}{2} \quad D\theta_s + D\theta_t + 6p_s - 6p_t + 3q_s - 3q_t - 9e/4. \quad 3f.$$

$$\frac{1}{2}, -\frac{1}{2} \quad 3f. \quad -D\theta_s - D\theta_t - 6p_s + 6p_t + 3q_s - 3q_t - e/4. \quad 4f.$$

$$-\frac{1}{2}, \frac{1}{2} \quad 4f. \quad -D\theta_s - D\theta_t + 6p_s - 6p_t - 3q_s + 3q_t - e/4. \quad 3f.$$

$$-\frac{3}{2}, \frac{3}{2} \quad 3f. \quad D\theta_s + D\theta_t - 6p_s + 6p_t - 3q_s + 3q_t - 9e/4.$$

$$\frac{1}{2}, -\frac{3}{2} \quad -G - D\theta_s + D\theta_t - 6p_s - 6p_t + 3q_s - 3q_t - 3e/4. \quad 2\sqrt{3}f.$$

$$-\frac{1}{2}, -\frac{1}{2} \quad 2\sqrt{3}f. \quad -G - D\theta_s - D\theta_t + 6p_s + 6p_t - 3q_s - 3q_t + e/4. \quad 2\sqrt{3}f.$$

$$-\frac{3}{2}, \frac{1}{2} \quad 2\sqrt{3}f. \quad -G + D\theta_s - D\theta_t - 6p_s - 6p_t - 3q_s + 3q_t - 3e/4.$$

$$-\frac{1}{2}, -\frac{3}{2} \quad -2G - D\theta_s + D\theta_t + 6p_s - 6p_t - 3q_s - 3q_t + 3e/4. \quad 3f.$$

$$-\frac{3}{2}, -\frac{1}{2} \quad 3f. \quad -2G + D\theta_s - D\theta_t - 6p_s + 6p_t - 3q_s - 3q_t + 3e/4.$$

$$-\frac{3}{2}, -\frac{3}{2} \quad -3G + D\theta_s + D\theta_t - 6p_s - 6p_t - 3q_s - 3q_t + 9e/4.$$

and $(D \sin^2 \theta)^2 / 8h\nu$ and θ is $g\beta H$. The subscripts s and t refer to the two spins in question.

There are three directions in the crystal (111), (110) and 001) in which it is convenient to study the nearest neighbour satellites, as in these directions the spectra of some of the four ions are identical and so are superimposed giving the spectrum a simpler structure. This gives a better chance of observing and identifying the satellites.

In the 111 direction the field is parallel to the crystal axis of one ion and at 55° to those of the other three. The $1/2$ to $-1/2$ lines of all the ions are superimposed and, as the other lines are well separated, good resolution should be obtained. The $\pm 3/2$ to $\pm 1/2$ lines of one ion are separated by $4D$, and of the other three are superimposed. (These lines are usually broad, perhaps due to inaccuracies in the mounting of the crystal so that they are unsuitable for these measurements). In the $3/2$ to $1/2$ transition the only satellites which need be considered are those produced by interaction between an ion having $\theta = 0^\circ$ with one having $\theta = 55^\circ$. For the $1/2$ to $-1/2$ transition however there are two cases: (a) interaction between ions where one has $\theta = 0^\circ$ and the other has $\theta = 55^\circ$; (b) interaction between ions both of which have $\theta = 55^\circ$.

These two possibilities have equal probability so that lines from each case with equal transition probability will have equal intensity.

In case (a) the $|\frac{1}{2}, -\frac{1}{2}\rangle$ and $|\frac{1}{2}, \frac{1}{2}\rangle$ states are degenerate so that they are replaced by a symmetric and antisymmetric combination. The transitions occurring are then:

transition	position	transition probability
$ \frac{3}{2}, \frac{3}{2}\rangle$ to $ \frac{1}{2}, \frac{3}{2}\rangle$	$G + 2D\theta_s + 3e/2$	3
$ \frac{3}{2}, \frac{1}{2}\rangle$ to $ \frac{1}{2}, \frac{1}{2}\rangle$	$G + 2D\theta_s + e/2$	3
$ \frac{3}{2}, -\frac{1}{2}\rangle$ to $\frac{1}{\sqrt{2}}(\frac{1}{2}, -\frac{1}{2}\rangle + -\frac{1}{2}, \frac{1}{2}\rangle)$	$G + 2D\theta_s - e/2 - 4f$	3/2
$ \frac{3}{2}, -\frac{1}{2}\rangle$ to $\frac{1}{\sqrt{2}}(\frac{1}{2}, -\frac{1}{2}\rangle - -\frac{1}{2}, \frac{1}{2}\rangle)$	$G + 2D\theta_s - e/2 + 4f$	3/2
$ \frac{3}{2}, -\frac{3}{2}\rangle$ to $ \frac{1}{2}, -\frac{3}{2}\rangle$	$G + 2D\theta_s - 3e/2$	3
$ \frac{1}{2}, \frac{3}{2}\rangle$ to $ \frac{1}{2}, -\frac{3}{2}\rangle$	$G + 3e/2$	4
$ \frac{1}{2}, \frac{1}{2}\rangle$ to $\frac{1}{\sqrt{2}}(\frac{1}{2}, -\frac{1}{2}\rangle + -\frac{1}{2}, \frac{1}{2}\rangle)$	$G + e/2 - 4f$	4
$\frac{1}{\sqrt{2}}(\frac{1}{2}, -\frac{1}{2}\rangle + -\frac{1}{2}, \frac{1}{2}\rangle)$ to $ \frac{1}{2}, -\frac{1}{2}\rangle$	$G - e/2 + 4f$	4
$ \frac{1}{2}, -\frac{3}{2}\rangle$ to $ \frac{1}{2}, \frac{3}{2}\rangle$	$G - 3e/2$	4

In case (b), as $D\theta_s = D\theta_t$, the 2x2 matrix is degenerate so that the $|\frac{3}{2}, \frac{1}{2}\rangle$ and $|\frac{1}{2}, \frac{3}{2}\rangle$ states are replaced by a symmetric and antisymmetric combination. The transitions occurring when S changes from 1/2 to -1/2 are:

transition	position	transition probability
$\frac{1}{\sqrt{2}}(\frac{1}{2}, \frac{3}{2}\rangle + \frac{3}{2}, \frac{1}{2}\rangle) \text{ to } -\frac{1}{2}, \frac{3}{2}\rangle$	$G + 3e/2 + 3f$	2
$\frac{1}{\sqrt{2}}(\frac{1}{2}, \frac{3}{2}\rangle - \frac{3}{2}, \frac{1}{2}\rangle) \text{ to } -\frac{1}{2}, \frac{3}{2}\rangle$	$G + 3e/2 - 3f$	2
$ \frac{1}{2}, \frac{1}{2}\rangle \text{ to } \frac{1}{\sqrt{2}}(\frac{1}{2}, -\frac{1}{2}\rangle + -\frac{1}{2}, \frac{1}{2}\rangle)$	$G + e/2 - 4f$	4
$\frac{1}{\sqrt{2}}(\frac{1}{2}, -\frac{1}{2}\rangle + -\frac{1}{2}, \frac{1}{2}\rangle) \text{ to } -\frac{1}{2}, -\frac{1}{2}\rangle$	$G - e/2 + 4f$	4
$ \frac{1}{2}, -\frac{3}{2}\rangle \text{ to } \frac{1}{\sqrt{2}}(-\frac{1}{2}, -\frac{3}{2}\rangle + -\frac{3}{2}, -\frac{1}{2}\rangle)$	$G - 3e/2 + 3f$	2
$ \frac{1}{2}, \frac{3}{2}\rangle \text{ to } \frac{1}{\sqrt{2}}(-\frac{1}{2}, -\frac{3}{2}\rangle - -\frac{3}{2}, -\frac{1}{2}\rangle)$	$G - 3e/2 - 3f$	2

Thus taking into account both cases (without allowing for the perturbation due to off diagonal elements) the lines around the $1/2$ to $-1/2$ transition occur at:

$G \pm 3e/2$	intensity	2
$G \pm (e/2 - 4f)$	"	4
$G \pm (3e/2 + 3f)$	"	1
$G \pm (3e/2 - 3f)$	"	1

The 100 direction is at 35° to the crystal axes of two ions and at 90° to those of the other two. Here four cases arise: (a) both ions having $\theta = 35^\circ$; (b) both ions having $\theta = 90^\circ$; (c) one ion having $\theta_s = 35^\circ$ and the other $\theta_t = 90^\circ$; (d) the same as (c) except that $\theta_s = 90^\circ$ and $\theta_t = 35^\circ$. Cases (a) and (b) are equally probable and cases (c) and (d) are both twice as probable as (a) or (b).

Cases (a) and (b) have degeneracy in the 2×2 matrix,

as $D\theta_s = D\theta_t$, so that the states and transitions which occur are the same as case (b) for the 111 direction.

These are listed above for the $S_z = 1/2$ to $-1/2$ transition and for the $3/2$ to $1/2$ transition the transitions are at:

transition	position	transition probability
$ \frac{3}{2}, \frac{3}{2}\rangle$ to $\frac{1}{\sqrt{2}}(\frac{3}{2}, \frac{1}{2}\rangle + \frac{1}{2}, \frac{3}{2}\rangle)$	$L + 3e/2 - 3f$	3
$\frac{1}{\sqrt{2}}(\frac{3}{2}, \frac{1}{2}\rangle + \frac{1}{2}, \frac{3}{2}\rangle)$ to $ \frac{1}{2}, \frac{1}{2}\rangle$	$L + e/2 + 3f$	3
$ \frac{3}{2}, -\frac{1}{2}\rangle$ to $\frac{1}{\sqrt{2}}(\frac{1}{2}, -\frac{1}{2}\rangle + -\frac{1}{2}, \frac{1}{2}\rangle)$	$L - e/2 - 4f$	3/2
$ \frac{3}{2}, -\frac{1}{2}\rangle$ to $\frac{1}{\sqrt{2}}(\frac{1}{2}, -\frac{1}{2}\rangle - -\frac{1}{2}, \frac{1}{2}\rangle)$	$L - e/2 + 4f$	3/2
$ \frac{3}{2}, -\frac{3}{2}\rangle$ to $ \frac{1}{2}, -\frac{3}{2}\rangle$	$L - 3e/2$	3

where L is the position of the lines produced by an isolated ion.

Cases (c) and (d) have $D\theta_s = -D\theta_t$ so that all the levels in the 4×4 matrix are degenerate. Even if values are assumed for the parameters e and f the matrix does not factorise, so that it is not easy to solve it by algebraic methods. However, as in this case the 2×2 matrix is not degenerate the following transitions exist:

transition	position	transition probability
$ \frac{3}{2}, \frac{3}{2}\rangle$ to $ \frac{1}{2}, \frac{3}{2}\rangle$	$L + 3e/2$	3
$ \frac{3}{2}, \frac{1}{2}\rangle$ to $ \frac{1}{2}, \frac{1}{2}\rangle$	$L + e/2$	3
$ \frac{3}{2}, -\frac{3}{2}\rangle$ to $ \frac{1}{2}, -\frac{3}{2}\rangle$	$L - 3e/2$	3
$ \frac{1}{2}, \frac{3}{2}\rangle$ to $ -\frac{1}{2}, \frac{3}{2}\rangle$	$L + 3e/2$	4
$ \frac{1}{2}, -\frac{3}{2}\rangle$ to $ -\frac{1}{2}, -\frac{3}{2}\rangle$	$L - 3e/2$	4

The 100 direction makes equal angles with all ions and $D_0 = 0$ so that all the matrices are degenerate. However, as $p_s = p_t$ and $q_s = q_t$ the 4x4 matrix and the 3x3 matrices factorise, so that if values are assumed for e and f they can be easily solved. The new states can be found and the transition probabilities for the allowed transitions calculated. The lines so predicted may then be compared with the observed spectrum.

Assuming the type of interaction postulated earlier it is possible to calculate the values of e and f in the various directions. In the 111 direction there are two types of ion. The six situated at $\pm \frac{1}{2}, \pm \frac{1}{2}, 0$; $\pm \frac{1}{2}, 0, \pm \frac{1}{2}$; and $0, \pm \frac{1}{2}, \pm \frac{1}{2}$ give: $e_1 = \frac{1}{3}(B + 2C)$, $f_1 = \frac{1}{12}(2B + C + 3A)$, and those at the other sites give $e_2 = \frac{1}{3}(B + 2A)$, $f_2 = \frac{1}{12}(2B + A + 3C)$. For magnetic interaction alone $B = A = k$ and $C = -2k$ so that $e_1 = e_2 = \frac{1}{3}k$ and $f_1 = f_2 = \pm \frac{1}{4}k$. There are also some interesting relations between the values of e and f :

$$e_1 - e_2 = -4(f_1 - f_2)$$

$$2e_1 - 4f_1 = \frac{3}{2}(e_1 - e_2).$$

In the 100 direction there are three sets of ions with the following values of e and f :

ions in the 001 plane $e = B$ $f = \frac{1}{4}(A + C)$

ions in the 100 plane $e = \frac{1}{2}(A + C)$ $f = \frac{1}{8}(A + C + 2B)$

ions in the 010 plane $e = \frac{1}{2}(B + C)$ $f = \frac{1}{8}(B + C + 2A)$

The last two are equivalent if the exchange has dipole-dipole form.

In the 110 direction there are four sets of ions with the following values of e and f :

ions at $\pm\frac{1}{2}, \pm\frac{1}{2}, 0$ $e = C$ $f = \frac{1}{4}(A + B)$

ions at $\pm\frac{1}{2}, \mp\frac{1}{2}, 0$ $e = A$ $f = \frac{1}{4}(B + C)$

ions in the 100 plane $e = \frac{1}{4}(C + B + 2A)$, $f = \frac{1}{16}(3C + 3B + 2A)$

ions in the 010 plane $e = \frac{1}{4}(C + A + 2B)$, $f = \frac{1}{16}(3C + 3A + 2B)$

The last two sets are equivalent if the exchange has dipole-dipole form.

EXPERIMENTAL RESULTS AND INTERPRETATION

Measurements have been made on crystals grown from solutions containing 20, 5 and 2 percent of Cr in $\text{AlK}(\text{SeO}_4)_2 \cdot 12\text{H}_2\text{O}$. They have been carried out at 90°K and at 20°K, but as the spin system is badly saturated at 20°K most of them have been done at the higher temperature. There was in fact no change in the satellite structure on cooling from 90°K to 20°K. Satellites can be seen in the three principle directions (111, 110 and 001) but it is impossible to follow their behaviour as the crystal is

rotated, because the spectrum also moves in a complex manner which obscures the satellites.

The theory so far described applies only to isolated pairs of ions. If either of the ions has a further neighbour the spectrum will be modified. It is therefore important to consider whether this theory is applicable to the crystals which were analysed.

In a crystal which contains one Cr^{+++} ion per n Al^{+++} ions the probability of any site being occupied by a Cr^{+++} ion is $1/n$. As there are 12 nearest neighbours the probability of a Cr having no neighbours is $(1 - 1/n)^{12}$, and of having one neighbour is $\frac{12}{n} (1 - 1/n)^{11}$. A pair of adjacent ions has 18 available sites for nearest neighbours, so that the probability of having an isolated pair is $\frac{12}{n} (1 - 1/n)^{17}$ and that of having a pair with one neighbour is $(66/n^2)(1 - 1/n)^{16}$. The values of these various factors for the dilutions of Cr^{+++} used are listed below:

percentage of Cr^{+++}	isolated ion	isolated pair	pair with one neighbour
20	.07	.20	.15
5	.54	.25	.07
2	.78	.17	.02

In the latter two cases the neighbours due to a pair with another neighbour will give satellites of much smaller

intensity than those due to isolated pairs. The satellites in the 5% crystal will be about 1/10th the intensity of the parent line and in the 2% crystal they will be about 1/19th of the parent line. However in the 20% case the satellites due to three adjacent ions should have comparable intensity to those due to isolated pairs, so that the theory is not applicable. The intensity of the satellites due to isolated pairs should be something greater than 1/8th the intensity of the parent line (as 1/8th is the figure obtained assuming that half the remaining possibilities contribute to the parent line).

Measurements have therefore been confined to an accurate determination of the positions of the satellites in these particular directions. Great care has always been taken to ensure that the crystal is well enough mounted in the desired direction that the width of a line composed of several superimposed lines is little greater than that of its widest component.

The crystal containing 2% Cr gave the best resolution of the satellites but they were faint. The intensity was greater in the 5% crystal though the resolution was poorer, and the positions of the satellites was the same. In the 20% crystal the intensity of the satellites was much greater but the resolution was only good enough to show the outermost

satellite on either side of the line; once again their position was the same as in the more dilute crystals. The positions of the satellites were measured using proton resonance in the two dilute crystals. Diagram 6.4 shows their positions in the three directions.

In the 20% crystal the satellites had $1/6$ th the intensity of the parent line. These lines may therefore be due to isolated pairs only, which would explain their being in the same position as those in the more dilute crystals. In the 111 and 100 directions the satellites in the 5% and 2% crystals have respectively $1/14$ th and $1/25$ th the intensity of the parent line. These are slightly smaller than expected, perhaps because there is less Cr^{+++} in the crystals than in the solutions from which they were grown. In the 110 direction the satellites have about half of the intensity that they have in the other two directions. A possible reason for this is suggested later.

The 111 direction will be discussed first as it has both the simplest spectrum and the simplest theory. If the interaction were purely magnetic the lines would be at (intensities in brackets) ± 42 gauss (6), ± 32 gauss (1) and ± 53 gauss (1), which is quite clearly not the case experimentally. The fact that the lines have not even the same ratio of intensity and separation shows that the

exchange is not purely of dipole-dipole form. The observed spectrum may be explained by three possible values of e and f :

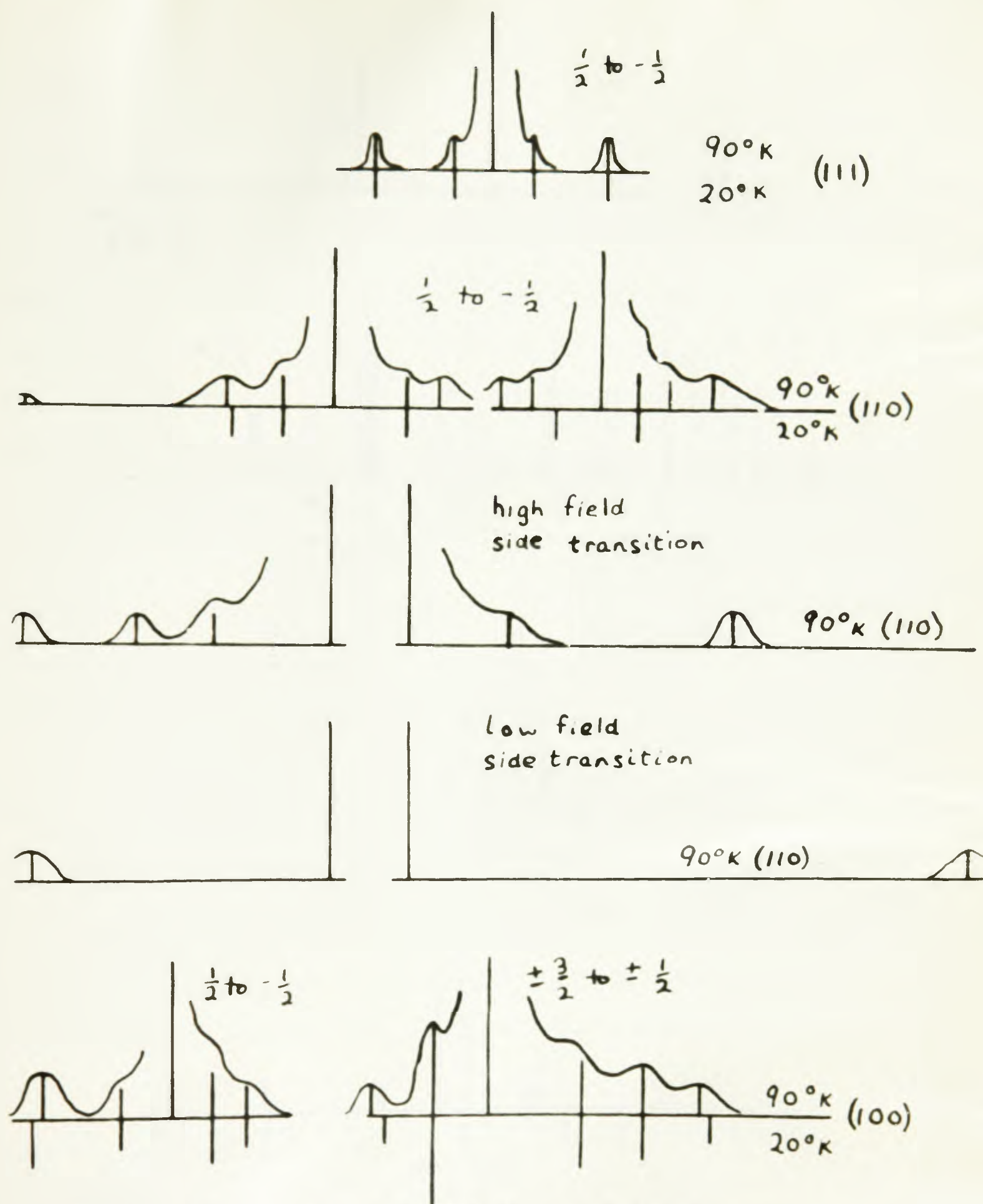
$$e = -14 \text{ gauss} \quad f = 17.2 \text{ gauss}$$

$$e = 51.2 \text{ gauss} \quad f = 1.2 \text{ gauss}$$

$$e = 0 \text{ gauss} \quad f = 18 \text{ gauss}$$

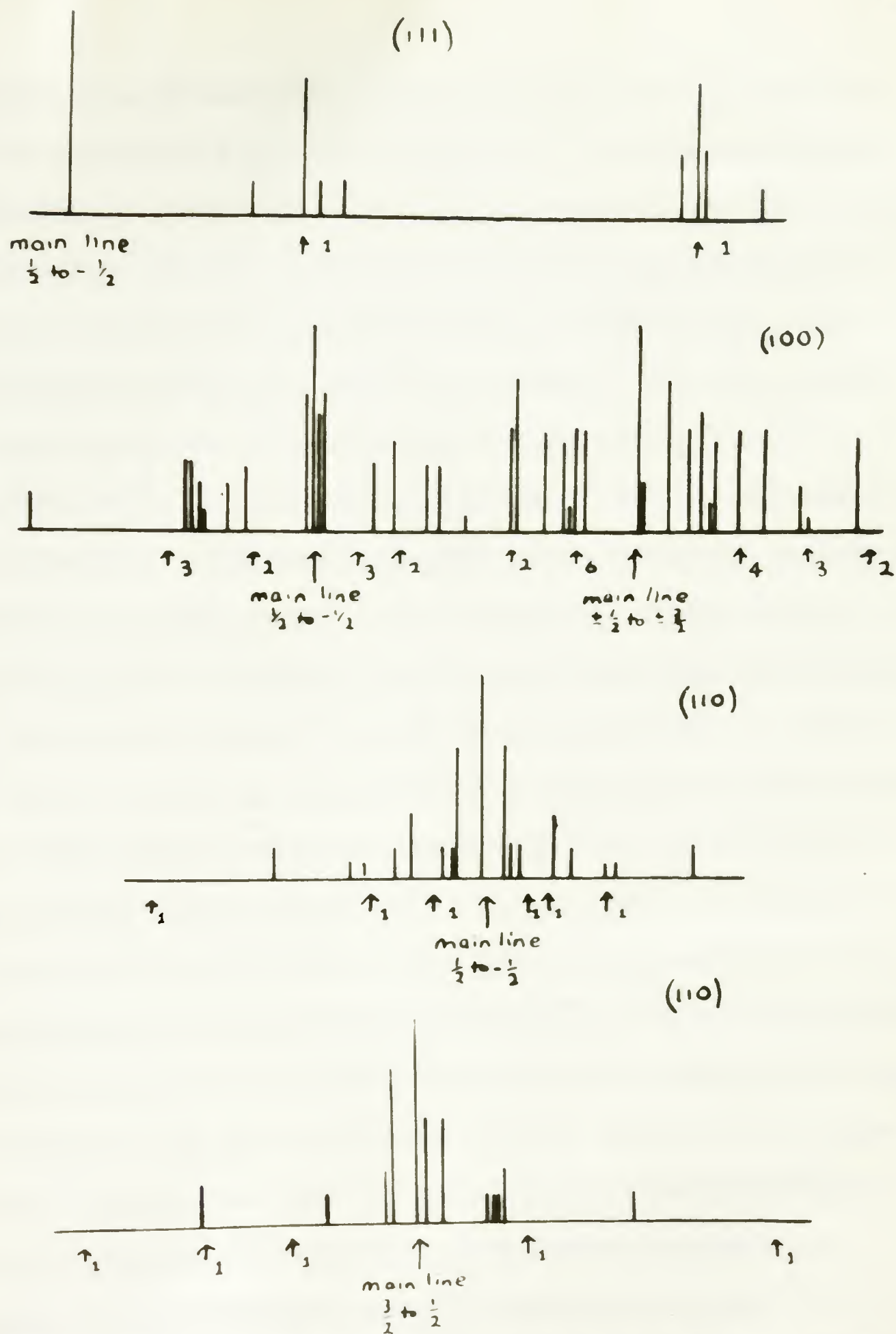
The first two sets are related by the equations quoted in the theoretical section. The third is not related to the other two in this way and is therefore not possible. The second order effects produced by the off diagonal elements in f have been taken into account when calculating these parameters. Diagram 6.5 shows a reconstruction of the satellites from these values.

These values of e and f can be obtained only if there is isotropic exchange $j = 18.8$ gauss. They also give the relation $C - A = 97.7$ gauss. If it is assumed that the anisotropic part of the exchange has the same form as magnetic interaction the constants A , B and C have values $A = B = -14.0$ gauss and $C = 84.0$ gauss. From these values the positions of the satellites in the 110 and 001 directions may be calculated and compared with the experimental values. Diagram 6.5 shows the reconstruction in these two directions (the 110 direction is not complete because the 4×4 matrix has not been solved). The 001



Satellites drawn above the horizontal lines were observed at 90°K and those drawn below at 20°K

Diagram 6.4



Reconstruction of positions and intensities of satellites. The arrows show the positions of the satellites which are observed and the number beside each arrow is the observed intensity.

Diagram 6.5

direction is a reasonable fit which could be improved by a slight adjustment of the parameters. The 110 direction is, however, a very poor fit. The missing lines may improve the fit close to the parent line but they cannot explain the lines which occur at ± 200 gauss, or those which are theoretically predicted and do not occur. The fact that the large lines are clustered near the parent line is consistent with the smaller intensity of the satellites in this direction. The lines at ± 200 gauss could be explained by putting $e = 133$ gauss. If, however, A, B and C are calculated from this value it is found that they necessitate a far too large value of e in the 001 direction. The lines might be due to cooperative effects of two neighbours, but if this were so similar lines ought to be visible in the 111 direction as well.

The next nearest neighbours give appreciable contribution only in the 001 direction if their interaction is purely magnetic. In this direction the ions at 0, 0, ± 1 give lines at ± 70 gauss. There is zero contribution from magnetic interaction from the next nearest neighbours in the 111 direction. If however there were appreciable exchange, either of an isotropic nature or, of an anisotropic kind but such that along the 111 direction it was the same for each ion, the satellites due to all six

neighbours would be superimposed. Such a phenomenon may account for the strong lines at ± 15 gauss which appear in this direction. It is unfortunately quite impossible to identify satellites which might be due to these neighbours in other directions so that this possibility cannot be investigated further.

Interesting light is thrown on this problem by adiabatic demagnetisation measurements by Kurti and Gardner (unpublished). In the concentrated chromic alum they find an excess specific heat of $84 \times 10^{-4} \text{ deg}^2$ which is presumably due to interactions (the contribution from pure magnetic interaction is $10 \times 10^{-4} \text{ deg}^2$). They also get a Curie-Weiss Δ of $0 \pm 0.02^\circ\text{K}$ which allows only a maximum of $9 \times 10^{-4} \text{ cm}^{-1}$ of isotropic exchange. This is only half as large as the exchange which the p.r. results suggest. A possibility, which seems a little improbable, is that the exchange from the next nearest neighbours is isotropic and of opposite sign to that from the nearest neighbours, so reducing the Curie-Weiss Δ .

However, this makes a negligible contribution to the specific heat which must be explained by anisotropic exchange. If it is assumed to have dipole-dipole form the value of A is $86 \times 10^{-4} \text{ cm}^{-1}$, which is far too large to explain the results in the 111 direction. If the values

of A, B and C are calculated accepting the results in the 111 direction the values of e and f in the 001 direction are far too large. The values of A, B and C which were assumed in the reconstructions made earlier give a contribution of only $12 \times 10^{-4} \text{ deg}^2$ to the specific heat. It is unlikely that such a large discrepancy can be accounted for by exchange from the six next nearest neighbours.

It is possible that the exchange interaction is larger in the concentrated salt than in the dilute salts on which all the p.r. measurements have been made. The line width of the $3/2$ to $1/2$ line of the concentrated salt was measured in the 111 direction. This particular line in this particular direction is the only one which ever becomes completely resolved from the other lines. Several crystals gave a change of line width between 90°K and 20°K , but as one was found which did not give it, and which also had the narrowest line, it was used for the final measurement. The mean square width was found to be 157 gauss.

Writing Van Vleck's formula (1.4) as:

$$h^2(\Delta \nu^2)_{av} = 5e^2/4$$

The width using the value of e derived from the measurements on the dilute salt is 149. The value computed from the position of the nearest neighbour satellites is 167 gauss. In the concentrated salt the satellites are

therefore particularly well in particular regions.

modified by the presence of other neighbours which tend to destroy the effects of off diagonal elements, and so make the value tend to that given by Van Vleck's formula. The fact that the experimental width lies between the two theoretical values is good support for the values of the parameters calculated from the satellites. It does however leave the specific heat results unexplained.

6.4 DISCUSSION

These two attempts to draw conclusions from the positions of nearest neighbour lines have been rather unsatisfactory. The Alum problem is complicated by the fact that there are four ions in the unit cell each giving a large number of satellites. For unambiguous results it is preferable to work with fewer ions per unit cell. A hexagonal crystal with one ion per unit cell, like the ethyl sulphates, is probably the best. Nickel fluosilicate is a salt of this type which might profitably be studied, the disadvantage being that there are six nearest neighbours which do not lie on the axis. More might be learned by studying a compound like Cr_2O_3 where the paramagnetic ions are close together and the exchange is large. The large number of neighbours which would give noticable contributions would, however, probably make the interpretation impossible. This type of analysis is therefore profitable only in particular compounds.

CHAPTER 7

RARE EARTH ETHYL SULPHATES

7.1 INTRODUCTION

The p.r. spectra of the rare earth ethyl sulphates have been studied extensively by several workers (see Bleaney and Stevens, 1953, for details). Most of the work has been done on ions with Kramer's degeneracy. Of those without Kramer's degeneracy Scovil has observed resonance in terbium and praseodymium. The Pr^{++} spectrum, comprising six hyperfine lines, has been interpreted (Bleaney and Scovil, 1952). The Tb^{++} spectrum comprised more than twenty lines which appeared to fall into groups of four, corresponding to hyperfine structure produced by a nuclear spin $I = 3/2$, but the behaviour of the groups was not interpreted (Scovil, 1951). All Scovil's work was done using lanthanum ethyl sulphate as an isomorphous diamagnetic dilutant.

While using various ethyl sulphates as dilutants for neodymium (chapter 6) a spectrum of four equally spaced, equally intense, lines was discovered in the salt made from some 98% pure yttrium. This was suspected to be due to terbium and was confirmed by adding some terbium to the yttrium salt and observing that the spectrum comprised four much broader lines in the same fields as before.

The spectrum of terbium has been fully investigated. In view of the success of yttrium as a dilutant the spectrum of praseodymium has also been studied using it. It also seems appropriate to mention here some work done on the radioactive promethium 147, which was studied using lanthanum as a dilutant; this work was unfortunately without success.

7.2 GENERAL THEORY

The ground state of the free rare earth ion is a multiplet characterised by the total angular momentum vector J . For an ion without Kramer's degeneracy, where J is integral, the axial components of the crystal field of D_{3h} symmetry splits this up into doublets $J_z = \pm J, \pm (J - 1), \dots, \pm 1$, and a singlet $J_z = 0$. The A_6^6 component of the field (chapter 1.2) admixes levels which differ in J_z by six. The $J_z = \pm 3$ levels are admixed and split into two singlets:

$$\begin{aligned} \frac{1}{\sqrt{2}} |J_z = +3\rangle + \frac{1}{\sqrt{2}} |J_z = -3\rangle \\ \frac{1}{\sqrt{2}} |J_z = +3\rangle - \frac{1}{\sqrt{2}} |J_z = -3\rangle \end{aligned}$$

The $J_z = \pm 6$ levels are admixed with the $J_z = 0$ level which splits the doublet, but by a smaller amount than the splitting of the ± 3 doublet. The other levels are admixed to form doublets of the type:

$$\begin{aligned} \cos \theta |J_z = +x\rangle &+ \sin \theta |J_z = (x-6)\rangle \\ \cos \theta |J_z = -x\rangle &+ \sin \theta |J_z = (-x+6)\rangle \end{aligned}$$

As these levels do not contain values of J_z which differ by unity the normal $\Delta M = 1$ transitions do not occur.

However, $\Delta M = 0$ transitions are allowed between the modified ± 3 and ± 6 doublets if the r.f. magnetic field is parallel to the crystal axis. If some dissymmetry in the crystal field, produced perhaps by the Jahn-Teller effect, admixes the two states of the other doublets it will produce a small splitting between the levels, and $\Delta M = 0$ transitions between the components of the doublet will be allowed. This latter effect was postulated to explain the spectrum of praseodymium (Bleaney and Scovil, 1952), and they allowed for it by adding a term ΔS_x to the spin hamiltonian which therefore became:

$$\mathcal{H} = g_{\parallel} \beta H_z S_z + A S_z I_z + \Delta S_x$$

where the effective spin is $1/2$. There are no terms in $g_{\perp} \beta (H_x S_x + H_y S_y)$ or $B (S_x I_x + S_y I_y)$ as these would introduce matrix elements between the two levels of the doublets, which, as explained above, do not exist. This hamiltonian gives energy levels:

$$W = \pm 1/2 \left[\Delta^2 + (g_{\parallel} \beta H_z + A m)^2 \right]^{1/2}$$

and, as only $\Delta M = 0$ transitions are allowed they occur at:

$$h\nu = \left[\Delta^2 + (g_{\parallel} \beta H + A m)^2 \right]^{1/2}$$

It should be possible to use this hamiltonian whatever the cause of the splitting Δ .

7.3 TERBIUM ETHYL SULPHATE: EXPERIMENTAL

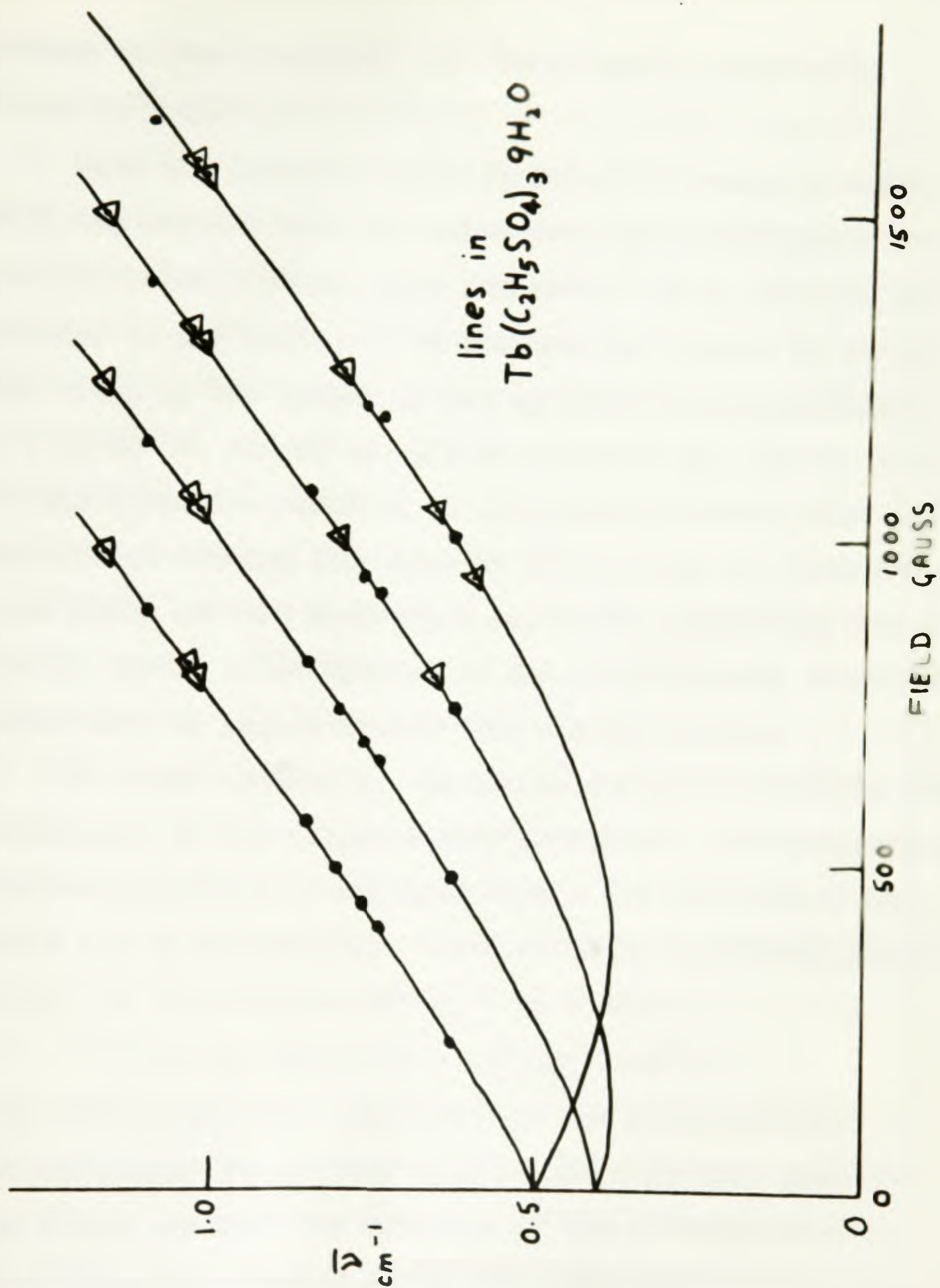
The spectrum was observed at 20°K only when there was a component of the r.f. magnetic field parallel to the crystal axis. At all frequencies and in all directions the spectrum consists of four equally spaced, equally intense lines; in any direction the spacing is the same at all frequencies. Measurements for determining the parameters of the hamiltonian were carried out with the external field accurately parallel to the crystal axis. Measurement at one frequency is not sufficient to determine all the parameters (it only enables one to calculate $A/g_{\parallel}$) so that measurements have been made at several frequencies from

$\bar{\nu} = 0.6$ to 1.2 . A plot of $(\bar{\nu})^2$ against H_0^2 should be a straight line if the proposed hamiltonian is correct; H_0 is the mean position of the four hyperfine lines corresponding to $m = 0$. The points, which are obtained by setting proton resonance pip on each line in turn, lie accurately on a straight line which gives the values of Δ , $g_{\parallel}$ and A . Table 7.1 shows the values of H_0 , calculated from $\bar{\nu}$ assuming the values for the parameters, compared with the measured value. The table also shows the value

TABLE 7.1

value of $\bar{\nu}$ cm ⁻¹	mean position of h.f.s. (gauss)		h.f.s. intervals (gauss)		
	observed	calculated			
1.180	1345.1	1346.4	251.2	253.0	-
1.047	1175.9	1175.3	252.3	255.4	252.2
1.047	1176.8	1175.5	249.7	251.8	251.7
1.031	1155.7	1154.7	249.9	251.5	253.0
0.814	864.4	865.4	-	-	252.6
0.6687	660.3	658.5	-	-	252.9
0.6045	560.9	560.6	-	-	-

of A in gauss measured by setting the proton pip on successive lines. It was not possible to make measurements of this sort below about 780 gauss as it was not possible to place the proton coil and the resonator between the pole pieces of the magnet simultaneously. One of the values for $\bar{\nu} = 1.180$ is missing because the high field line lay in a region between the extremes of two coils. Diagram 7.1 shows how the energy of the transitions vary with magnetic field; the experimental points are plotted for comparison with the lines which are calculated from the parameters. The points surrounded with triangles are the measurements made with proton resonance quoted in table 7.1, the others have been measured using the magnet calibration or by using the magnet without pole pieces so that it behaves as a solenoid and there is little resonance. The values of A , $g_{\parallel}$ and Δ which fit the observations best are $\Delta = 0.387 \pm 0.001 \text{ cm}^{-1}$, $g_{\parallel} = 17.72 \pm 0.02$ and $A = 0.209 \pm 0.002 \text{ cm}^{-1}$. This value of A is much bigger than that found by Bleaney and Scovill in praseodymium where $\Delta = 0.04 \text{ cm}^{-1}$. In zero field there will be two absorption lines, one at $\bar{\nu} = 0.401 \text{ cm}^{-1}$, corresponding to $m = \pm 1/2$, and the other at $\bar{\nu} = 0.498 \text{ cm}^{-1}$, corresponding to $m = \pm 3/2$. The lowest frequency at which it is possible for a transition to occur is $\bar{\nu} = 0.387$, which explains why no spectrum was seen at $\bar{\nu} = 0.32 \text{ cm}^{-1}$. The energy



levels in zero field are at: 0.000 cm^{-1} , 0.049 cm^{-1} , 0.449 cm^{-1} and 0.498 cm^{-1} .

When the magnetic field is rotated to make an angle with the crystal axis the lines move to higher fields and the separation between them increases. If $g_{\perp}$ is zero the g -value at any angle θ to the axis is $g_{\parallel} \cos \theta$, so that the field at the centre of the spectrum (corresponding to $m = 0$) is $H_{\parallel} \sec \theta$, as $g\mu H$ is constant ($H_{\parallel}$ is the field in the direction parallel to the crystal axis); also the separation between the lines is $(A/g_{\parallel}) \sec \theta$. Both the mean field and the separation appear to follow this $\sec \theta$ law to within a few degrees of the perpendicular where the lines move to higher fields than can be reached.

To check whether $g_{\perp}$ is really zero, measurements were done close to the perpendicular direction. Measurements of the mean position of the line enable the accuracy of the $\sec \theta$ law to be checked; there would be departures from it if $g_{\perp} \neq 0$ as then, if $g_{\perp}$ is small:

$$g = g_{\parallel} \cos \theta (1 + (g_{\perp}^2/2g_{\parallel}^2) \tan^2 \theta)$$

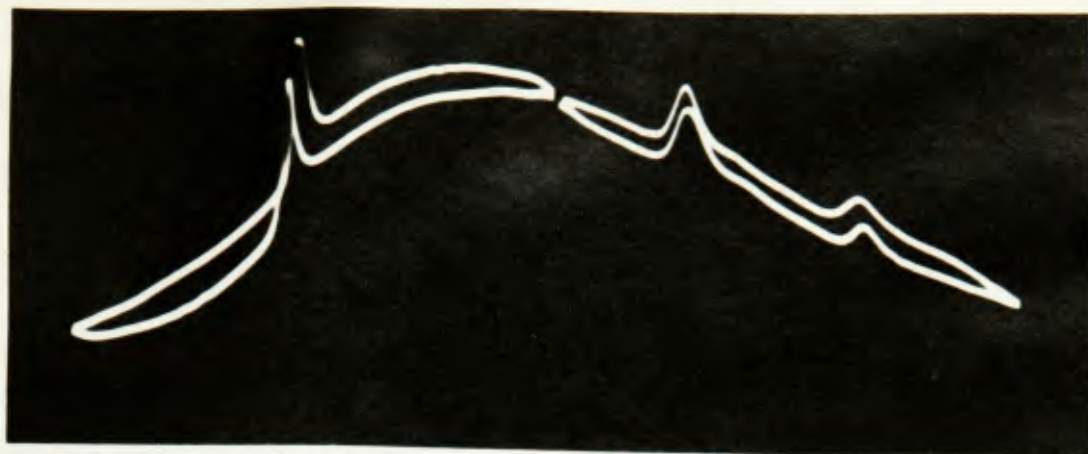
Thus the smaller the angle between the field and the perpendicular the greater will be the departure from the $\sec \theta$ law, so that the accuracy of the determination is limited by the size of θ when the field becomes too high. To check that both the mean field and the separation of the lines obey the $\sec \theta$ law would require proton

measurements on all four lines at various angles close to the perpendicular. These are quite lengthy measurements and at such high fields the magnet would become very hot. The measurement was therefore done by setting the field at a value, requiring only one proton resonance measurement, and rotating the field so that each of the four lines occurred in turn at that field. The angle at which each line occurred was measured using a lamp and scale which enabled the angle between the field and the perpendicular to be measured to about 1%. Measurements were made on both sides of the perpendicular so that the perpendicular direction was accurately defined. Assuming that $g_{\perp} = 0$ the angle at which each line should occur at the set field of 11.32 Kgauss. was calculated and compared with the observed angle at which it occurred. This comparison is shown in table 7.2. Taking the angle of $2^{\circ}16'$ where the error of $2'$ is within the error of angular measurement of about $3'$, where the departure from the sec θ law should be most evident the total error in $g_{\perp}$ is ± 0.1 . A measurement of the separation of the lines was made when $(90 - \theta) = 6^{\circ}16'$ which was 2.30 ± 0.02 Kgauss. while the calculated value of $A\sec\theta/g_{\parallel}$ is 2.31 Kgauss.

The quantity of terbium in the crystal used is not known. The yttrium contains 2% impurity much of which, judging from the p.r. spectrum, is gadolinium, so that

there is probably much less than 1% terbium in it. Thus there should be little contribution to the line width from the neighbouring Tb^{+++} ions. The line width at 20°K is 20 gauss which is reduced to 12 gauss at about 15°K. In the ethyl sulphates the line width due to waters of crystallisation is about 7 gauss. The variation of line width with temperature suggests that the additional width is due to the fact that the spin-lattice relaxation time is still too long at 15°K. Expressed in terms of frequency the line width remains constant as the orientation of the external magnetic field is altered. This behaviour would be expected if the width were due to spin-lattice effects as the relaxation time is independent of the orientation of the external field. The line is quite symmetrical (diagram 7.2) which indicates that there is little Jahn-Teller effect. This effect appears to produce broad lines which have a steep slope on one side and a shallow one on the other; such lines were found in praseodymium ethyl sulphate by Bleaney and Scovill.

In a more concentrated crystal the lines were much broader but still symmetrical. There were nearest neighbour lines (see chapter 6) outside either end of the spectrum, but as these had low intensity and were very broad an accurate determination of their position was not possible. The low field one was 380 gauss below the lowest

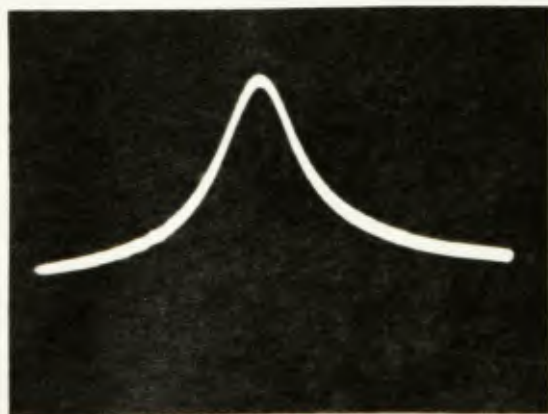


Line shape in 1:100 Pr:Yb ethyl sulphate



Reconstructed line shape assuming

$$I \propto \frac{\Delta H}{\Delta H_{\max}} e^{-\frac{\Delta H}{\Delta H_{\max}}}$$



Line shape in diluted
terbium ethyl sulphate

Diagram 7.2

line and the high field one 540 gauss above the highest hyperfine line. The mean of these agrees with the expected displacement of 460 gauss calculated assuming only dipole-dipole interaction but the experimental accuracy was not sufficient to attribute any significance to the asymmetry of the lines.

No other lines appear in the spectrum at all when the dilute crystal gives a signal/noise of 100 and the concentrated a little larger.

7.4 DISCUSSION: TERBIUM ETHYL SULPHATE

Scovil (1951) suggests that the distortion of the crystal by the Jahn-Teller effect may cause the complex spectrum which he observed using lanthanum as a dilutant. There is no preferential direction for an axis of distortion perpendicular to the crystal axis so that different parts of the crystal may distort in different directions. Bleaney and Bowers (1952) have found a similar effect in copper fluosilicate.

The indications are, however, that there is little Jahn-Teller effect, and the probable cause of Scovil's spectrum is the distortion of the lanthanum ethyl sulphate lattice by the introduction of terbium which has a different ion size. The relative sizes of the unit cells of the ethyl sulphates given by Ketelaar (1937) gives a measure of

the ion size. For lanthanum $a = 14.080\text{\AA}$ while for yttrium $a = 13.90\text{\AA}$, which is much closer to the value for terbium where $a = 13.92\text{\AA}$ (this figure is extrapolated by taking the mean of the salts of the neighbouring elements gadolinium and dysprosium). It is likely, therefore, that less distortion is caused when the Tb^{+++} ion is put into a Yt lattice than when it is put into a La lattice.

The Lande g -value for Tb^{+++} is $\Lambda = 3/2$ and the g -values for the doublets $J_z = \pm 6, \pm 5, \dots, \pm 1$ produced by the axial components of the crystal field are $g_{||} = 12\Lambda, 10\Lambda, \dots, 2\Lambda$. The measured g -value of 17.72 makes it quite clear that it is the $J_z = \pm 6$ doublet which lies lowest, as the next doublet $J_z = \pm 5$ has a maximum g -value of 15.

The F_6^6 term in the crystal field admixes the $J_z = \pm 6$ doublet with the $J_z = 0$ level. Suppose that the latter singlet lies d energy units above the former doublet, then the matrix for these three states in zero external field is:

$$\begin{array}{c|ccc} +6 & 0 & c & 0 \\ 0 & c & d & c \\ -6 & 0 & c & 0 \end{array}$$

where c is the matrix element introduced by A_6^6 .

Diagonalization of this matrix leads to the following states:

* ground state of free ion $4f^8, {}^7F_6$

$$\frac{1}{\sqrt{2}}(|+6\rangle - |-6\rangle)$$

$$W_1 = 0$$

$$\cos\theta \frac{1}{\sqrt{2}}(|+6\rangle + |-6\rangle) - \sin\theta |0\rangle$$

$$W_2 = \frac{1}{2}(d - \sqrt{d^2 + 8c^2})$$

$$\sin\theta \frac{1}{\sqrt{2}}(|+6\rangle + |-6\rangle) + \cos\theta |0\rangle$$

$$W_3 = \frac{1}{2}(d + \sqrt{d^2 + 8c^2})$$

where $\tan \theta = 2c/W_3$. If $c \ll d$ these energies become $W_1 = 0$, $W_2 = -2c^2/d$ and $W_3 = d + 2c^2/d$. The first two levels form a split doublet as observed experimentally with $\Delta = 2c^2/d$ and having $g_{||} = 18.014 \cos \theta$. The observed g -value gives $\cos \theta$ to be 0.984, which together with the measured value of Δ gives $c = 1.5 \text{ cm}^{-1}$ and $d \approx W_3 = 12 \text{ cm}^{-1}$. The theory of Elliott and Stevens gives for Tb^{+++} that $c = 1.23 \cdot 10^{-2} A_6^6 r^6$. This gives a value for $A_6^6 r^6$ of 120 cm^{-1} which is somewhat smaller than the values of this expression used by Elliott and Stevens to fit the spectra of the neighbouring ions Sm^{+++} (590 cm^{-1} .) and Er^{+++} (330 cm^{-1} .). The relation between d and the crystal field parameters is complicated, but if values of these constants are extrapolated from the values assumed by Elliott and Stevens for the neighbouring ions in the rare earth group, the separation between the doublets may be found. An overall splitting of $\sim 20 \text{ cm}^{-1}$ is found, which is much smaller than other ions in this group. The $J_z = \pm 3$ doublet is admixed by the A_6^6 term and split by 8.4 cm^{-1} . assuming the value of c found above, so that these levels would not give rise to transitions. The other doublets

are expected to be split by the Jahn-Teller distortion, and as all the levels are within 20 cm^{-1} of the ground state transitions within them should be visible. If the admixtures of the components of the doublets due to the Jahn-Teller effect are very small the intensity of the transitions between the levels would be small. This might explain the fact that no other transitions are visible. However, with such a small overall separation of the energy levels of the lowest term the spin-lattice relaxation time should be much shorter than it appears to be, judging from the width of the spectral lines. A possible interpretation is that the very small departure of $g_{\parallel}$ from 18.014 may be due to other effects, such as incipient j - j coupling, making considerable contributions. If this is so the values of c and d will be different and the overall separation of the lowest term may be larger so that the other doublets are not in fact populated.

From the observed h.f.s. the nuclear magnetic moment of ^{159}Pr may be calculated. There is no term in κ to be allowed for (chapter 1.3)*. The only non zero matrix element to the $J = 5$ term some 2000 cm^{-1} above $J = 6$ is $\langle J=5, J_z=0 | A_6^6 P_6^6 | J=6, J_z=6 \rangle$ which is only a few cm^{-1} , so that the effect of admixture of $J = 5$ is negligible. In this case the formula derived by Elliott and Stevens (1953) can be used:

* see note at the end of chapter 4

$$\frac{A}{g_{\parallel}} = \frac{2\beta\beta_N \gamma(r^{-3})}{I} \frac{\langle J|N|J \rangle}{\langle J|\Lambda|J \rangle}$$

For Terbium $\langle J|N|J \rangle = 49/90$ and $\langle J|\Lambda|J \rangle = \Lambda = 3/2$.

Elliott and Stevens assumed a value for $r^{-3} = (12 \pm 3)(2-55)^{3/4}$ which gives a value 68 ± 17 A as $Z = 65$. This gives a value for the magnetic moment of 1.5 ± 0.4 nuclear magnetons. According to Klinkenberg (1952) the odd proton is in a $d_{3/2}$ state which explains the nuclear spin, but the magnetic moment is considerably larger than those of other $d_{3/2}$ nuclei.

7.5 PRASEODYMIUM ETHYL SULPHATE

The size of the unit cell of praseodymium ethyl sulphate, $a = 14.007$ A, lies closer to the value for yttrium than that for lanthanum ethyl sulphate. The effects due to distortion of the lattice might be expected to be smaller using the former as a dilutant. A crystal of yttrium ethyl sulphate containing about 1% of praseodymium was therefore investigated. The lines were asymmetrical, similar to the lines found by Bleaney and Scovil using lanthanum as dilutant.

The ground state of the free Pr^{+++} ion is $4f^2$, 3H_4 . The axial components of the crystal field give doublets $J_z = \pm 4, \pm 3, \pm 2, \pm 1$ and a singlet $J_z = 0$, and the A_6^6 term admixes states differing by 6 in J_z . The theory of

Elliott and Stevens (unpublished) shows that the ground doublet is:

$$\cos\theta |J_z = \pm 4\rangle + \sin\theta |J_z = \mp 2\rangle$$

If some dissymmetry in the crystal field admixes the two components of the doublet, $\Delta M = 0$ transitions are allowed when the r.f. magnetic field is parallel to the crystal axis. The spin hamiltonian has already been quoted.

7.6 THE LINE SHAPE

It was suggested by Pryce (see e.g. Bleaney, Hall, Llewellyn and Pryce, 1954)^b that the parameter Δ introduced by dissymmetry in the crystal field is not single valued but may have all values. In absence of any knowledge of the mechanism of the splitting a Gaussian distribution of values will be assumed.

The term to be added to the hamiltonian may be more generally written $\Delta_x S_x + \Delta_y S_y$. The energy levels are unchanged where $\Delta^2 = \Delta_x^2 + \Delta_y^2$, and the transitions occurring (assuming no hyperfine structure) are: $(h\nu)^2 = (g\beta H)^2 + \Delta^2$, or, if Δ is small, $h\nu - g\beta H = \Delta^2/2h\nu$. . . (1)

If a Gaussian distribution is assumed for Δ_x and Δ_y then the number of ions with a given value of Δ is

$$n(\Delta)d\Delta = n_0 e^{-a\Delta^2} \Delta d\Delta$$

The transition probability for these ions is proportional to $\Delta/h\nu$ so that the intensity of the line produced by

then is:

$$I(\Delta)d\Delta = \frac{\Delta^2}{(h\nu)^2} e^{-a\Delta^2} d(\Delta^2)$$

$$= 2(1 - g\beta H/h\nu) e^{-2a(h\nu)^2(1 - g\beta H/h\nu)} h\nu g\beta dH$$

The value of H at which I is a maximum is given by putting $dI/dH = 0$ giving:

$$g\beta H_{\max} = h\nu(1 - 1/2a(h\nu)^2)$$

This compared with equation (1) gives $\Delta^2 = 1/a$

When $\Delta = 0$, $g\beta H_0 = h\nu$ so that:

$$g\beta(H_{\max} - H_0) = -1/2ah\nu = -\Delta^2/2h\nu$$

$$\text{and } I_{\max} = e^{-1} g\beta/ah\nu$$

Writing $H - H_0 = \Delta H$ we have:

$$I(\Delta H) = \frac{g\beta}{h\nu a} \frac{\Delta H}{\Delta H_{\max}} e^{-\frac{\Delta H}{\Delta H_{\max}}}$$

Thus the line shape is independent of any parameter; the line width is proportional to $1/ah\nu$ and the intensity to $1/ah\nu$. In diagram 7.2 a photograph of one of the Praseodymium lines at $\bar{\nu} = 0.8\text{cm}^{-1}$ is compared with a reconstruction of the above line shape. The agreement is seen to be excellent. The above treatment has assumed zero natural width for the lines. The fact that they have natural width causes the curve to have the rounded tail seen in this diagram.

Measurements of ΔH were made at three wavelengths by setting the proton pip on the peak and then at the point where the extrapolation of the steepest part of the high field slope cuts the base line. At each wavelength the average value over several lines was taken. There was unfortunately too little praseodymium in the crystal to make a line width measurement possible at 0.3 cm^{-1} . The results which were obtained are shown in table 7.3.

TABLE 7.3

$\bar{\nu} \text{ cm}^{-1}$	average ΔH gauss	$\Delta H \text{ cm}^{-1}$	$2\Delta H \bar{\nu} = \Delta^2$
0.805	213	.015	.024
0.672	271	.019	.026
1.05	202	.014	.029

An attempt was made to compare the intensity of the lines with those of some gadolinium impurity. This however proved too difficult and the results are worthless.

7.7 PRASEODYMIUM ETHYL SULPHATE: EXPERIMENTAL

The nuclear spin of ^{141}Pr is $5/2$ so that the spectrum consists of six equally spaced hyperfine lines. The spacing in any direction is the same at all frequencies, and obeys the $\sec\theta$ law at angles to the crystal axis. Measurements were made at 20°K with the r.f. and steady

fields parallel to the crystal axis to determine the parameters in the hamiltonian. The results at the four frequencies used are shown in table 7.4. The table shows the observed mean field of the spectrum (where $m = 0$) and the value for this field calculated from the parameters assumed. The general intensity of the spectrum at Q-band was low so that the measurements were not precise. At X-band the spectrum of praseodymium was very faint, though judging by the intensity of the spectrum of gadolinium impurity the sensitivity of the apparatus was good, so that these results too are imprecise. The measurements were all made on the peak of the line with proton resonance, but as the lines are several hundred gauss broad, and faint, the accuracy obtained is low. The values of the parameters which the experiments give are:

$$g_{\parallel} = 1.525 \pm 0.020, \Delta = 0.11 \pm 0.04 \text{ cm}^{-1}, A = 0.076 \pm 0.002 \text{ cm}^{-1} \text{ and } A/g_{\parallel} = 1059 \pm 29 \text{ gauss.}$$

This value of Δ agrees quite well with the value ($.16 \text{ cm}^{-1}$) obtained from line width measurements. The discrepancy may be partially due to a systematic error in the extrapolation of the steep part of the line, which would tend to make Δ measured in that way too large, because the line width tends to make the estimated ΔH too large.

TABLE 7.4

Value of $\bar{\nu}$ cm ⁻¹	Mean position of h.f.s. (Kgauss)	
	observed	calculated
0.998	13.84 $\pm$ 0.10	13.93
0.7917	11.04 $\pm$ 0.03	11.01
0.5913	8.13 $\pm$ 0.03	8.15
0.3122	4.22 $\pm$ 0.20	4.08

The values obtained by Bleaney and Scovil are:
 $g_{\parallel} = 1.69 \pm 0.01$, $\Delta = 0.04 \text{ cm}^{-1}$, $A = 0.083 \pm 0.001 \text{ cm}^{-1}$
 and $A/g_{\parallel} = 1052 \pm 15 \text{ gauss}$. The value of $g_{\parallel}$ found by
 Van den Handel (1941) by susceptibility measurements is
 1.56. The unit cell size of praseodymium ethyl sulphate,
 $a = 14.007 \text{ \AA}$, lies nearly midway between those for the
 La and Yt salts ($14.080 \text{ \AA}$ and $13.903 \text{ \AA}$ respectively). It
 may be therefore that the size of the A_6^6 component of the
 crystal field around the praseodymium ion is different
 for the different lattice sizes and that this alters the
 admixture of the $J_z = \pm 2$ and $J_z = \pm 4$ doublets so that
 the g -value is changed. This is supported by the fact
 that the g -value in praseodymium lies between the values
 in the other dilutants. This effect of change of g -value
 with size of lattice constant of the dilutant has also been
 observed in neodymium ethyl sulphate (see chapter 6.2).

Line width measurements on a crystal of lanthanum
 ethyl sulphate containing about 1% praseodymium gave a
 value of $\Delta H = 332 \text{ gauss}$ at $\bar{\nu} = .808 \text{ cm}^{-1}$. The value
 of $\Delta = 0.19 \text{ cm}^{-1}$ is much larger than that found by Bleaney
 and Scovil. Assuming that $\Delta = 0.19$ this crystal gave
 $g_{\parallel} = 1.63$. If however $\Delta = 0.04$ is assumed, the g -value
 becomes 1.69 so that this measurement would fit with the
 results of Bleaney and Scovil. This small value of Δ

would give a line width of only 15 gauss at $\bar{\nu} = .8$ which is unreasonable. Unfortunately no record of the line width which Bleaney and Scovil obtained has been kept, but it was certainly of the order of hundreds of gauss. It is reasonable that Δ should have a larger value in the lanthanum salt because it is also produced by lattice distortions, and the g-value measurements have shown that there is larger distortion in the lanthanum salt. This would suggest therefore that the extrapolation made by Bleaney and Scovil to obtain the values of Δ and $g_{||}$ is slightly in error. The value of $A/g_{||} = 1051$ gauss found in this crystal is in excellent agreement with that quoted for the other two workers.

Elliott and Stevens (1953) show that if admixture from higher J multiplets is negligible, $A/g_{||}$ may be expressed in terms of factors which are constants for the ion (see chapter 7.4). Thus the value of $A/g_{||}$ should be the same in different dilutants, which is seen to be the case.

With this value of $A/g_{||}$ the nuclear magnetic moment may be estimated as in terbium. The value of $\langle J|N|J \rangle$ is $296/225$ and $\langle J|\Lambda|J \rangle$ is $\Lambda = 4/5$; $Z = 59$ so that r^{-3} is 34 ± 9 A; these give a magnetic moment of 4.5 ± 1.1 nuclear magnetons. The odd proton, according

to Klinkenberg (1952) is in a $d_{5/2}$ state which explains the nuclear spin. The magnetic moment is close to that expected on the Schmidt model.

7.8 PROMETHIUM ETHYL SULPHATE

Twenty micrograms of promethium 147 were obtained from the Radiochemical Centre, Amersham; this isotope is a fission product which has a half-life of 3.6 years. This was made into the ethyl sulphate and diluted with a thousand times as much spectrographically pure lanthanum ethyl sulphate. A crystal was grown, using a heavy water crystallisation unit (chapter 2.1).

The ground state of the free Pm^{+++} ion is $4f^4, {}^5I_4$. The energy levels of this are much the same as terbium except that there is an additional $J_z = \pm 7$ doublet which is admixed with the $J_z = \pm 1$ and $J_z = \mp 5$ doublets. ~~As~~ The Lande g-value is $3/5$. ~~the g-values will be lower.~~ Elliott (unpublished) suggests that the ground state is:

$$\cos\theta |J_z = \pm 2\rangle - \sin\theta |J_z = \mp 4\rangle$$

He also suggests a value of θ which would make $g_{||} = 0.21$. If this value is correct then the measurements become extremely difficult. The field necessary even at

$\bar{\nu} = 0.1 \text{ cm}^{-1}$ is 10 Kgauss and as the g-value is so low and the line width is likely to be large as in praseodymium the lines will be very faint. It was estimated that the

lines would be too faint to be seen using a 10 cm apparatus, even when the lock-in detector is used in conjunction with it. Measurements have been made at $\bar{\nu} = 0.32 \text{ cm}^{-1}$ up to 8.2 Kgauss corresponding to $g_{\parallel} = 0.85$, and at 0.8 cm^{-1} up to 12.8 Kgauss corresponding to $g_{\parallel} = 1.3$. In neither of these measurements was any spectrum seen which was attributable to promethium. The spectrum from some neodymium impurity enabled the crystal to be accurately lined up in the external field.

Recent calculations by Mr. B.R. Judd show that in a field of the type which exists in the double nitrate, $2\text{Pm}(\text{NO}_3)_3 \cdot 3\text{Mg}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$, the lowest level is either a singlet, or a doublet:

$$.7 | \pm 1 \rangle + .5 | \pm 4 \rangle + .3 | \mp 2 \rangle$$

which is lower depending upon the crystal field parameters. If the doublet is lowest then resonance should be observed easily. The double nitrate would appear then to be the most suitable substance in which to continue the investigation.

APPENDIX 1Specific Heat and Curie-Weiss Δ produced by interactions

By setting up an expression for the partition function Van Vleck (1937) calculates an expression for the specific heat which is, neglecting powers of T greater than the second:

$$\frac{CT^2}{R} = \sum_{s,t} \frac{\text{spur}(\mathcal{H}_{st}^2)}{k^2 \text{spur}(1)} = \frac{1}{3N} \sum_s \frac{\text{spur}(\mathcal{H}_{st}^2)}{k^2 \text{spur}(1)}$$

If the interactions between the ions add to the hamiltonian a term:

$$A \sum_{st} S_x T_x + B \sum_{st} S_y T_y + C \sum_{st} S_z T_z$$

these contribute to the value of $\text{spur}(\mathcal{H}_{st}^2)/\text{spur}(1)$:

$$\frac{s^2(s+1)^2}{3} \times \frac{(A^2 + B^2 + C^2)}{3}$$

so that,

$$\frac{CT^2}{R} = \frac{s^2(s+1)^2}{6k^2} \sum_s \frac{(A^2 + B^2 + C^2)}{3} = 2.34 \sum_s \frac{(A^2 + B^2 + C^2)}{3}$$

Writing A , B and C as $(\alpha + a + j)$, $(\beta + b + j)$ and

$(\gamma + c + j)$ as has been suggested in chapter 1.4

$$(A^2 + B^2 + C^2) = (\alpha^2 + \beta^2 + \gamma^2) + (a^2 + b^2 + c^2) + 3j^2 + 2(\alpha a + \beta b + \gamma c).$$

As $(a + b + c) = 0$ and $\alpha = \beta = \gamma$ the last term reduces to $-6\alpha c$. Summing magnetic interaction over all neighbours,

$$\sum_s \frac{(\alpha^2 + \beta^2 + \gamma^2)}{3} = 4.8(\alpha^2 + \beta^2 + \gamma^2)$$

and summing the exchange over the twelve nearest neighbours,

$$\begin{aligned} \sum_s \frac{(a^2 + b^2 + c^2)}{3} + j^2 - 2\alpha c \\ = 4(a^2 + b^2 + c^2) + 12j^2 - 24\alpha c \end{aligned}$$

The contribution to CT^2/R is simply the sum of these two terms.

Calculating the magnetic susceptibility from the partition function Daniels (1953) obtains:

$$\Delta = \frac{1}{3k^2} \frac{\text{coeff. of } H^2 \text{ in spur } (W^3)}{\text{Curie constant} \times \text{spur } (1)}$$

The coefficient of H^2 in spur (W^3) averaged over all directions for the above hamiltonian is $75(A + B + C)$ so that,

$$\Delta = \frac{J(J+1)}{3k} \sum_s \frac{(A + B + C)}{3}$$

As $(A + B + C) = 3j$ and there are 12 neighbours over which to do the sum,

$$\Delta = \frac{4J(J+1)}{k} j$$

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