

ABSTRACT

The susceptibilities and specific heats of various paramagnetic substances have been measured at temperatures between 20°K and 0.005°K, and the results compared with theoretical predictions. In some cases the agreement

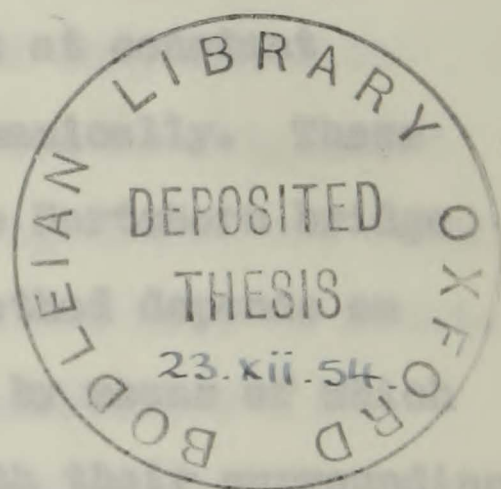
SOME PROPERTIES OF PARAMAGNETIC SALTS

Susceptibilities at temperatures as low as 0.005°K were measured from the change of resistance of coils of coils surrounding the specimens, using a Wheatstone bridge. This involved the construction of an accurate decade inductometer which is described in full detail.

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by

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ABSTRACT

The susceptibilities and specific heats of various paramagnetic substances have been measured at temperatures between 20°K and 0.006°K, and the results compared with theoretical predictions. In some cases the agreement between theory and experiment was found to be very good.

Susceptibilities were measured by an a.c. method from the change of mutual inductance of a pair of coils surrounding the specimen, using a Hartshorn bridge. This involved the construction of an accurate decade inductometer which is described in full detail.

Magnetic specific heats above 1°K were measured in terms of the adiabatic and isothermal susceptibilities, from the ratio of which the specific heat at constant magnetization can be calculated thermodynamically. These susceptibilities can be measured with the Hartshorn bridge using suitable audio frequencies. The method depends on the mechanism of spin lattice relaxation by means of which the magnetic ions can exchange energy with their surroundings. If the relaxation time is sufficiently long, then the susceptibility measured in the presence of a large steady field using the audio frequency method is equal to the

adiabatic susceptibility. The isothermal susceptibility is equal to the susceptibility in zero external field for all measuring frequencies. The method measures only the specific heat of the assembly of paramagnetic ions and is independent of the lattice specific heat of the substance.

Below 1°K entropies and hence specific heats were measured by the method of adiabatic demagnetization in terms of the magnetic temperature T^* . This is defined as $T^* = \frac{\lambda}{\chi}$, where χ is the susceptibility, and λ is determined from measurements in the helium range. The dependence of T^* on the shape of the specimen is discussed.

The Results

The susceptibility of oxygen trapped in a "clathrate" enclosure compound of β quinol was measured and the temperature variation between 20°K and 1°K compared with that of an assembly of free oxygen molecules as calculated from spectroscopic data. Almost perfect agreement was found down to 2°K indicating that the molecules are free to rotate within the cage of quinol. However, below about 2°K a discrepancy was observed suggesting a "freezing in" of the rotation. This conclusion was supported by a second experiment on oxygen enriched in $O^{16}O^{18}$. The susceptibility of this "gas" at very low temperatures would be expected to

differ from that of normal oxygen on the basis of free rotation, but no appreciable difference was found in the range 1-5°K.

The magnetic specific heat of Cerium Magnesium Nitrate was measured at 1°K by the relaxation method and between 1°K and 0.006°K by the method of adiabatic demagnetization. It was found that the specific heat is very small, being given in this range of temperatures by $C_M = 7.3 \times 10^{-6} R/T^2$, and that it can be accounted for almost entirely by magnetic dipole-dipole interaction. The uses of the salt for work below 1°K are discussed.

Specific heat measurements by the relaxation method were also made on four other substances:-

Cerium zinc nitrate. This was found to have very nearly the same properties as the magnesium salt, its susceptibility being exactly the same and its specific heat being given by $C_M = 6.4 \times 10^{-6} R/T^2$.

Neodymium magnesium nitrate. The specific heat of this salt was measured at 1°K and found to be given by $C_M = 8.73 \times 10^{-4} R/T^2$, in good agreement with the value calculated on the basis of magnetic dipole-dipole interaction plus the effect of hyperfine splittings. In view of the good agreement between theory and experiment at 1°K, the theory

will almost certainly hold down to temperatures of the order of 0.01°K where the interaction energy becomes comparable with kT . An expression for the deviation from Curie's law in the temperature range 1°K to 0.05°K is derived and the uses of the salt for work below 1°K are discussed.

Chromic methyamine alum. The value of the specific heat near 1°K was found to be $C_M = 0.0192 R/T^2$ in excellent agreement with the values derived from adiabatic demagnetization data. However, when compared with the value calculated from dipole-dipole interaction plus the effect of the Stark splittings it was found that there was a 12% discrepancy. Possible explanations are discussed but the discrepancy remains unresolved.

Ferric Rubidium alum. The value of the specific heat near 1°K was found to be $C_M = 8.2 \times 10^{-3} R/T^2$. This is compared with the value $10.0 \times 10^{-3} R/T^2$ deduced from demagnetization experiments, and the value $5.8 \times 10^{-3} R/T^2$ calculated from the splittings and the dipole-dipole interactions. Possible explanations for the discrepancy with the theoretical value are discussed.

Finally a new method of relating magnetic temperatures below 1°K to absolute temperatures is described. Cerium magnesium nitrate, which is known to obey Curie's law down

to 0.006°K , was used as a thermometer since its very anisotropic susceptibility can be measured in the presence of another isotropic paramagnetic substance. The design and construction of a system of mutual inductance coils to measure susceptibilities in two directions at right angles is discussed in detail. The method has been used to determine the $T-T^2$ relation for manganous ammonium sulphate from its Curie point to 1°K . The temperature of the Curie point was determined as $0.127^{\circ}\text{K} \pm 0.003$. The advantages of this method over the conventional thermodynamic method are discussed with special reference to measurements in the Curie point region.

unfailing sense of humor in the face of all my bright ideas.

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- 1) Determination of magnetic specific heat in the temperature range 4.2°K to 1°K by paramagnetic relaxation (Ch. 2, chapters 6 and 7).
- 2) Determination of entropy as a function of temperature below 1°K by the method of continuous extrapolation (Ch. 4; results Ch. 6.)
- 3) A new method of determining the absolute temperature scale below 1°K by interpolation of the magnetic specific heats (Ch. 8).

The first CHAPTER 1. are well established and have been described in detail in the literature so that only a summary will be given in Part I of this thesis together with references and INTRODUCTION.

In Part II we give the experimental results compared with the During the work to be described in this thesis, the following methods were used to investigate the properties of paramagnetic substances at low temperatures

1) Susceptibility measurements by an a.c. method in the ranges 4.2° to 1°K and 20°K to 10°K (Ch. 2; results Chs. 5 and 7).

2) Measurements of magnetic specific heat in the temperature range 4.2°K to 1°K by paramagnetic relaxation (Ch. 3; results Chs. 6 and 7).

3) Determination of entropy as a function of magnetic temperature below 1°K by the method of adiabatic demagnetization. (Ch. 4; results Ch. 6.)

4) A new method of determining an absolute temperature scale below 1°K by intercomparison of two paramagnetic substances. (Ch. 8).

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The first three of these methods are well established and have been described in detail in the literature so that only a summary will be given in Part I of this thesis together with references and details of new techniques.

In Part II we give the experimental results compared with the present theories, with a view to being able to predict the properties below 1°K from measurements above 1°K.

In Part III we describe the method of using a substance for which the theoretical predictions are well borne out by experiment, for investigating the properties of other paramagnetic substances by intercomparison.

In this introduction we shall compare briefly the properties of an ideal paramagnetic with those of the substances actually used.

The perfect paramagnetic

Let us define a perfect paramagnetic as an assembly of dipoles, each of strength μ , which are perfectly free except for their interaction with an applied field. This is the model for which Langevin (1905) worked out the temperature variation of susceptibility in small fields, now universally known as Curie's law

$$\chi = \frac{N\mu^2}{3kT}$$

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where N is the number of dipoles and k is Boltzmann's constant. In quantum mechanical terms we can regard the magnetic moment of the particles as arising from angular momentum or spin $\underline{J}$, having a magnetogyric ratio γ so that

$$\begin{aligned}\underline{\mu} &= \gamma \underline{J} \\ &= g\beta \underline{J}\end{aligned}$$

where β is the Bohr magneton $\frac{eh}{4\pi mc}$, and g is the spectroscopic splitting factor. We can thus write Curie's law for a set of free particles as

$$\chi = \frac{N g^2 \beta^2 J(J+1)}{3kT} \quad (1)$$

since $\underline{J}^2 = J(J+1)$. This extension of the Langevin formula was first made by Brillouin (1927).

The entropy of such an assembly is $N k \log_e(2J+1)$ independent of temperature. We see therefore that this model cannot represent a real substance at all temperatures since it would violate the third law of thermodynamics.

Real paramagnetism

In a real paramagnetic, the magnetic particles are ions with unpaired electrons and the magnetic moment arises from their orbital angular momentum $\underline{L}$ and spin $\underline{S}$. In the free ion $\underline{L}$ and $\underline{S}$ are coupled by the spin orbit coupling ($\lambda \underline{L} \cdot \underline{S}$) to

give states of total angular momentum J as described by the vector model of the atom. However, the ions are not free and we must consider the effect of their surroundings. The most important of these are the forces in the crystal lattice in which they are arranged.

The electric crystalline field

In ionic crystals there are large electric forces between the ions and these affect the orbits of the electrons in a way analogous to the Stark effect in atoms. In the salts of the iron group, where the unpaired electrons are in the outermost (3d) shell, the effect of the electric field is very large and in consequence the energies of the various orbital states are very different. Hence, at ordinary temperatures ($< 10^4$ °K) all the ions will be in the same state and have the same orbital energy. We say that L has been quenched.

As the spin is not affected directly by an electric field, the orbital ground state is still degenerate with respect to spin. Interaction between the spin and the electric field occurs only through the spin orbit coupling and therefore the ions behave as very nearly like free particles with angular momentum S and magnetic moment $gS\mu_B$ where $g = 2$ as for a free

electron. The effect of the spin orbit coupling is to modify the value of g and also make the effective value of g different for different directions in the crystal. The deviations from the value 2 are however small (except for Cobalt and Titanium salts, which we shall not consider here), and we speak of "spin only" paramagnetism.

The combined effect of the spin orbit coupling and the crystal field also lifts the spin degeneracy of the ground state and causes small splittings of the order of 0.1°K . The magnitude of the splittings can be deduced from paramagnetic resonance. It has been found, however, that in some substances they are very structure sensitive and change with temperature (and "dilution", see page 7.20), so that in applying the results of resonance measurements to other experiments care must be exercised to ensure that the conditions are exactly reproduced.

As the temperature is lowered there will be a repopulation of the different levels according to a Boltzmann distribution which, at low temperatures, gives rise to a specific heat 'anomaly' of the Schottky type and deviations from Curie's law. Both these effects can

* For ions in an S state ($L=0$) splittings are also found and a different mechanism has been suggested (Abragam & Pryce, 1951).

calculated from the splittings, but as pointed out above these may change with temperature so that resonance experiments at 'high' temperatures may lead to the wrong result at low temperatures.

In the salts of the rare earths the position is very different. The unpaired electrons are in the 4f shell and are shielded by the 5s and 5p shells so that the effect of the crystal field is much smaller than in the iron group and is comparable with the spin orbit coupling. Hence, to a first approximation, L and S still combine to form J as in the free ion. Each state of J is then split by the combined effect of electric field and spin orbit coupling into sub levels. However, for ions with an odd number of electrons not all the degeneracy can be removed in this way, since by Kramer's (1930) theorem, an electric field acting on a system with half integral spin must leave each state at least doubly degenerate. In all experiments we have confined ourselves to ions with an odd number of electrons, for which this theorem holds. If the splitting by the crystalline field is fairly large, then at low temperatures only one doublet will be populated and the ions will behave like particles with a spin of $S = \frac{1}{2}$. This is normally referred to as a "fictitious spin" of $S = \frac{1}{2}$.

If a magnetic field is applied to such an ion the two levels will, however, behave very differently from those of a free spin. In a field H the energy levels of a free spin are $\pm \beta H$ irrespective of the direction of H . For a fictitious spin the levels are in general $\pm \frac{1}{2} g \beta H$ where the value of g depends on the angle between the field and the axes of symmetry of the crystal. g transforms like a tensor of second rank and has symmetry properties closely related to those of the crystal field. Thus if the field has axial symmetry then so will g and its value for any direction θ of the field relative to the axis, will be given in terms of two principal values $g_{\parallel}$ and $g_{\perp}$ by

$$g^2 = g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta$$

As the susceptibility is proportional to g^2 , this leads to an anisotropic susceptibility whose principal values are proportional to $g_{\parallel}^2$ and $g_{\perp}^2$. For example, in Cerium Magnesium Nitrate, the only two states populated at low temperatures ($< 10^\circ K$) are $|J = 5/2 \quad J_z = \pm \frac{1}{2}\rangle$ and this leads to a ground state which can be described by:

$S = \frac{1}{2}$; $g_{\perp} = 1.84$, $g_{\parallel} = 0.25$ (see Chapter 6), so that the ratio of $\chi_{\perp} : \chi_{\parallel} = (1.84)^2 : (0.25)^2 = 54:1$.

We can summarize the effect of the crystal field by

saying that in the salts of the iron group it quenches the orbital part of the angular momentum leaving the ion with a paramagnetism due to its spin only, while in the rare earths it combines with the spin orbit coupling. In cases where Kramers' theorem applies, this gives rise to a series of doublets, so that at sufficiently low temperatures the ion can be regarded as a fictitious spin $S = \frac{1}{2}$ with an anisotropic splitting factor g .

$$\chi = \chi_0 \left(1 - \frac{T_0}{T} \right)$$

Hyperfine structure

If the paramagnetic ion has a non zero nuclear spin I , then there will be an interaction between the nucleus and the electronic shell which gives rise to a hyperfine splitting of the ground state. This effect has long been known for atomic spectra but was only recently observed for ions in a crystal by Penrose (1949) using paramagnetic resonance. The theory for the interaction has been given by Abragam and Pryce (1951) who express the effect in terms of an operator which is a function of the nuclear spin I and the effective electron spin S (see Appendix II). The constants in this operator (called the spin hamiltonian) are found from the paramagnetic resonance spectrum. The effect of the hyperfine splittings on the specific heat

and susceptibility can be calculated from the hamiltonian, and approximate expressions are derived in Appendix II. For most salts the splittings are of the order of 0.1°K to 0.01°K so that their effect will not become appreciable until very low temperatures.

At temperatures high compared with the splittings it can be shown (Bleaney, 1950b) that the susceptibility follows a law of the form

$$\chi = \chi_c \left(1 - \frac{\tau}{T^2}\right)$$

where χ_c is the Curie law of susceptibility $\frac{\lambda}{T}$, and τ is a constant of the same order as the splittings which can be calculated from the resonance data.

It can also be shown that at 'high' temperatures the tail of the Schottky anomaly associated with the splittings gives a specific heat of the form $\left(\frac{\tau'}{T}\right)^2$ where τ' is another constant which can be calculated. It is thus possible to subtract the effect of the "nuclear specific heat" from measurements of the total specific heat and to examine the effect of other contributing factors.

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Interactions - Magnetic dipole-dipole forces

Another important contribution to the deviation of real paramagnetics from the ideal case is the interaction between the magnetic ions themselves. In the types of crystal most usually studied (e.g. alums or double nitrates), the paramagnetic ions are situated in a regular lattice some 6 to 10 Å apart. In the absence of an external field the orientation of the ions will be random and the field which each sets up at its neighbour will have an average value of zero. However the mean square value of the internal field will be finite and have an average value of the order of $\frac{\mu^2}{r^3}$ where r is the distance between the ions. It has been shown by Van Vleck (1937) that this mean square field gives rise to an interaction specific heat which at high temperatures is given by

$$C = \frac{\lambda (\overline{\Pi_{int.}^2})}{2T^2}$$

where λ is the Curie constant per cc. The criterion of a high temperature is that the energy of interaction should be small compared with kT . It is then possible to expand the partition function of the assembly as a power series in $\frac{1}{T}$ and to use the first terms to a good approximation.

The original calculation by Van Vleck was applicable only to substances with an isotropic susceptibility and this has been extended in Chapter 6 to include the case where the susceptibility is anisotropic.

There are three main theories for estimating the effect of the magnetic forces on the susceptibility. The simplest of these is the theory of Lorentz (1909) which agrees to a first order with the more refined theories of Onsager (1936) and Van Vleck (1937).

In order to consider the effect of the magnetic forces on any one particular ion Lorentz divides the specimen into two parts by drawing an imaginary sphere around the ion and considers the contribution from ions inside the sphere separately from those outside. He showed that for the case of either a cubic lattice or for a completely random arrangement, the average field due to the ions within the sphere was zero. In order to consider the effect of the ions outside the sphere he replaced them by a continuum of uniform magnetization M , which can be shown to produce a field equal to $\frac{4\pi}{3} M$ at the centre of the sphere. This is usually called the Lorentz internal field. This treatment however holds only for a body of infinite size; for a finite body we also have to consider the

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distribution of "surface charge" on the outside of the specimen. In the case of an ellipsoid the field inside the body is uniform, and it can be shown from simple macroscopic considerations that the field inside due to the surface distribution is equal to $N \cdot M$ where N is a factor depending on the proportions of the ellipsoid (Maxwell 1873). N is usually called the demagnetizing factor, and the substance is well above its Curie point. At

Thus on the basis of the Lorentz theory the field acting on any ion is given by

$$H_{act} = H_0 + \frac{4\pi}{3} M - N M$$

where H_0 is the applied field. If the assembly of 'free' ions obeys Curie's law, regarded as a continuous, is

$$\begin{aligned} M &= \frac{\lambda}{T} H_{act} \\ &= \frac{\lambda}{T} (H_0 + \frac{4\pi}{3} M - N M), \end{aligned}$$

then in general

$$\chi = \frac{M}{H_0} = \frac{\lambda}{T - \theta} \quad (2)$$

where $\theta = \lambda (\frac{4\pi}{3} - N)$ is explained in section (3) and Appendix II: consists of writing down the partition

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In the case of a spherical specimen $N = \frac{4\pi}{3}$, so that the Lorentz field exactly cancels the demagnetizing correction and the susceptibility still follows Curie's law. For this reason measurements of susceptibility at low temperatures are always corrected to a sphere (see Chapter 4). The Lorentz theory is essentially a static calculation and holds only if the internal field is small. This is the case when $\chi \ll 1$ and the substance is well above its Curie point. At very low temperatures a better approximation is needed.

In the Onsager theory, which is superficially similar to that of Lorentz, the ion under consideration is supposed to be situated at the centre of a small spherical cavity scooped out of the body. The effect of the ion on the substance outside the cavity, regarded as a continuum, is calculated, and from the magnetisation produced the "reaction field" back on the ion can be deduced. The result of the theory, which is well summarized by Van Vleck (1937), reduces to the Lorentz theory when $\chi \ll 1$ but is ^{more} accurate at low temperatures.

In the same article Van Vleck gives another more accurate theory which agrees with that of Lorentz to a first approximation. The method which is explained in section 6.4 and Appendix II, consists of writing down the partition

function in terms of the interaction energy between pairs of neighbouring dipoles and expanding it in powers of $\frac{1}{T}$. The coefficients of $\frac{1}{T^n}$, which are proportional to the mean of the n th powers of the interaction energy, are calculated very neatly from the diagonal sums of the matrices representing the hamiltonian and its n th powers.

Experimental results of measurements at low temperatures (Cooke 1949) show that the behaviour of real substances falls somewhere between the last two theories. In trying to find a substance whose behaviour at low temperatures can be calculated with good accuracy, it is advantageous therefore to choose one which has a small susceptibility per unit volume, when even the Lorentz approximation is fairly close.

where n is the number of nearest neighbours and S is the

Exchange interaction

In order to explain the discrepancy between the observed specific heat and the specific heat calculated from all other known effects, it has been suggested that the ions are also coupled by exchange forces. The observed line slopes in paramagnetic resonance are also explained by this fact.

It can be shown (see, for example, Van Vleck 1932 p.318) that the exchange forces between two ions can be represented, apart from an additive constant, by an operator of the form

$-J \underline{S}_i \underline{S}_j$ where J is a constant depending on the distance between the ions and $\underline{S}_i$ and $\underline{S}_j$ are their effective spins. This type of interaction energy, which depends only on the cosine of the angle between $\underline{S}_i$ and $\underline{S}_j$ is called isotropic or direct exchange. The value of J decreases very rapidly with distance, so that in calculating the effect on any one ion, we have to consider only the effect of the nearest neighbours. Using the same method of expanding the partition function as for magnetic interaction, Van Vleck showed that the contribution to the specific heat from exchange, at high temperatures, is given by

$$C = \frac{2}{3} \frac{N}{k} \frac{J^2 S^2 (S+1)^2}{T^2} \cdot z \quad (4)$$

where z is the number of nearest neighbours and N is the number of ions in the assembly. He also showed that to a first approximation the effect on the susceptibility can be represented in the form of a Curie-Weiss law

$$\chi = \frac{\lambda}{T - \Delta} \quad (5)$$

where $\Delta = \frac{3}{2} \frac{J}{k} S(S+1) \cdot z \quad (6)$

We can eliminate the unknown constant J between equations (4) and (6) and write

to the specific heat but not necessarily to the susceptibility.

$$\frac{C_{\text{exch}} T^2}{R} = \frac{3}{2} \frac{\Delta^2}{z}, \quad (7)$$

where $R = N k$. If we consider a gm. mole then N is Avogadro's number and R is the gas constant.

Equation (7) is, however, not always verified in practice. It has been found that for many substances for which the specific heat is larger than that calculated from all other causes so that exchange is indicated, Curie's law is obeyed accurately if account is taken of the internal and demagnetizing fields. It seems therefore that there must be some other kind of exchange which leads to a specific heat but no Weiss Δ .

A more general interaction between spins of the form

$$\mathcal{H} = \sum_{i,j} C_{xx} \overset{(i)}{S}_x \overset{(j)}{S}_x + C_{xy} \overset{(i)}{S}_x \overset{(j)}{S}_y + \quad (8)$$

has been suggested by Opechowski (1948). In the particular case where

$$C_{xx} = C_{yy} = C_{zz} = J$$

$$C_{xy} = C_{yx} \text{ etc.} = 0$$

this reduces to the isotropic case. It was shown by Opechowski that a general interaction of this type gives rise to a contribution to the specific heat but not necessarily to the susceptibility.

A particular case of the general interaction (8) was suggested by Ollam and Van Vleck in 1950, who postulated an interaction of the form

$$\mathcal{K} = f(r) \left[\underline{S}_1 \cdot \underline{S}_2 - \frac{3}{r_{12}^3} (\underline{S}_1 \cdot \underline{r}_{12})(\underline{S}_2 \cdot \underline{r}_{12}) \right]$$

analogous to magnetic dipole interaction, where $f(r)$ is a function of the distance between the spins. It can be shown that if $f(r)$ fall off more rapidly than $\frac{1}{r^3}$ (which is to be expected for exchange) then this type of interaction does not give rise to a Weiss Λ and that deviations from Curie's law occur only in higher order terms.

The mechanism for anisotropic exchange is not yet fully understood but in particular cases of very concentrated substances it has been shown that the intermediate diamagnetic atoms play an important role. For this reason any exchange not of the form $-J \underline{S}_1 \cdot \underline{S}_2$ is often referred to as "indirect" or "super exchange".

A new technique for studying the general interactions by means of paramagnetic resonance has recently been developed by Baker and Bleaney (unpublished). By working with semi diluted crystals of Neodymium in Lanthanum ethyl sulphate (about 10% Nd to 90% La), they were able to observe the interaction between isolated pairs of ions and to

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measure the shift of resonance of one ion due to the field of another. They were able to distinguish between the interactions between similar and dissimilar ions since some of the Nd ions have a nuclear spin (and hence hyperfine structure) and some do not. They found that the exchange interaction between nearest neighbours was not isotropic and that its magnitude was only 10% of the magnetic interaction. Since the specific heat involves the mean square energy the effect is thus too small to be measured on a macroscopic scale. However similar experiments on substances known to have large exchange interactions should lead to a clearer understanding of the mechanism.

Conclusion

We conclude this introduction with a summary of the properties which a real substance must have to approximate to those of a perfect paramagnetic as nearly as possible:

- 1) In zero field at low temperatures all the populated energy levels must be degenerate, and in practice this restricts us to substances with an effective spin of $S = \frac{1}{2}$, as for all others splittings by the crystal field are likely. States with $S = \frac{1}{2}$ can not be split on account

of Kramers' theorem. The magnitude of the g value is not of importance since it can be measured accurately by paramagnetic resonance and allowance made in calculating the susceptibility etc.

2) If possible none of the isotopes should have any nuclear spin so that there is no hyperfine structure. In cases where there is hyperfine structure allowance for its effect can be made from paramagnetic resonance data. There is however a small possibility that this may lead to the wrong result since the resonance is performed on diluted crystals, while the macroscopic properties are investigated in the pure salt, and there may be small differences in the hyperfine parameters. Such differences have however not yet been observed. Such a case is described in Chapter 3.

3) The substance should be magnetically dilute i.e. have a small susceptibility per unit volume. This reduces the effect of magnetic dipole-dipole interaction which leads to deviations from Curie's law at low temperatures. The correction due to this effect can be largely reduced by using spherical specimens for which the first order correction is zero, or by using a spheroid and applying

a demagnetizing correction to reduce the measurements to those of a sphere (see eq.4.4).

4) The interionic distance should be as large as possible since exchange effects decrease rapidly with distance. Exchange and dipole-dipole forces can be artificially reduced by making mixed crystals consisting of the paramagnetic salt diluted in an isomorphous diamagnetic salt.

In the course the work described in this thesis we have found a substance, Cerium Magnesium Nitrate, which very nearly fulfils all these requirements (see Chapter 6). Such a substance can be used as a standard thermometer in the region below 1°K where the susceptibilities of other substances no longer obey any known laws. Such a thermometer is described in Chapter 8.

$$M = M_0 + \Delta M$$

$$= M_0 + C\chi$$

where C depends on the size of the sample and the dimensions of the specimen. C can be determined from measurements on substances with known magnetic properties and hence changes in χ can be measured in terms of changes in M . The absolute value of χ can only be determined if M can be found. In

2.1

PART I. EXPERIMENTAL METHODS AND TECHNIQUES.

temperatures could not be made, so that the value of M_0

to be found by CHAPTER 2.

MEASUREMENT OF SUSCEPTIBILITY USING A MUTUAL INDUCTANCE BRIDGE

passing through M_0 at $\frac{1}{T} = 0$. As measurements could

be made from $1^\circ K$ to $20^\circ K$ ($\frac{1}{T} = 0.05$), this involved some

1. Introduction extrapolation. For specimens with an
 Let us consider the change of mutual inductance of a
 pair of coils surrounding a paramagnetic specimen as the
 temperature T is varied. When T is very high the
 susceptibility is small and the inductance corresponds to
 that of the empty coil. Let this value be M_0 . At low
 temperatures the susceptibility of the specimen becomes
 larger and the inductance increases by an amount ΔM which
 is directly proportional to the susceptibility. Thus
 we can write

$$M = M_0 + \Delta M \quad (1)$$

$$= M_0 + C \chi$$

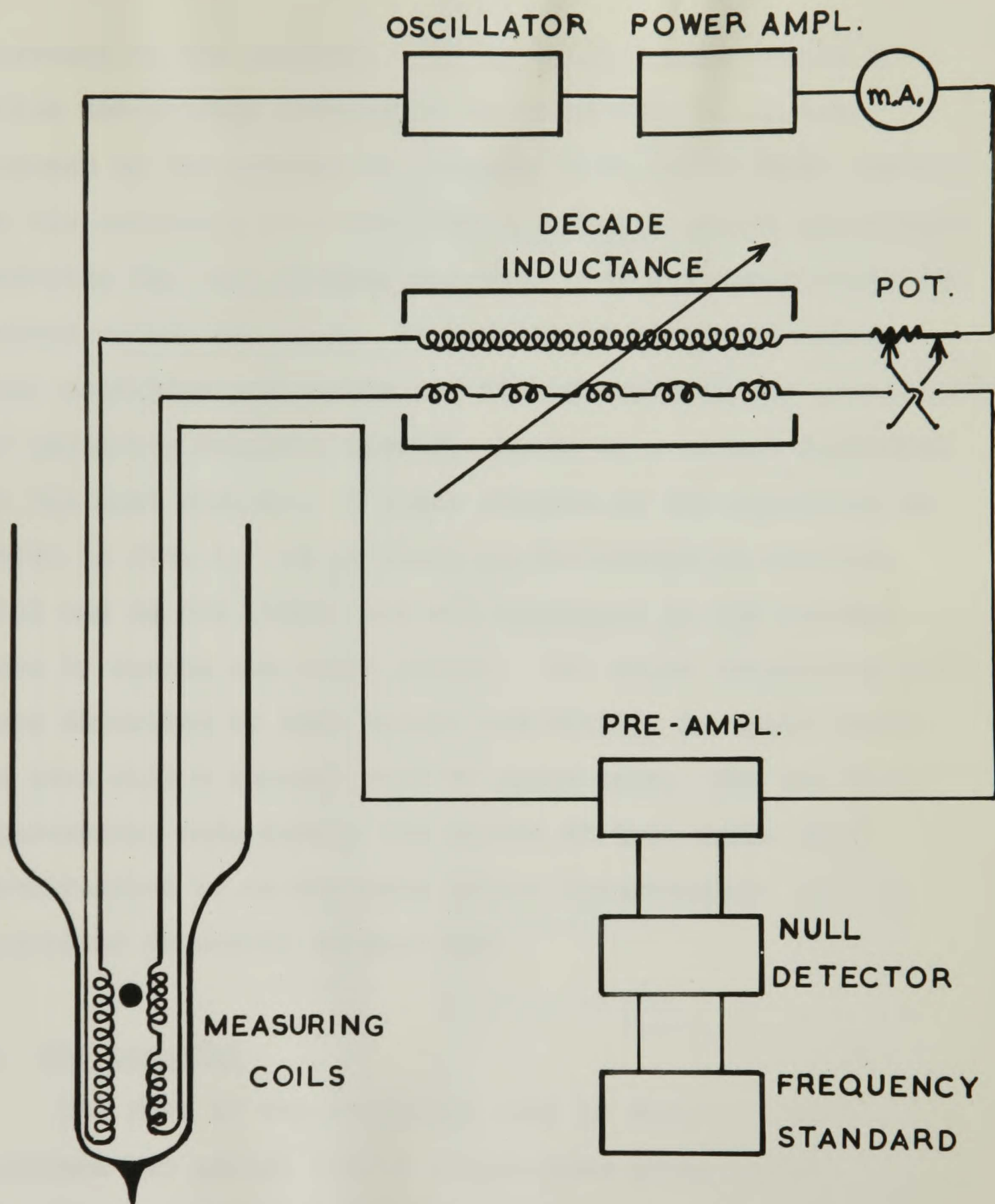
where C depends on the size of the coils and the dimensions
 of the specimen. C can be determined from experiments on
 substances with known magnetic properties, and hence changes
 in χ can be measured in terms of changes in M . The absolute
 value of χ can only be determined if M_0 can be found. In

2.2

the present experimental arrangement measurements at high temperatures could not be made, so that the value of M_0 had to be found by extrapolation from a graph of M against $\frac{1}{T}$. For specimens which obeyed Curie's law this gave a straight line passing through M_0 at $\frac{1}{T} = 0$. As measurements could be made from 1°K to 20°K ($\frac{1}{T} = 0.05$), this involved only a relatively small extrapolation. For specimens with an appreciable Weiss θ the approximate value of M_0 found in this way was used to plot $\frac{M - M_0}{M_0} \left(\propto \frac{1}{X} \right)$ against T to determine θ . Then, using this value of θ a more accurate value of M_0 was found by plotting M against $\frac{1}{T - \theta}$. In this way M_0 and θ were determined by successive approximations.

It must be pointed out that if M_0 is found in this way the susceptibility measured includes only temperature dependent terms. Diamagnetic and temperature independent paramagnetic susceptibilities are not measured. The alternative method of determining M_0 directly from the inductance of the empty coil was impossible in the present experimental arrangement, as the cryostat had to be completely dismantled to remove the specimen. The mutual inductance M can be measured in one of two ways: (1) By using a ballistic galvanometer to measure the voltage induced in the secondary when a known d.c. current is

FIG 1.



Block Diagram of Hartshorn Bridge

FIG 1.

2.3

reversed in the primary. (2) By using a null method in which the voltage induced in the secondary by an a.c. current in the primary is compared with the voltage induced in the secondary of a calibrated variable mutual inductance carrying the same primary current. For our experiments the second method was used. It has the advantage of being more sensitive and stable and it also affords the possibility of measuring magnetic specific heats by a method described in the next chapter. A block diagram of the apparatus is shown in fig. 1. It is based on the design of Casimir, Bijl and de Pre (1941) and was developed in its present form by Benzie and Cooke (1950). The major components have been described by both Benzie and Whitley in their theses so that only a summary will be given here. The one major improvement made during the course of this work, the construction of an accurate decade inductometer, will be described in detail on page 2.9.

2. The cryostat

The form of the apparatus used is shown in fig. 2. The specimen was sealed into a simple lead glass cryostat which was attached by two tubes to a standard Simon liquefier (Pickard, 1937). The cryostat was made of glass to avoid

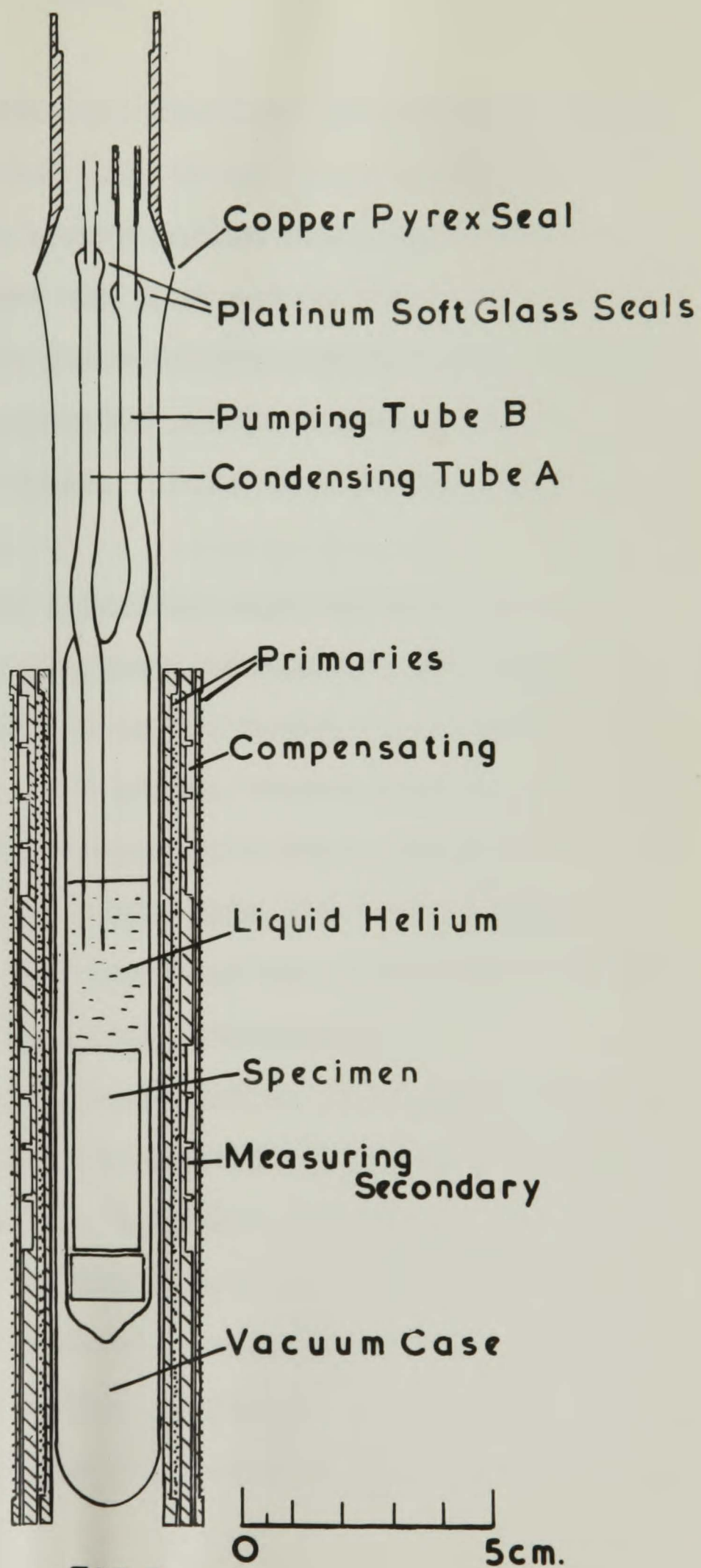


FIG. 2

2.4

eddy currents from the a.c. field of the measuring coil and the specimen sealed into it as it is difficult to produce an efficient liquid helium tight seal in any other way. Lead glass was used rather than pyrex so that the joins between the glass of the cryostat and the metal of the rest of the apparatus could be made by means of platinum soft glass seals. These have proved highly satisfactory in use.

The cryostat and liquefier were enclosed in a vacuum case of which the part surrounding the cryostat was made of pyrex, joined to the metal above by means of a copper-glass seal. The entire vacuum case was surrounded by liquid hydrogen in a dewar vessel. The measuring coil fitted closely into the space between the vacuum case and the dewar and was immersed in liquid hydrogen throughout the whole experiment.

The production of liquid helium in the bomb of the Simon liquefier has been described by Pickard. In order to cool the specimen to 4°K , helium gas was passed through a heat exchanger in the expansion bomb at a pressure of about $1\frac{1}{2}$ atmospheres and was condensed into the cryostat through tube A. The helium, which had to be very pure to avoid blocking the narrow tubes was obtained from a low

2.5

pressure cylinder. This was filled during each experiment with gas from the expansion bomb of the liquefier. About 8 - 10 ccs. of liquid were usually condensed, enough for an experiment of 4 to 6 hours.

To vary the temperature of the specimen the vapour pressure of the liquid helium in the cryostat was reduced by pumping through tube A. The temperature was determined from the vapour pressure as measured through the second tube, (B) which dipped below the surface of the liquid helium, thus eliminating the pressure drop down the pumping tube. At pressures below 1 mm. Hg, an empirical correction of 0.01 mm. was made to allow for thermo-molecular pressure. The lowest temperature that could be reached was about 1°K corresponding to a vapour pressure of about 0.1 mm.

In order to obtain temperatures in the range 20°K to 10°K, hydrogen was condensed into the cryostat in place of helium. The cryostat was put into thermal contact with the liquid hydrogen in the dewar vessel by admitting helium "exchange" gas into the vacuum case. Hydrogen gas from a cylinder was then condensed into the cryostat at a small over pressure. The temperature was reduced and measured as before. Although it was possible to reach temperatures down to 8°K, it was found that measurements below the triple

2.6

point (13.96°K) were sometimes inconsistent on account of the poor thermal conductivity of solid hydrogen.

When measurements in both the hydrogen and helium range were required in one experiment (see Ch. 5) it was found more satisfactory to carry out the latter first, as it was difficult to remove all traces of the hydrogen before condensing the helium.

3. The Measuring Coil

A cross section of this is shown in fig. 2. The primary consisted of two solenoids wound on separate formers mounted co-axially. The radii of the formers r_1 and r_2 and the number of turns per cm. on each (n_1 and n_2), were arranged in such a way that

$$n_1 r_1^2 = n_2 r_2^2.$$

If two such coils are connected in anti-phase the arrangement has a very small external field so that any spurious effects due to nearby pieces of metal are greatly reduced. The field inside the coils is proportional to $n_1 - n_2$. For our case of a single layer solenoid of 30 s.w.g. wire surrounding a double layer solenoid, the field at the specimen was about 40 gauss/amp. As sufficient sensitivity

2.7

was obtained using primary currents of the order of 0.1 amp., the mutual inductance method gives a measure of the susceptibility in very small fields.

The secondary was wound on a separate former which fitted between the two primaries. It was wound in two similar parts connected in antiphase so that in the absence of a specimen the whole system had only a small mutual inductance ($\sim \frac{1}{2}$ mH.) and when the specimen was placed at the centre of one of the two halves the relative effect on the mutual inductance was a maximum. Each part of the secondary was wound with 6000 turns of 47 s.w.g. enamelled, silk covered copper wire in 4 channels 9 mm. wide, 1 mm. spacers being left between the channels to reduce the effect of self capacity. As the specimens were also about 4 cm. long allowance had to be made for their finite size. (see appendix 1). For example, the value of ΔM in eq. 1 is 13% less for a cylindrical specimen 3.6 cm. long than for a point dipole of the same strength placed at the centre of the secondary.

4. The Hartshorn Bridge

The change of mutual inductance produced by the specimen was measured by a Hartshorn bridge. The measuring coil was level, and by adding smaller units to eq.

2.8

connected in opposition to a variable mutual inductance, M_2 , and the value for zero voltage in the secondary circuit found using a cathode ray oscilloscope as null detector. In practice there was also a small voltage in phase with the primary current due to eddy currents and the self capacity of the measuring coil and also the imaginary component of susceptibility (see 3.4). This was balanced out by means of a potentiometer device described on page 2.16.

The accuracy of this method of measuring mutual inductance depends on (i) how exactly the variable inductance M_2 can be subdivided and (ii) how small an out of balance signal can be detected. In the decade inductometer described in the next section, the smallest unit was 0.015μ Henry with all other units (5 decades in all) exact multiples of this to within 0.01μ H. At the frequency normally used, 175 c/s. and a primary current of $1/10$ amp., a change of mutual inductance of 0.015μ H changes the voltage in the secondary by $M \frac{di}{dt} = 1.5 \mu$ Volt. This was just on the limit of detection for the amplifier used and was amply sufficient for the present work. For the measuring coil described above it corresponded to a change of about 4×10^{-6} e.m.u. of magnetization. Greater sensitivity could, however have been attained by increasing the gain of the amplifier, which was used well below noise level, and by adding smaller units to M_2 .

2.9

5. The Decade Variable Inductance

As no suitable inductance was available commercially a special one was constructed. The essential features of the design are as follows:

- (i) Within any one decade all the units must be exactly the same. The maximum error in each unit must be less than one unit of the smallest decade, in order to make the last figure significant. For a 5 decade inductance this represents an accuracy of at least 1 in 10^4 in the largest units.
- (ii) Ten units of any one decade must be exactly equal to one unit of the next, the criterion of accuracy being the same as in (i) above.

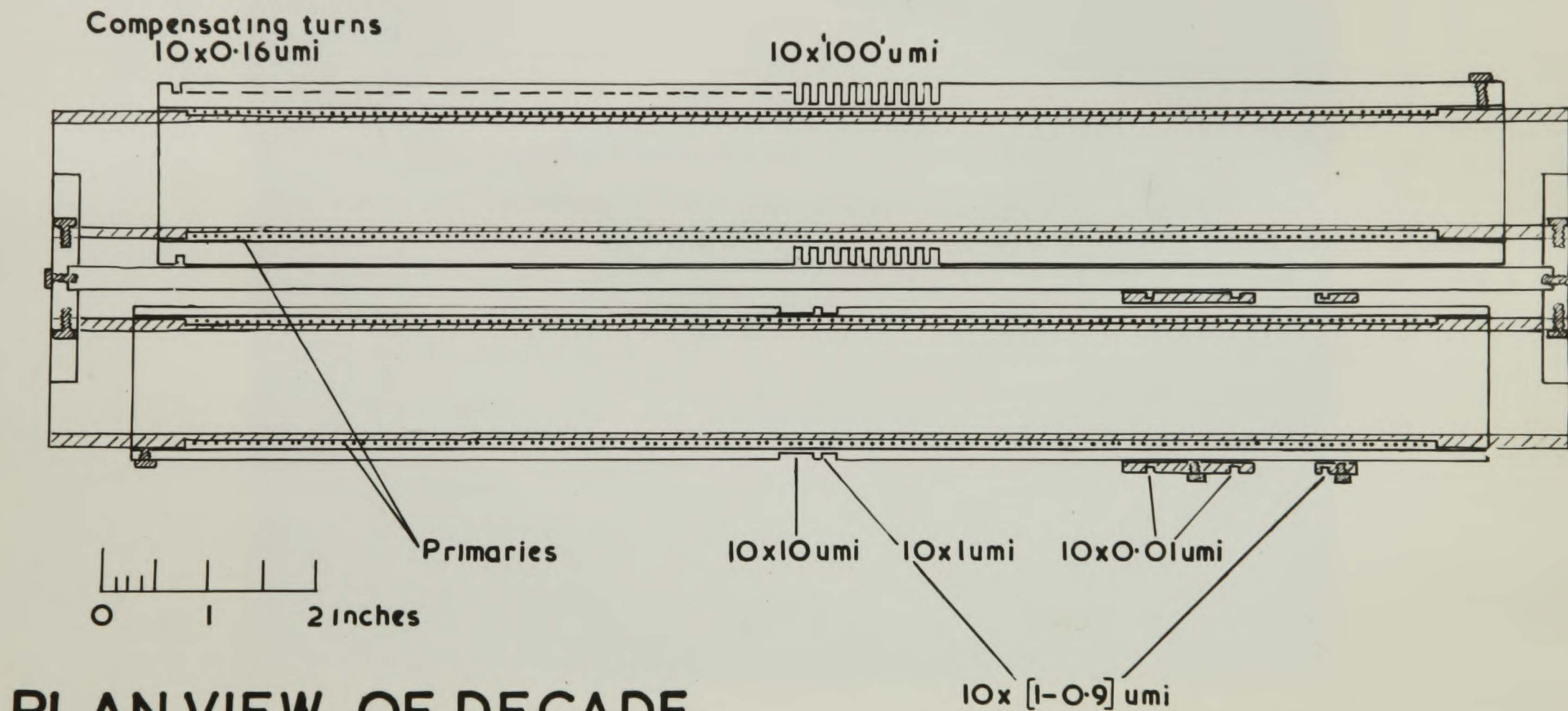
In the present design these two conditions were met in fundamentally different ways. The first was ensured by using stranded wire for the secondary turns so that each of the ten strands had an exactly equivalent geometrical path around the primary. The second was ensured by winding the secondaries of the different decades on separate formers, the flux through which could then be adjusted by moving them along the common primary until the relative values were correct. This could be done after the instrument had been completed. No attempt was made to make the basic unit any exact value of μ Henries as the constant of proportionality between susceptibility and mutual inductance depends on the

particular measuring coil used, and can be determined experimentally from substances with known susceptibilities. Various determinations of this calibration constant are listed in Ch. 7.

Details of the construction are shown in figs. 3 and 4. In order to eliminate eddy currents (which produce a secondary voltage in phase with the primary current), the coil formers were made of Tufnol (Carp brand) and were mounted on a Tufnol chassis with small brass screws. The whole unit was enclosed in a wooden box.

The primary

The primary was wound in two identical halves which were mounted side by side and were connected in antiphase. Such an astatic arrangement produces a very small field at some distance from the coils so that, as in the case of the measuring coil, the system was very insensitive to any external influences. The coils were wound as uniformly as possible with a single layer of 20 s.w.g. enamelled cotton covered copper wire held in position with a dystrene in amylacetate varnish. This rather heavy gauge wire was used to ensure that the coils would not be heated appreciably by the current, even with only air cooling.



PLAN VIEW OF DECADE
MUTUAL INDUCTANCE

FIG.3

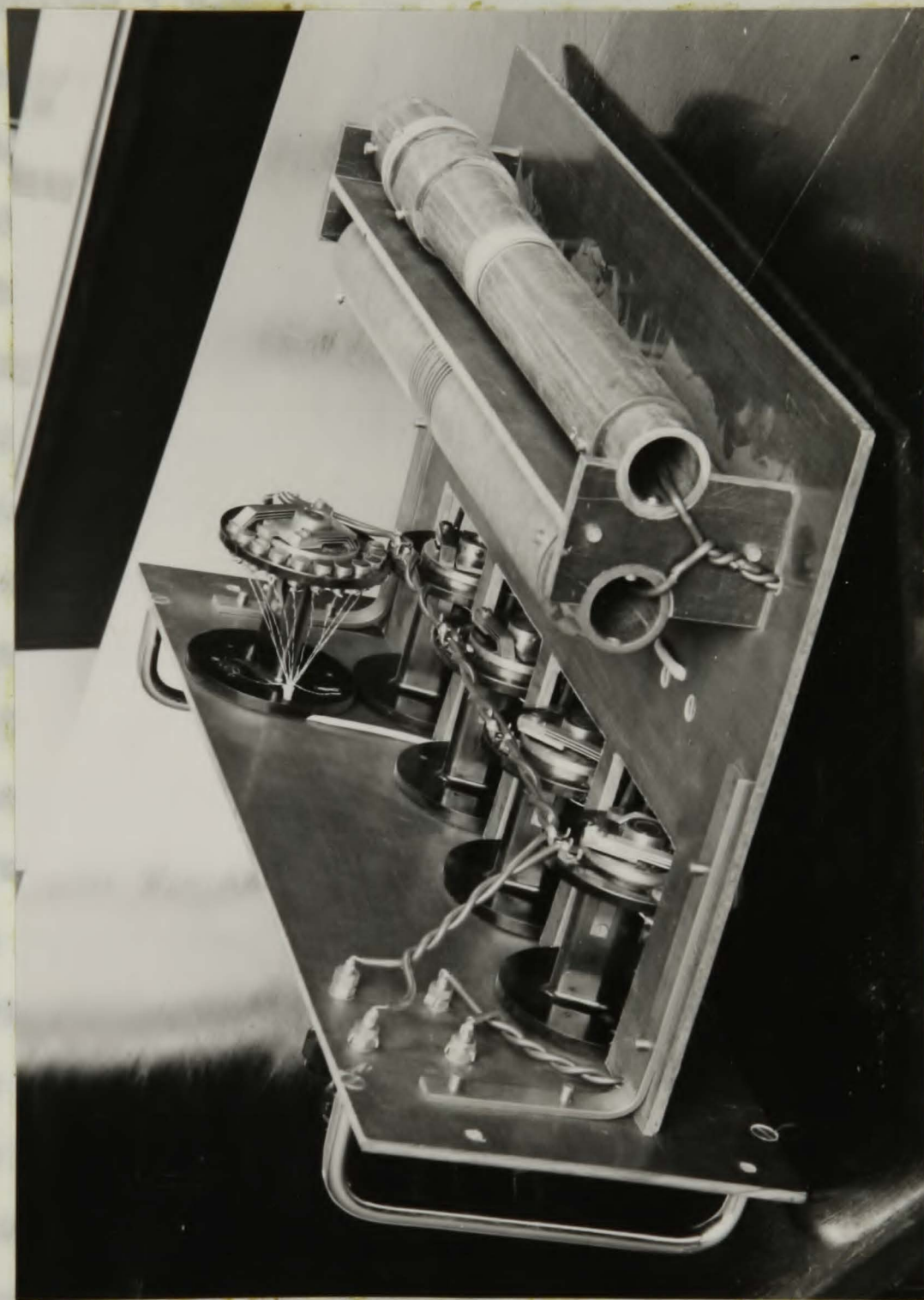


Fig. 4 The decade indicator.

2.11

The secondaries

(a) The units: The basic unit of mutual inductance, henceforth called 1 u.m.i., was defined as the inductance of two turns wound around the centre of one of the primaries. The other decades (10 times 100, 10, 0.1 and 0.01 u.m.i.) were adjusted to be exact multiples or submultiples of this.

The stranded wire used to wind the secondaries was made in the following way: 12 pieces of 36 s.w.g. enamelled silk covered copper wire about 50 yards long were stretched between two hooks and the lengths adjusted until all the wires were under the same tension. One of the hooks was then put into the chuck of an electric pistol drill and about 5000 turns applied. The overall diameter of the finished cable was 0.9 mm.

Two turns of this cable were wound in a groove at the centre of a Tufnol tube which fitted closely around one of the primaries and the ends connected to a high quality decade switch (Muirhead). The lengths of wire between the former and the switch were twisted together as closely and as evenly as possible to avoid stray inductances, and rigidly fixed to the chassis. At the switch all the strands were taken to their respective contacts by as similar paths as possible. These connections are not shown in the diagram

2.12

but can be seen in the photograph. Each strand now had a mutual inductance of exactly 1 u.m.i. and this was verified by connecting pairs of turns in opposition and checking that their effects exactly cancelled out. Two of the strands were left unconnected to act as spares in the event of a breakage.

(b) The tens: These were wound with 20 turns of stranded cable in a second groove as close to the units as possible. It was found that the primary field was sufficiently uniform to make one of these strands exactly equal to ten of the units without any further adjustment. (A small degree of adjustment would have been possible by moving the whole secondary former along the primary to bring the two sets of coils into a more uniform part of the field).

(c) The tenths: The principle employed in making units smaller than 1 u.m.i. was to connect two sets of similar coils in series opposition and then, by adjusting their positions on the primary, find a point where the difference between their inductances was exactly 1/10th of one unit of the next highest decade (Bijl, Thesis).

To make the tenths, two turns of stranded cable,

2.13

corresponding to 1 u.m.i., were wound at the centre of the secondary former next to the units and tens and connected in opposition to a similar pair of turns on a sliding collar. As the collar was moved along the primary the inductance of each strand increased, being equal to the difference in inductance of the two pairs of turns. The difference was equal to 0.1 u.m.i. when the collar was about 12 cm. from the centre. The adjustment was made, as before, by connecting the 10 'tenths' in series and opposing them with 1 unit. After the final adjustment the movable former was glued in position on the main secondary former.

(d) The Hundredths: These were constructed similarly to the tenths except that only one turn of stranded cable was used for each of the opposing coils. Both turns were wound 2 cm. apart on the same former and moved along the primary together. It was found that when the turns were about 8 cm. and 10 cm. respectively from the centre of the primary the mutual inductance of each strand was 0.01 u.m.i. The exact adjustment was made as before and the former then glued in place.

Using this principle it would be possible to make even

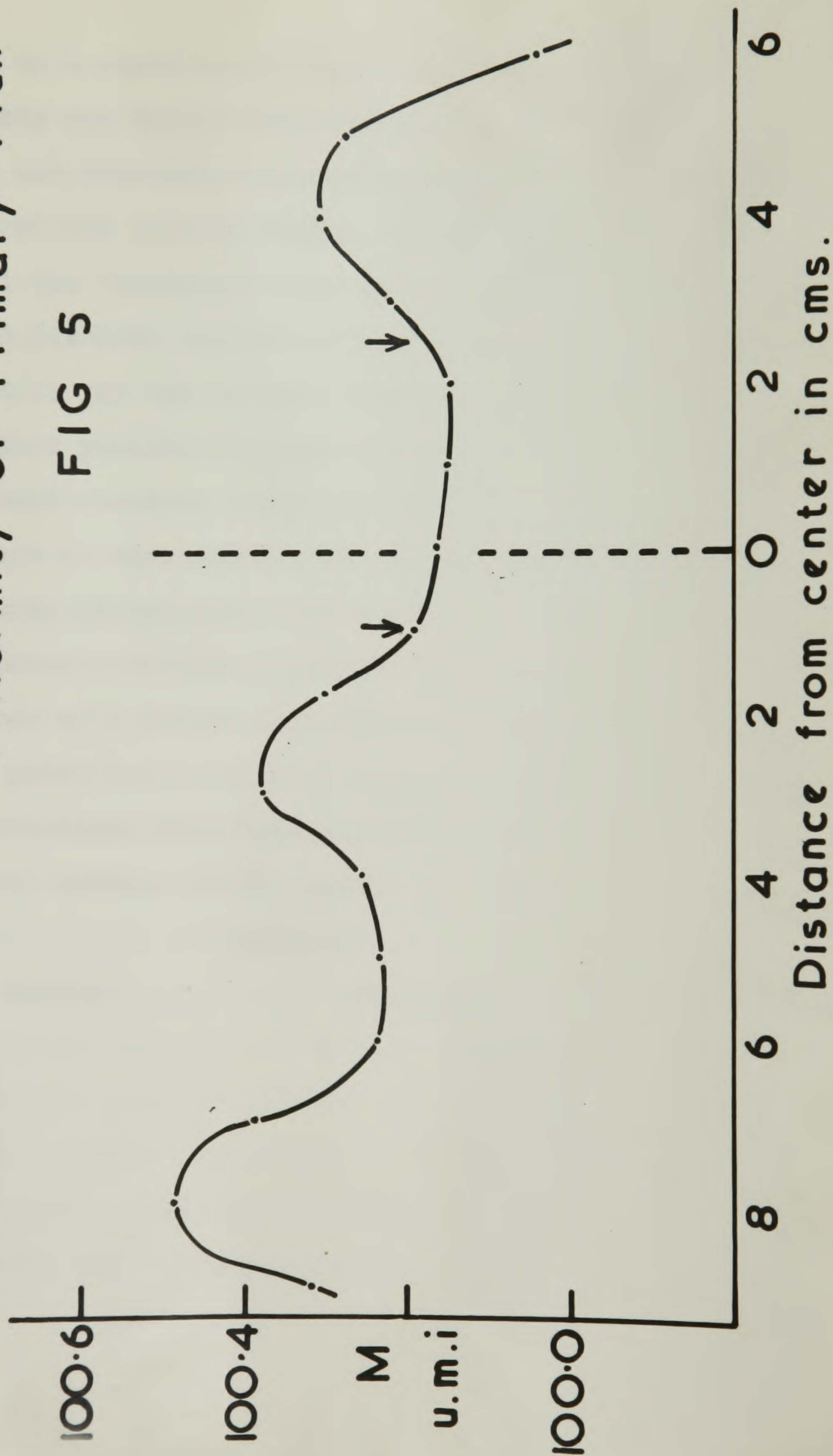
2.14

smaller units of mutual inductance by having the two opposing turns very close together and mounting them on a primary whose field was very nearly uniform. However, for the present set of experiments 0.01 i.m.i. ($\approx 0.015 \mu\text{H}$) was a sufficiently small unit.

(e) The Hundreds: We have deferred until now the description of the largest units as these required a different construction from the rest. When at first an attempt was made to extend the method of making the tens to the hundreds by using 200 turns of stranded cable, it was found that the system had such a large self-capacity that no balance could be obtained. The complex problem of transfer capacities has been treated in a very general way by Bijl in his thesis but on account of the complexity of the problem, empirical remedies were sought. It was found, however, that no screening made any appreciable difference. It was therefore decided to abandon the stranded wire and to wind ten separate coils side by side each with 200 turns. Before doing this the uniformity of the field of the second primary P_2 was explored by means of a single movable coil of 200 turns. The result is shown in fig.5. It will be seen that within a distance +1 cm. to -2.5 cm. from the centre the flux was

Uniformity of Primary Flux

FIG 5



2.15

uniform to 4 parts in 10^4 while from -1 to -2 cm. the uniformity was better than 1 in 10^4 . Thus, by arranging for the ten separate coils to be situated in this uniform section of the primary field, it was possible to ensure that all the 'hundreds' were equal to an accuracy of 0.04 u.m.i., with several of them equal to better than 0.01 u.m.i. It can be seen from the graph that, although it was thus possible to make all the hundreds nearly the same, their absolute value was about 100.16 u.m.i. As there were no more degrees of freedom available in the adjustment, it was necessary to wind a compensating turn in antiphase with the main turns at a point where the inductance of a single turn was 0.16 u.m.i. The position of this point was found in a separate experiment. The final deviations from the nominal value 100 u.m.i. for the individual members of the decade is shown in table 1.

which was divided into Table 1.

Coil number	Deviation from 100 u.m.i.
1	- 0.015 u.m.i.
2	+ 0.005
3	- 0.005
4	- 0.015
5	0.00
6	- 0.02
7	- 0.02
8	+ 0.04
9	+ 0.08
10	+ 0.09

2.16

In practice a fixed compensator M_3 cooled in liquid oxygen was used in series with the inductometer to balance out the major part of the inductance of the empty measuring coil (M_0). In this way only small changes of M were read on the bridge and only the first 3 hundreds were used for susceptibility measurements above $1^\circ K$. Below $1^\circ K$, where the larger units were used, the percentage error in the total M value was negligible. The construction M_3 is described in detail in Benzle's thesis.

6. The Potentiometer

In order to balance out the signal in phase with the primary current a voltage across a tapped resistance in the primary circuit was injected into the secondary. This resistance consisted of 29 non-inductive, 0.1 ohm coils in series with a slide wire of 0.13 ohms. The slide wire, which was divided into 130 parts, was constructed in such a way that, when the tapping point was moved, the inductance between the primary and secondary systems remained unaltered. The principle used was similar to that in making a non-inductive variable resistance. In order to obtain very small transfer voltages without the difficulties of contact resistances, the whole potentiometer could be shunted by a

2.17

factor of 10 or 100. Thus, the smallest unit by which the tapped resistance could be altered was 10^{-5} ohms. For a primary current of 0.1 amp this corresponds to 1 μ Volt injected into the secondary.

7. The oscillator

The alternating current to the primary circuit was supplied by a Solatron resistance - capacity oscillator feeding into a power amplifier. The power available was about 4 watts corresponding to a primary current of 200 mA. The frequency range of this type of oscillator is 25 c/s to 250 kc/s though in practice only frequencies between 75 c/s and 500 c/s were found to be satisfactory for our bridge. This was partly due to the design of the detector and partly due to the self capacity of the measuring coil which made the mutual inductance very frequency dependent at high frequencies.

8. The Detector

This consisted of a "General Radio cathode ray null detector" preceded by a three stage battery operated preamplifier. Both the null detector and the preamplifier were turned by twin-Tee feed back networks to the frequencies

2.18

33, 75, 175, 300 and 500 c/s. Above 500 c/s phase changes through the amplifier caused instability due to spontaneous oscillations.

The signal from the secondaries was applied to the Y plates of the cathode ray tube, and a standard 50 c/s sine wave from a quartz crystal clock to the X plates. The frequency of the oscillator could then be set accurately by observing Lissajon's patterns. The voltage sensitivity of the detector was about 1.5μ Volts.

Dynamic formulas used to analyze the behavior of the system.

The laws of thermodynamics for a closed system can be written as

$$dU = TdS - PdV + \sum \mu_i dN_i$$

If we define

$$C_H = T \left(\frac{\partial^2 S}{\partial T^2} \right)_P = \text{specific heat at constant pressure.}$$

$$C_V = T \left(\frac{\partial^2 S}{\partial T^2} \right)_V = \text{specific heat at constant volume.}$$

$$\alpha = \left(\frac{\partial S}{\partial T} \right)_P = \text{thermal expansivity}$$

$$\beta = \left(\frac{\partial S}{\partial P} \right)_T = \text{adiabatic compressibility.}$$

then it can be shown that

3.1

CHAPTER 3.

THE MAGNETIC METHOD OF MEASURING SPECIFIC HEATS.

1. Introduction

This method of measuring specific heats was first described by de Haas and du Pre (1939) and was developed in its present form by Benzie and Cooke (1950). Before discussing the method we give a summary of the thermodynamic formulae used to describe an assembly of magnetic systems.

The laws of thermodynamics for a magnetic system can be written as

$$TdS = dU - HdM.$$

If we define

$$C_H = T \left(\frac{\partial S}{\partial T} \right)_H = \text{Specific heat at constant field.}$$

$$C_M = T \left(\frac{\partial S}{\partial T} \right)_M = \text{Specific heat at constant magnetization}$$

$$\chi = \left(\frac{\partial M}{\partial H} \right)_T = \text{Isothermal susceptibility}$$

$$\chi_s = \left(\frac{\partial M}{\partial H} \right)_S = \text{Adiabatic susceptibility.}$$

then it can be shown that in the previous section

3.2

$$\frac{C_M}{C_H} = \frac{\chi_S}{\chi_T} \quad (1)$$

and
$$C_H - C_M = \frac{T}{\chi_T} \left(\frac{\partial M}{\partial T} \right)_H \quad (2)$$

whence
$$C_M = T \left(\frac{\partial M}{\partial T} \right)_H^2 \frac{\chi_S}{\chi_T(\chi_T - \chi_S)} \quad (3)$$

For a substance for which $M = f\left(\frac{H}{T}\right)$,

$$\frac{C_M}{H} T = T f'\left(\frac{H}{T}\right) \left(\frac{\partial^2 M}{\partial T^2} \right)_H = 0$$

so that C_M is independent of H at a given temperature.

Hence C_M is equal to the specific heat in zero field, the quantity most readily calculated from theory.

For a substance which obeys a Curie-Weiss law of susceptibility,

$$M = \frac{\lambda H}{T - \theta}$$

(λ = Curie constant, θ = Weiss constant), equation 3 reduces to

$$\frac{C_M T^2}{\lambda} = \frac{H^2 \chi_S}{\chi_T - \chi_S} \cdot \left(1 - \frac{\theta}{T}\right)^{-3} \quad (4)$$

λ and θ can both be determined from susceptibility measurements as described in the previous section.

3.3

However, for a substance which obeys Curie's law λ can be calculated more accurately from g value obtained from paramagnetic resonance data, using equation (1) of Ch. 1.

For a substance for which the deviations from Curie's law are mainly due to the magnetic interaction between the ions, the value of Θ can also be calculated. The expression for Θ is given in Ch.4, eq. 4. In cases where the deviations are due to exchange interaction, Θ must be determined experimentally from the susceptibility curve. For most specimens Θ is less than 0.05°K .

2. Measurement of χ_g and χ_T

From eq. 3 it can be seen that the specific heat can be calculated from a measurement of χ_g and χ_T in a magnetic field H . Before we can discuss the measurement of these quantities, we must consider the processes which take place in the assembly of spins when the external magnetic field is varied.

Let us assume that initially the magnetic systems (spins) are all in thermal equilibrium with one another and with the surrounding crystal lattice of non-magnetic atoms. Corresponding to the different energy levels E_i , there will

3.4

be a Boltzmann distribution proportional to $e^{-E_i/kT}$, characterized by the temperature of the spins T_s . If now the field is changed, the energy levels will alter accordingly, and a new equilibrium state will be established. However, this will require a finite time which depends on (i) how quickly the spins can exchange energy with one another and (ii) how quickly the spin system as a whole can exchange energy with its surroundings. These surroundings consist of the crystal lattice plus the liquid helium in the cryostat and can be assumed to constitute a constant temperature bath with an effectively infinite heat capacity. The two processes can be characterized by two relaxation times: (i) by a spin-spin time τ_s and (ii) by a spin lattice time τ_L . The mechanisms which give rise to these are very different.

Spin-spin interaction arises mainly from the magnetic dipole forces between the ions and is well understood for crystals in which exchange effects are negligible. For cases where the exchange forces are large no complete theory has yet been given. However it is possible to estimate the magnitude of τ_s experimentally from the line width of paramagnetic resonance absorption. It is found in nearly all cases, that τ_s is of the order of 10^{-9} seconds.

3.5

Thus for any magnetic measurements which are made at audio frequencies, the spins will always reach an internal equilibrium in a time very much shorter than the period of the applied field. We can therefore speak of the spins as a thermodynamic substance with a spin temperature T_S .

Spin lattice interaction, on the other hand, is not well understood. The electric crystalline field, which acts on the ions (see Ch. 1), to a first order affects only the orbits of the electrons. These are coupled to the spins through the spin-orbit interaction. Thus any fluctuations of the crystal field are transmitted to the spins indirectly and this makes the problem of energy-transfer a very complex one. Furthermore, as the nature of the fluctuations depends on the thermal vibrations of the lattice, the whole process is very temperature dependent. A review of the present theories has been compiled by Cooke (1950), who points out that none of the theories agree more than qualitatively with experiment. However, both theory and experiment agree that the relaxation time for spin lattice interaction increases at low temperatures, in some cases by as much as T^{-9} . For many substances it is of the order of 20 milliseconds at 1°K and it is this fact which makes it possible to measure specific heats in terms of χ_S and χ_T using an audio frequency method.

3.6

If we measure the susceptibility in the presence of a steady magnetic field H using a measuring frequency of say 500 c/s (corresponding to a periodic time of 2 milliseconds.) then, as the spin system will not have sufficient time to exchange energy with the lattice, the measurement will be adiabatic and the susceptibility equal to χ_s . It was found that a factor of 3 to 4 times between the relaxation time and the measuring time was sufficient to ensure effectively adiabatic conditions.

The isothermal susceptibility can be measured in one of two ways: By extension of the above argument, if we use a frequency such that the relaxation time is short compared with the measuring time, then the spins will have time to exchange energy with their surroundings at constant temperature and the susceptibility measured will be χ_T . In our experiment the low frequency was obtained by reversing a d.c. field and measuring the inductance with a ballistic galvanometer instead of the a.c. bridge. By this method χ_T can be measured in the same field H as that used in the measurement of χ_s .

For substances with a small saturation correction χ_T can also be measured using the a.c. method: From the thermodynamic equations it will be seen that in zero field

3.7

$\chi_T = \chi_S$, so that the value of χ measured by the a.c. method at any frequency corresponds to χ_T at $H = 0$. The small saturation correction to obtain χ_T in the magnetic field H can be determined from the Brillouin function.

For small $\frac{H}{T}$,

$$(\chi_T)_H \approx (\chi_T)_{H=0} \left[1 - \alpha \frac{H^2}{T^2} \right] \quad (5)$$

where

$$\begin{aligned} \alpha &= \frac{1}{10} \frac{g\beta}{k}^2 (2S^2 + 2S + 1) \\ &= 4.52 \times 10^{-10} \text{ g}^2 (2S^2 + 2S + 1), \end{aligned}$$

using the symbols as in eq(1.1). This second method avoids the use of a ballistic galvanometer and has proved satisfactory for most of the substances investigated for which the saturation is only a few percent.

However, for a substance with a large specific heat, big fields have to be used to measure χ_S (eq.4) and the saturation correction becomes important. Recent experiments have shown (Gardner priv. com.) that in some cases the Brillouin function does not represent the variation of χ_T with H accurately so that for these substances the ballistic method must be used.

3.8

3. Experimental procedure

The apparatus was the same as that described in the previous chapter. The d.c. field H was provided by an iron free solenoid placed coaxially with the measuring coil around the outside of the dewar. The current through the solenoid was provided by batteries and was measured in terms of the voltage across a standard 0.05 ohm resistance using a Tinsley potentiometer. The constant of proportionality between field and current was found to be 52.7 gauss/amp. using proton resonance.

In order for the spin lattice relaxation time to be as long as possible all measurements were made near 1°K. While pumping down the helium to reach this temperature, readings of vapour pressure and mutual inductance were taken and M plotted against $\frac{1}{T}$. From this curve the value of M_0 , corresponding to the empty coil, was found as described in the previous chapter.

In zero field $M-M_0$ gave a measure of χ_T . When the d.c. field H was switched on the value of M was reduced to a new value M_H . For a sufficiently high measuring frequency M_H-M_0 corresponded to the adiabatic susceptibility χ_S . Thus, neglecting saturation, the change of M produced by the field was proportional to $\chi_T - \chi_S$. The ratio

3.9

$\frac{\chi_s}{\chi_T - \chi_s}$ in equation (4) is therefore equal to $\frac{M_H - M_0}{M - M_H}$ and is thus independent of the calibration constant which relates the change of mutual inductance of the measuring coil to the susceptibility. This was very convenient as it made the measurement of specific heat independent of the position of the specimen in the measuring coil.

4. The measurement of spin lattice relaxation times

When the a.c. frequency is not sufficiently high, the spins can exchange energy with the lattice and the measurement is no longer adiabatic. The magnetization then has a component out of phase with the measuring field so that we can write for the susceptibility

$$\chi = \chi' + i\chi'' \quad \text{where} \quad i = \sqrt{-1}$$

The theory for the general variation of χ' and χ'' with frequency has been given by Casimir and du Pre (1938). Recent work by Benzie and Cooke (1950) has shown that their results are only approximately true when the measuring time, $\frac{1}{2\pi\omega}$, is long compared with τ_L but the good agreement is obtained when $\frac{1}{\omega}$ is less than τ_L . In this case it can be shown that in a given field H

$$\frac{\chi''}{\chi'} \approx \frac{\chi_T - \chi_S}{\omega \tau \chi_S} \approx \frac{1}{\omega \tau} \cdot \frac{M - M_H}{M - M_0} \quad (6)$$

The ratio of χ' to χ'' was obtained from the bridge readings of mutual inductance and resistance: χ' , in units of susceptibility, is equal to $C(M_H - M_0)$ where M_H and M_0 are measured in u.m.i. (eq. 2.1). χ'' was measured from the change of resistance δR which had to be tapped to restore balance when the field was switched on. In zero field $\chi'' = 0$ (eq. 3.6). When the field is applied the effect of χ'' is equivalent to a change of "imaginary inductance" i.e. resistance, which is equal to $\frac{\delta R}{\omega}$, in Henries where δR is measured in ohms. In a separate experiment it was found that 1 u.m.i. = 1.53μ Henries so that

$$= \frac{1}{1.53 \times 10^{-6}} \cdot \frac{\delta R}{\omega} \quad \text{Substituting for } \chi' \text{ and } \chi'' \text{ in eq. 6}$$

$$\tau_L \approx 1.53 \times 10^{-6} \cdot \frac{M - M_H}{\delta R} \quad \text{seconds} \quad (7)$$

From this approximate value of the spin lattice relaxation time it was possible to estimate whether the measuring frequency was sufficiently high to ensure adiabatic conditions.

3.11

5. Extrapolation to higher frequencies

As the highest frequency available was 500 c/s it was not always possible to measure χ'' directly. Thus for a substance whose relaxation time was shorter than about 8 milliseconds at 1°K, an extrapolation to higher frequencies had to be made. It can be shown from the theory of Casimir and du Pre, that if we plot $\chi'' (= \frac{\delta R}{\omega})$ against $\chi' (= M_H - M_0)$ for different values of ω at a given value of H , then the points will lie on a curve (ideally a semi circle) one of whose intersections with the axis gives the value of χ'' . If τ is not much shorter than 8 milliseconds this extrapolation can be made with good accuracy.

The final expression for the specific heat in terms of the quantities measured is

$$\frac{C_M}{R} = \frac{1}{T^2} \left[\frac{\lambda H^2}{R} \left(1 - \frac{\theta}{T}\right)^{-3} \frac{1}{\frac{M - M_H}{M_H - M_0} - \frac{\alpha H^2}{T^2}} \right] \quad (8)$$

It is usual to express the specific heat in terms of R , the gas constant (8.31×10^7 ergs/mole) since C/R is then a dimensionless number. For most substances $C_M \propto \frac{1}{T^2}$

3.12

so that the quantity inside the square bracket should be independent of temperature. Our experiments could therefore be checked by measuring at several temperatures and comparing the values of $\frac{CT^2}{R}$. It should be emphasized that the specific heat measured by this method includes only the magnetic specific heat of the spin system and is independent of the lattice contribution from the rest of the crystal.

The present work was carried out using an almost identical apparatus except that the susceptibility of the specimen was measured by the e.s.r. method described in Chapter 2, so that the whole of the lower part of the apparatus had to be made of glass to avoid eddy currents. The essential components are shown in Fig. 4.

1. THE CRYSTAL

The double walled apparatus was made of 1/2 inch glass and was attached to the metal part of the glass liquidator through two ground glass tubes by means of glass and glass seals. One of the tubes was connected to the vacuum space between the two walls of the apparatus, into which helium was condensed as described in Chapter 2. The other was connected to the inner space containing the specimen, usually referred to as the i.s.s., or inner vacuum space.

CHAPTER 4.

MEASUREMENT OF ENTROPY BY ADIABATIC DEMAGNETIZATION
EXPERIMENTS

The technique for adiabatic demagnetization experiments in the region below 1°K has been described in detail by Hull (1947). The present work was carried out using an almost identical apparatus except that the susceptibility of the specimen was measured by the a.c. method described in Chapter 2, so that the whole of the lower part of the apparatus had to be made of glass to avoid eddy currents. The essential components are shown in fig. 6.

1. The cryostat

The double walled cryostat was made of C8 hard glass and was attached to the metal part of the Simon liquefier through two graded glass tubes by means of platinum soft glass seals. One of the tubes was connected to the annular space between the two walls of the cryostat, into which helium was condensed as described in Chapter 2. The other was connected to the inner space containing the specimen, usually referred to as the I.V.C., or inner vacuum space.

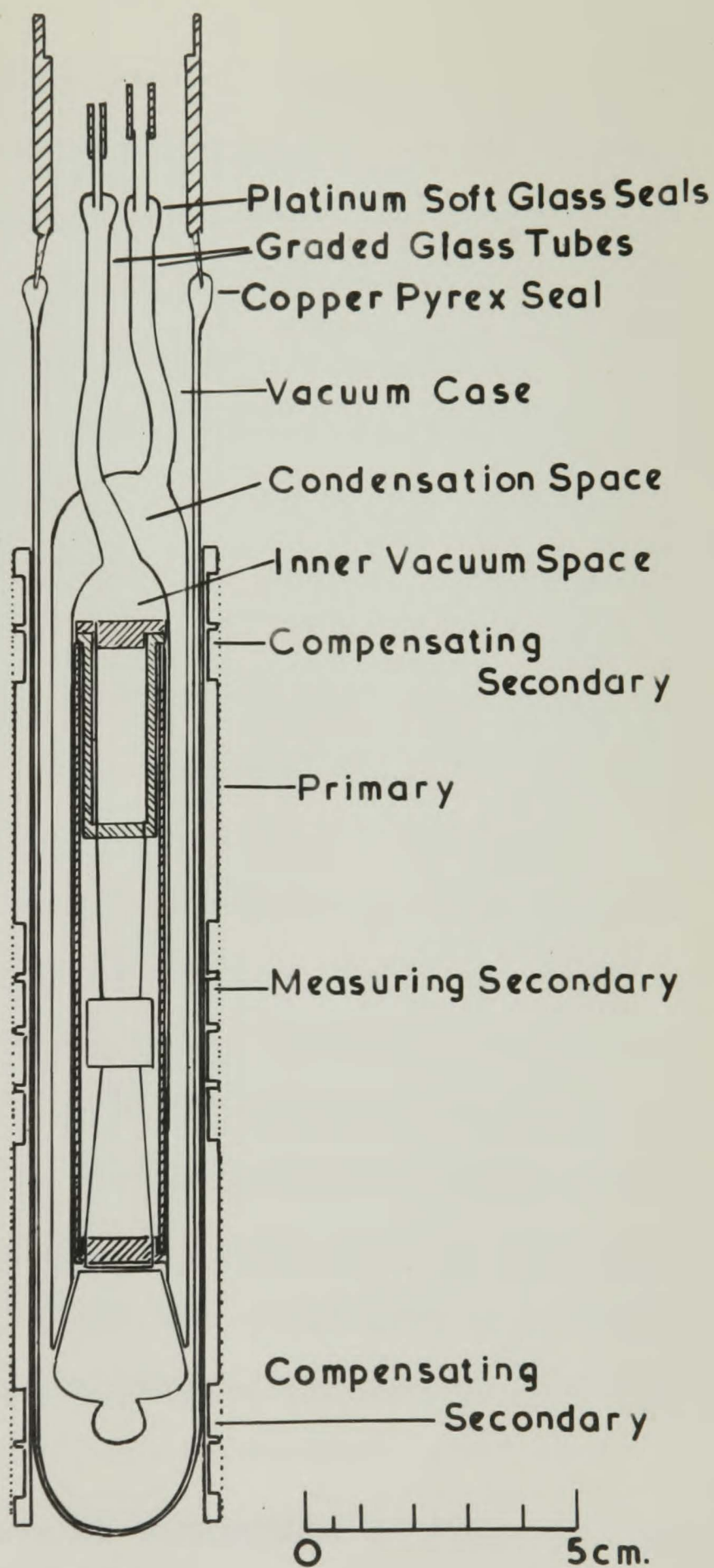


FIG. 6

4.2

By admitting helium 'exchange' gas into this space, thermal contact between the cryostat and the specimen could be established, while by pumping the specimen could be thermally insulated. The bottom of the I.V.C. was closed with a ground glass stopper which was made vacuum tight with glycerol. At low temperatures this forms a glass which makes the seal tight even to helium. However, such a seal is reliable only when the ground surfaces fit very closely and the film of glycerol is correspondingly thin since a thicker film may crack at low temperatures.

The suspension of the specimen provided a problem whose satisfactory solution was found only after a considerable amount of trial and error. Most of the suspensions which were tried became slack at low temperatures due to the contraction of the surrounding cage. This led to vibrations of the specimen which were found to cause an appreciable amount of heating below 1°K . (Note: The kinetic energy of 1 gm. falling through 1 cm. is about 1000 ergs, 8 times the total heat capacity of 1 gm. of Cerium Magnesium Nitrate between 0.006°K and 1°K . - see Chapter 6).

The final form of the suspension is shown in fig. 6. The main part of the cage was made of pyrex glass and the ends closed with perspex caps. The suspension consisted

4.3

of 8 cotton threads attached to the end caps one of which was made in a re-entrant form. It was found that when the 'cradle' was cooled the contraction of the perapex was just sufficient to counteract the contraction of the glass and the threads remained taught.

Another important source of heating below 1°K was found to be thermal radiation from the surrounding liquid hydrogen. Contrary to expectation, the far-infrared light given out at 20°K was found to be not absorbed by the glass of the cryostat. As soon as this was silvered the heat influx to the specimen was reduced from 300 ergs/min. to about 30 ergs/min.

2. The measuring coil

A cross section of the measuring coil is shown in fig. 6. In order to accommodate the larger cryostat in a standard dewar vessel, a simpler coil had to be used in place of the one described in Chapter 2. It was decided to dispense with the double primary and to use instead a single layer of 30 gauge wire wound on the same former as the secondary. This reduced the wall thickness of the coil from 8 to 3 mm. The secondary was wound in 3 parts. The middle part, surrounding the specimen, was 4 cm. long

and consisted of 6000 turns of 46 s.w.g. enamelled silk covered copper wire. The other two parts were wound at the ends of the Tufnol former each with 3000 turns. These were connected in antiphase with the main secondary to reduce the mutual inductance of the empty coil, as before. Each of the sets of windings was again divided into sections to reduce the self capacity.

3. The magnet

The magnetic field was produced by a Savage and Parsons water cooled magnet. The maximum power which could be dissipated by the cooling system was 20 Kwatt, corresponding to a current of 100 amps. This produced a field of 14 Kilogauss with a pole gap of 5.2 cm. (standard 'tailed' dewar vessel), and 9 Kg. with a pole gap of 10 cm. (standard 'wide' dewar). The field was calibrated in terms of the current using proton resonance up to 10 Kg. (40 amps), and a search coil and ballistic galvanometer from 10 to 14 Kg. The current was measured on a Turner sub standard ammeter. A photograph of the magnet is shown in fig. 7.

Fig. 7 The Magnet.

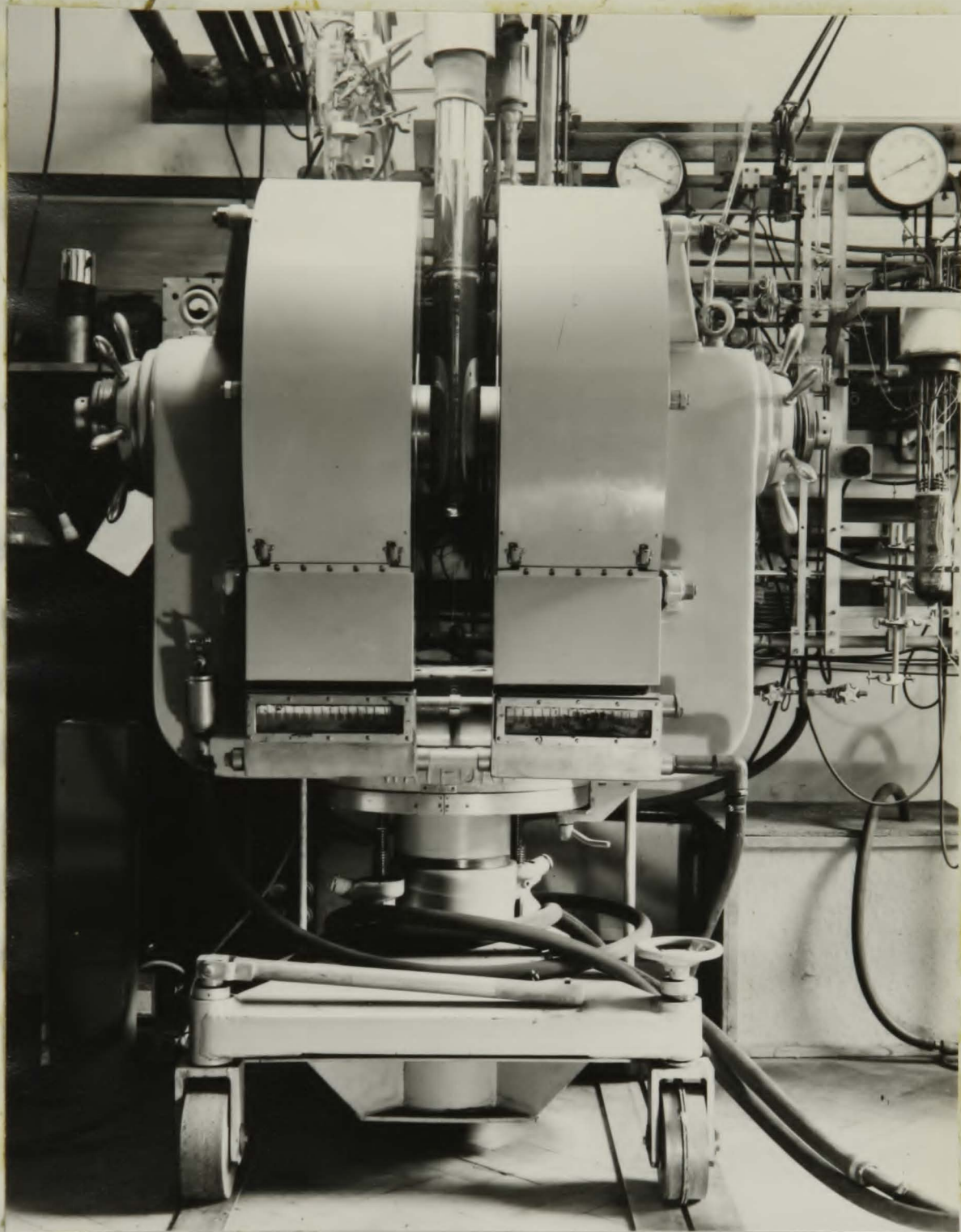


Fig. 7 The Magnet.

4.5

4. Thermometry

The usual magnetic scale of temperature T^* was employed at temperatures below 1°K . This was defined (Kurti and Simon, 1938) by the relation

$$\chi = \frac{\lambda}{T^*} \quad (1)$$

where λ was found (in terms of u.m.i.) from the slope of the M vs. $\frac{1}{T}$ plot in the helium range, as described in Chapter 2. Since χ depends on the shape of the specimen all measurements were corrected to those of a sphere, as in this case the demagnetizing correction is equal to the effect of the internal field at temperatures well above the Curie point (see Chapter 1). The relation between the measured susceptibility per unit volume and that of a sphere has been given by Kurti and Simon:

$$\chi_{sp} = \frac{\chi}{1 + \left(\frac{4\pi}{3} - N\right)\chi}$$

where N is the demagnetizing factor which can be calculated from the shape of the specimen. For a prolate spheroid of eccentricity e with its long axis parallel to the field

$$N = 4\pi \left(\frac{1-e^2}{e^2} \right) \left(\frac{1}{2e} \ln \frac{1+e}{1-e} - 1 \right)$$

... (2)

4.6

(Maxwell 1873 p.65), which reduces to $\frac{4\pi}{3}$ for a sphere.

Thus if we define $T^{\odot} = \frac{\lambda}{\chi_{sp}}$

$$T^{\odot} = T^* - \Theta \quad (3)$$

$$\text{where } \Theta = \lambda \left(\frac{4\pi}{3} - N \right) \quad (4)$$

and λ is the susceptibility in e.m.u. per cc. of specimen.

5. Experimental technique for entropy determination

The principle of the method is well known. With the cryostat at 4°K and about 12 ccs. of liquid helium in the angular space, exchange gas was admitted into the I.V.C. and the pressure adjusted to about 0.1 mm. Hg. The temperature was then reduced by pumping down the liquid helium.

As in the demagnetizing cryostat there was only one tube down to the liquid helium the vapour pressure could be measured only while pumping was stopped. This led to a small uncertainty in the temperature. It was attempted to remove this in some of the later experiments by joining a second tube to the main pumping line about 8 cm. above the cryostat so that it was then possible to measure the pressure near the cryostat while pumping continuously. About 10 calibration points were taken between 4.2°K and 1.3°K.

When the cryostat was at its lowest temperature,

4.7

(0.95°K) the a.c. current through the measuring coil was switched off and the magnet wheeled up to the apparatus. The field was then switched on and maintained at a steady value for about 10 minutes. During this time the heat of magnetization was carried away by the exchange gas to the helium in the cryostat, reducing the entropy by a known amount. The I.V.C. was then pumped to remove the exchange gas for a period depending on the degree of thermal insulation it was desired to obtain. For entropy determinations about 10 minutes sufficed but for other experiments, where it was necessary to reduce the heating up rate to a minimum, about $1\frac{1}{2}$ hours were needed. Before switching off the magnet the I.V.C. was isolated from the rest of the pumping system so that any gas still remaining in it would be condensed on the specimen when this was cooled. The field was then reduced to zero, a stop watch started and the magnet wheeled away from the apparatus. The current through the measuring coil was switched on and the bridge balanced as quickly as possible. Several readings were taken as the specimen warmed up so that the M value immediately after demagnetizing could be found by extrapolation. M at time $t = 0$ was converted to magnetic temperature T^* using eq. 1.

For specimens with a very small heat capacity, such

4.8

as Cerium Magnesium Nitrate (Ch.6) a special technique had to be used in order to get readings sufficiently quickly. From previous preliminary experiments an estimate was made of the approximate M value to be expected immediately after demagnetizing and the bridge set at a value slightly lower than this. It was then possible, using the stop watch, to determine the exact time after demagnetizing at which the inductance passed through this value of M , by waiting for the null reading on the detector. The bridge was then reset at a value slightly 'ahead' of the measuring coil and the null moment again recorded. By reading the time for a given value of M measurements could be taken very quickly (every 5 seconds) and with good accuracy. This technique was essential for the work on Cerium Magnesium Nitrate where the specimen warmed up to the temperature of the cryostat after only a few minutes.

The entropy in zero field immediately after demagnetizing is equal to the entropy in the magnetic field before demagnetizing. This can be calculated from the partition function if the energy levels are known. For cases where the ground state has 2, 4 or 6 fold degeneracy in the absence of a field, and the energy levels in a field can be written in the form $W_m = mg\beta H$, (m is the magnetic quantum

number and g the spectroscopic splitting factor), the entropy has been tabulated by Hull and Hull (1941) as a function of $\frac{g\beta H}{kT}$.

For substances with an anisotropic g , the value of g depends on the relative orientation of the crystal and the field. Thus if a powder of such a substance is used, different amounts of entropy are extracted from the individual grains and hence on demagnetizing, the different grains do not all reach the same temperature, and a measurement of the mean susceptibility is therefore meaningless. If, on the other hand, time is allowed to elapse for the attainment of thermal equilibrium, entropy is gained by the system due to the irreversible nature of heat transfer, thus in neither case is it possible to obtain a point on the $S - T^2$ curve. Hence in all experiments on anisotropic substances, quantitative results can be obtained only by using single crystals.

The results of an entropy determination on a single crystal of Cerium Magnesium Nitrate are given in Chapter 6.

The method of adiabatic demagnetization was also used to establish a new method of measuring absolute temperatures below 1°K. This is described in detail in Chapter 8.

and the results of the measurements are given in Chapter 9 and 10.

PART II. EXPERIMENTAL RESULTS.

CHAPTER 5.

THE MAGNETIC SUSCEPTIBILITY OF OXYGEN IN A
CLATHRATE COMPOUND1. Introduction: the Paramagnetism of Oxygen.

The electronic ground state of the oxygen molecule O_2 is $^3\Sigma$, and at high temperatures this gives rise to a paramagnetic susceptibility appropriate to an assembly of particles having spin $S = 1$ and splitting factor $g = 2$ (Van Vleck 1932, p.266). In agreement with experiments on the gas the temperature dependence is then given by Curie's law:-

$$\chi = 8N\beta^2/3kT = \frac{1.000}{T} \quad (1)$$

where χ is the molar susceptibility at an absolute temperature T , N is Avogadro's number, k is Boltzmann's constant, and β is the Bohr magneton. At low temperatures the effect of molecular rotation becomes important, and Curie's law no longer holds. The theory for the susceptibility variation at low temperatures is given in Section 5 below, and the result of the calculation is given in figures 8 and 9.

5.2

It will be seen that down to about 40°K the deviations from Curie's law are negligible.

As measurements on the gas cannot be made below about 70°K , the theoretical predictions cannot be checked experimentally. Measurements on liquid oxygen diluted in liquid nitrogen (Perrier and Onnes, 1914) show that a Curie-Weiss law is obeyed with a large Weiss constant depending on concentration, showing that there are strong interaction forces between the molecules. These forces become even more important in the solid where they cause the diamagnetic dimer O_4 to form. The effect is further complicated by crystalline transitions which cause sudden discontinuities in the susceptibility.

Measurements have also been made on oxygen adsorbed on charcoal (Aharoni and Simon 1929) though only at one temperature (77°K). The susceptibility was less than that calculated for free Oxygen, suggesting that here too interaction effects are important. The variation of susceptibility with the amount of gas adsorbed showed a sharp discontinuity, probably due to increased interactions as second molecular surface layer is formed. The same authors also reported similar experiments on oxygen in chabazite. This substance, $\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 5$ to $7 \text{ H}_2\text{O}$, contains

5.3

free water molecules which can be driven off without affecting the rest of the lattice. Gas molecules can then enter the holes thus formed. The susceptibility at 77°K was again found to be less than that of free oxygen, with similar discontinuities corresponding to an average of one, two, etc. molecules per chabazite molecule. Simon (1928) has discussed the interaction between the matrix and the enclosed gas in such a compound.

A new approach to the problem of overcoming the interaction effects and measuring virtually free oxygen molecules was recently made possible by the discovery (Powell, 1948) of a group of "clathrate" compounds of β -quinol. This substance crystallizes in an open lattice in such a way that certain gas molecules, including those of oxygen, can be trapped in regularly spaced holes with one molecule in each. The holes are about 8Å apart so that interaction effects between the O_2 molecules can be expected to be very small. It was first pointed out by Evans and Richards (1952) that the influence of the surrounding cage on the magnetic properties could also be expected to be small and that the oxygen would behave like a gas of free molecules down to very low temperatures. They measured the susceptibility at room temperature and found agreement with the value

5.4

corresponding to oxygen gas. At low temperatures, however, some small departures from the behaviour of free oxygen would be expected and these could be interpreted as a measure of the degree of interaction of the molecule with its cage. Below we give an account of susceptibility measurements on specimens of the oxygen clathrate compound with β -quinol, at temperatures down to 1°K. Susceptibility measurements have also been reported by Cooke and Duffus (1954) using a clathrate compound containing nitric oxide.

2. The Experiments

The preparation and estimation of the samples was carried out for us by Drs. Evans and Richards as described in their paper. Quinol was crystallized from alcohol under suitable conditions in the presence of oxygen gas at about 30 atm. pressure. About 60% of the available holes in the lattice could be filled, corresponding to about 0.07 gm. of oxygen per cc. of solid. (This concentration is equivalent to a gas pressure of 50 atm. at room temperature). About 3 gm. of the substance, in the form of small crystallites, were loosely packed into a cylindrical perspex container 3.6 cm. long and 1.3 cm. in diameter. Measurements were made on several specimens using the

5.5

method described in Chapter 2. At temperatures between 20°K and 40°K the susceptibility obeyed Curie's law within the accuracy of the experiment. The Curie constants of the different specimens showed some scatter. For different samples the values obtained were 0.99, 1.05, 0.97 per mole of gas, the value for free O_2 at high temperatures being 1.000 per mole (Equation 1). Some uncertainty in the determination of the absolute value of the Curie constant is, however, to be expected as it depends on comparison with other substances of known susceptibilities. In order to change the specimens, the cryostat has to be completely dismantled and the small differences in positioning which are thus likely to occur can give rise to an error of up to 2%.

Another error in determining the Curie constant arises in the estimation of the oxygen content of the specimen. This was carried out using a nitrometer to determine the gas content but it was unfortunately not always possible to check the purity of the evolved gas. The errors due to impurity and inaccuracies in the nitrometer are estimated however to be less than 3%.

We see therefore that the susceptibility in the temperature region 20°K to 40°K is consistent with that of a 'gas' and is shown on the left of Figure 10. The main part of the susceptibility of O_2 (22.6) for which symmetry

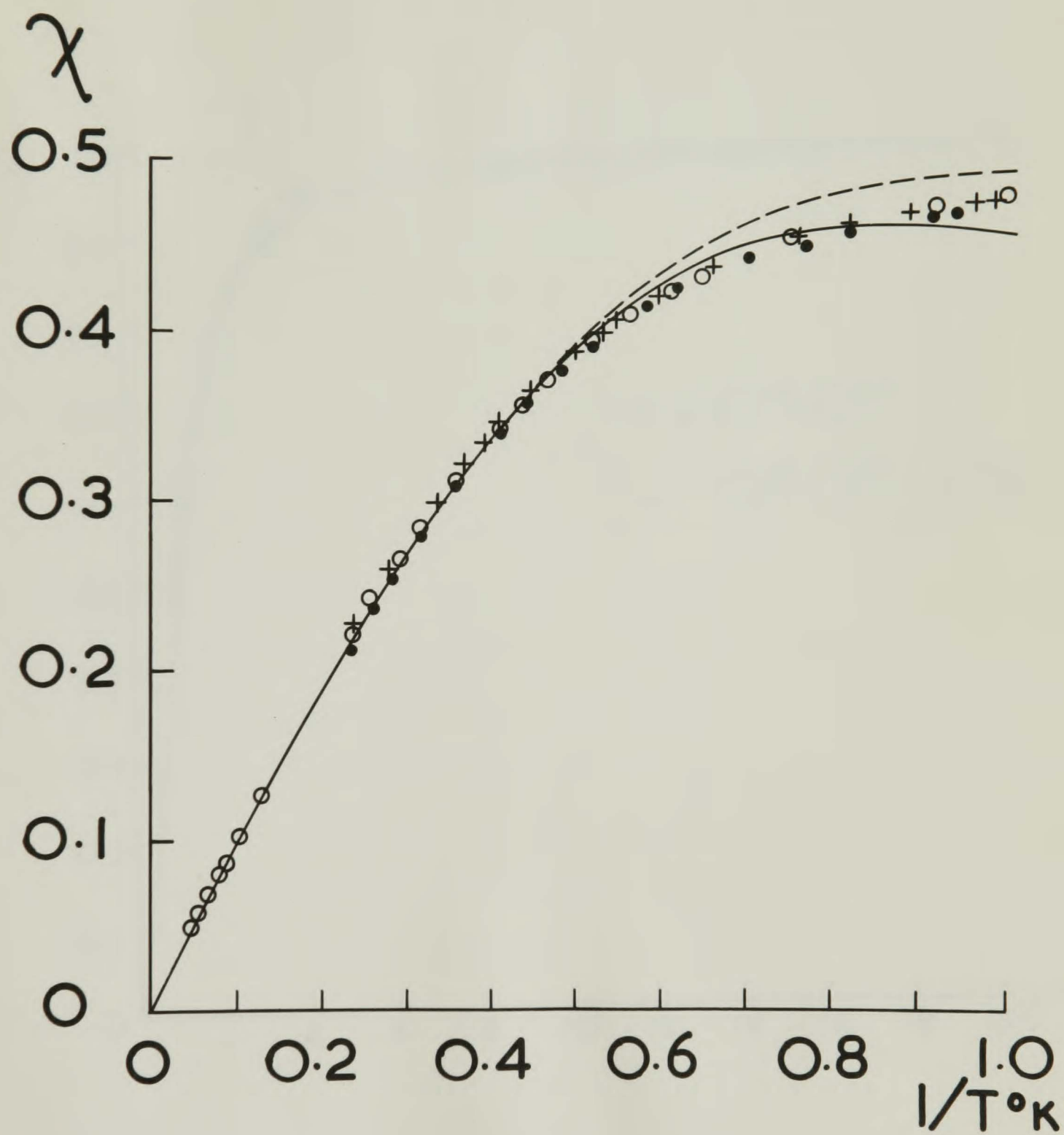
5.6

of free oxygen molecules within the limits of experimental error.

In order to investigate the temperature variation at lower temperatures, where Curie's law is no longer obeyed, it seems reasonable to normalize all experiments to fit the behaviour of free oxygen at high temperatures. In this way the two systematic errors mentioned above are eliminated and the full internal accuracy of each experiment (better than 1%) can be utilized. The results of two runs are shown in figure 8, where the molar susceptibility χ is plotted against $1/T$. In figure 9 the results are shown as a plot of χT against T . χT is proportional to the square of the effective magneton number p defined from $p^2 = 3 \chi T \cdot \frac{k}{N\beta^2}$ and, from eq. 1, is equal to 1.000 at high temperatures.

3. Discussion of the Experimental Results

At low temperatures, the approximate representation of the O_2 molecule as a spin $S = 1$ is no longer accurate and we must consider the effect of molecular rotation. This superposes on the $^3\Sigma$ ground state a series of energy levels given by $BK(K+1)$ where B is a constant (2.0683° for $^{16}O^{16}O$) and K is an integer. The levels for $K = 0, 1, 2$ and 3 are shown on the left of figure 10. Normal oxygen consists mainly of $^{16}O^{16}O$ (99.6%), for which symmetry



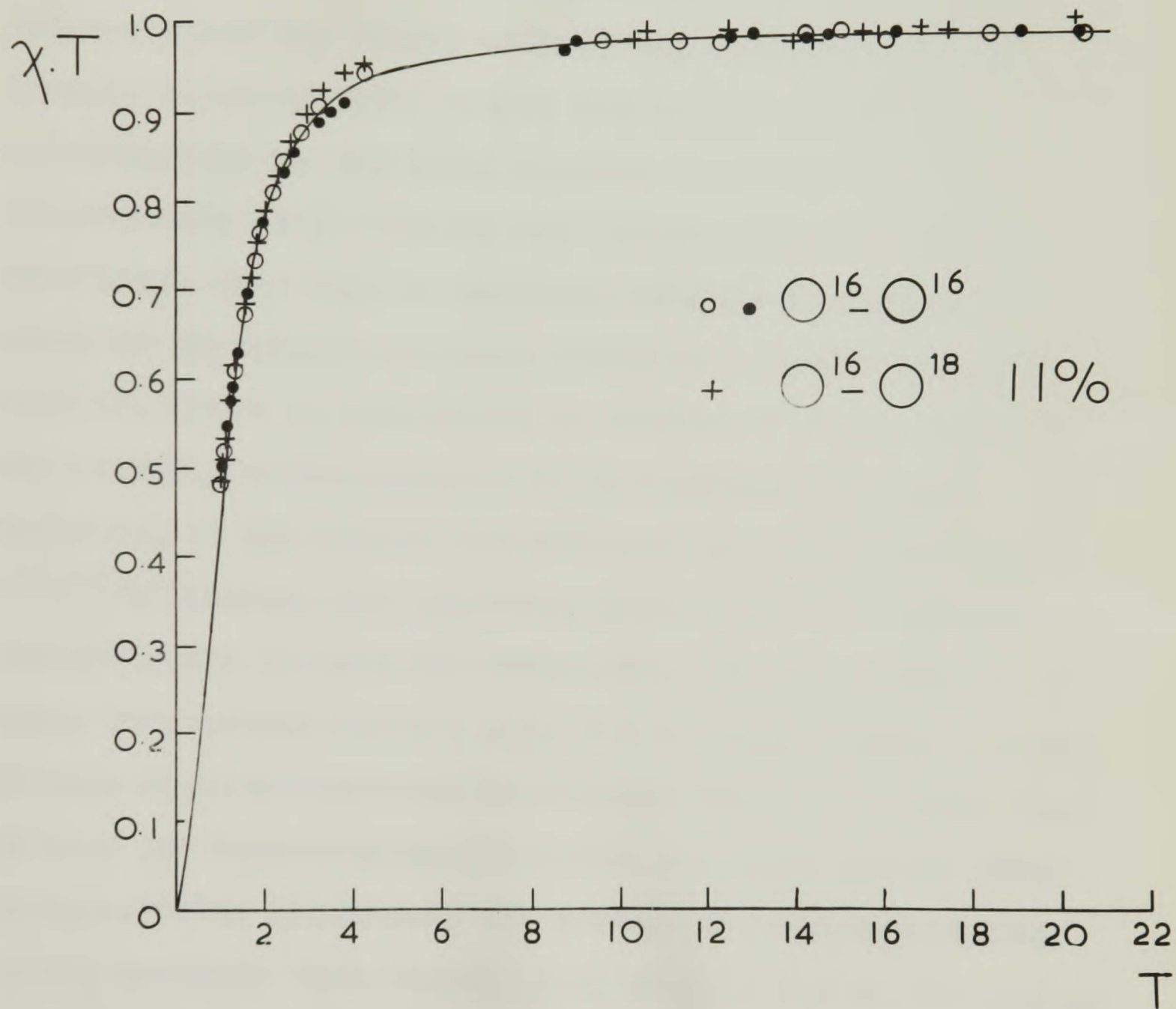


FIG 9

5.7

conditions on the wave functions of a homopolar molecule with zero nuclear spin restrict K to odd values. Each of the K -states has a threefold degeneracy due to the spin. This is lifted by the interaction between K and S and between S and the figure axis of the molecule (see for example Herzberg 1950) and we are left with states characterized by the total angular momentum $J = K + S$, (Hund's case 'b'). Miller and Townes (1953) have shown that while this type of coupling closely represents the state of the oxygen molecule there is a slight departure from it. This is considered in Section 5 below, where the magnetic susceptibility of an assembly of oxygen molecules at the lowest temperatures is calculated. For $O^{16}O^{16}$ molecules, the important feature of the scheme of energy levels is that the restriction to odd values of K leads to a ground state $K = 1$, $J = 0$, which, being a state of zero angular momentum, is diamagnetic. It follows that at very low temperatures, at which only this ground state is appreciably populated, the paramagnetic susceptibility arises entirely from second order effects due to the higher levels (Van Vleck 1932), and is independent of temperature. This effect is clearly seen in figure 8. Comparing the theoretical curve for free oxygen with the experimental again carried out by Richards and Townes using a slight

5.8

points, it will be seen that there is a close similarity between the behaviour of the clathrates and the gas. It seems then, at first sight, that the oxygen is relatively unhindered by the cage and behaves magnetically like a gas of free O_2 with only a small effect from its surroundings.

4. Experiments with $O^{16}O^{18}$

There is however a further experiment which can be performed to investigate the rotational freedom of the O_2 molecule at the lowest temperatures. In a molecule of $O^{16}O^{18}$ the value $K = 0$ will be allowed and this, together with $B = 1$ leads to a paramagnetic ground state $J = 1$, 0.81° below the diamagnetic state $K = 1, J = 0$. Thus at very low temperatures the susceptibility of $O^{16}O^{18}$ will tend to Curie's law whereas that of $O^{16}O^{16}$ becomes temperature independent. This distinction between the behaviour of the two kinds of O_2 molecules of course depends on the molecule being able to rotate within the cage. If the molecule is completely frozen in we should expect no difference between the two cases.

As no pure $O^{16}O^{18}$ was available, experiments were carried out using oxygen enriched to about 11% in this class of molecule. The preparation of the samples was again carried out by Richards and Evans using a slight

5.9

modification of their technique for normal oxygen. The O^{18} was available from A.E.R.E. in the form of water containing 6.18% H_2O^{18} . This was completely electrolysed, using a little sodium hydroxide as electrolyte. No attempt was made to keep the hydrogen and oxygen separate. The mixture of gases was then slowly pumped through two traps cooled in liquid hydrogen and the oxygen frozen out. The oxygen was then allowed to evaporate back into the storage globe and the separation repeated to remove all traces of hydrogen. A small brass bomb, coated inside with several layers of Bakelite varnish to avoid risk of contamination from the metal, was connected through a diaphragm valve to a vertical stainless steel tube which in turn could be connected through a needle valve to the storage globe and glass vacuum system. The bomb was nearly filled with an oxygen free saturated solution of quinol in n-propyl alcohol together with an appropriate amount of solid α -quinol, and the system was cautiously evacuated to remove air. The diaphragm valve was closed and the enriched oxygen condensed into the stainless steel trap using liquid hydrogen. The needle valve was closed and the diaphragm valve opened, and the trap allowed to warm up to room temperature. The dimensions of the apparatus were chosen to give a final pressure of

5.10

oxygen in the bomb of about 30 atmospheres. The crystallisation was then carried out as described previously.

In this way it was possible to prepare 4 gas. of clathrate containing 0.17 gas. of oxygen starting from 2 gas. of water. We are very much indebted to Dr. Danby for carrying out the isotope analysis of the oxygen contained in the clathrate. The relative abundances were:

a) $^{16}\text{O}^{16}\text{O}$ 88.02

$^{16}\text{O}^{16}\text{O}^{17}$ 0.42

$^{16}\text{O}^{16}\text{O}^{18}$ 11.05

$^{17}\text{O}^{16}\text{O}^{18}$ 0.05

$^{18}\text{O}^{16}\text{O}^{18}$ 0.45

The results of the measurements on the enriched sample are shown in fig.(8) as is the curve to be expected for a gas of oxygen molecules of the same isotopic abundance. It will be seen that within the errors of the experiment the results do not differ from the previous experimental points, although a difference of 9% would be expected at 1°K if the gas was free. While this fact does not give a measure of the effect of the cage on the oxygen molecules, it indicates that they are not entirely free to rotate.

An attempt to detect paramagnetic resonance absorption at 3 cm. wavelength has been made by Dr. H.J. Duffus

gives the coupling between the spin and the rotation. The

(Private communication) using a powder specimen of the compound enriched in $^{16}\text{O}^{18}$. No adsorption was detected in magnetic fields up to 14 K gauss. It is possible that the spin-lattice relaxation time is too short, even at 4.2°K , to permit the observation of resonant absorption.

5. The theory of free oxygen

a) The energy levels in zero field

An accurate matrix for the energy levels in zero magnetic field has been given by Miller and Townes (1953) using a representation in which $\underline{J}$ and $\underline{K}$ are diagonal. (Hund case b). The energies for a given value of J and $K = J+1, J,$ and $J-1$ are given by

$$\begin{array}{l}
 K=J+1 \quad \left| \begin{array}{cc} \frac{2\lambda J}{2J+1} + B(J+1)(J+2) & 0 \\ -\mu(J+2) - W & \frac{2\lambda}{2J+1} [J(J+1)]^{\frac{1}{2}} \end{array} \right| \\
 K=J \quad \left| \begin{array}{cc} 0 & 2\lambda - \mu + BJ(J+1) - W \\ & 0 \end{array} \right| \\
 K=J-1 \quad \left| \begin{array}{cc} \frac{2\lambda}{2J+1} [J(J+1)]^{\frac{1}{2}} & 0 \\ \frac{2\lambda(J+1)}{2J+1} + BJ(J-1) + \mu(J-1) - W & \end{array} \right|
 \end{array}$$

... (3)

where λ ($=2.8553^\circ\text{K}$) determines the magnitude of the spin-spin interaction (Kramers 1929; Hebb, 1936) and μ ($=-0.0121^\circ\text{K}$) gives the coupling between the spin and the rotation. The

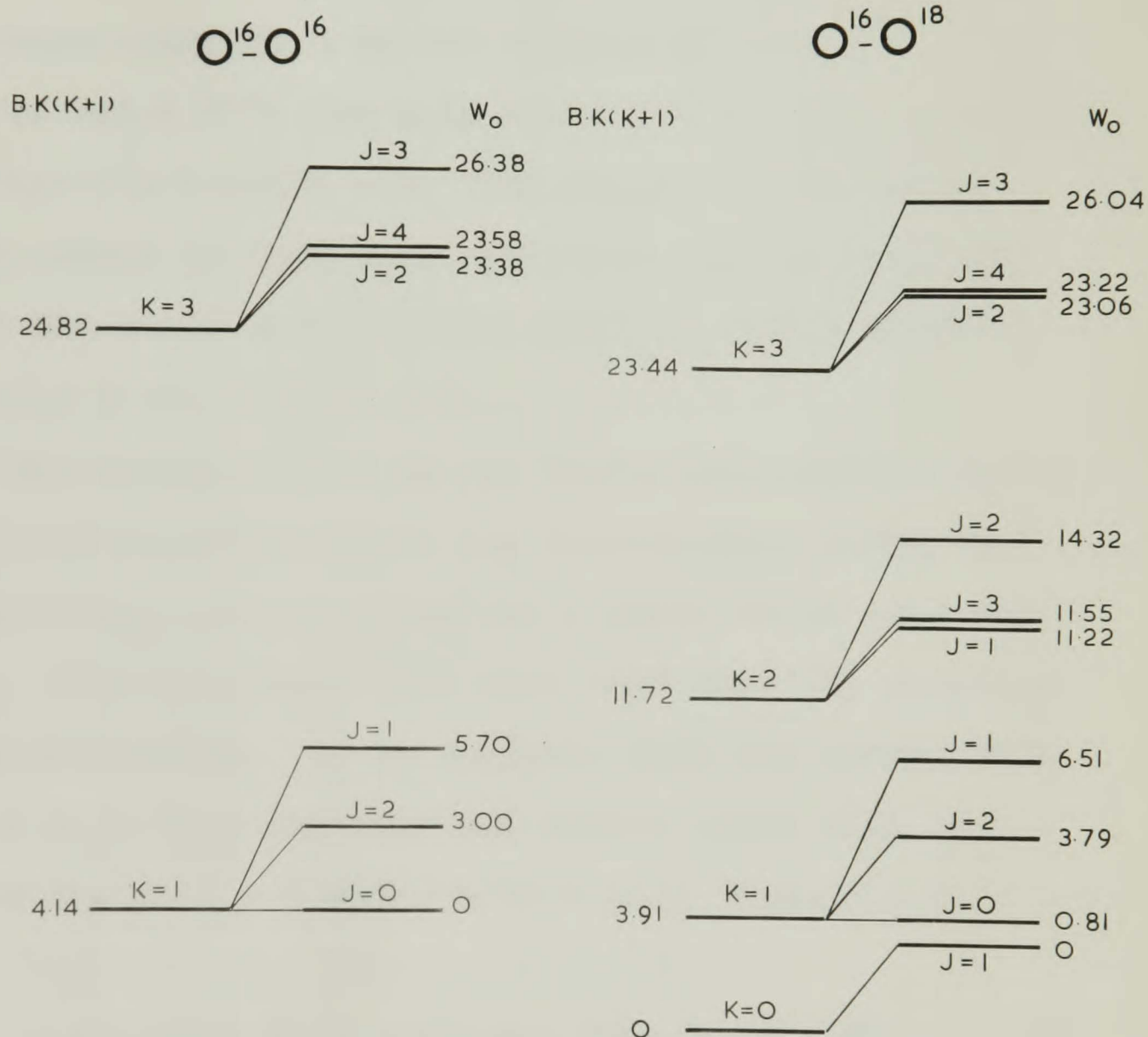


FIG 10

5.12

rotational energy levels neglecting spin are given by $B K (K + 1)$ where $B = 2.0683^\circ\text{K}$ for $\text{O}^{16}\text{O}^{16}$. Fig. 10 shows the solutions of this equation for $K = 0, 1, 2$ and 3 .

In the case of $\text{O}^{16}\text{O}^{16}$, as pointed out above, symmetry considerations restrict K to odd values, so that at temperatures below 20°K the only states which are appreciably populated are $K = 1$ and $K = 3$. The effect of the higher rotational states is thus very small and will be neglected except for the small second order shift of energy produced by $J = 4, K = 5$ on $J = 4, K = 3$.

From the energy matrix we see that, although the states with $J = K$ are eigen states of the Hamiltonian, there is a small interaction between states of a given value of J and $K = J \pm 1$. This departure from true Hund case (b) coupling is readily calculated. If we consider only the states with $K = 1$ and $K = 3$, then the only two states which will be admixed are $J = 2, K = 3$ and $J = 2, K = 1$. Thus $J = 2, K = 1$ becomes

$$|\alpha\rangle = a_{13} |J = 2, K = 1\rangle - b_{13} |J = 2, K = 3\rangle \quad (4)$$

and $J = 2, K = 3$ becomes

$$|\beta\rangle = a_{13} |J = 2, K = 3\rangle + b_{13} |J = 2, K = 1\rangle \quad (5)$$

where $a_{13} = 0.990$ and $b_{13} = 0.138$.

The admixture to $J = 4, K = 3$ from $J = 4, K = 5$ is very small and will be neglected.

5.13

b) The energy levels in a magnetic field

The effect of a magnetic field on the energy levels of oxygen has been accurately calculated by Henry (1950) who considers the partial decoupling of K and S by a large magnetic field. However, as in our case the field produced by the primary of the measuring coil was only about 3 gauss, it is more convenient to calculate the effect of the field as a small perturbation on the field-free states. For the manifolds of $K = 1$ and $K = 3$ this leads to a 30 by 30 matrix the elements of which are, however, readily calculated.

Taking the magnetic field H as axis of quantization, the perturbation is given by

$$\mathcal{H}_m = 2 \beta H \cdot \underline{S} = 2 \beta H S_z$$

The matrix elements of S_z in a representation in which $\underline{J} = \underline{K} + \underline{S}$, $\underline{K} \cdot \underline{S}$ and $J_z (=M)$ are diagonal (Hund case b) are readily obtained by the standard methods. The non vanishing ones are (Van Vleck 1932, p.167)

$$\langle J, K, S, M | S_z | J, K, S, M \rangle = \frac{M}{2J(J+1)} [J(J+1) + S(S+1) - K(K+1)]$$

and

$$\langle J, K, S, M | S_z | J+1, K, S, M \rangle = \left[\frac{(J+K+S+2)(-J+S+K)(J+S-K+1)}{4(J+K-S+1)(J+1-M)(J+1+M)} \right]^{\frac{1}{2}} \\ \left[\frac{4(J+1)^2 (2J+1)(2J+3)}{4(J+1)^2 (2J+1)(2J+3)} \right]^{\frac{1}{2}}$$

		J	0
K	J	J	0
1	0	0	0
		1	
1	1	0	$\sqrt{\frac{2}{3}}$
		-1	
		2	
$a \leq k=1$		1	a
$-b \leq k=3$	2	0	
		-1	
		-2	
		2	
$a \leq k=1$		1	b
$+b \leq k=3$	2	0	
		-1	
		-2	
		3	
		2	
		1	
3	3	0	
		-1	
		-2	
		-3	
		4	
		3	
		2	
		1	
3	4	0	
		-1	
		-2	
		-2	

		$a K=1\rangle - b K=3\rangle$										$a K=1\rangle + b K=3\rangle$																				
K	J	0	1	0	-1	2	1	0	-1	-2	2	1	0	-1	-2	3	2	1	0	-1	-2	-3	4	3	2	1	0	-1	-2	-3	-4	
1	0	0	0	$\sqrt{\frac{2}{3}}$																												
1	1	0	$\frac{1}{2}$	0		$a\sqrt{\frac{1}{2}}$					$b\sqrt{\frac{1}{2}}$																					
	2				$-\frac{1}{2}$	$\frac{2}{3}a^2$					$\frac{5ab}{3}$																					
$a K=1\rangle$ $-b K=3\rangle$	2					$a\sqrt{\frac{1}{2}}$	$\frac{2}{3}a^2$				$\frac{5ab}{6}$																					
	-1				$a\sqrt{\frac{1}{2}}$			0			0																					
	-2					$\frac{b^2}{3} - \frac{a^2}{2}$	$\frac{2b^2}{3} - a^2$				$-\frac{5ab}{6}$																					
	2					$\frac{5ab}{3}$					$\frac{5ab}{3}$																					
	1		$b\sqrt{\frac{1}{2}}$			$\frac{5ab}{6}$					$\frac{b^2}{2} - \frac{a^2}{3}$																					
$a K=1\rangle$ $+b K=3\rangle$	2					$b\sqrt{\frac{1}{2}}$		0			0																					
	-1				$b\sqrt{\frac{1}{2}}$			$-\frac{5ab}{6}$			$\frac{a^2}{3} - \frac{b^2}{2}$																					
	-2					$-\frac{5ab}{3}$					$\frac{2b^2}{3} - a^2$																					
	3										$\frac{1}{4}$																					
	2										$\frac{1}{6}$																					
	1										$\frac{1}{12}$																					
3	3	0									$\sqrt{\frac{20}{63}}$																					
	-1										$\sqrt{\frac{36}{63}}$																					
	-2										$\sqrt{\frac{32}{63}}$																					
	-3										$\sqrt{\frac{20}{63}}$																					
	4																															
	3																															
	2																															
	1																															
3	4	0																														
	-1																															
	-2																															
	-3																															
	-4																															

MATRIX of S_8

Fig.11

MATRIX of S_y

Fig. 11

5.14

using the Dirac notation to denote matrix elements. The matrix elements between the zero field states of oxygen are now found using the admixture coefficients given in eq. (4) and (5). For example -

$$\langle J = 1, K = 1 | S_z | \alpha \rangle$$

$$= a_{13} \langle J = 1, K = 1 | S_z | J = 2, K = 1 \rangle$$

$$- b_{13} \langle J = 1, K = 1 | S_z | J = 2, K = 3 \rangle$$

$$= a_{13} \left[\frac{4 - J^2}{12} \right]^{\frac{1}{2}} = 0$$

while

$$\langle J = 1, K = 1 | S_z | \beta \rangle$$

$$= b_{13} \left[\frac{4 - J^2}{12} \right]^{\frac{1}{2}}$$

The whole matrix is reproduced in fig. 11.

c) The susceptibility of O^{16-16} below $20^\circ K$

Following the calculation given by Van Vleck (1932 p.182) we express the energy levels in a magnetic field in the form

$$W(J, M) = W_0(J, M) + H W_1(J, M) + H^2 W_2(J, M) + \dots$$

The susceptibility in small fields is then

$$-\left[3.089 - 0.194 \right] e^{-23.38/T}$$

... (6)

5.15

$$\chi = \frac{N \sum_{J,M} \left\{ \frac{[W_1(J,M)]^2}{kT} - 2W_2(J,M) \right\} e^{-W_0(J,M)/kT}}{\sum_{J,M} \exp[-W_0(J,M)/kT]}$$

If the perturbation of the magnetic field does not couple degenerate states, W_1 and W_2 are respectively the first and second order perturbations to W_0 and are given by 5.95, as computed with the data temperature values of

$$W_1(J,M) = \langle J,M | \mathcal{H}_m | J,M \rangle$$

$$W_2(J,M) = \sum_{J',M'} \left[\frac{|\langle J,M | \mathcal{H}_m | J',M' \rangle|^2}{W_0(J,M) - W_0(J',M')} \right]$$

Thus, at temperatures where only $K = 1$ and $K = 3$ are populated, the susceptibility of oxygen gas is given by

$$\chi = \frac{4N\beta^2}{k} \cdot \frac{1}{Z} \left\{ \left[0.234 - \left(0.838 - \frac{1}{2T} \right) e^{-\frac{5.70}{T}} + \left(\frac{2.346}{T} + 0.618 \right) e^{-\frac{3.00}{T}} \right] \right. \\ \left. + \left[\left(\frac{1.008}{T} + 1.467 \right) e^{-\frac{23.38}{T}} + \left(\frac{3.750}{T} + 1.607 \right) e^{-\frac{23.58}{T}} \right. \right. \\ \left. \left. - \left(3.089 - \frac{0.194}{T} \right) e^{-\frac{26.38}{T}} \right] \right\},$$

... (6)

5.16

where

$$Z = \left[1 + 3e^{-\frac{5.70}{T}} + 5e^{-\frac{3.80}{T}} \right] + \left[5e^{-\frac{23.38}{T}} + 9e^{-\frac{23.58}{T}} + 7e^{-\frac{26.38}{T}} \right]$$

This equation is shown as the solid line in figs. 8 and 9.

A close examination of the formula shows that, in the temperature range 20°K to 14°K the susceptibility very nearly follows Curie's law for a free spin. There is, however, a small deviation which over this small temperature range can be represented by a modified Curie constant of 0.98, as compared with the high temperature value of 1.000. This correction is important as the experiments on the clathrate were normalized to the behaviour of free oxygen in this temperature range.

At very low temperatures, when only $J = 0$ is populated, the susceptibility tends to a temperature independent value of 0.312 c.m.u. per mole. The maximum which occurs at about 1°K corresponds to the 'draining' of the $J = 1$ levels into the more paramagnetic $J = 2$ levels before these in turn are drained into $J = 0$.

d) The Susceptibility of $O^{16}O^{18}$

When considering the levels of $O^{16}O^{18}$ populated below 20°K account must be taken of the states with $K = 0$ and

5.17

$K = 2$ in addition to $K = 1$ and 3 . The positions are again calculated from (3) but with B and μ varied inversely as the reduced mass of the molecule to allow for the change of isotopic mass. Thus $B^{16-18} = 1.9532^\circ K$ and $\mu^{16-18} = -0.0114^\circ K$ in agreement with the microwave spectrum (Miller and Townes, 1953). The values for $K = 0$ to 3 are given in fig. 10.

The susceptibility can now be calculated as above and an expression analogous to eq. (6) obtained. However, down to $5^\circ K$ the differences from the previous formula are negligible, both curves nearly following Curie's law for a free spin.

If we consider, then, only the temperature range below $5^\circ K$, we can neglect the population of all but the levels $K = 1$ and $K = 0$ and obtain for the susceptibility of $O^{16}O^{18}$

$$\chi_{16-18} = \frac{4N\beta^2}{k} \frac{1}{Z'} \left\{ 0.234 e^{-0.81} - \left(0.834 - \frac{1}{2T}\right) e^{-\frac{2.51}{T}} + \left(\frac{2.323}{T} + 0.615\right) e^{-\frac{3.79}{T}} + \left(\frac{1.650}{T} + 0.046\right) \right\}$$

$$\frac{1}{T} < 0.2$$

where $Z' = 3 + e^{-\frac{0.81}{T}} + 5e^{-\frac{3.79}{T}} + 3e^{-\frac{6.51}{T}}$.

5.18

The broken line in fig.8 shows the susceptibility to be expected for a gas consisting of 11% O^{16-18} and 89% O^{16-16} .

6. Conclusion

It will be seen that above $2^{\circ}K$ the magnetic susceptibility of the oxygen in the clathrate compound agrees within our experimental error with that calculated for a gas of non-interacting molecules. Below $2^{\circ}K$ however there is an appreciable departure from the "free gas" behaviour, and moreover there is no detectable difference between the specimens of different isotopic constitution. We have to conclude therefore that the interaction of the oxygen molecules with the cage enclosing them is sufficient to affect their rotational freedom at temperatures in the helium range. It is not possible to be more precise, on account of the insensitivity of macroscopic quantities like susceptibility to any perturbation of the energy levels when several of them are populated. The only other evidence on the rotational freedom of molecules in these compounds is afforded by the experiments of Dryden and Meakins (1952) on the dielectric constants of β -quinol clathrate compounds containing polar molecules. These indicate that at room

temperature small molecules such as hydrogen sulphide, methanol, and hydrogen cyanide can rotate within the cage. In view of the indication from our experiments that the rotational freedom may persist to very low temperatures, it would be interesting to have more direct evidence on the rotational freedom at low temperatures, either from such dielectric measurements, or from nuclear resonance studies.

Of other possible experiments, specific heat measurements over a wide range of temperatures would give information on the freedom of motion of the enclosed molecules. For example, translational or vibrational motion could be studied in a compound containing a monatomic gas, such as argon, while rotational motion could be studied using a polyatomic gas such as nitrogen or methane.

CHAPTER 6.

THE MAGNETIC PROPERTIES AND SPECIFIC HEAT OF CERIUM
MAGNESIUM NITRATE1. Introduction

This salt is one of the isomorphous series of rare earth double nitrates which have the formula $A_2B_3(NO_3)_{12} \cdot 24H_2O$, where A is one of the trivalent rare earth ions between Lanthanum and Gadolinium, and B is a divalent metal, for example magnesium or zinc. Bleaney (priv.Comm.) has pointed out that comparison of the specific heats of different paramagnetic salts shows that exchange interaction between the magnetic ions falls very rapidly with increasing ionic volume, and that as the double nitrates have a particularly large ionic volume, interactions between the ions may be expected to be very small. It follows that adiabatic demagnetization of suitable salts of this series (that is, those in which the magnetic ions have Kramers degeneracy) should yield very low temperatures. Of the different salts, cerium salts are especially interesting since, as the naturally occurring cerium nuclei have no magnetic moment, the electronic states have no nuclear hyperfine structure, and at low temperatures there is

6.2

no contribution to the specific heat save that due to interaction between the magnetic ions.

The rare earth double nitrates are very soluble in water, from which they crystallize readily in thick plates of trigonal symmetry. Their external morphology has been described by Groth (1908). The crystal structure is not known in detail, and we are indebted to Mr. H. M. Powell, who has determined the structure of the lattice formed by the cerium ions in cerium magnesium nitrate. These lie on a rhombohedral lattice, with a unit cell of side 8.51 Å., and interaxial angle $79\frac{1}{2}^\circ$.

Measurements of the susceptibility and the magnetic anisotropy were made at room temperature on several salts of the series by Krishnan and Mookherji (1938) in their survey of rare earth paramagnetic salts. The only measurements at low temperatures so far reported are those of Becquerel, de Haas, and van den Handel (1931) who measured the Faraday effect when a magnetic field was applied along the trigonal axis of a crystal of cerium magnesium nitrate at temperatures in the helium range. The effect they found was too small to allow an accurate estimate of the magnetic susceptibility to be made; they concluded that the effective magnetic moment of the cerium ion in the direction of

6.3

measurement was not greater than 0.2 Bohr magnetons. More recent work on this substance has been carried out in this laboratory using paramagnetic resonance at a wavelength of 3.33 cm. (Cooke, Duffus and Wolf, 1953). Resonance was observed only at temperatures below 10°K showing that at higher temperatures the spin lattice relaxation time is so short ($\sim 10^{-11}$ secs.) that the line was broadened beyond the limit of detection. Measurements at 4.2°K gave a single resonance line, indicating that, as in the comparable case of gadolinium magnesium nitrate (Trenam, 1953) all the rare earth ions occupy equivalent positions in the crystal and that only one doublet is populated at low temperatures. It was found that the splitting in a magnetic field could be expressed in terms of an axial g tensor whose principal values perpendicular and parallel to the trigonal axis are $g_{\perp} = 1.84 \pm 0.02$ and $g_{\parallel} = 0.25 \pm 0.05$, respectively. Thus one can represent the ion at temperatures below 10°K as a spin $S = \frac{1}{2}$ allowing for the proper J value (or admixtures from other levels) via the anisotropic g tensor. This leads to a susceptibility which, in one plane of the crystal, is comparable with other paramagnetic substances, while in a direction at right angles it is smaller by a factor of 50. It is interesting to compare this anisotropy

6.4

with that of another Cerium salt - the ethyl sulphate- (Bogle, Cooke and Whitley, 1952) which has a large susceptibility along its axis and a very small one perpendicular to it. As there are many potential uses for such highly anisotropic substances it was decided to investigate the double nitrate further, first by the method of paramagnetic relaxation and later by adiabatic demagnetization.

2. Relaxation Measurements

The specimen used was a piece of single crystal (45 x 10 x 8 mm.) cut from a plate 6 cm. in diameter and 8 mm. thick, which was grown in a period of three weeks in a dessicator over sulphuric acid. It was mounted in the cryostat so that in all measurements the magnetic field was normal to the trigonal axis of the crystal. The spin lattice relaxation time was measured as described in Chapter 3. The results are shown in Table 1.

Table 1.

T°K	$\frac{M-M_H}{M} \approx \tau$ Lsecs.
4.2	$< 10^{-5}$
2.14	$4 \cdot 10^{-4}$
1.38	$3 \cdot 10^{-2}$
1.03	$\sim 5 \cdot 10^{-2}$

6.5

It will be seen that τ is very temperature dependent, varying approximately as T^{-7} . At 1.03°K the relaxation time was long enough for the adiabatic susceptibility to be measured at 175 c/s without extrapolation, and the specific heat was determined using equation 3.4. As expected the value of $\frac{CT}{\lambda}^2$ was extremely small and it was thus necessary to correct for several factors which are usually negligible.

- (i) The d.c. field H which had to be applied to measure was only of the order of 50 gauss so that the vertical component of the earth's field had to be eliminated. This was done by reversing the current through the solenoid and taking the mean result.
- (ii) There was a small temperature dependent effect on M due to the cryostat, which was ascribed to either the paramagnetism of lead glass or to some superconducting woods metal joins about 10 cm. from the specimen. The effect was however very small on account of the internal compensation of the coil and was estimated by repeating the experiment with an empty cryostat. It was found very approximately that at 1°K the cryostat contributed -0.07 u.m.i. to M in zero field and -0.05 u.m.i. in a field of 50 gauss.
- (iii) It was also found that there was a small diamagnetic displacement in the calibration curve (~ 0.1 u.m.i.) near the

6.6

A point probably due to a superconductor. In extrapolating to find M_0 it was necessary to allow for this.

For a substance with a very small value of $\frac{CT^2}{\lambda}$ it is possible to find M_0 without extrapolation. From eq. 3.4 it will be seen that if $\frac{CT^2}{\lambda}$ is small and H is large, χ_s is very small so that $\chi_s = c(M_H - M_0) \approx 0$. Thus the value of M_H measured in a 'large' field corresponds closely to M_0 . This was verified by using several different large fields and observing that M_H remained virtually constant. We can estimate the criterion of a 'large' field in any given case from the following consideration: If we let H_1 be the field which makes the ratio $\frac{\chi_s}{\chi_T - \chi_s} = 1$, then a field $10H_1$ will make $\frac{\chi_s}{\chi_T} \approx \frac{1}{100}$. Thus for χ_s to be less than 1% of χ_T , the applied field must be 10 times greater than H_1 . For Cerium Magnesium Nitrate H_1 was about 45 gauss so that it was possible to apply fields of the order $20H_1$.

Results

For a salt as dilute as this demagnetizing corrections are negligible and the ratio $H^2 \frac{M_H - M_0}{M_H - M_H}$ gives the value of $\frac{CT^2}{\lambda}$ directly. Measurements of this quantity were made in fields between 20 and 60 gauss. For these fields the saturation correction was less than 0.01%. The results are shown in Table 2.

6.7

Table 2.

$$T = 1.03^{\circ}\text{K}$$

$$M_0 = 144.265 \text{ u.m.1.}$$

H	$M=M-M_H$	$\Delta M=M_H-M_0$	M_{corr}^*	ΔM_{corr}^*	$\frac{CT^2}{\lambda} = \frac{H^2 \Delta M_c}{M_c}$	$\frac{CT^2}{\lambda} \text{ avg.}$
+59.2	2.935	1.615	2.955	1.665	1989	1969
-58.3	2.92	1.63	2.94	1.68	1949	
+58.1	2.905	1.67	2.925	1.72	1993	1966
-57.5	2.91	1.665	2.93	1.715	1939	
-47.4	2.465	2.10	2.485	2.15	1949	1974
+47.9	2.46	2.105	2.48	1.155	1999	
+40.3	2.06	2.505	2.08	2.555	1999	1966
-39.9	2.08	2.485	2.10	2.535	1933	
-32.3	1.60	2.97	1.62	3.02	1949	1980
+32.5	1.58	2.99	1.60	3.04	2011	
+26.0	1.145	3.425	1.165	3.475	2016	1971
-25.8	1.175	3.395	1.195	3.445	1926	
+21.2	0.825	3.745	0.845	3.795	2027	1966
-21.1	0.87	3.70	0.89	3.75	1905	

Avg. values of $\frac{CT^2}{\lambda} = 1968$

* corrected for effect of empty cryostat

The Curie constant λ was calculated from the g value.

For a spin $S = \frac{1}{2}$ eq.1.1 becomes

$$\lambda = 0.09375 g^2 \text{ e.m.u./gm. ion,} \quad (1)$$

Thus, taking $g = g_{\perp} = 1.84$

$$\lambda = 0.318 \text{ emu/gm. ion.}$$

This gives for the specific heat

per cc, was calculated from the following equation

$$\frac{C_M}{R} = \frac{7.5 \times 10^{-6}}{T^2}$$

given by Brinkman and Gorter

In view of the uncertainty of some of the corrections it was decided to check the value of the specific heat constant by measuring the entropy using the method of adiabatic demagnetization. At the same time it would be possible to see whether very low temperatures could be reached as expected.

3. Demagnetization Experiments

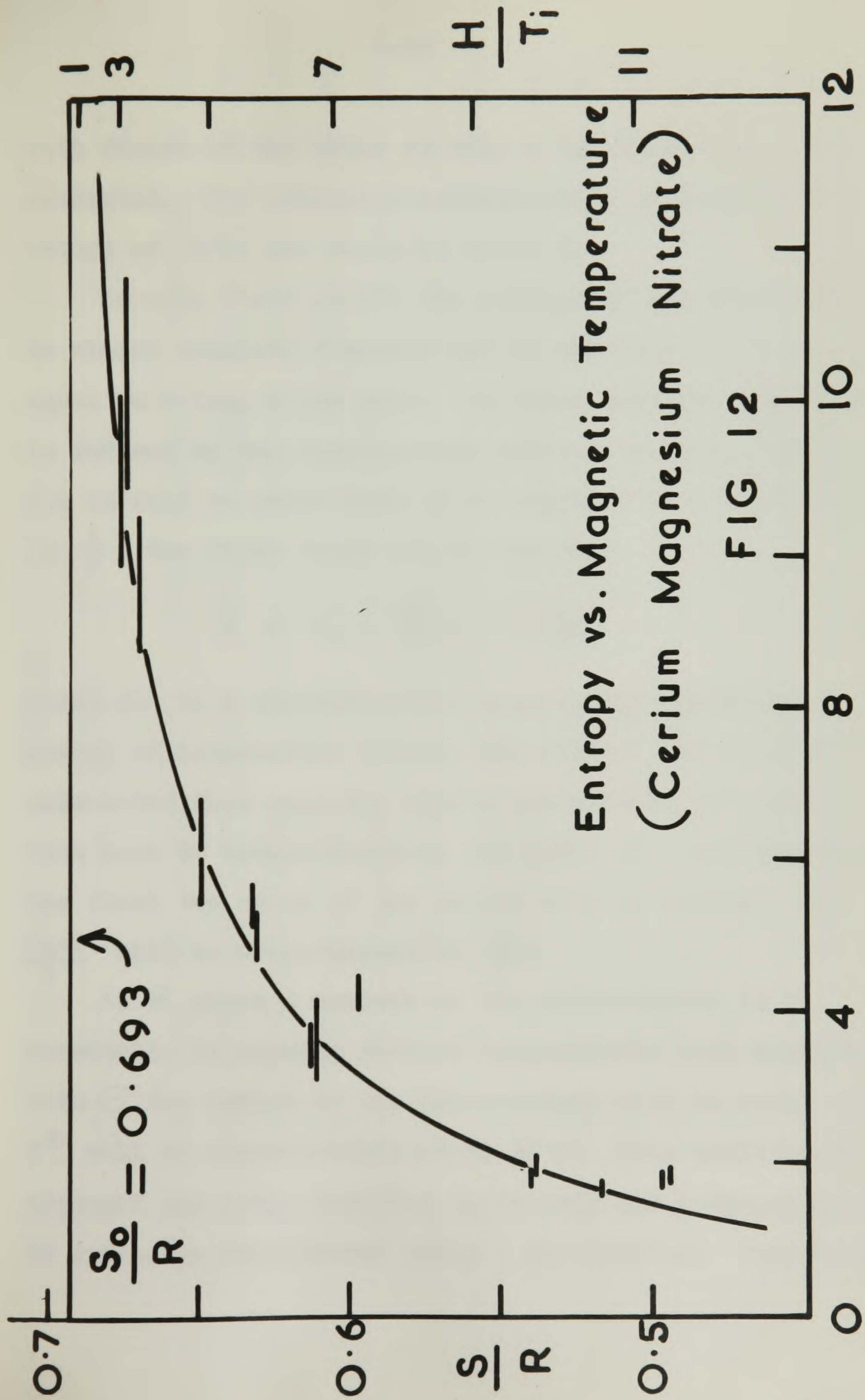
The method of measuring entropy as a function of magnetic temperature has been outlined in Chapter 4. The same specimen was used as for the relaxation measurements. It was suspended in the cryostat so that its trigonal axis (direction of small susceptibility) was perpendicular to both the field of the measuring coil and the field of the magnet. The appropriate value of g for calculating both the susceptibility

and entropy was therefore $g_{\perp} = 1.84$. The importance of using a single crystal for determining the entropy has already been stressed in Chapter 4.

The demagnetizing correction to convert T^* to T° was calculated from eq.(4.4). Taking the crystal to be a 5:1 ellipsoid, $N \approx 0.7$, so that $\Theta = 0.003^{\circ}\text{K}$. The Curie constant per cc. was calculated from eq. 1 and the density of the specimen. The density of Cerium Magnesium Nitrate has been given by Krishnan and Mookherji (1938) as 2.01, but the value calculated from the X-ray crystal structure is 2.12. It was therefore decided to measure the density of the actual crystal used from the weight in air and the weight in benzene. The density found was 2.07. This is nearer the calculated value than the previous experimental determination, but it must be concluded that in both cases there were small inclusions of free water which reduced the density.

Results

The results of demagnetizations can be expressed most directly by plotting H/T_i (the ratio of field to initial temperature) against the magnetic temperature reached T^*_f . The experimental points are shown in fig.12. The errors on the points were estimated from the amount of extrapolation necessary to find M at time $t = 0$. It will be seen that magnetic temperatures in the millidegree region were reached



with fields of the order of only a few kilogauss, as predicted. The entropies corresponding to the various values of H/T are shown in Table 3.

In zero field at 1°K the entropy of the spins corresponds to almost complete disorder and we may take its value, S_0 equal to $R \log_2 2$ per mole. At lower temperatures the entropy is reduced by the interactions between the ions. In section 6.4 it will be shown that if we expand S as a power series in $\frac{1}{T}$, the first terms are of the form

$$S = S_0 - \frac{\Theta^2}{T^2} R + O\left(\frac{1}{T^3}\right) \quad (2)$$

where Θ is a characteristic temperature depending on the energy of interaction between the spins. The value of Θ calculated from magnetic dipole interaction is $1.8 \times 10^{-3}^\circ\text{K}$. Thus down to temperatures of the order of a few millidegrees the first two terms of the series will be dominant and $\frac{S_0 - S}{R}$ will be proportional to $\frac{1}{T^2}$.

As Θ gives a measure of the interactions it is reasonable to suppose that at temperatures high compared with Θ the effect of the interactions will be small and that $T \gg \Theta$ will be approximately equal to T . This qualitative argument was later verified by Daniels and Robinson (1953) by extensive experiments using γ ray heating. They found

Table 3.

H	$T_1^{\circ}\text{K}$	$\frac{H}{T_1}$	x	S/R	$\frac{\Delta S}{R} = \frac{S_0 - S}{R}$	$\frac{\Delta S}{R}$	T_F°	$T = T_F + 3.0$	$\frac{1}{T}$
2.9	0.98	2.95	0.36	0.677	0.016	0.126	10.9-13.6	13.9-16.6	72 - 60
2.9	0.98	2.95	0.36	0.677	0.016	0.126	9.9-12.1	12.9-15.1	77 - 66
4.8 $\pm$	1.42	3.38	0.42	0.674	0.022	0.148	8.8-10.5	11.8-13.5	85 - 74
6.9 $\pm$	1.42	4.85	0.60	0.650	0.043	0.207	6.1-6.8	9.1-9.8	110 -102
4.8	0.98	4.9	0.61	0.649	0.044	0.240	5.4-6.0	8.4-9.0	119 -111
8.2	1.42	5.8	0.72	0.632	0.064	0.247	5.1-5.7	8.1-8.7	123 -115
8.2	1.42	5.8	0.72	0.632	0.064	0.247	4.7-5.3	7.7-8.3	130 -120
9.6	1.42	6.77	0.84	0.613	0.080	0.283	3.3-3.9	6.3-6.9	160 -145
9.6	1.42	6.77	0.84	0.613	0.080	0.283	3.1-4.2	6.1-7.2	165 -140
10.5	1.42	7.4	0.92	0.597	0.096	0.310	4.0-4.5	7.0-7.5	143 -133
9.6	0.98	9.8	1.21	0.539	0.154	0.392	1.8-2.1	4.8-5.1	208 -196
9.6	0.98	9.8	1.21	0.539	0.154	0.392	1.7-1.9	4.7-4.9	213 -204
10.5	0.99	10.6	1.34	0.517	0.176	0.420	1.5-1.7	4.5-4.7	222 -213
10.5 $\pm$	0.93	11.3	1.40	0.497	0.196	0.443	1.7-2.0	4.7-5.0	213 -200

$\pm$ denotes: Two identical points obtained H in Kilo gauss

$$T_0, T \text{ in millidegrees absolute} \quad x = \frac{20H}{KT_1} = 0.124 \frac{H}{T_1}$$

6.12

that down to 0.006°K $T^* = T^* + 0.0027 = T$ to an accuracy of 2%. Using fields of up to 27 K gauss they also investigated the Curie point region and determined the absolute temperature of the Curie point as 0.0031°K .

Fig. 13 shows a plot of $\left(\frac{S_0 - S}{R}\right)^{\frac{1}{2}}$ against $\frac{1}{T}$ in the temperature range $T^* = 5$ to 15 millidegrees. It will be seen that despite the rather large scatter, which was due to the experimental difficulties already discussed in Chapter 4, a straight line can be drawn through the points to an accuracy of about 8%. The slope of the line gives

$$\frac{\Delta S}{R} = \frac{3.6 \times 10^{-6}}{T^2}$$

whence

$$\frac{C_M}{R} = \frac{7.2 \times 10^{-6}}{T^2}$$

This value is in good agreement with that derived from the relaxation measurements $\frac{7.5 \times 10^{-6}}{T^2}$, and can be compared with the value found by Daniels and Robinson $\frac{6.4 \times 10^{-6}}{T^2}$. No explanation can be offered for the discrepancy except to stress the difficulties of measuring a specific heat which is so much smaller than that of any other paramagnetic salt so far reported. For example the

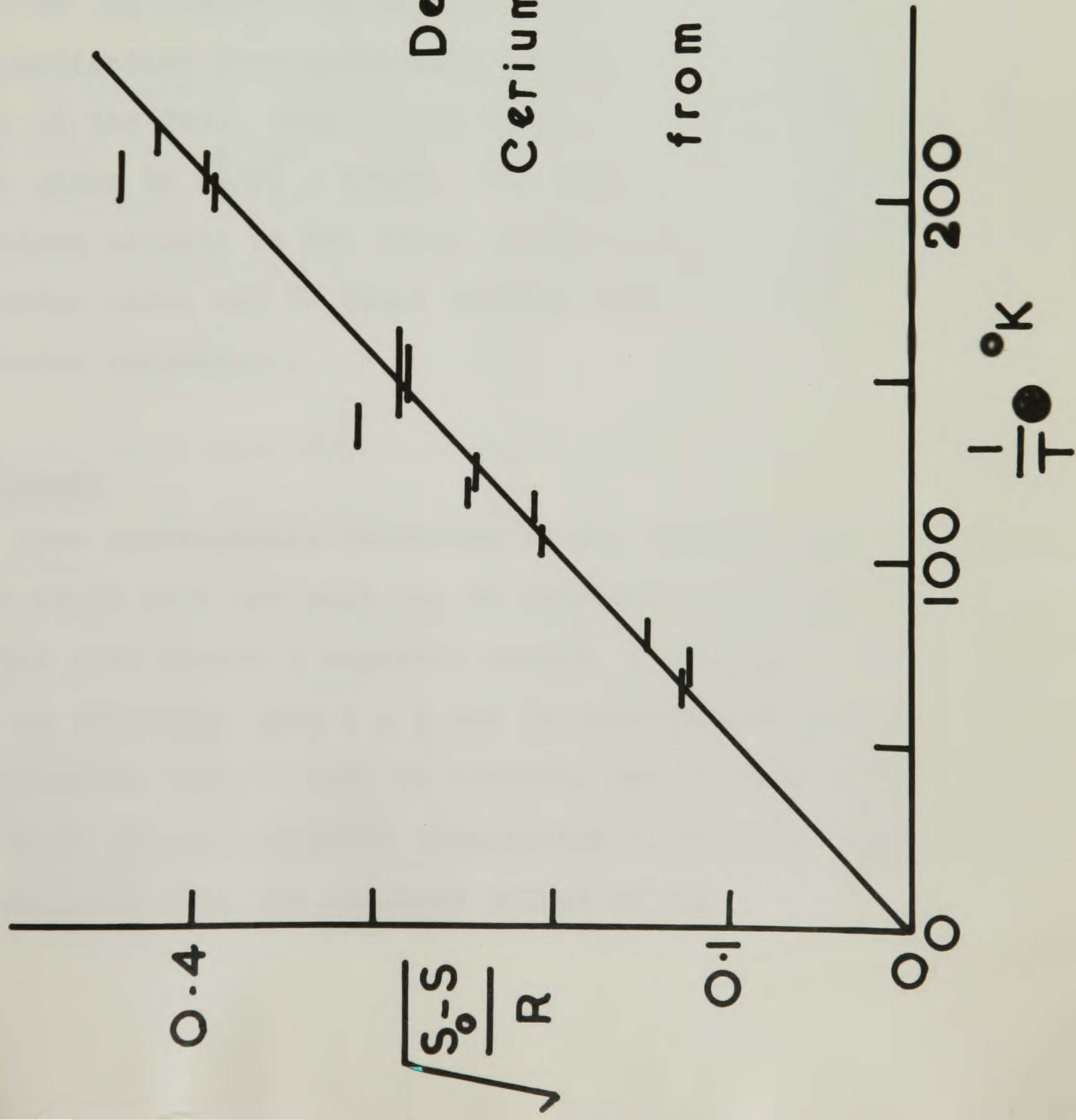


Fig 13

Demagnetisation of
Cerium Magnesium Nitrate

from slope:—

$$\frac{S_0 - S}{R} = \frac{3.6 \times 10^{-6}}{T^2} \pm 8\%$$

6.13

specific heat of chromium potassium alum is 2,300 times greater, and that of copper potassium sulphate is 85 times greater than that of cerium magnesium nitrate at the same temperature. From the practical point of view, the chief interest of the comparison lies in the use of the salts for obtaining very low temperatures by adiabatic demagnetization. A useful figure is the ratio of the specific heat constant b , given by $C_M = b/T^2$, to the Curie constant λ , since in demagnetization from moderately high magnetic fields the ratio of the final temperature T_f to the initial temperature T_i is given by $T_f^2/T_i^2 = b/\lambda H^2$. The value of b/λ for cerium magnesium nitrate is 380 times smaller than for chromium potassium alum, and 60 times smaller than for copper potassium sulphate.

4. Theory

From paramagnetic resonance we see that at temperatures below about 10°K the salt may be regarded as an assembly of dipoles each having a magnetic moment $\mu = \beta g S$, (3) with an effective spin $S = \frac{1}{2}$ and an anisotropic g factor. The specific heat of such an assembly can be calculated on the basis of pure magnetic interaction between the dipoles and compared with the measured values of C_M .

6.14

Following the treatment of Van Vleck (1937) we derive the specific heat (and entropy) from the partition function Z .

$$Z = \sum_{\lambda} \exp(-W_{\lambda}/kT) \quad (4)$$

since

$$S = \frac{\partial}{\partial T} (kT \log Z) \quad (5)$$

and

$$C_M = T \frac{\partial^2}{\partial T^2} (kT \log Z) \quad (6)$$

where W_{λ} is one of the eigen-values of the Hamiltonian $\mathcal{H}$ describing the system. Expanding Z in powers of $\frac{W_{\lambda}}{kT}$ we get expressions for C_M and S in terms of $\sum_{\lambda} W_{\lambda}^n$. In order to evaluate these sums we make use of the fact that

$$\sum_{\lambda} W_{\lambda}^n = \text{Spur } \mathcal{H}^n \quad (7)$$

where the right hand side represents the sum of the diagonal elements of the matrix representing $\mathcal{H}$. This can be proved as follows:

If the basic vectors (wave functions) used to represent $\mathcal{H}$ are the eigen vectors of $\mathcal{H}$, then the matrix will have elements only along the diagonal and these will be the eigen-values W_{λ} . It follows from the law of matrix multiplication that the matrix of any power of $\mathcal{H}$ will then also be diagonal with elements W_{λ}^n . Thus in a representation in which the

6.15

basic vectors are the eigen vectors of $\mathcal{H}$ the theorem is proved. Using now the fact that a change of representation (from one set of "wave functions" to another) transforms a matrix into its equivalent matrix (see for example Margenau and Murphy) then, as any two equivalent matrices have the same spur, it follows that the spur of $\mathcal{H}$ in any representation is equal to $\sum_{\lambda} w_{\lambda}$. Thus from eqs. (5), (6) and (7)

$$S = S_0 - \frac{1}{2kT^2} \cdot \left[\left(\frac{S_p \mathcal{H}}{S_{p1}} \right)^2 - \frac{S_p \mathcal{H}^2}{S_{p1}} \right] + \dots \quad (8)$$

$$C_M = \frac{1}{kT^2} \left[\left(\frac{S_p \mathcal{H}}{S_{p1}} \right)^2 - \frac{S_p \mathcal{H}^2}{S_{p1}} \right] + \dots \quad (9)$$

Now, as we can regard the spur of any operator divided by the number of its eigen values as the mean (or expectation) value of the physical quantity which it represents, it follows that we can always choose $\mathcal{H}$ so that

$$\text{Spur } \frac{\mathcal{H}}{S_{p1}} = 0,$$

since the mean energy of the system has no fixed zero. Thus eqs. (8) and (9) simplify to

$$S = S_0 - \frac{1}{2kT^2} \cdot \frac{S_p \mathcal{H}^2}{S_{p1}} + o\left(\frac{1}{T^3}\right) \quad (10)$$

$$C_M = \frac{1}{kT^2} \cdot \frac{S_p \mathcal{H}^2}{S_{p1}} + o\left(\frac{1}{T^3}\right) \quad (11)$$

6.16

From (3), the Hamiltonian for magnetic dipole-dipole interaction is

$$\mathcal{H} = \sum_{i>j} \frac{\beta^2}{r_{ij}^3} \left\{ (\underline{S}_i \cdot \underline{g})(\underline{g} \cdot \underline{S}_j) - \frac{3}{r_{ij}^2} [(\underline{S}_i \cdot \underline{g}) \cdot \underline{r}_{ij}] [(\underline{S}_j \cdot \underline{g}) \cdot \underline{r}_{ij}] \right\} \quad \dots (12)$$

or in Cartesians

$$\begin{aligned} \mathcal{H} = \sum_{i>j} \frac{\beta^2}{r_{ij}^3} \left\{ g_1^2 (S_{xi} S_{xj} + S_{yi} S_{yj}) + g_2^2 S_{zi} S_{zj} \right. \\ \left. - \frac{3}{r_{ij}^2} \left[g_1 (x_{ij} S_{xi} + y_{ij} S_{yi}) + g_2 z_{ij} S_{zi} \right] \right. \\ \left. \times \left[g_1 (x_{ij} S_{xj} + y_{ij} S_{yj}) + g_2 z_{ij} S_{zj} \right] \right\} \quad \dots (13) \end{aligned}$$

As in the isotropic case, the trace of this is zero.

This follows from the fact that if $f(\underline{S}_i)$ and $g(\underline{S}_j)$ are any two functions of the operators S_x, S_y, S_z of the i th and j th ion respectively then

$$Sp \left[f(\underline{S}_i) \cdot g(\underline{S}_j) \right] = \left[Sp f(\underline{S}_i) \right] \left[Sp g(\underline{S}_j) \right]$$

and further that

$$Sp(S_x) = Sp(S_y) = Sp(S_z) = 0$$

(see also Appendix II).

In order to calculate $Sp \mathcal{H}^2$ we need to know Spurs of

6.17

cross products of the form $S_x S_y$ etc. These are given by

$$Sp (S_\alpha S_\beta) = \frac{1}{2} \delta_{\alpha\beta} \quad (\text{see Appendix II})$$

where α, β are x, y or z and $\delta_{\alpha\beta} = \begin{cases} 0 & \text{if } \alpha \neq \beta \\ 1 & \text{if } \alpha = \beta \end{cases}$

Thus $Spur \mathcal{H}^2$ is given by

$$\begin{aligned} Sp \mathcal{H}^2 = \beta^4 \sum_{j>i} \frac{1}{4 r_{ij}^6} \left\{ [g_{\perp}^4 (1 - \frac{3x_{ij}^2}{r_{ij}^2})^2 + (1 - \frac{3y_{ij}^2}{r_{ij}^2})^2] \right. \\ \left. + g_{\parallel}^4 (1 - \frac{3z_{ij}^2}{r_{ij}^2})^2 + 18 g_{\perp}^4 \frac{x_{ij}^2 y_{ij}^2}{r_{ij}^4} \right. \\ \left. + 18 g_{\parallel}^2 g_{\perp}^2 \frac{(x_{ij}^2 + y_{ij}^2) z_{ij}^2}{r_{ij}^4} \right\} \end{aligned}$$

... (14)

Summing over i , and writing x_j, y_j, z_j for the co-ordinates of the j th ion relative to any one fixed ion

$$\begin{aligned} Sp \mathcal{H}^2 = \frac{n\beta^4}{2} \sum_j \frac{1}{4 r_j^6} \left\{ g_{\perp}^4 \left[2 - 6 \frac{(x_j^2 + y_j^2)}{r_j^2} + 9 \frac{(x_j^4 + y_j^4)}{r_j^4} \right] \right. \\ \left. + g_{\parallel}^4 \left[1 - \frac{6z_j^2}{r_j^2} + \frac{9z_j^4}{r_j^4} \right] + 18 g_{\perp}^4 \frac{x_j^2 y_j^2}{r_j^4} \right. \\ \left. + 18 g_{\parallel}^2 g_{\perp}^2 \frac{(x_j^2 + y_j^2) z_j^2}{r_j^4} \right\} \end{aligned}$$

... (15)

6.18

On account of axial symmetry, this may be expressed in terms of ρ_j the distance of the j th ion from the z axis:

$$\rho_j^2 = x_j^2 + y_j^2; \quad r_j^2 = \rho_j^2 + z_j^2 \quad (16)$$

Then

$$\begin{aligned} S_p \kappa^2 = \frac{n p^4}{2} \sum_j \frac{1}{4 r_j^6} \left\{ g_{\perp}^4 \left(2 - \frac{6 \rho_j^2}{r_j^2} + \frac{9 \rho_j^4}{r_j^4} \right) \right. \\ \left. + g_{\parallel}^4 \left(1 - \frac{6 z_j^2}{r_j^2} + \frac{9 z_j^4}{r_j^4} \right) \right. \\ \left. + 18 g_{\parallel}^2 g_{\perp}^2 \frac{\rho_j^2 z_j^2}{r_j^4} \right\} \end{aligned} \quad \dots (17)$$

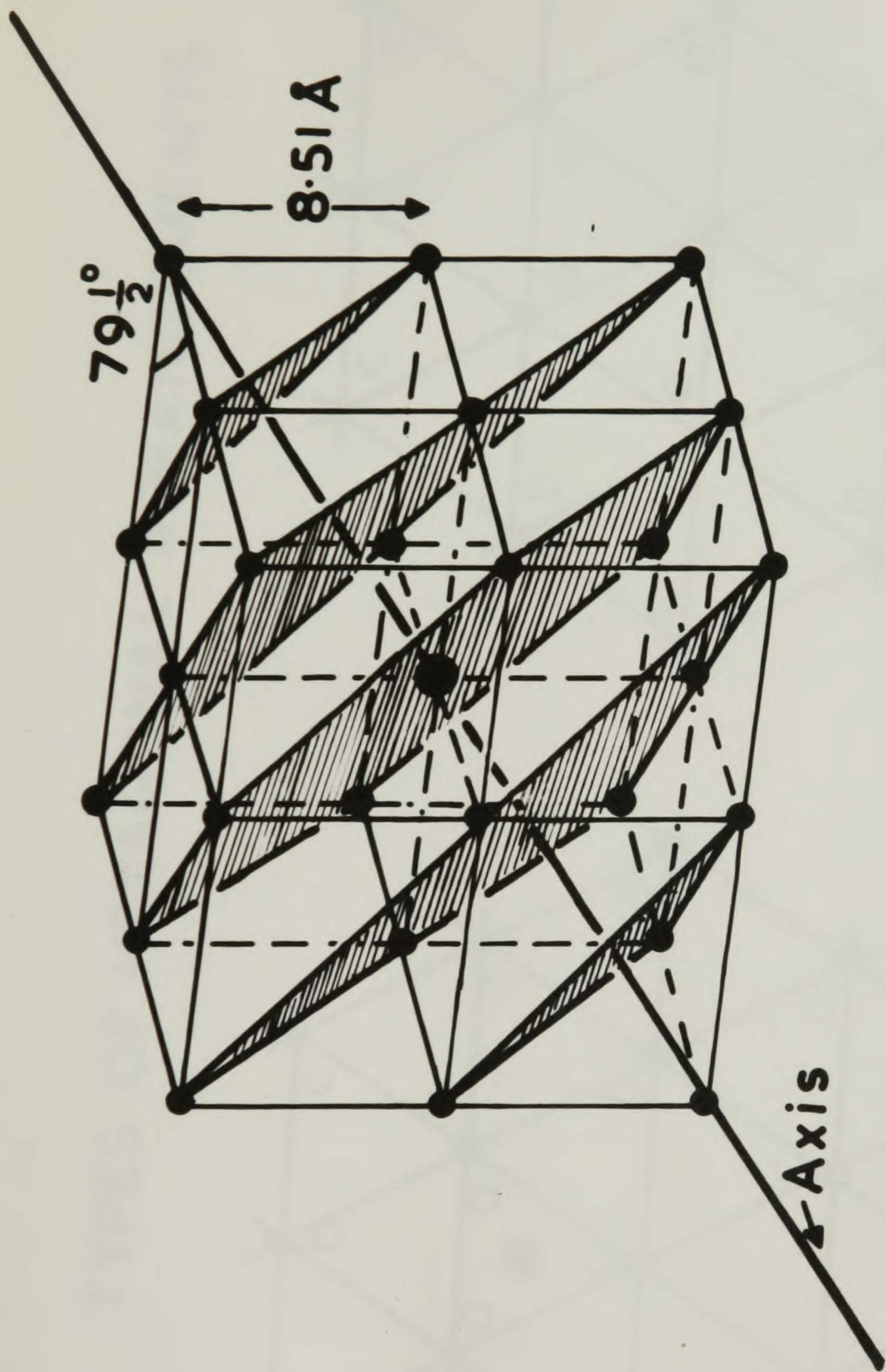
To obtain the specific heat per gram-ion, the summation over j must be taken over $n = N$ ions, where $N =$ Avogadro's number. The lattice sum over j in equation (17) need be taken in practice, only over relatively close neighbours, since it converges rapidly, its terms being of order $1/r^4$. In this particular case, inclusion of the 326 nearest neighbours gives a result accurate to better than 1%. Further, because of the uncertainty in the value of $g_{\parallel}$, we neglect the terms in $g_{\parallel}^2$, $g_{\perp}^2$ and $g_{\parallel}^4$, retaining only the term in $g_{\perp}^4$. On account of the great anisotropy, the resulting uncertainty in the

6.19

value of the specific heat is less than 3%. The expression for the specific heat is then

$$C_M = \frac{N\beta^4 g_1^4}{32RT^2} \cdot \sum_j \frac{1}{r_j^6} \left(2 - \frac{6p_j^2}{r_j^2} + \frac{9p_j^4}{r_j^4} \right) \dots (18)$$

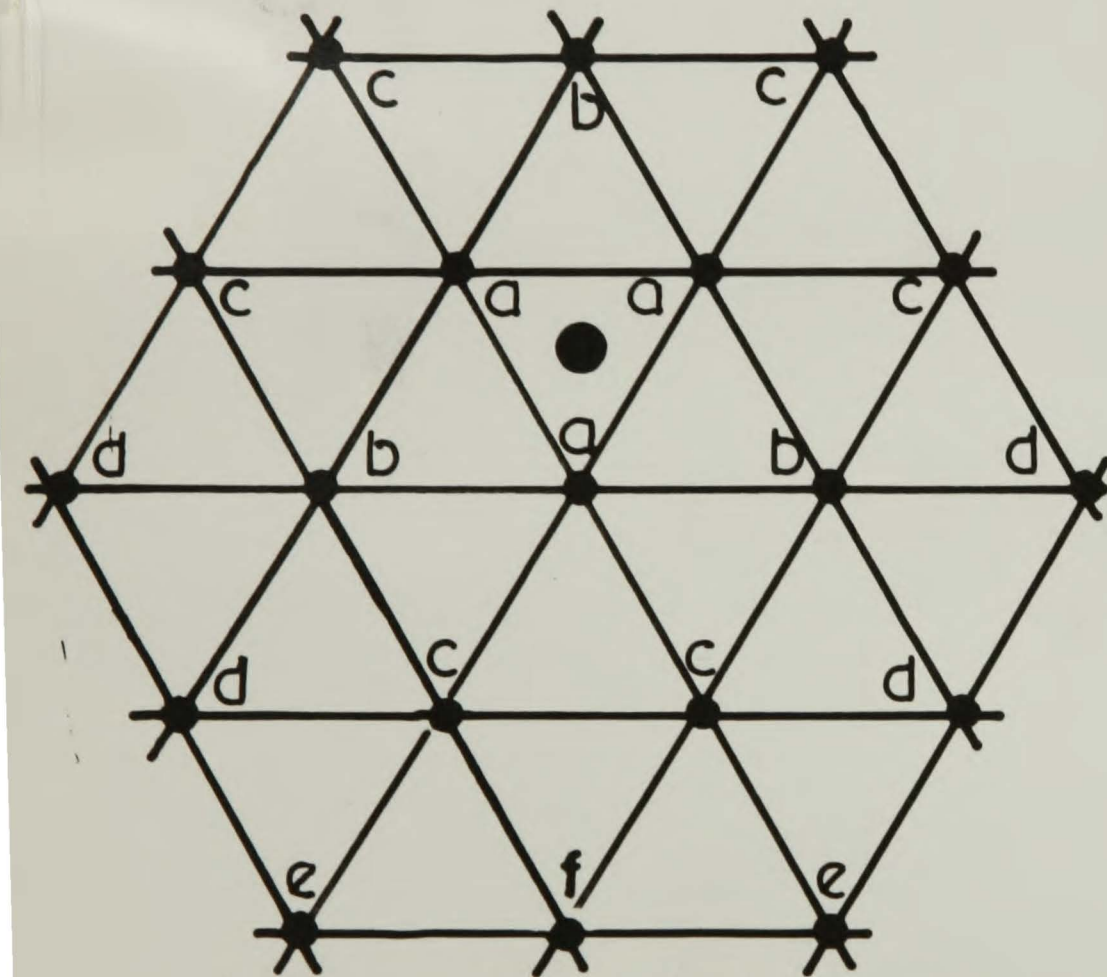
In order to perform the lattice sum we must consider the crystal structure more closely. Fig. (14) shows the arrangement of Cerium ions surrounding any one particular lattice site. It will be seen that one way of regarding the lattice is to consider it as a set of planes perpendicular to the trigonal axis XX' within each of which the ions are arranged in regular hexagons. If we take the line XX' to pass through one particular ion A, then there will be two types of hexagonal arrangements with respect to this axis. For one type the axis will pass through an ion in the plane, as for A, while in the second type it will pass through a point which is equidistant from three of the ions. From the point of view of computing p_j , the distance of the various ions from the axis, we consider these two types separately. The two arrangements are shown in fig. (15). Every third plane starting from the one containing the ion A will be of the first type while the intermediate planes will be of the second type. From Powell's measurements we can calculate the length of the side of each hexagon and



DOUBLE NITRATE LATTICE

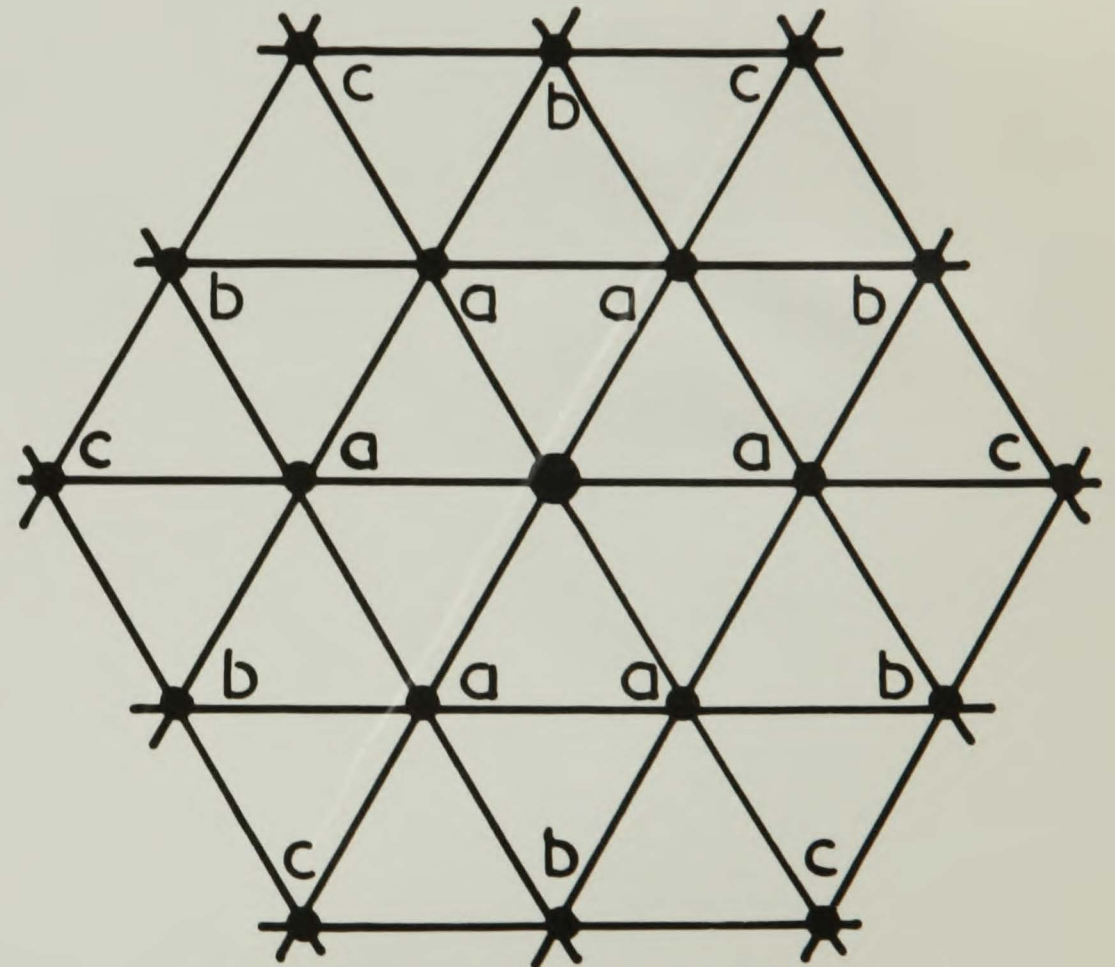
FIG.14

TYPES OF HEXAGONAL ARRANGEMENTS



Axis passing between
3 lattice sites

FIG.15



Axis passing through
a point in the plane

6.20

also the distance between the planes. They are $15.43 \text{ \AA}$ and $5.74 \text{ \AA}$ respectively. It is now simple to compute z^2 for each plane and $\sum \frac{1}{r_{ij}^6}$ for each ion in the plane. To find the lattice sum accurate to 1% we have to include contributions to it of up to 0.01% and this involves the 32 nearest neighbours of A. Thus we find that

$$\sum_j \frac{1}{r_{ij}^6} (2 - 6 \frac{p_{ij}^2}{r_{ij}^2} + 9 \frac{p_{ij}^4}{r_{ij}^4}) = 48.7 \times 10^{42} \text{ cm}^{-6}$$

and this gives

$$C_M = \frac{6.7 \times 10^{-6}}{T^2}$$

accounting for approximately the whole of the observed specific heat. Exchange interaction must thus be very small.

5. Conclusion

It seems that the behaviour of this salt can be entirely accounted for on the basis of an assembly of ions interacting only through magnetic forces. As the crystal structure is such that the ions are relatively far apart ($>10.9 \text{ \AA}$) these forces are very small and the substance approximates very closely to an ideal paramagnetic down to very low temperatures. This fact together with its very small heat capacity should make it a very good thermometric standard below 1°K . (see Ch. 8).

6.21

The highly anisotropic susceptibility also makes it possible to use the salt in experiments below 1°K which require the application of a magnetic field after demagnetization, since by applying the magnetic field along the axis of low susceptibility the temperature is raised by only a small amount. In an experiment on the alignment of Co^{60} nuclei reported by Ambler, et al. (1953) using cerium magnesium nitrate as a cooling agent, a field of 430 gauss was applied at a temperature of 0.007°K , producing a 50% anisotropy in the gamma-radiation.

1. CERIUM MAGNESIUM NITRATE $\text{Ce}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

This salt is very similar in all respects to the magnesium nitrate and a check experiment was carried out to verify that the properties were not appreciably different. The g values have been measured by Shuler and Huffer and were found to be 1.84 and 0.89 as before. Measurements of the spin lattice relaxation time in a field of about 50 gauss gave the following results:

Table 1.

$T^{\circ}\text{K}$	$T_{1\rho}$ sec
2.48	2×10^{-3}
1.05	8×10^{-4}

7.1

CHAPTER 7.

OTHER SPECIFIC HEAT MEASUREMENTS

Relaxation measurements similar to those on Cerium Magnesium Nitrate have been made on several other substances. These included 2 salts in the double nitrate series and 2 of the alums. In this chapter we shall briefly summarize the results.

1. CERIUM ZINC NITRATE $Ce_2Zn_3(NO_3)_{12} \cdot 24H_2O$

This salt is very similar in all respects to the magnesium nitrate and a check experiment was carried out to verify that the properties were not appreciably different. The g values have been measured by Cooke and Duffus and were found to be 1.84 and 0.25 as before. Measurements of the spin lattice relaxation time in a field of about 40 gauss gave the following results:

Table 1.

$T^{\circ}K$	τ_L secs
2.18	2×10^{-4}
1.05	8×10^{-3}

7.2

Using 450 c/s it was thus possible to measure χ_s at 1.05°K without extrapolation. The effect of the earth's field was again eliminated by reversing the field through the solenoid and taking the mean result. The correction for the effect of the empty cryostat was made as before, by adding 0.05 u.m.i. to $M_H - M_0$ and 0.02 to $M - M_H$. The value of M_0 was found by measuring the inductance in a field of about 1700 gauss, large enough to make χ_s effectively zero. In this experiment there was no discontinuity in the calibration curve due to a superconductor. As for the magnesium salt demagnetizing and saturation effects were negligible. The results are shown in table 2.

Table 2.

$T^{\circ}K = 1.05$		$M_0 = 937.26$					$\frac{CT^2}{\lambda} = \frac{H^2 \Delta M_C}{\delta M_C}$
H	M	$\Delta M = M_H - M_0$	$\delta M = M - M_H$	ΔM_{cor}	δM_{cor}		
0	944.85	7.59	0	7.66	0	-	
+42.1	940.87	3.61	3.98	3.66	4.00	1660	
-42.1	940.95	3.69	3.90	3.74	3.92		
-47.9	940.48	3.22	4.37	3.27	4.39	1690	
+47.4	940.48	3.22	4.37	3.27	4.39		

$$\frac{CT^2}{\lambda} = 1675$$

7.3

Taking $\lambda = 0.09375 \times 1.84^2$ (eq. 6.1) we get

$$\frac{G_2^2}{R} = 6.4 \times 10^{-6}$$

This is of the same order of magnitude as the value for Ce Mg Nitrate and is in good agreement with the calculated value which is the same for both salts. It has thus been established that there is no significant difference between the zinc and magnesium double nitrate so that either can be used for experiments where a very low specific heat or great anisotropy is required.

These are $\text{Nd}^{3+}(\text{f}^3, \text{L}^3, \text{S}^3)$ and $\text{Mg}^{2+}(\text{f}^0, \text{L}^0, \text{S}^0)$ each with spin

2. NEODYMIUM MAGNESIUM NITRATE $\text{Nd}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$

is represented by a spin Hamiltonian of the form

The ground state of the free Nd^{3+} ion is $^4\text{I}_{9/2}$ and in a crystalline electric field of sufficiently low symmetry this is split into 5 Kramers' doublets. To a first approximation these may be specified by $J_z = \pm\frac{1}{2}, \pm\frac{3}{2}, \dots, \pm\frac{9}{2}$. However a more accurate theory shows, (Elliott and Stevens, 1953) that a crystal field of C_{3h} symmetry such as would be expected in the double nitrates, will admix certain states with different values of J_z and also that the effect of higher levels on the ground state must be considered. The theoretical problems connected with this substance have not

7.4

yet been fully solved. However it has been shown experimentally by Cooke and Duffus (1954) that in the double nitrate below 4°K only one doublet is populated and that the magnetic properties of the ions can be expressed in terms of a fictitious spin $S = \frac{1}{2}$ and an anisotropic g value, as for Cerium Magnesium Nitrate. The principal values of the g tensor were found to be 0.45 ± 0.05 along the trigonal axis and 2.72 ± 0.02 perpendicular to it.

Cooke and Duffus also resolved the hyperfine structure due to the two Nd isotopes with non zero nuclear spin. These are Nd^{143} (12.2%) and Nd^{145} (8.29%) each with nuclear spin $I = 7/2$. They found that the hyperfine splittings could be represented by a spin hamiltonian of the form

$$A S_z I_z + B(S_x I_x + S_y I_y) \quad (1)$$

where A and B have the values

$$\begin{aligned} \text{Nd}^{143}: \quad A &= 5 \times 10^{-4} \text{ cm}^{-1} = 0.07 \times 10^{-2} \text{ }^{\circ}\text{K} \\ B &= 312 \times 10^{-4} \text{ cm}^{-1} = 4.49 \times 10^{-2} \text{ }^{\circ}\text{K} \\ \text{Nd}^{145}: \quad A &= 3 \times 10^{-4} \text{ cm}^{-1} = 0.04 \times 10^{-2} \text{ }^{\circ}\text{K} \\ B &= 193 \times 10^{-4} \text{ cm}^{-1} = 2.79 \times 10^{-2} \text{ }^{\circ}\text{K} \end{aligned}$$

These splittings give rise to a Schottky anomaly at very low temperatures ($\sim 0.05^{\circ}\text{K}$), the tail of which can be measured at 1°K .

The Measurements

The specimen consisted of two pieces of single crystal each $25 \times 10 \times 4$ mm., mounted on a perspex frame with the trigonal axis perpendicular to the measuring field. Measurements of the spin lattice relaxation time in a field of about 200 gauss gave the following results:

Table 3

$T^{\circ}K$	τ_L secs
2.05	8×10^{-3}
1.37	11×10^{-3}
1.03	14×10^{-3}

It is interesting to compare the slow variation of with temperature in this salt ($\sim \frac{1}{T}$) with that in the Cerium double nitrate in which τ varies approximately as T^{-7} .

At the lowest temperature the relaxation time was long enough to measure the specific heat without extrapolation using 175c/s. The field needed to make $\frac{\chi_2}{\chi_1 - \chi_2} \approx 1$ was about 300 gauss so that the effect of saturation was negligible. The demagnetizing correction, calculated as for Cerium Magnesium Nitrate was less than $0.005^{\circ}K$. The quantity $H^2 \frac{M_H - M_0}{M - M_H}$ therefore gives $\frac{CT^2}{\lambda}$ directly. Table 4 shows the results of 6 measurements of $\frac{CT^2}{\lambda}$ in fields between 200 and 420 gauss.

7.6

Table 4.

$T=1.03^\circ\text{K}$ $f=175 \text{ c/s}$ $M_0=736.42 \text{ u.m.i.}$

H gauss	M u.m.i.	$\Delta M = M_H - M_0$	$\delta M = M - M_H$	$\frac{CT^2}{\lambda} = H^2 \frac{\Delta M}{\delta M}$
0	746.01	9.59	0	
-215.5	743.03	6.61	2.98	1.025×10^5
-316	741.31	4.89	4.70	1.05
-421	739.94	3.52	6.07	1.03
+208.5	743.21	6.79	2.78	1.06
+312	741.40	4.98	4.60	1.055
+422	740.00	3.58	6.03	1.055

Average value of $\frac{CT^2}{\lambda} = 1.045 \times 10^5$

The Curie constant λ was calculated from the g value giving

$$\lambda = 0.698 \text{ e.m.u./mole}$$

so that

$$\frac{CT^2}{R} = 8.73 \times 10^{-4}$$

Discussion

The measured value of the specific heat can be compared with that calculated from the hyperfine structure plus the effect of dipole-dipole interaction. It can be shown that, exchange interaction is very small.

7.7

(Daniels, 1953) that in the region where the specific heat is proportional to $\frac{1}{T^2}$ the two contributions are additive. The calculation for the 'hyperfine' specific heat is given in Appendix II where a series expansion is derived in terms of the constants of the spin hamiltonian (eq. 1).

This gives

$$\frac{C_{\text{hyp}} T^2}{R} = 8.10 \times 10^{-4} \left(1 + \frac{4.8 \times 10^{-4}}{T} \right)$$

At 1°K the second term may be neglected.

The dipole-dipole specific heat may be derived directly from the calculation for Ce Mg Nitrate (6.6), since the two salts have the same lattice constants. As C is proportional to g^4 we multiply the value for the Cerium salt by $\left(\frac{g_{\text{Nd}}}{g_{\text{Ce}}}\right)^4 = \left(\frac{2.72}{1.84}\right)^4 = 4.8$ so that for Nd Mg Nitrate

$$\frac{C_{\text{dipole}} T^2}{R} = 3.3 \times 10^{-5}$$

Thus the total calculated specific heat is given by

$$\frac{C_{\text{calc}} T^2}{R} = 8.43 \times 10^{-4}$$

This is in very good agreement with the experimental value of 8.73×10^{-4} . The small discrepancy can be ascribed to experimental errors in measuring either the specific heat or the parameters derived from paramagnetic resonance. In any case, exchange interaction is very small.

7.8

Conclusion

It seems therefore, that the behaviour of the salt above 1°K is adequately described in terms of the hyperfine splittings and dipole-dipole interaction. No measurements have so far been made below 1°K but it seems reasonable to predict that the same theory will hold at least down to temperatures where the hyperfine splittings become comparable with kT ($\sim 0.05^{\circ}\text{K}$). As in Ce Mg Nitrate, the theory for the dipole-dipole interaction will hold down to much lower temperatures ($\sim 0.01^{\circ}\text{K}$). It would therefore be possible to use Nd Mg Nitrate as a standard magnetic substance below 1°K instead of the Cerium salt, in experiments where a specific heat about 100 times larger would be advantageous.

The salt should also prove very useful for experiments in nuclear alignment.

3. CHROMIC METHYLAMINE ALUM $\text{Cr}(\text{CH}_3\text{NH}_2)_2(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

The properties of this salt below 1°K have been investigated extensively by Gardner and Kurti (1954), and it was decided to measure the specific heat above 1°K to check their extrapolated value.

7.9

The specimen used was a 4:1 ellipsoid of compressed powder enclosed in a hollow perspex mould. It was 3.9 cm. long and weighed 2.7 gms. Measurements of the spin lattice relaxation time in a field of 470 gauss give the following results:

Table 5.

$T^{\circ}\text{K}$	$\tau_L \text{secs}$
2.14	6×10^{-3}
1.38	18×10^{-3}
1.03	28×10^{-3}

The specific heat was therefore measured at the two lower temperatures using 175 c/s. The results are shown in tables 6 and 7.

Table 6.

$f=175 \text{ c/s}$			$M_0 = 628.50 \text{ u.m.i.}$		
T	H	M	$\Delta M = M_H - M_0$	$\delta M = M - M_H$	$r = \frac{\delta M}{\Delta M}$
1.38	0	647.91	19.41	0	-
1.38	465	643.83	15.33	4.08	0.266
1.38	625	641.57	13.07	6.34	0.485
1.03	0	654.45	25.95	0	-
1.03	456	649.09	20.59	5.36	0.260
1.03	610	646.18	17.68	8.27	0.467
1.03	773	643.30	14.80	11.15	0.754

7.10

As this substance has a relatively large value of $\frac{CT^2}{\lambda}$, fields of the order of 700 gauss had to be used to measure χ_s and account had to be taken of saturation effects. The saturation correction was calculated from eq.(3.5) which gives $\alpha = 1.58 \times 10^{-8}$. The corrections to the ratio $r = \frac{\delta M}{\Delta M}$ are tabulated below.

Table 7.

H	T	$\frac{H^2}{T^2}$	r	$r' = r - \alpha \frac{H^2}{T^2}$	$\frac{H^2}{r'}$
465	1.38	1.75×10^{-3}	266×10^{-3}	264×10^{-3}	8.18×10^5
625	1.38	3.14	485	482	8.12
456	1.03	3.01	260	257	8.09
610	1.03	5.35	467	462	8.05
773	1.03	8.62	754	745	8.02
					8.09

Account also had to be taken of the effect of the demagnetizing correction as the volume susceptibility of this substance is fairly large. The value of ϕ was calculated from eq.(4.4) using the value of λ corresponding to a spin $S = 3/2$ and $g = 1.98$:

$$\lambda = 1.876 \text{ e.m.u./mole}$$

$$= 0.00632 \text{ e.m.u./cc.}$$

7.11

For a 4:1 ellipsoid θ is equal to 0.016°K . The specific heat can now be calculated from the ratio $\frac{\chi^2}{R}$ using eq.(3.8). This gives

$$\frac{\chi^2}{R} = 0.0192,$$

in excellent agreement with the value 0.0193 found by Gardner and Kurti from demagnetization experiments and also with the value 0.020 found by de Klerk and Hudson (1953).

Discussion

Extensive paramagnetic resonance work has been done on this substance by Bleaney (1950) and by Baker (unpublished). The ^4F ground state of the free Cr^{3+} ion is 'quenched' by the large cubic crystalline field so that only one orbital level is populated at normal temperatures. This level, which has a 4 fold degeneracy due to spin, is split by a trigonal field into 2 doublets which are characterized by $S_z = \pm 3/2$ and $S_z = \pm 1/2$. However, the variation of paramagnetic resonance absorption with angle showed that the simple model which ascribed the splitting solely to a trigonal distortion of the cubic field was not exact and that a rhombic component was also involved. The magnitude of the splitting in zero field was found to be 0.255°K . This splitting gives rise to a Schottky type specific heat anomaly with its maximum at

7.12

about 0.11°K , so that above 1°K only the 'tail' can be observed. It can be shown that in this region the specific heat follows the law

$$\frac{C}{R} = \frac{\delta^2}{4k^2T^2}$$

where δ is the splitting. Thus the contribution to the specific heat due to the Stark effect is

$$\frac{C_{\text{st}}T^2}{R} = 0.0163$$

(11) The contribution due to dipole-dipole interaction can be calculated from the formula of Van Vleck (1937)

$$\frac{C_T T^2}{R} = \frac{3}{2} \lambda'^2 Q \quad (1)$$

where λ' is the Curie constant per cc. and Q is a dimensionless constant depending on the lattice arrangement of the nearest neighbours (c.f. eq. 6.18). For a face centred cubic lattice, corresponding to the alum structure $Q = 14.4$. Thus

$$\frac{C_{\text{dipole}} T^2}{R} = 8.7 \times 10^{-4}$$

This gives for the total calculated specific heat

$$\frac{C_{\text{total}} T^2}{R} = 0.0171$$

7.13

It will be seen that there is a discrepancy between this value and the experimental value amounting to 12%. Three possible reasons for the 'excess' specific heat have been advanced:

(i) The resonance measurements were made at 20°K and it is possible that there might be a small change in the crystal field which would alter the splitting as the temperature is reduced. To agree with the experimental specific heat would have to be 0.27°K.

(ii) In the resonance experiments, the splitting was deduced from measurements of transitions in large magnetic fields. Any deviations of the crystal field theory from the assumed symmetry would lead to the wrong value of δ . Work is at present in progress (Baker) to find the zero field transitions more directly by using different microwave frequencies.

(iii) The interactions between the ions may not be entirely due to magnetic dipole-dipole forces and there may be a contribution from exchange. However isotropic exchange of the form $J \underline{S}_1 \cdot \underline{S}_2$ leads to a Weiss Δ , (see Chapter 4) and this was not observed, since it was found that Curie's law was obeyed accurately if allowance was made for the demagnetizing correction. Any exchange must therefore be of the anisotropic

7.14

kind. Recent examination of the line shape has shown (Baker unpublished) that this possibility can be ruled out so that the exchange interaction must be negligible.

At present there is no indication which of the other two explanations is correct and the position still needs clarifying.

4. FERRIC RUBIDIUM ALUM $\text{Fe Rb}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

Paramagnetic resonance in this salt has been investigated by Bleaney and Trenam (1952) who found that the ^6S ground state of the free Fe^{3+} ion was split into three doublets with energies corresponding to 0, 0.0026 and 0.063°K. These splittings are much smaller than in any of the other alums. Consequently the 'Stark' specific heat associated with the splittings should be very small, so that almost the entire specific heat should arise from dipole-dipole interaction. This would make the properties of the substance very interesting near its Curie point as the theory of Sauer and Temperley (1940) should then be applicable. When demagnetizing experiments were started by Gardner and Kurti with a view to investigating this region, it was found that the specific heat was much larger than expected.

7.15

They also found that the magnetization did not follow a Brillouin function even for small fields of the order of a few hundred gauss. In order to confirm the first of these findings it was decided to measure the magnetic part of the specific heat by the relaxation method.

The Measurements

Measurements were made on the same specimen as that used by Gardner and Kurti, a single crystal shaped into a cylinder 4 cm. long and 5 mm. in diameter, with its axis parallel to the (1, 1, 0) direction. In a field of about 250 gauss the following relaxation times were obtained.

Table 8.

T	τ_L
-----	----------

4.2°K 7×10^{-4} sec.

2.19 4×10^{-3}

1.35 15×10^{-3}

1.05 30×10^{-3}

It was thus possible to measure the specific heat at the two lower temperatures using 175 c/s without any extrapolation. The results are summarized in table (9).

The demagnetizing correction was calculated from eq. (4.4) assuming the specimen to be an 8:1 ellipsoid.

7.16

This gives $\Theta = 0.059^\circ\text{K}$. The Curie constant, calculated from the g values, was

$$\begin{aligned}\lambda &= 4.38 \text{ e.m.u./mole} \\ &= 0.0152 \text{ e.m.u./cc.}\end{aligned}$$

As it had been shown by Gardner that the magnetization did not follow a Brillouin function, it was necessary to investigate the saturation experimentally. This was done by Gardner and Meyer and the full results are discussed in Gardner's thesis. Using a ballistic galvanometer to measure the (differential) susceptibility in fields of up to 1400 gauss, they found that near 1°K the susceptibility could be expressed in the form

$$\chi_H = \chi_0 \left[1 - \frac{\alpha'^2 H^2}{(T - \Theta)^2} \right]$$

where α' has the value $1.2 \times 10^{-7} \pm 15\%$. If the substance had followed a Brillouin function the value of α' would have been 3.34×10^{-8} (eq. 3.5). Thus the saturation correction to the ratio $r = \frac{\delta M}{\Delta M}$ is about 4 times bigger than that calculated theoretically. However for the fields used to measure χ_s (~ 800 gauss) the correction to the final value of the specific heat only amounted to about 1%. The results are shown in Table 9.

$$1.275 \times 10^5 \text{ at } 4.35^\circ\text{K}$$

$$\text{and } 1.245 \times 10^5 \text{ at } 4.05^\circ\text{K}$$

7.17

Table 9.

T	H	$\Delta M = M - M_0$	M	$r = \frac{\delta M}{\Delta M}$	$\frac{H^2}{(T-\theta)^2}$	$r' = r - \frac{H^2}{(T-\theta)^2}$	$\frac{H^2}{r'}$
1.35	191	16.79	4.39	0.262	2.6×10^{-3}	0.259	1.42×10^5
	235	15.07	6.15	0.408	4.0	0.404	1.37
	272	13.74	7.54	0.552	5.3	0.547	1.35
	400	9.70	11.51	1.185	11.6	1.173	1.37
	511	7.22	14.00	1.94	18.8	1.92	1.36
							1.37
1.05	233	19.56	8.27	0.421	6.6×10^{-3}	0.414	1.31
	289	16.91	10.92	0.645	10.2	0.635	1.31
	330	15.10	12.72	0.843	13.2	0.830	1.31
	358	13.95	13.87	0.994	15.6	0.978	1.31
	419	11.78	16.04	1.36	21.4	1.34	1.31
	514	9.08	18.30	2.02	32.1	1.99	1.33
	785	4.75	23.03	4.85	75	4.77	1.29
	991	3.31	24.69	7.8	120	7.7	1.27
							1.30

The value of $(1 - \frac{\theta}{T})^{-3}$ at 1.35°K is 1.15, and 1.19 at 1.05°K so that

$$\frac{CT^2}{\lambda} = \frac{H^2}{r'} (1 - \frac{\theta}{T})^{-3}$$

$$= 1.575 \times 10^5 \text{ at } 1.35^\circ\text{K}$$

$$\text{and } 1.545 \times 10^5 \text{ at } 1.05^\circ\text{K}$$

7.18

Taking the average value of $\frac{CT^2}{\lambda} = 1.56 \times 10^5$, we find that

$$\frac{CT^2}{R} = 8.2 \times 10^{-3}$$

Discussion

This value of the specific heat can be compared with the value calculated for dipole-dipole interaction plus the effect of the Stark splittings. Using eq.(1) we get for the dipole-dipole contribution

$$\frac{C_{\text{dipole}}T^2}{R} = 4.98 \times 10^{-3}$$

The contribution to the specific heat from the Stark splittings has been given by Bleaney and Trenam as

$$\frac{C_{\text{stark}}T^2}{R} = 8.58 \times 10^{-4}$$

Thus the total calculated value of $\frac{CT^2}{R}$ is

$$\frac{C_{\text{calc}}T^2}{R} = 5.84 \times 10^{-3}$$

Comparing this with our measured value 8.2×10^{-3} we see that there is a discrepancy of 25%.

An estimate of the magnetic specific heat has also been made by Gardner from his demagnetization results by analysing the total specific heat into a $\frac{1}{12}$ part, corresponding to

the tail of the Stark and interaction anomalies, and a "non magnetic" contribution C_N . After correcting for the effect of saturation, he found that

$$\frac{C}{R} = \frac{10.0 \times 10^{-3}}{T^2} + C_N$$

An attempt to fit the non magnetic part to a Debye function has so far proved unsuccessful, and it may be that a simple analysis of the specific heat cannot be made in this case. The discrepancy between his value and ours cannot be explained but it must be pointed out that the relaxation method measures only the spin dependent part of the specific heat while demagnetization measurements involve the lattice as well. In any case the discrepancy between Gardner's value and the theoretical value is even greater than ours.

Two possible explanations of the 'excess' specific heat have been suggested: One is that there is a large exchange interaction between the ions. However, direct (isotropic) exchange is unlikely as no Weiss Δ was observed and also as the ions are very far apart. Hence a large amount of anisotropic indirect exchange would have to be involved. The second, and much more likely cause of the discrepancy is that the splittings in the concentrated salt are different from those in the diluted salt in which the

7.20

resonance measurements were made. In order to reduce the line width due to spin-spin interaction, Bleaney and Trenam found it necessary to use crystals containing only very small quantities of the ferric alum diluted in several hundred parts of the isomorphous aluminium salt. It does not seem at all unlikely that the crystalline field acting on the Fe^{3+} ions should have been slightly different from that in the concentrated salt, particularly in view of the fact that the splittings are only caused by distortions of the field from cubic symmetry. (A field of true cubic symmetry affects an S state only in a very high order of perturbation (Van Vleck and Penney, 1934)). A subsequent examination of the unresolved line shape in the concentrated salt indicated that this explanation is probably correct.

However the anomalous variation of magnetization with field as well as the discrepancy between the relaxation and demagnetization measurements of $\frac{CT^2}{R}$ have yet to be explained.

5. SUMMARY OF PART II.

We conclude this part with a table of results showing the specific heats and also the slopes of the calibration curves of M against $\frac{1}{T}$ (or $\frac{1}{T-\theta}$ where there is an appreciable demagnetizing correction). For a substance with known g values it is possible to deduce the constant of proportionality between the Curie constant and the change of mutual inductance of the measuring coil, since from equation 2.1

$$\lambda = C(M_{\frac{1}{T}=1} - M_0) = C \cdot \text{Slope}$$

and hence

$$\begin{aligned} \text{Slope (uni)} &= \left[\frac{1}{C} \frac{Ng^2}{3k} \right] g^2 J(J+1) \frac{m}{M} f \\ &= A g^2 J(J+1) \frac{m}{M} f \end{aligned} \quad (2)$$

where m is the mass of the specimen, M the gram ionic mass and f is a function of the size of the specimen which allows for the fact that not all the flux passes through the secondary. For a very short specimen $f = 1$ (see Appendix I).

Two measurements have been included in table 10 which have not been referred to above. One was a measurement on determination of λ . This was on a specimen enclosed in an

7.22

a specimen of manganous ammonium sulphate, the purpose of which was to establish the constant A to greater accuracy by using a substance with a large susceptibility. The specimen which was freshly recrystallized, was contained in a standard cylindrical perspex container 3.65cm. long. The demagnetizing correction was calculated on the assumption that the cylinder approximated to a 3:1 ellipsoid giving the value $\Theta = 0.029^\circ\text{K}$. It will be seen from the table that the value of A deduced is in good agreement with the mean of all the other experiments.

The other experiment was an attempt to measure the specific heat of Ferric methylvamine alum. In this substance the splittings of the ^6S ground state are very large (Bleaney and Trenam, 1954) and the calculated value of $\frac{CT^2}{R}$ at 1°K is about 0.4. This is 50 times larger than the value for the rubidium salt. It was found, however, that $\frac{CT^2}{\lambda}$ was too big to be measured by the relaxation method as such large fields had to be applied to measure χ_s that the saturation correction became comparable with the ratio $\frac{\delta M}{\Delta M}$. In view of the uncertainty of the correction it was decided to postpone further measurements until an experimental investigation of the saturation curve had been made.

However, the experiment was useful in providing another determination of A , this time on a specimen enclosed in an

7.23

ellipsoidal container for which θ can be calculated accurately (0.025°K). A calculation was also made to estimate the effect of the large crystalline splittings on the susceptibility, but it was found that down to 1°K the effect was less than 1% and could therefore be neglected.

The results of all the experiments are collected in Table 10. It will be seen that the average value of $A = 363 \pm 10$ so that for any substance for which the g values are not known, the Curie constant can now be calculated from eq.(2) using the experimentally determined slope.

Table 10

Substance	$\bar{g}$	Mass m, gms	Length (cm)	f	Slope (exp u.m.l.)	Slope/mole $\times f$	A	$\frac{C_A^2}{R}$
$Ce_2Mg_3(NO_3)_{12} \cdot 24H_2O$	1.84	$4.95^{\frac{1}{2}}$	4.2	1.17	$4.86 \pm 0.07^{\frac{1}{2}}$	893	352	7.5×10^{-6}
$Ce_2Zn_3(NO_3)_{12} \cdot 24H_2O$	1.84	$7.97^{\frac{1}{2}}$	3.55	1.12	$8.08 \pm 0.07^{\frac{1}{2}}$	943	372	6.4×10^{-6}
$Nd_2Mg_3(NO_3)_{12} \cdot 24H_2O$	2.72	$4.00^{\frac{1}{2}}$	2.5	1.07	$9.90 \pm 0.07^{\frac{1}{2}}$	2042	369	8.73×10^{-4}
$Pr(CH_3NH_3)_2(SO_4)_2 \cdot 12H_2O$	1.98	2.70	3.9	$1.09^{\frac{1}{2}}$	26.4	5200	359	1.92×10^{-2}
$Pr(CH_3NH_3)_2(SO_4)_2 \cdot 12H_2O$	2.00	1.72	3.9	$1.09^{\frac{1}{2}}$	40.2	1270	363	0.4 (too large to measure)
$Prb(SO_4)_2 \cdot 12H_2O$	2.00	1.40	4.0	1.165	27.8	1273	364	8.2×10^{-3}
$Mn(NH_4SO_4)_2 \cdot 6H_2O$	2.00	5.55	3.65	1.13	158.8	1260	359	not measured

$\frac{1}{2}$ 0.07 u.m.l. to allow for paramagnetism of the glass cryostat

$\frac{1}{2}$ These masses have been corrected for 2.3% inclusion of water deduced from the density measurements (page 6.9)

$\times$ 4:1 ellipsoid container.

PART III

CHAPTER 8.

A NEW METHOD OF DETERMINING A RELATION BETWEEN
'MAGNETIC' AND ABSOLUTE TEMPERATURES BELOW 1°K.

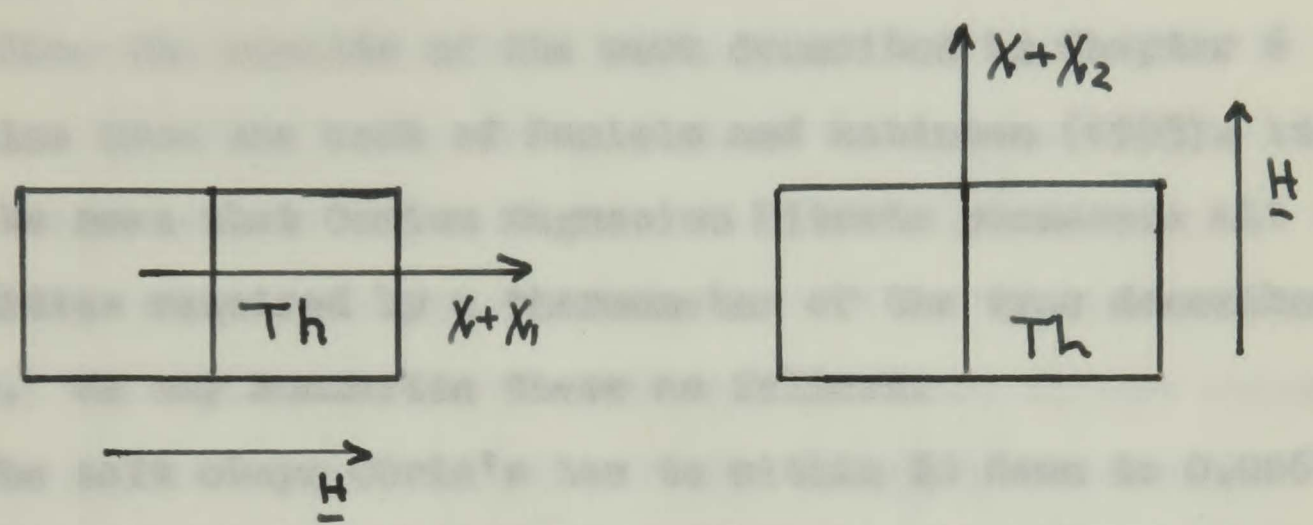
1. Introduction

At temperatures reached by adiabatic demagnetisation, we define a magnetic scale of temperature T^* by extrapolating Curie's law, $\chi = \frac{\lambda}{T^*}$, using measurements made in the range 4°K to 1°K to calculate λ (see Chapter 4). However, as we have seen in Chapter 1 Curie's law does not hold accurately at very low temperatures for most substances used, especially those with a large specific heat. We therefore require to find the variation of χ with absolute temperature so that T^* can be corrected to T . One method of measuring T is to use a thermometer substance which is known to obey Curie's law in the temperature range required, when T can be deduced from measurement of its susceptibility. The problem is then one of measuring simultaneously the susceptibilities for two salts in thermal contact.

Consider the case of a composite specimen consisting of two substances one of which has an isotropic susceptibility

8.2

while the other, the thermometer, is a single crystal having a susceptibility χ_1 in one direction and χ_2 in a perpendicular direction.



Measurements on the composite specimen in these two directions give $(\chi + \chi_1)$ and $(\chi + \chi_2)$. If χ_1 and χ_2 are known to obey Curie's law the variation of χ with temperature can be deduced. The problem is particularly simple if χ_2 negligibly small.

However, the magnetic moments of the two substances will be additive only to a first approximation, and at low temperatures, where the susceptibilities become large, demagnetizing corrections must be applied. The potential problem of a composite specimen can be solved most simply for the case of an anisotropic sphere surrounded by a concentric isotropic spherical shell (see Appendix III). If the thermometer salt has a small thermal capacity, as all salts obeying Curie's law will, such an arrangement has the further advantage of being a specimen consisting of a single crystal sphere of the substance under investigation.

of providing a guard ring of large heat capacity for the thermometer and ensuring optimum conditions for thermal contact.

From the results of the work described in Chapter 6 and also from the work of Daniels and Robinson (1953), it will be seen that Cerium Magnesium Nitrate possesses all the properties required by a thermometer of the type described above. We may summarize these as follows:

- 1) The salt obeys Curie's law to within 2% down to 0.006°K.
- 2) The susceptibility parallel to the crystalline axis is very much smaller than that perpendicular to the axis

$$\chi_{\perp} : \chi_{\parallel} \approx 50:1.$$

- 3) The specific heat below 1°K is very small

$$C = \frac{0.8}{T^2} \text{ ergs/}^{\circ}\text{K/gm.}, \quad (1)$$

This has the advantage of ensuring a short response time in spite of poor thermal contact at low temperatures.

The main problems in devising such a method of measuring temperatures are as follows:

- 1) Constructing a system of mutual inductance coils to measure susceptibilities in two directions at right angles.
- 2) Making a specimen consisting of a single crystal sphere of Cerium Magnesium Nitrate surrounded by a concentric shell of the substance under investigation.

8.4

3) Making good thermal contact between the substances since after demagnetization they may be at very different temperatures.

The advantage of such a thermometer is that, once a specimen has been made, the variation of susceptibility with temperature can be measured from the lowest temperature attainable with that substance up to 4°K in one demagnetization, so that the entire T - T^* relation can be found in one experiment. This is a great improvement over the thermodynamic method of determining absolute temperatures which requires a large number of demagnetizations. ^{T_c} method. is particularly useful in the Curie point region where the susceptibility of the salt itself becomes practically temperature independent.

2. The design and construction of a coil to measure susceptibility in two directions at right angles.

We have seen in Chapter 2 that the susceptibility of a specimen can be measured very conveniently in terms of the mutual inductance of a pair of coils surrounding the specimen. The main problem in designing a coil to measure in two directions at right angles is one of space, since the whole measuring system must be accommodated in a dewar vessel and placed between the poles of a magnet. A simple extension of

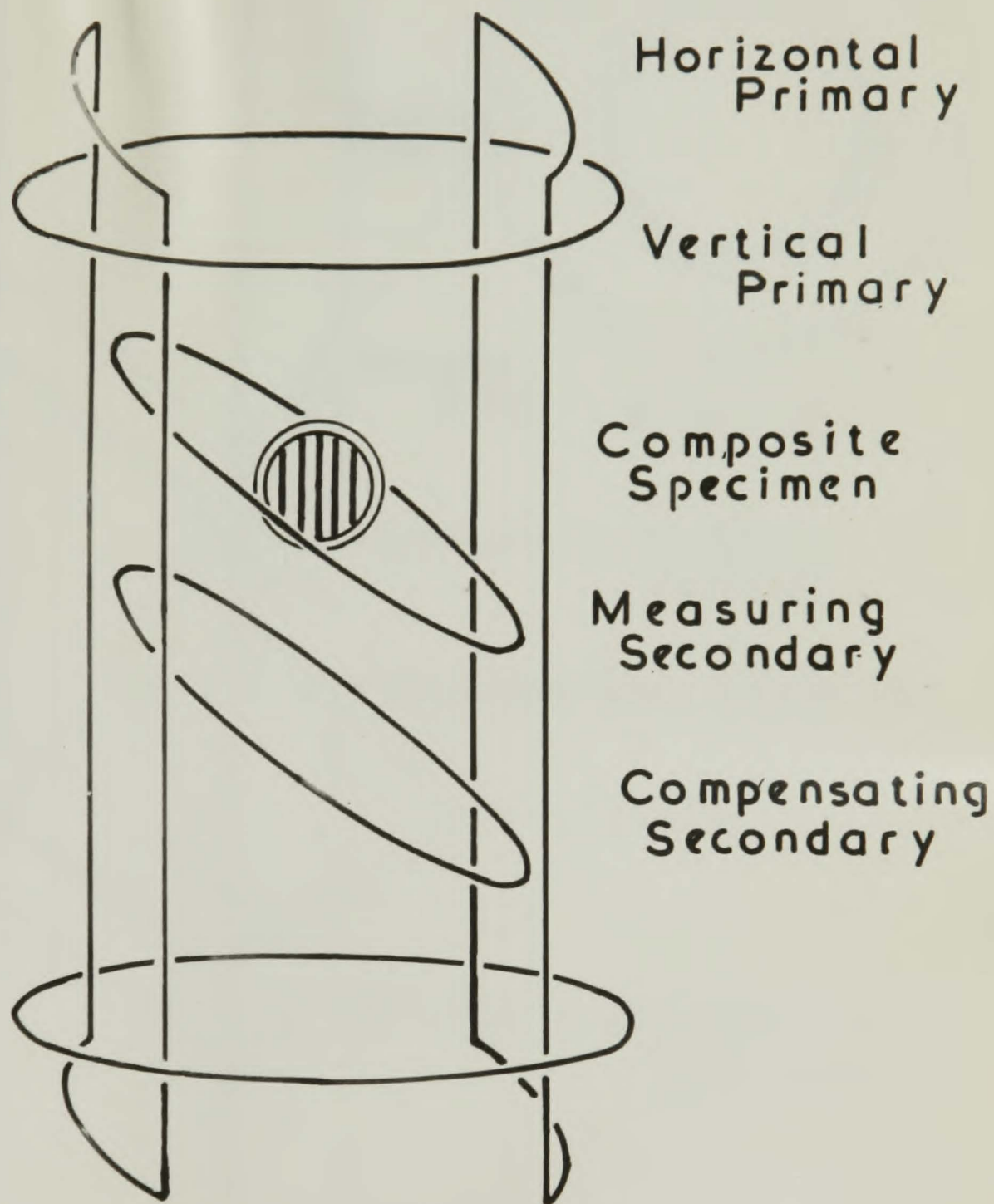
8.5

the conventional arrangement of coaxial solenoids was thus ruled out. However a much less bulky arrangement can be designed since the coils can be wound in any shape and also it can be shown from first principles that a single secondary wound at an angle to two primaries at right angles is sufficient.

Let us consider an anisotropic paramagnetic specimen in a magnetic field H due to the primary of a mutual inductance coil. If the field is parallel to one of the principal axes of susceptibility, then the magnetic moment induced in the specimen, $\underline{h}$, will be parallel to H and proportional to the corresponding principal susceptibility. If we now surround the specimen by any secondary coil and vary H , then the change of flux through the secondary due to the specimen will be proportional to the change of $\underline{h}$ and hence to the principal susceptibility in the direction of H . Further, if a second primary is used to produce a variable field along one of the other principal axes, the principal susceptibility in this direction can be measured from the change of flux through the same secondary. The two constants of proportionality between susceptibility and flux will depend only on geometrical factors and can be found using an isotropic specimen of known susceptibility.

Two experimental arrangements were tried: In the first the inductance of the empty coil was backed off by an external compensator cooled in liquid Oxygen. The small changes due to the specimen were then measured on the Hartshorn bridge. However, this arrangement proved unsatisfactory due to insufficient stability in the compensator and it was therefore decided to construct a second coil compensated internally as for normal demagnetization experiments (see Chapter 4). The construction of this coil is shown in figs. 16, 17 and 18.

The secondary consisted of two identical halves connected in antiphase, each wound with 3800 turns of 38 s.w.g. enamelled silk covered wire in two channels 7 cm. apart. Each channel was 2 cm. wide and was divided in the middle by a thin spacer to reduce self capacity. To wind the secondary, two steel rods were screwed into the former at an angle of 35° to the axis of the coil, exactly at right angles to the channels, and held between the centres of a lathe. As the two parts of the secondary were elliptical, there was a variation in winding speed which was allowed for by feeding the wire from an automatic tensioning device. Bakelite varnish was applied after each layer to hold the wires in place. When the coil was finished the varnish was carefully dried out at 80°C for



Schematic Diagram of
CROSSED COILS SYSTEM.

FIG. 16

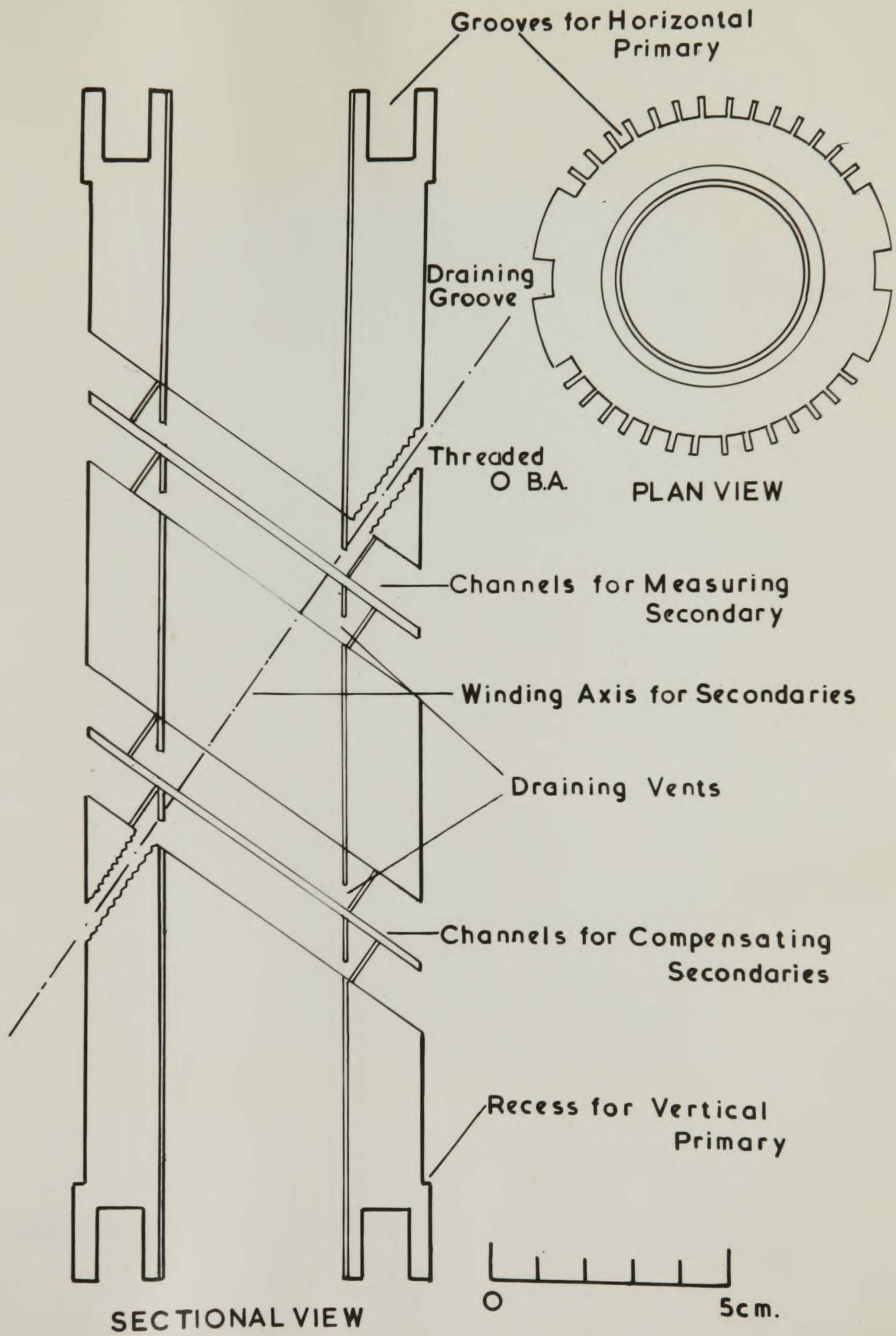


FIG 17

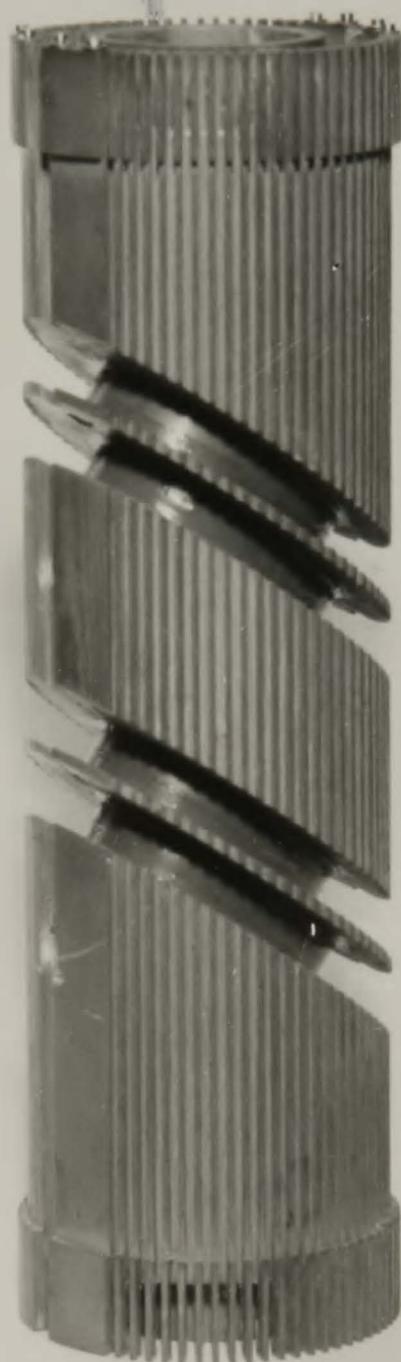


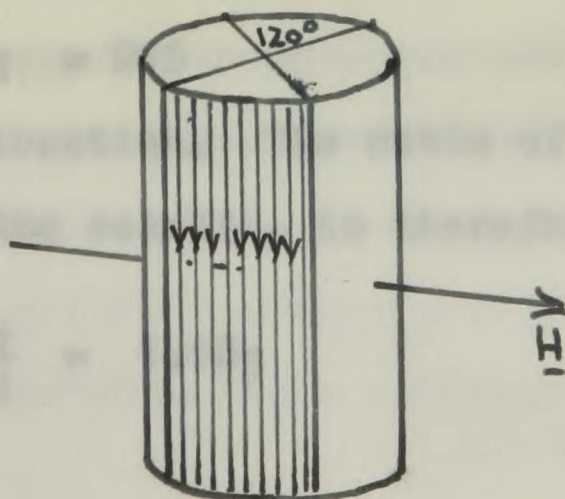
Fig. 18 The Crossed Coil Mutual Inductance Former.

8.7

several hours to remove the solvent and was then polymerized at 140°C for 1 hour. The ends of the wires were brought out to terminal blocks consisting of small brass screws.

The primary was also wound in two parts: one to provide a field perpendicular to the axis of the coil (the horizontal field), the other to provide a field along the axis (the vertical field).

The primary for the horizontal field was wound in grooves running along the length of the coil distributed over the surface of the former in such a way that the uniformity at the centre was a maximum. It can be shown by extending the calculation for a Helmholtz coil, that the condition for this is satisfied by a uniform current distribution over the curved surface of the coil subtending an angle of 120° at the axis, plus a similar distribution flowing in the other direction on the opposite side of the coil.



In practice the uniform current distribution was achieved by winding 30 turns of 32 s.w.g. wire in each of 15 slots 2 mm. wide and 1 mm. apart producing a field at the centre of 69 gauss/amp. The winding was done by hand.

The primary for the vertical field consisted of a double layer solenoid of 34 s.w.g. wire. This was wound on top of the other primary, a piece of X-ray film being placed between the two to facilitate smooth winding. The field produced at the centre was 63 gauss/amp.

The constants relating mutual inductance to susceptibility were found by calibrating in the helium range, using a sphere of powdered potassium chrome alum. In the notation of section 7.5

$$\text{Slope} = \left[\Delta M \right]_{\frac{1}{T}=0}^{\frac{1}{T}=1} = AS(S+1)g^2 \frac{M}{H}$$

whence the values for A were found to be

$$A_V = 223$$

for the vertical direction, and

$$A_H = 205$$

for the horizontal direction. The ratio of the sensitivities, needed to calculate the results, is therefore

$$\frac{A_V}{A_H} = 1.085 \quad (2)$$

8.9

The error in this ratio is about 2% but as it affects the final answer only to a second order, this is negligible.

By demagnetizing the same sphere of chrome alum it was possible to investigate the accuracy with which temperatures can be measured with this coil below 1°K. For an isotropic sphere, the values of T^* deduced by extrapolating a plot of M against $\frac{1}{T}$ in the helium range should be very accurately the same, for a given temperature of the sphere, whichever of the primaries is used. The following values were obtained by taking alternate readings to find the simultaneous values of M at different temperatures:

T^*_V	T^*_H
0.1285	0.129
0.130	0.131
0.1615	0.163
0.2395	0.240
0.351	0.352

We thus see that, as regards sensitivity and stability of the system, deviations in the T - T^* relation of the order of 0.001°K can be measured.

8.10

3. The specimens

As explained in the introduction, the most convenient form of specimen is one consisting of a single crystal sphere of the anisotropic thermometer substance surrounded by a shell of the isotropic substance under investigation. The thickness of the shell was chosen so that the magnetic moments of the shell and sphere were roughly equal and was determined by the relative volume susceptibilities of the two substances. As Ce Mg Nitrate has a rather small susceptibility ($S = \frac{1}{2}$ $g_1 = 1.84$) this implies, for most substances, very thin shells of the order of 1 mm. thick. Two different techniques were evolved for making the concentric spheres according as a single crystal or compressed powder was used for the shell. For both types of specimen the inner sphere of Ce Mg Nitrate was made in the same way: The flat face (perpendicular to the trigonal axis) of a piece of single crystal of Ce Mg Nitrate was glued with Araldite (101) to a piece of paper and this in turn was glued with Durofix to the end of a cylindrical wooden mandrel. In this way the crystal could be turned in a lathe and shaped into a hemisphere using sandpaper, and could then be detached from the mandrel by cleaving the piece of paper with a razor blade. However, for making

8.11

a specimen with a single crystal shell this last operation was deferred. First a hemispherical hole was cut into a piece of the outer crystal attached to another wooden mandrel as described above. The cutter used for making the hole was a simple steel disc of the required size machined flat on one face and backed off at 5° to provide a cutting edge. It was attached to a brass holder which was gripped in the tailstock of the lathe. No lubricant was used for cutting. The operation of cutting a hole took about 2 hours and even then the crystal frequently broke on account of flaws, and for this reason later experiments used shells of compressed powder. The Ce Mg Nitrate hemisphere, still attached to its mandrel was then glued into the hole using Araldite, care being taken to ensure that the axis of the mandrel, (and hence the crystal) was exactly perpendicular to the equatorial plane of the hole. When the glue had set the mandrel was put back into the lathe and the outer crystal shaped away using sandpaper until a thin shell remained. In this way it was possible to make extremely thin shells (~ 0.7 mm-thick) out of single crystals, which were exactly concentric with the inner hemisphere. Two such compound hemispheres were made and glued together with araldite. The line of the join clearly

8.12

defined the plane of the Cerium crystals and hence the axis of low susceptibility. The respective masses of shell and sphere were deduced from weighings made at the different stages of the process.

In view of the difficulties of machining single crystals, it was decided to use compressed powder for the outer shell and the following technique was evolved:

A piece of perspex was turned down in a lathe till its diameter was about 2 mm. greater than the outside of the shell and a hemispherical hole cut into one end using a steel disc similar to the one described above. The diameter of the hole, which was always about 0.5 mm. bigger than that of the cutter, was made equal to that of the outside of the shell. The hole was then packed with some very finely crushed powder of the substance out of which it was desired to make the shell, using a hydraulic ram to provide pressures of up to 6 tons/sq. inch. The perspex "cup" was then put back into the lathe and a hole corresponding to the size of the Cerium sphere turned out of the powder using a second steel cutter. Due to the uniform nature of the compressed powder and the absence of flaws this proved to be considerably easier than for a single crystal. One of the Cerium hemispheres, detached from its mandrel, was then

8.13

gently pressed into the hole using Apiezon J oil to fill any small gaps. It was found that this made good thermal contact between the shell and the sphere down to at least 0.1°K (see below). Two such composite hemispheres were made and joined together using chloroform to seal the perspex. The advantage of having the specimen totally enclosed in perspex is that the masses of the salts will remain constant with time so that the calibration slopes for different experiments can be compared. The method also avoids the use of any glue except for sealing the perspex, so that chemical decomposition of the specimens is far less likely. It was found that the perspex did not influence the heat transfer between the specimen and the cryostat, and it seems that it would be very good practice in all demagnetization experiments on powdered samples to use similar plastic moulds to protect the specimens.

For the preliminary experiments chrome alum was used for the shell, but for the first quantitative experiments it was decided to use manganous ammonium sulphate for which the deviations from Curie's law are large and have already been determined by the standard γ ray method (Cooke, 1949). The volume susceptibility of this salt is about 24 times that of Ce Mg Nitrate, so that for the magnetic moment of the shell

8.14

and sphere to be comparable only a small amount had to be used. To avoid the difficulties of making a shell 0.2 mm. thick, the manganese salt was mixed with exactly two parts of diamagnetic zinc sulphate to act as filler, making it possible to work with volumes 3 times as big. The salts were both made from Analar chemicals and were freshly recrystallized before being finely crushed and mixed. To avoid dehydration of the finely divided powder it was compressed into the perspex mould immediately after crushing. The dimensions of the specimen were as follows -

Radius of Ce Mg Nitrate sphere, R_1	= 8.0 mm.
Mass of Ce Mg Nitrate sphere, R_1	= 4.39 gms.
Mass of Mn + Zn shell	= 0.61 gms.
Mass of Mn ammonium sulphate	= 0.203 gms.
Effective outer radius of shell, R_2	= 0.4 mm.
Hence, $\left(\frac{R_1}{R_2}\right)^3 = n$	= 0.87

The effective outer radius was deduced from the thickness of the shell which was calculated from the mass and the density. The ratio $\left(\frac{R_1}{R_2}\right)^3$ is needed in some of the calculations of correction factors given in Appendix III.

4. Thermal Contact

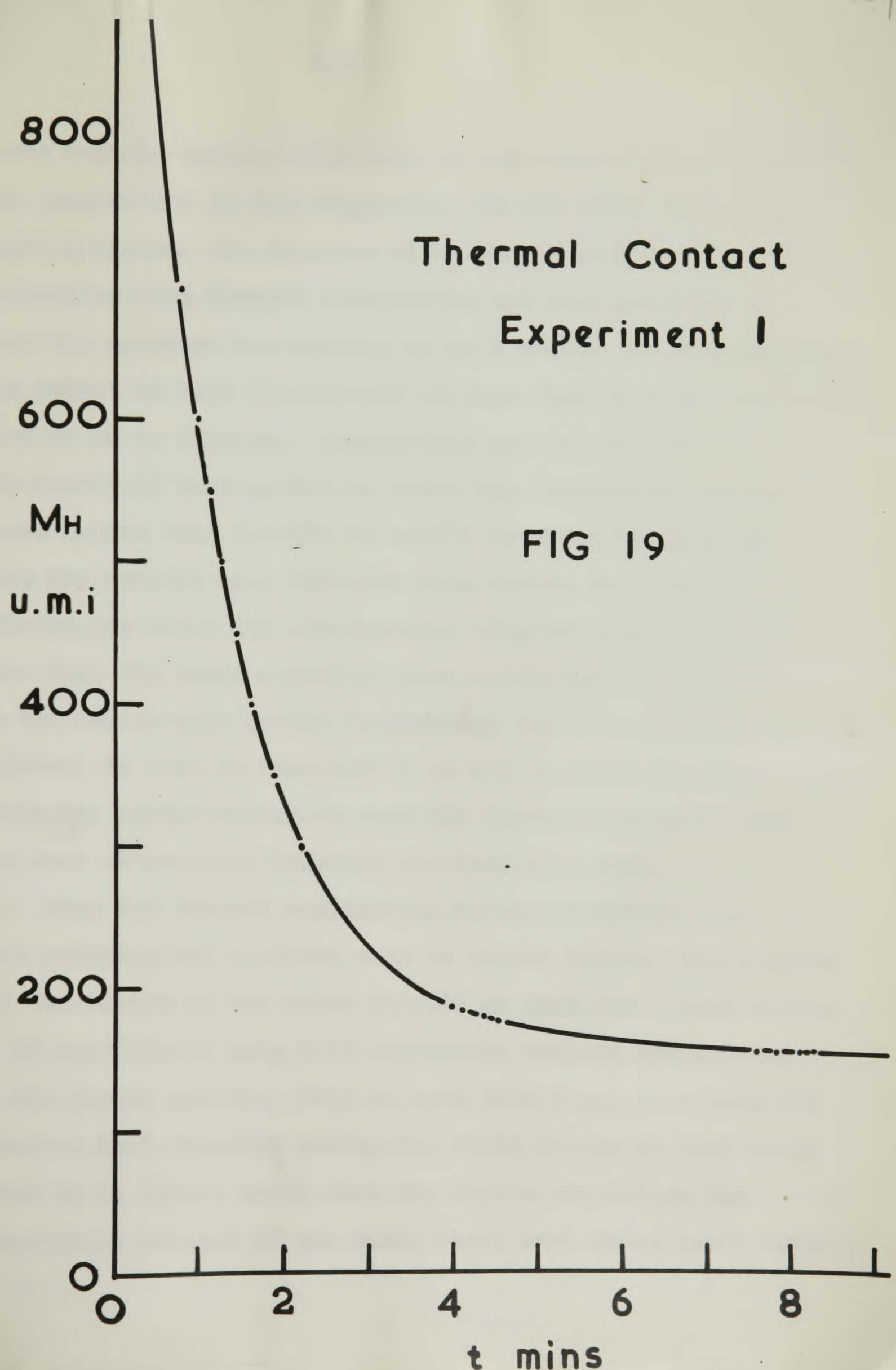
The thermal contact between the shell and the inner sphere was investigated in the following experiment: The composite specimen with an outer shell of Chrome alum, was demagnetized from a field of about 7 K gauss applied along the direction of large susceptibility of the Cerium salt. This cooled the inner sphere to about 0.006°K and the surrounding Chrome alum to about 0.16°K. The M value was read on the Hartshorn bridge as soon after demagnetizing as possible and plotted as a function of time. A typical result is shown in fig. 19.

In the temperature region where the effect of the two salts is approximately additive ($T > 0.1^\circ\text{K}$, see Appendix III) the value of mutual inductance for the direction of maximum susceptibility is given by

$$M_H = M_0 + \frac{\alpha_{ce}}{T_{ce}} + \frac{\alpha_{cr}}{T_{cr}} \quad (3)$$

where the constant α_{ce} and α_{cr} are approximately equal (see p. 8.9). Since the Cerium is cooled to such a low temperature its initial effect on M, through the second term in eq.(1), is very much greater than that of the manganese (in the ratio 0.16:0.006). Hence, as can be seen from fig. 19, the initial of M_H is very large and





Thermal Contact
Experiment I

FIG 19

8.16

grows rapidly smaller with time as the Cerium warms up to the temperature of the Manganese. It was found that after about 4 minutes the decrease of M_H became very much slower, indicating that thermal equilibrium had been reached and that the specimen was warming up as a whole. We can estimate the amount of heat transferred in this time from the specific heat of Ce Mg Nitrate. Integrating eq. (1) we find that the amount of heat needed to raise the temperature of the inner sphere from 0.006°K to 0.16°K is about 500 ergs so that the average heat transfer rate during the first four minutes was about 125 ergs/minute. Similar calculations show that the total amount of heat which must be supplied to the Cerium spin system (neglecting the effect of the lattice) to warm it from 0.16°K to 1°K is about 20 ergs while the amount needed to warm the Chrome alum shell over the same temperature interval is about 8000 ergs.

Thus for thermal equilibrium to be maintained, any heat reaching the specimen must be shared between the outside and the inside in the ratio 8000:20 so that for a heat influx of 40 ergs/minute only $1/10$ erg/minute must be transferred to the Cerium sphere. This is some 1000 times less than the observed heat transfer during the first minute so that there seems to be little doubt that the Cerium can follow the temperature changes of the outer shell down to at least 0.16°K .

236

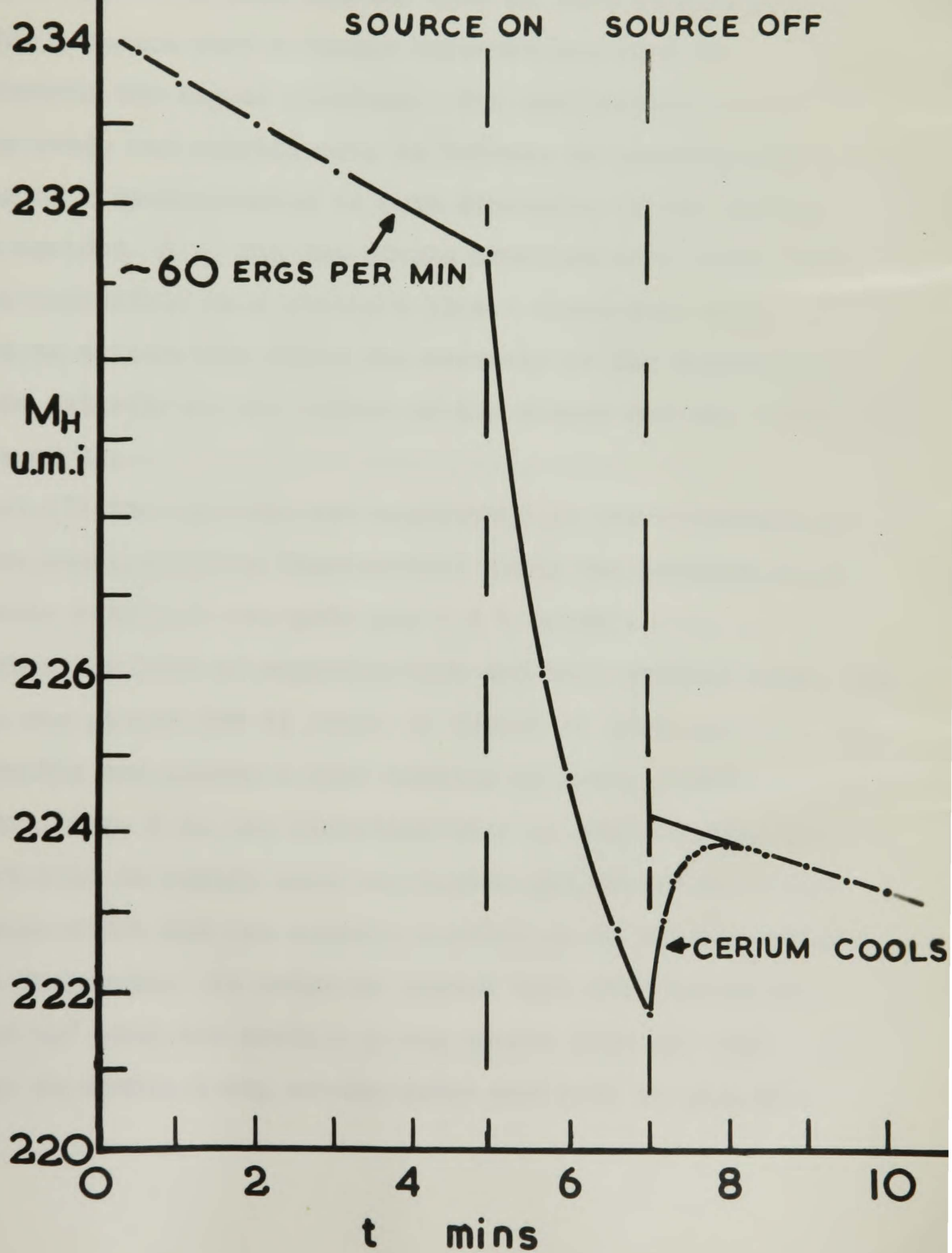
In order to check this conclusion a second experiment was performed: The specimen was heated with γ rays from a 250 millicurie source for a period of 2 minutes and the change of M was observed during and after the heating. The direction of measurement was Ce + Cr as before. The absorption of γ rays is roughly the same for both the Chromium and Cerium salts while the specific heats are in the ratio 2000:1. Thus if there were poor heat transfer, the inner sphere would be raised in temperature far above the outer shell. On removing the γ ray source the inner sphere would then cool to the temperature of the shell at a rate depending on the heat contact. The result of the experiment is shown in fig. 20. By extrapolating the final drift-rate back to the time the source was removed, it was possible to calculate that the inner sphere had been raised only about 0.032°K above the shell at 0.2°K , inspite of the fact that the γ rays supplied to it about 300 ergs, more than 20 times the amount needed to raise its temperature to 1°K .

The specimen used for this experiment was made with araldite between the sphere and shell. When the experiment was repeated with a new specimen in which Apiezon oil had been used to make thermal contact it was found that the equilibrium time was even shorter and it seems therefore that down to at least 0.1°K the problem of heat contact has been solved.

t mins

FIG 20.

Thermal Contact Experiment 2



5. The Measurements

The apparatus used was the same as that described in Chapter 4 except that a larger cryostat was used to accommodate the bigger specimen. The calibration in the helium range was carried out, as before, by plotting the values of M corresponding to each direction of the primary field against $\frac{1}{T}$. The two graphs obtained were each found to lie accurately on a straight line. Great care was needed in calibrating since the accuracy of the experiment depends entirely on the values of the slopes and the respective values of M_0 .

At 1°K the specimen was magnetized in the direction of maximum susceptibility (horizontal) using the largest field available with a 10 cm. pole gap (9 K gauss).

When the heat of magnetization had been carried away, the I.V.C. was pumped for $1\frac{1}{2}$ hours to remove as much exchange gas as possible and ensure a slow heating up rate. After demagnetizing, M in the direction $Mn + Ce$ was observed for a short time to verify that the Cerium had cooled to a very low temperature and was rapidly warming up to the temperature of the Manganese. In order to ensure that the inside had "caught up" with the shell, a γ ray source (250 mCi) was brought to within 5 cm. of the dewar and left in position

8.19

for 30 seconds. This raised the temperature of the Cerium above that of the shell as described in section 4, so that after one further minute complete thermal equilibrium between the sphere and shell can be considered to have been established. Alternate values of M were then taken every 30 seconds for the next 30 minutes. During this time the values of M in both directions remained almost constant indicating that the manganese was near its Curie point. In order to warm up the specimen more quickly than through the natural heat leak, the γ ray source was then brought back and the specimen heated for about 30 seconds. After allowing 1 minute to ensure thermal equilibrium, alternate readings of M (vertical) and M (horizontal) were again taken every 30 seconds, and the simultaneous values found by interpolation. This procedure was repeated until the specimen reached 1°K .

While the specimen was at low temperatures, the primary currents were reduced to as small a value as possible to avoid heating of the specimen by hysteresis near the Curie point. It was found possible to use currents of the order of 10 ma (corresponding to 0.7 gauss) and still read M to within 0.1 u.m.i. When the specimen was at about 0.7°K the I.V.C. was connected to the pumping system to remove exchange

gas which is desorbed at higher temperatures. If this is not done, the heating up rate increases very rapidly as 1°K is approached and it becomes very difficult to take accurate readings. These are very important in this region since it is essential to verify that near 1°K $T = T^*$ to check that the correct extrapolation of the calibration curves has been made.

6. Calculation of the Results

The results can be expressed most directly by plotting M (vertical) against M (horizontal) since these are approximately proportional to χ (manganese) and $\chi(\text{Mn}) + \chi(\text{Ce})$. In the range in which both substances obey Curie's law this gives a straight line which could be extrapolated to lower temperatures and compared with the experimental points obtained. Deviations from this line below 1°K indicate a deviation from Curie's law. In order to get a quantitative measure of the deviations it is necessary to proceed numerically and to apply various corrections which we have so far neglected. The steps in the calculation of a $T = T^*$ relation from the simultaneous values of M_V and M_H may be summarized as follows:

From the calibration curves in the helium range we find either graphically or by least squares the values of

8.21

$(M_0)_V$, $(M_0)_H$, $(\text{slope})_V$ and $(\text{slope})_H$. The slopes can be compared with those calculated from the masses of Mn and Ce, using the constants given on page 8.8. It was found that the differences were never greater than about 2%. Any small error may be ascribed to a slight tilt of the specimen. This can be allowed for but as it affects the final answer only to a second order it can usually be neglected.

We can now subtract the appropriate value of M_0 from the readings of M in each direction and obtain the changes in M , ΔM_V and ΔM_H , which are proportional to the susceptibilities in arbitrary units. In order to bring both sets of ΔM to the same units we multiply the values of ΔM_V by $\frac{\Delta H}{\Delta V} = \frac{1}{1.085}$ (see p. 8.8).

ΔM_V represents the effect of the manganese shell plus a small effect from the parallel susceptibility of the Cerium. The latter can be calculated to sufficient accuracy from the mass of the inner sphere and the value of g_u , and was found to be 1.6% of the total magnetic moment in the vertical direction. Thus in units of ΔM_H

$$\begin{aligned}\Delta M(\text{shell}) &= \left(1 - \frac{1.6}{100}\right) \cdot \frac{1}{1.085} \cdot \Delta M_V \\ &= 0.9 \Delta M_V \\ &= 0.9 (M_V - M_{0V}).\end{aligned}$$

8.22

ΔM (shell) is proportional to the magnetic moment of the shell of manganese. It can be related to the magnetic moment of a sphere of the same volume by means of a simple magnetostatic calculation. This is given in Appendix III. It is found that in the helium range the correction is negligible but that at 0.15°K the magnetic moment of the shell is about 4% larger than that of a sphere. Using the general formula the values of $\Delta M_{Mn}(\text{shell})$ can thus be corrected to $\Delta M_{Mn}(\text{sphere})$ and the values of $T^{\otimes}$ deduced.

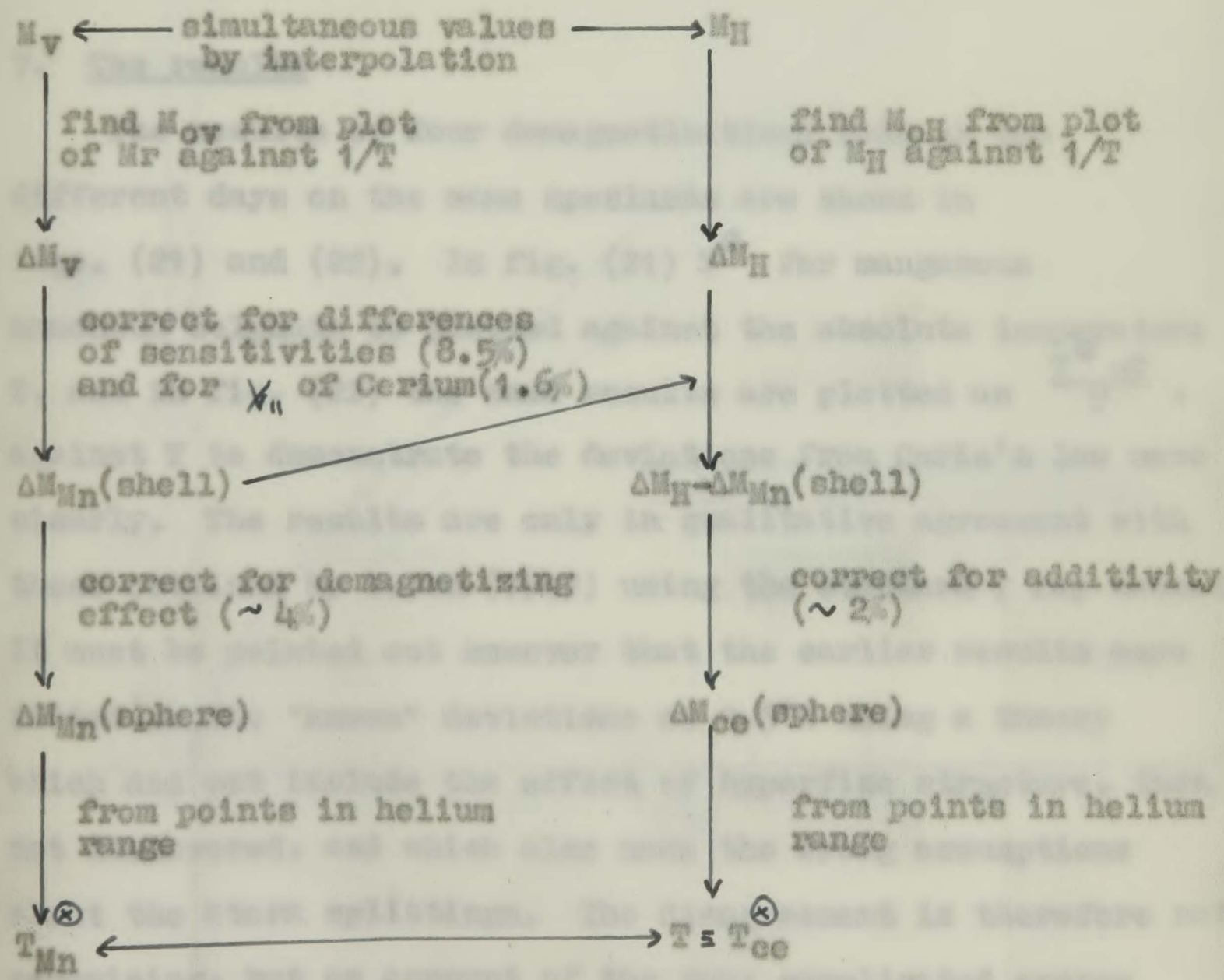
In order to calculate the corresponding values of the absolute temperature we must find the magnetic moment of the sphere of Cerium Magnesium Nitrate. To a first order this is proportional to $\Delta M_H - \Delta M(\text{shell})$. However at low temperatures the magnetic moment of the compound specimen is not exactly equal to the sum of the moments of the two components and we must take account of the interaction between them by means of an "additivity" correction. This is given in section 4 of Appendix III. It is shown that the magnetic moment of the shell plus the magnetic moment of the sphere of Ce Mg Nitrate is greater than the compound specimen and an expression for the percentage difference is derived. However the effect is small (3% at 0.1°K) and can be neglected at all but the lowest temperatures.

8.23

The values of ΔM_{ce} for an isolated sphere of Ce Mg Nitrate can now be calculated from the values of $\Delta M_H - \Delta M(\text{shell})$ and the absolute temperature deduced from the formula

$$\Delta M_{ce}(\text{sphere}) = \frac{[\Delta M_{ce}]_{\frac{1}{T}=0}}{T}$$

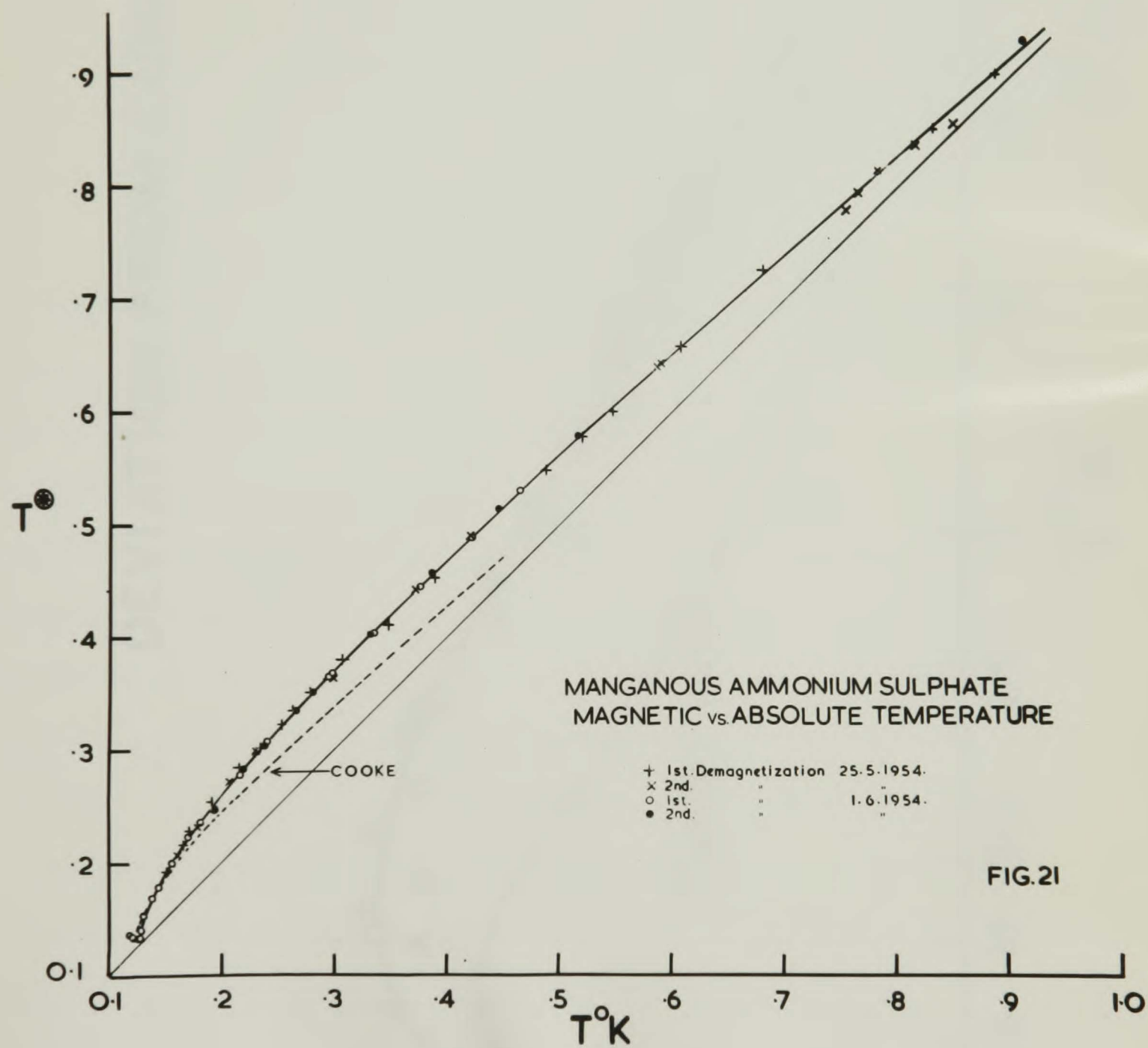
which holds to within 2% down to a temperature of 0.006°K. To make this sequence of calculations somewhat clearer, we may represent it diagrammatically as follows:



It must be pointed out that, although the calculation of the results is performed in several stages, all the "correction" factors arise from classical magneto-static considerations, so that there is no question of finding the results by successive approximations. Since the corrections are all very small it is simply more convenient to allow for the effects separately.

7. The results

The results of four demagnetizations made on two different days on the same specimens are shown in figs. (21) and (22). In fig. (21) T° for manganous ammonium sulphate is plotted against the absolute temperature T , and in fig. (22) the same results are plotted as $\frac{T^{\circ} - T}{T}$, against T to demonstrate the deviations from Curie's law more clearly. The results are only in qualitative agreement with those obtained by Cooke (1949) using the standard γ ray method. It must be pointed out however that the earlier results were fitted to the "known" deviations at 0.5°K using a theory which did not include the effect of hyperfine structure, then not discovered, and which also made the wrong assumptions about the Stark splittings. The disagreement is therefore not surprising, but on account of the very complicated energy



DEVIATION FROM CURIE'S LAW

$\frac{T}{T_c}$

0.4

0.2

0

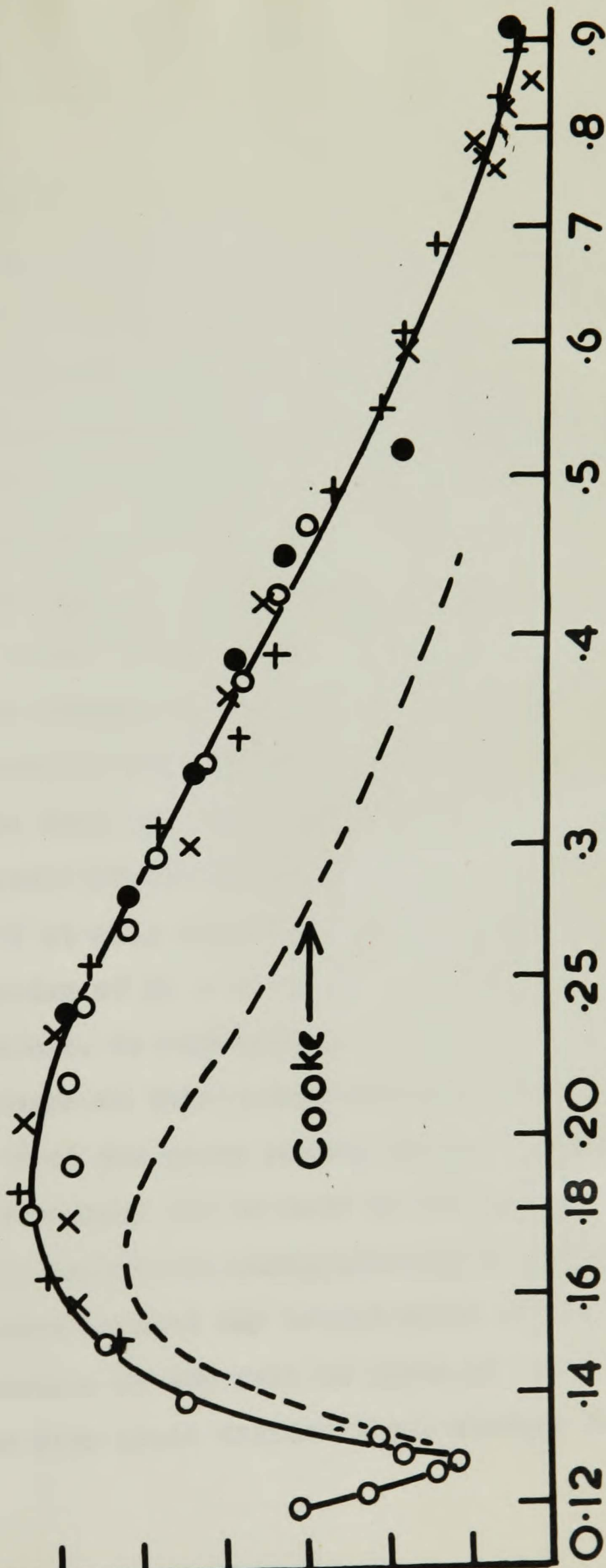


FIG.22

level scheme found from paramagnetic resonance (Bleaney, Ingram, 1951) it would be difficult to recalculate his results.

It will be seen from the graphs that the consistency of the new method is very good, the scatter nowhere exceeding a few percent. The only serious error which affects the results appears to be the uncertainty of the slopes of the calibration curves in the helium range. It seems that this error arises not from lack of sensitivity, but from a lack of stability of the whole system which from time to time causes small spurious changes of M . However the shifts are very small (< 0.1 u.m.i.) and it is estimated that the error in the slopes is less than 3%. It must be noted that any small shifts which occur at low temperatures hardly affect the value of T^* or T at all, since the measured values of ΔM are then of the order of 30 - 50 u.m.i. so that an uncertainty of 0.1 u.m.i. is negligible.

The chief advantage of this method over the standard γ ray method, apart from the great saving in time, is the ease with which measurements can be made in the region of the Curie point. In this region the susceptibility is practically temperature independent so that any method which relies on measuring the temperature of the salt in terms of its own susceptibility meets with great difficulties, whereas in our

method we can follow small changes of temperature easily in terms of the susceptibility of the Cerium thermometer. We can determine the value of the Curie point from fig.(22) as the temperature at which T° passes through a minimum, (i.e. the susceptibility passes through a maximum.) We find that with this definition of the Curie point

$$\begin{aligned} T_c &= 0.127^\circ\text{K} \\ T_c^{\circ} &= 0.134^\circ\text{K} \quad \pm 0.003^\circ\text{K} \end{aligned}$$

and it would be interesting at a later date to investigate how this temperature compares with the Neel point defined as the temperature at which remanence sets in. It may be noted that the value of T_c° obtained by Cooke was independent of the fitting at 0.5°K , and was 0.14°K , in good agreement with ours.

It is hoped in the near future to use this thermometer to measure the specific heat in the Curie point region by applying known amounts of heat from a γ ray source. Such experiments would provide new and very interesting information on the onset of antiferromagnetism about which very little is known at present. On account of the very large number of measurements which can be made during each demagnetization (the time required to measure T is about 2 minutes) it should

8.27

be possible to measure the entire specific heat curve in one single experiment, and so open up a field in which progress up to now has been slow on account of very time consuming experiments.

Consider a specimen with a primary magnetization curve of the form $M = H.A.$ where A is a constant. Then the dipole moment of the specimen is M and the flux is $\Phi = M.A.$

$$\Phi = M.A.$$

Calculating the flux due to this magnetization curve of the specimen, taking $M = H.A.$ as a function of the field H , we get

$$\Phi = \int H.dM = \int H.A.dH = \frac{A}{2} H^2.$$

Then for a secondary of N turns/cm, extending from z_1 to z_2 , the flux is

$$\Phi = N \int_{z_1}^{z_2} \frac{a^2 dz}{2(a^2 + z^2)}.$$

i.e. For a dipole a distance a from the centre of a secondary of length $2a$, the flux is

I.1.

APPENDIX I.

$$\phi(x) = n \mu \int_{-b}^{+b} \frac{a^2 dz}{2(a^2 + z^2)^{3/2}}$$

CORRECTION FOR THE FINITE LENGTH OF THE SPECIMEN
INSIDE A SECONDARY 4CM. LONG

Consider a specimen with a uniform cross section A, whose magnetization due to the primary field is $M = 2$ e.m.u./cc. Then the dipole moment of a short length

dx is $\mu = M.A.dx$. In order to find the flux due to a specimen of finite length (2b) we must now integrate $\phi(x)$ with respect to x between the limits $x = -b$ to $x = +b$. This integration is again

performed by calculating the flux due to this through a single turn of the secondary, radius a , at a distance z along the axis of the dipole, we get

$$d\phi = \int H.ds = \frac{a^2}{2(a^2 + z^2)^{3/2}} \cdot \mu.$$

Thus for a secondary of n turns/cm. extending from $z = z_1$ to $z = z_2$, the flux is

$$\phi = n \mu \int_{z_1}^{z_2} \frac{a^2 dz}{2(a^2 + z^2)^{3/2}}$$

i.e. For a dipole a distance x from the centre of a secondary of length $2b$, the flux is

that for a specimen 3.5 cm. long the correction is about 13%.

$$\begin{aligned}\phi(x) &= n \mu \int_{x-b}^{x+b} \frac{a^2 dz}{2(a^2+z^2)^{3/2}} \\ &= n \mu F(x) = n.M.A. dx F(x)\end{aligned}$$

This integration is best carried out graphically using the actual dimensions of the coil: $a = 1.5$ cm. and $2b = 4$ cm. Fig. 23 shows $F(x)$ as a function of x .

In order to find the flux due to a specimen of finite length (21) we must now integrate $\phi(x)$ with respect to x between the limits $x = \pm l$. This integration is again performed graphically and the result is shown in fig. 24. Comparing the flux with that due to a specimen of similar strength (2 M.A.1) but concentrated at the centre,

$$\Phi_0 = 2 M.A.1.n.F(0),$$

we can calculate a correction factor f to allow for the flux linkage lost by the specimen of length $2l$.

f is defined as

$$f = \frac{\int_{-l}^{+l} n.M.A.F(x) dx}{2n.M.A.1.F(0)}$$

as is shown as a function of l in fig. 22. It will be seen, that for a specimen 3.6 cm. long the correction is about 13%.

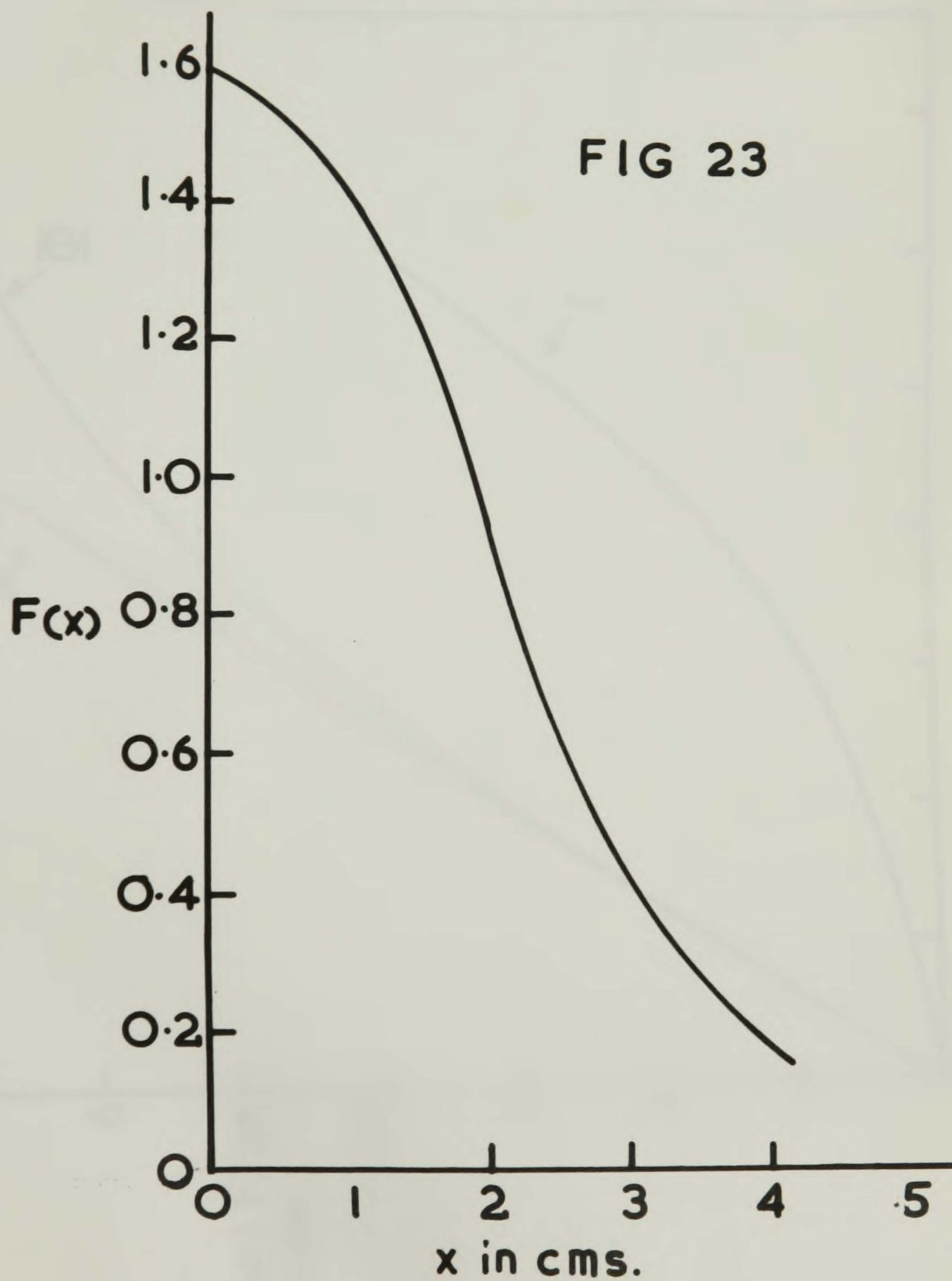
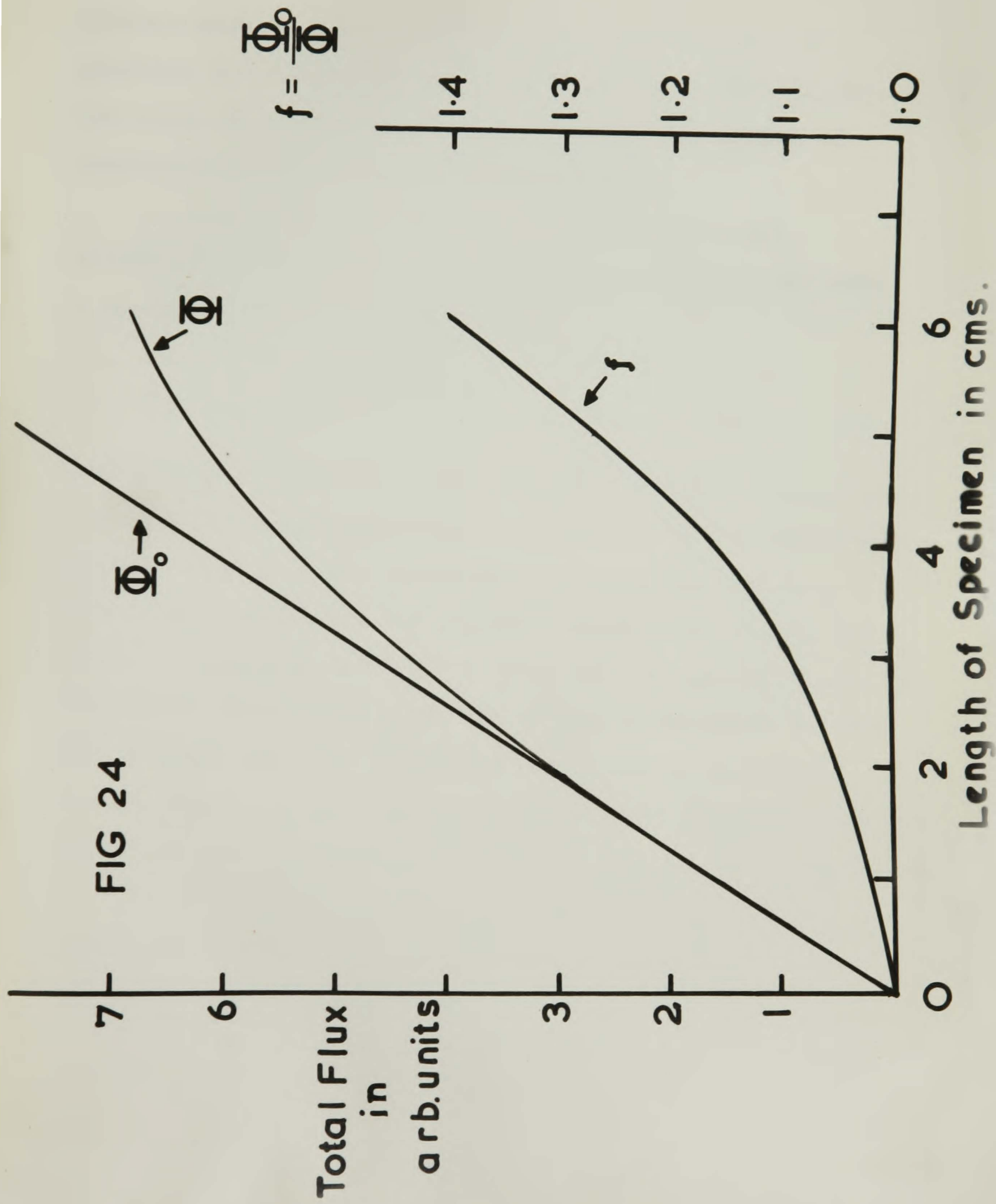


FIG 24



I.3

However most of this correction can be eliminated in practice by always using specimens of comparable lengths. The curve is then used only to normalize the effect of specimens which are necessarily smaller.

A similar calculation has been made for a 4:1 ellipsoid 3.9 cm. long. The correction factor f for such a specimen was found to be 1.095.

$$\mathcal{H} = \mathcal{H}_A + \mathcal{H}_B + \mathcal{H}_C + \mathcal{H}_D + \mathcal{H}_E \quad (1)$$

(see Abragam and Pryce, 1951) where the terms $\mathcal{H}_A$ through $\mathcal{H}_E$ represent the interaction between the electron spin $\mathbf{S}$ and the nuclear spin $\mathbf{I}$, $\mathcal{H}_B$ the interaction between the nuclear quadrupole moment and the electric crystalline field, and $\mathcal{H}_C$ the interaction between the spin and the applied field, $\mathcal{H}_D$. The fourth term which gives the direct interaction between the nuclear magnetic moment and the field is negligible except when H is very big. The fifth term $\mathcal{H}_E$ represents the effect of the crystalline electric field. For $S = \frac{1}{2}$, $\mathcal{H}_E = 0$.

If we consider the case of $\mathbf{I}$ along the z axis of a coordinate system in which A , B and C are diagonal, then (1) reduces, for $S = \frac{1}{2}$, to

$$\begin{aligned} \mathcal{H} = & A_x S_x I_x + A_y S_y I_y + A_z S_z I_z \\ & + B_x I_x^2 + B_y I_y^2 + B_z I_z^2 + C S^2 I^2 \end{aligned}$$

II.1

APPENDIX II.

THE EFFECT OF NUCLEAR HYPERFINE STRUCTURE ON
SUSCEPTIBILITY AND SPECIFIC HEAT

1. The Hamiltonian

The general spin hamiltonian for an ion with hyperfine structure in a magnetic field may be written as

$$\mathcal{H} = \underline{S} \cdot \underline{A} \cdot \underline{I} + \underline{I} \cdot \underline{P} \cdot \underline{I} + \beta \underline{H} \cdot \underline{g} \cdot \underline{S} - \gamma \beta \underline{H} \cdot \underline{I} + \mathcal{H}_{st} \quad (1)$$

(see Abragam and Pryce, 1954) where the tensor $\underline{A}$ characterizes the interaction between the electron spin $\underline{S}$ and the nuclear spin $\underline{I}$, $\underline{P}$ the interaction between the nuclear quadrupole moment and the electric crystalline field, and $\underline{g}$ the interaction between the spin and the applied field, $\underline{H}$. The fourth term which gives the direct interaction between the nuclear magnetic moment and the field is negligible except when $\underline{H}$ is very big. The fifth term $\mathcal{H}_{st}$ represents the effect of the crystalline electric field. For $S = \frac{1}{2}$, $\mathcal{H}_{st} = 0$.

If we consider the case of $\underline{H}$ along the z axis of a coordinate system in which $\underline{A}$, $\underline{P}$ and $\underline{g}$ are diagonal, then (1) reduces, for $S = \frac{1}{2}$, to

$$\begin{aligned} \mathcal{H} = & A_x S_x I_x + A_y S_y I_y + A_z S_z I_z \\ & + P_x I_x^2 + P_y I_y^2 + P_z I_z^2 + g_z \beta H S_z \end{aligned} \quad (2)$$

II.2

For many substances the coefficients P are negligible and also $A_x = A_y$ on account of axial symmetry, but for the sake of generality we shall use eq. 2 in its unsimplified form.

2. The expansion of the partition function

The method of obtaining approximate values of specific heat and entropy from the hamiltonian has been explained in Chapter 6. The same method can be used for the susceptibility. We set up a partition function

$$Z = \sum_{\lambda} \exp(-W_{\lambda}/kT) \quad (3)$$

and expand it in powers of $1/T$. The coefficients $\sum_{\lambda} W_{\lambda}^n$ can be calculated directly from the energy levels, if these are known explicitly, but as pointed out before this is not necessary. By using the theorem

$$\sum_{\lambda} W_{\lambda}^n = \text{Spur} \quad (4)$$

and writing down the full expression for $\mathcal{H}$ (eq.2), we can find the $\sum_{\lambda} W_{\lambda}^n$ in terms of the Spurs of functions of the operators $S_x, S_y, S_z; I_x, I_y$ and I_z . These diagonal sums can be calculated once and for all and are given in table 1 below. It can be shown from simple symmetry considerations

II.3

that many of them are zero and that some of the non zero ones are equal, so that the actual number which has to be computed is small.

Expanding Z and using eq.(4) we have

$$Z = Sp e^{1 - \frac{Sp \mathcal{H}}{kT} + \frac{Sp \mathcal{H}^2}{2! k^2 T^2} - \frac{Sp \mathcal{H}^3}{3! k^3 T^3} + \frac{Sp \mathcal{H}^4}{4! k^4 T^4} - \dots} \quad \dots (5)$$

whence, retaining only powers of $\frac{1}{T}$ up to $\frac{1}{T^4}$

$$\begin{aligned} \log_e Z &= \log_e(Sp) + \frac{1}{Sp} \left[-\frac{Sp \mathcal{H}}{kT} + \frac{Sp \mathcal{H}^2}{2! k^2 T^2} - \frac{Sp \mathcal{H}^3}{3! k^3 T^3} + \frac{Sp \mathcal{H}^4}{4! k^4 T^4} \right] \\ &\quad - \frac{1}{2(Sp)^2} \left[\frac{(Sp \mathcal{H})^2}{k^2} - \frac{Sp \mathcal{H} Sp \mathcal{H}^2}{k^3 T^3} + \frac{Sp \mathcal{H} Sp \mathcal{H}^3}{3 k^4 T^4} + \frac{(Sp \mathcal{H}^2)^2}{4 k^4 T^4} \right] \\ &\quad + \frac{1}{3(Sp)^3} \left[\frac{-(Sp \mathcal{H})^3}{k^3 T^3} + \frac{3(Sp \mathcal{H})^2 Sp \mathcal{H}^2}{2 k^4 T^4} \right] \\ &\quad - \frac{1}{4(Sp)^4} \left[\frac{(Sp \mathcal{H})^4}{k^4 T^4} \right] + O\left(\frac{1}{T^5}\right) \quad \dots (6) \end{aligned}$$

We can write the hamiltonian $\mathcal{H}$ in eq.(2) in the form

$$\mathcal{H} = \mathcal{H}_0 + H \mathcal{H}_m \quad (7)$$

II.4

where $\mathcal{H}_m$ is the part depending on the magnetic field (i.e. $g\beta Sz$) and $\mathcal{H}_0$ is the nuclear part. Substituting for $\mathcal{H}_0$ in equation (6), we can then simplify the expression for $\log_e Z$ since, as will be shown below, (see eq.19)

$$\text{Sp } \mathcal{H}_0 = \text{Sp } \mathcal{H}_m = \text{Sp } \mathcal{H}_m \mathcal{H}_0 = \text{Sp } \mathcal{H}_m \mathcal{H}_0^2 = 0$$

and also

$$\text{Sp } \mathcal{H}_m^2 \mathcal{H}_0 = 0$$

Retaining only 2nd powers in H we get

$$\log_e Z = \log_e(\text{Sp } 1) + \frac{1}{\text{Sp } 1} \left[\frac{\text{Sp } \mathcal{H}_0^2 + H^2 \text{Sp } \mathcal{H}_m^2}{2k^2 T^2} - \frac{\text{Sp } \mathcal{H}_0^3}{6k^3 T^3} \right.$$

$$+ \frac{H^2}{4! k^4 T^4} \left(\text{Sp } \mathcal{H}_0^2 \mathcal{H}_m^2 + \text{Sp } \mathcal{H}_m^2 \text{Sp } \mathcal{H}_0^2 + \text{Sp } \mathcal{H}_m \mathcal{H}_0^2 \mathcal{H}_m \right. \\ \left. + \text{Sp } \mathcal{H}_m \mathcal{H}_0 \mathcal{H}_m \mathcal{H}_0 + \text{Sp } \mathcal{H}_0 \mathcal{H}_m \mathcal{H}_0 \mathcal{H}_m \right) \Big]$$

$$- \frac{1}{2(\text{Sp } 1)^2} \left[\frac{(\text{Sp } \mathcal{H}_0^2)^2}{4k^4 T^4} + 2H^2 (\text{Sp } \mathcal{H}_0^2)(\text{Sp } \mathcal{H}_m^2) \right]$$

.... (8)

From this expression for $\log Z$ we can calculate the susceptibility χ , since

$$\chi = \frac{KT}{H} \frac{\partial}{\partial H} (\log Z) \quad (9)$$

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while by putting $H = 0$ we get the entropy and specific heat in zero field from the relations

$$S_{H=0} = k \frac{\partial}{\partial T} (T \log Z_{H=0}) \quad (10)$$

and $C_{H=0} = T \left(\frac{\partial S}{\partial T} \right)$ (11)

Since we have retained only powers of H up to H^2 in (8), the expression for the susceptibility (9) will contain only the part of χ independent of field, i.e. the susceptibility in small fields. In order to investigate the variation of χ with H we would have to include higher powers of H in $\log Z$.

3. The calculation of the spurs of angular momentum operators

a) Symmetry considerations

In order to calculate the spurs which occur in the numerators of eq.(8), let us first consider the spurs of the 3 angular momentum operators L_x , L_y and L_z , representing the components of either the nuclear spin $\underline{I}$ or the electronic spin $\underline{S}$.

We have shown in Chapter 6 that the spurs of an operator is invariant under a change of representation and this fact

II.6

often makes possible to deduce the spur of one operator from that of another, by rotating the coordinate axes. Thus, quite generally, the spur of any function of L_x is equal to the spur of the same function of L_y or L_z . Now $\text{Spur } f(L_z)$ can be calculated very simply. The usual representation of angular momentum is one in which the total square of the angular momentum and its component along Oz are defined (good quantum numbers) so that the matrix of L_z is

$$\begin{array}{c}
 |L^2, L_z=L\rangle \quad \dots \quad |L^2, L_z=-L\rangle \\
 \begin{array}{c} \langle L^2, L_z=L | \\ \vdots \\ \langle L^2, L_z=-L | \end{array} \left[\begin{array}{c} L \\ \vdots \\ L-1 \\ \vdots \\ -L+1 \\ -L \end{array} \right]
 \end{array} \tag{12}$$

It follows that the only non vanishing elements of any operator, which is a function of L_z , are

$$\langle L^2, L_z' | f(L_z) | L^2, L_z' \rangle = f(L_z').$$

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so that

$$\text{Sp } f(L_z) = \sum_{L_z' = -L}^{+L} \langle L_z' | f(L_z) | L_z' \rangle$$

$$= \sum_{L_z' = -L}^{+L} f(L_z') \quad (13)$$

$$\text{Thus } \text{Sp } L_z = \sum_{L_z' = -L}^{+L} L_z' = 0 \quad (14)$$

and hence, by rotation of axes

$$\text{Sp } L_x = \text{Sp } L_y = 0 \quad (14a)$$

Similarly

$$\text{Sp } L_z^2 = \sum_{L_z' = -L}^{+L} (L_z')^2 = \frac{1}{3} L(L+1)(2L+1)$$

$$= \text{Sp } L_x^2 = \text{Sp } L_y^2 \quad (15)$$

Spurs of higher powers are deduced in a similar way.

In calculating the spurs of functions involving more than one operator (eg. $L_x L_y$) account must be taken of the fact that operators in general do not commute. Thus

$$L_x^2 L_z - L_z L_x^2 = 2L_y \neq 0.$$

However, it can be shown that for any operators A, B, C ... that

$$\text{Spur}(ABC...) = \text{Spur}(BC...A) \text{ etc.} \quad (16)$$

as long as the cyclic order of the factors remains unaltered.

On the other hand, $\text{Spur } ABC$ is not necessarily equal to

II.8

Sp BAC. Thus for any set of functions which are products of a number of operators it is only necessary to compute the spurs of all the different cyclic permutations of the factors.

eg. Although H^4 involves terms in $H_0^2 H_m^2$, $H_m H_0^2 H_m$, $H_0 H_m^2 H_0$, $H_m^2 H_0^2$, $H_0 H_m H_m H_0 \rightarrow H_m H_0 H_m H_0$ the spur of only one of the first four products and one of the last two have to be calculated.

There is a further theorem which often enables us to reduce the number of spurs which have to be computed. This enables us to say from the symmetry of the matrices representing factors that the spur of a certain product will be zero. We call this:

b) The theorem of "diagonally antisymmetric" matrices

Consider a square $n \times n$ matrix A whose elements are such that

$$a_{ij} = a_{n-j+1, n-i+1}. \quad (17)$$

Let us call such a matrix diagonally symmetrical about the line from the top right to the bottom left hand corner.

It is simple to show that any power of A will also exhibit diagonal symmetry.

Consider now a second $n \times n$ matrix B which is diagonally antisymmetrical

i.e. $b_{ij} = -b_{n-j+1, n-i+1}$ the spur will be (18)

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We can show that even powers of B are diagonally symmetrical while odd powers are antisymmetrical. The spur of a diagonally antisymmetrical matrix is zero since the elements which occur along the main diagonal occur in equal and opposite pairs. Thus

$$\text{Spur } B^{2q-1} = 0 \quad \text{where } q \text{ is any integer } \geq 1.$$

If we now consider the product of a diagonally symmetrical matrix with any diagonally antisymmetrical matrix of the same order, e.g. $A^p B^{2q-1}$, then, as we can show that the resulting product is anti symmetrical, it follows that the spur of all products of the form $A^p B^{2q-1}$ is zero. A simple example of a diagonally symmetrical matrix is $\mathcal{H}_0$ above; a simple antisymmetrical matrix is $\mathcal{H}_m$. Thus we can conclude without any further calculation that for all p and $q \geq 1$.

$$\text{Spur } \mathcal{H}_0^p \mathcal{H}_m^{2q-1} = 0 \quad (19)$$

c) The Spur of the product of two commuting operators

We have so far considered only products of operators of one physical variable, e.g. nuclear angular momentum. Now any operator describing the interaction between a nucleus $\mathbf{I}$ and an electron $\mathbf{J}$ must be represented in terms of both $\mathbf{J}$ and $\mathbf{I}$. The spin dependent part of the operator will be

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represented by a $(2S+1) \times (2S+1)$ matrix, while the part depending on the nucleus will be represented by a $(2I+1) \times (2I+1)$ matrix. In order to represent the whole operator we therefore need an 'outer product space' which has $(2I+1) \times (2S+1)$ rows and columns. It follows that the spur of any operator of the form $f(\underline{S}) \cdot g(\underline{I})$ will be equal to the product of $\text{Sp } f(\underline{S}) \cdot \text{Sp } g(\underline{I})$ where $\text{Sp } f(\underline{S})$ and $\text{Sp } g(\underline{I})$ are computed respectively in a $2S+1$ and $2I+1$ dimensional representation. It is important to note that if we use an outer product space for any one part of our hamiltonian e.g. $A \times S \times I$, then we must use the same representation for all the other operators in $\mathcal{H}$. Thus $P \times I \times I^2$ must be written as $P \times I \times I^2 \cdot 1_S$ where 1_S is the unit operator in a $(2S+1)$ dimensional representation. Similarly

$$\begin{aligned} \text{Spur } 1_{\text{total}} &= \text{Sp } 1_S \cdot \text{Sp } 1_I \\ &= (2S+1) \cdot (2I+1). \end{aligned}$$

d) The terms in $\log_e Z$

We are now in a position to calculate the non vanishing spurs which occur in the expansion of $\mathcal{H}^n$. Considering only terms included in eq.(8) we find, taking account that the operators in $\underline{S}$ commute with those in $\underline{I}$ but not among themselves,

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that the terms we need are of the form

$$\text{Sp } L_{\alpha}^2, \text{Sp } L_{\alpha}^4, \text{Sp } L^2 L_{\beta}^2, \text{Sp } L_{\alpha} L_{\beta} L_{\gamma} \quad (20)$$

where L stands for either $\underline{x}$ or $\underline{y}$ and α, β, γ represent x, y or z . The values of these spurs are readily calculated. We have already seen that the spurs of operators involving only the z component of angular momentum can be written down by inspection, eq.(13), and that those involving only L_y or L_x can be obtained from them by rotating the axes.

As a typical example of computing the spur of a product of different operators, let us consider:

Spur $L_x L_y L_z$

From the commutation relation

$$L_x L_y - L_y L_x = i L_z \quad (21)$$

(units of $\hbar$ implied throughout), we have

$$\text{Sp } L_x^2 = \text{Sp } L_x L_y L_z = i L_z^2 + L_y L_x L_z$$

whence

$$\text{Sp } L_x^2 \text{Sp}(L_x L_y L_z) = i \text{Sp}(L_z^2) + \text{Sp}(L_y L_x L_y) \quad (22)$$

Consider now the function $(L_x L_y + L_y L_x)L_z$

as the product of two operators. Since the first factor

remains invariant when z is changed to $-z$, it follows that

the matrix of $(L_x L_y + L_y L_x)$ must be diagonally symmetrical i.e. $(L_x L_y + L_y L_x)$ is an operator of the type A in section (3b). Similarly L_z is antisymmetrical of the type B. Thus by the above theorem the product $(L_x L_y + L_y L_x)L_z$ is antisymmetrical so that its spur is zero.

$$\text{Hence } \text{Sp}(L_x L_y L_z) + \text{Sp}(L_y L_x L_z) = 0 \quad (23)$$

Thus from (22)

$$2\text{Sp}(L_x L_y L_z) = 1 \text{ Sp } L_z^2 \quad \dots (25)$$

From eq. (15) it follows that

$$\text{Spur } (L_x L_y L_z) = \frac{i}{6} L(L+1)(2L+1) \quad (24)$$

The spurs of other functions of L up to the fourth power are given in table (1).

Table 1.

$$\text{Sp } L_x = \text{Sp } L_y = \text{Sp } L_z = 0$$

$$\text{Sp } L_x L_y = \text{Sp } L_y L_z \text{ etc.} = 0$$

$$\text{Sp } L_x^2 = \text{Sp } L_y^2 \text{ etc.} = 1/3 L(L+1)(2L+1)$$

$$\text{Sp } L_x^2 L_y \text{ etc.} = 0$$

$$\text{Sp } L_x^3 \text{ etc.} = 0$$

$$\text{Sp } L_x L_y L_z = -\text{Sp } L_y L_x L_z = L(L+1)(2L+1)$$

$$\text{Sp } L_x L_y \text{ etc.} = 1/30 L(L+1)(2L+1)(2L^2+2L+1)$$

$$\text{Sp } L_x^3 L_y \text{ etc.} = 0$$

$$\text{Sp } L_x^4 \text{ etc.} = 1/15 L(L+1)(2L+1)(3L^2+3L-1)$$

$$\text{Sp } L_x L_y L_x L_y = 1/30 L(L+1)(2L+1)(2L^2+2L+1-5)$$

4. Resultsa) Susceptibility

Substituting in the expression for $\log Z$ (8) and carrying out the differentiations we get

$$\chi_z = \frac{g^2 \beta^2 S(S+1)}{3kT} \left[1 - \frac{I(I+1)}{15kT^2} \left\{ (A_x^2 + A_y^2) \left(\frac{26S^2 + 26S - 7}{8} \right) - A_z^2 \left(\frac{4S^2 + 4S - 3}{6} \right) \right\} \right] \dots (25)$$

For a spin $S = \frac{1}{2}$ this reduces to

$$\chi_z = \frac{g^2 \beta^2}{4kT} \left[1 - \frac{5 I(I+1) (A_x^2 + A_y^2)}{288 kT^2} \right] \dots (26)$$

Two similar expressions hold for χ_x and χ_y

For a powder the average susceptibility is given by

$$\chi = \frac{1}{3} (\chi_x + \chi_y + \chi_z)$$

It is interesting to note (Bleaney 1950) that there is no term in $\frac{1}{T^2}$ so that the deviations from Curie's law will be very small down to the lowest temperature ($\sim \frac{\Delta}{k} ^\circ K$).

b) Entropy and Specific heat

The expression for the entropy to powers of $\frac{1}{T^3}$ is

$$\begin{aligned} \frac{S}{R} = & \log_e (2S+1)(2I+1) - \frac{1}{k^2 T^2} \left[\frac{A^2 I(I+1)S(S+1)}{18} \right. \\ & + \frac{P^2 I(I+1)(2I-1)(2I-3)}{60} \left. \right] \\ & - \frac{1}{k^3 T^3} \left[\frac{A_x A_y A_z}{18} S(S+1)I(I+1) \right. \\ & - \frac{(A_x^2 P_x + A_y^2 P_y + A_z^2 P_z) S(S+1)I(I+1)(2I-1)(2I-3)}{90} \left. \right] \\ & \dots (27) \end{aligned}$$

a) Specific heat

where $A^2 = \sum A_x^2$; $P^2 = \sum P_x^2$

This is equivalent to a specific heat

$$\begin{aligned} \frac{C_{H=0}}{R} = & \frac{1}{k^2 T^2} \left[\frac{A^2 I(I+1)S(S+1)}{9} + \frac{P^2 I(I+1)(2I-1)(2I+3)}{30} \right] \\ & + \frac{1}{k^3 T^3} \left[\frac{A_x A_y A_z}{6} S(S+1)I(I+1) \right. \\ & - \frac{(A_x^2 P_x + A_y^2 P_y + A_z^2 P_z) S(S+1)I(I+1) \times (2I-1)(2I-3)}{30} \left. \right] \\ & \dots (28) \end{aligned}$$

The values of the coefficients of $Ax^2 + Ay^2 + Az^2$ agree with those calculated by Bleaney (loc.cit) who did not consider the expansion any further.

5. Application

We can now apply these formulae to the case of Neodymium Magnesium Nitrate for which the coefficients in the spin hamiltonian have been given on page 7.4 .

Identifying our notation with the more usual one for cases of axial symmetry we find that Curie's law is obeyed ($T > 0.05^\circ K$)

the entropy $B = Ax = Ay$ both follow a $\frac{1}{T}$ law to very good accuracy $A = -Az$.

No quadrupole shift was measured and we take $Px = Py = Pz = 0$.

a) Susceptibility

On account of the large anisotropy ($g_{||} = 0.45 \pm 0.05$, $g_{\perp} = 2.72 \pm 0.02$) single crystals must be used for demagnetization work (see 4.4) so that we need only calculate the susceptibility in the direction of large g . Substituting in eq. (26) we get

$$\text{energy level} = \frac{0.698}{T} \left[1 - \frac{85 \times 10^{-5}}{T^2} \right]$$

This formula will hold down to about $0.05^\circ K$ where the deviation from Curie's law amounts to 3.5%. At lower

general theory has yet been worked out. The contribution

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temperatures the next term in the series, $\frac{B^3}{T^3}$, will become important and a more exact calculation is needed.

b) Specific Heat and Entropy

Substituting in eqs. (27) and (28) we get

$$\frac{S}{R} = \log 16 - \left(\frac{4.05 \times 10^{-4}}{T^2} + \frac{1.3 \times 10^{-7}}{T^3} \dots \right)$$

$$\text{and } \frac{C_{H=0}}{R} = \frac{8.10 \times 10^{-4}}{T^2} + \frac{3.9 \times 10^{-7}}{T^3} \dots$$

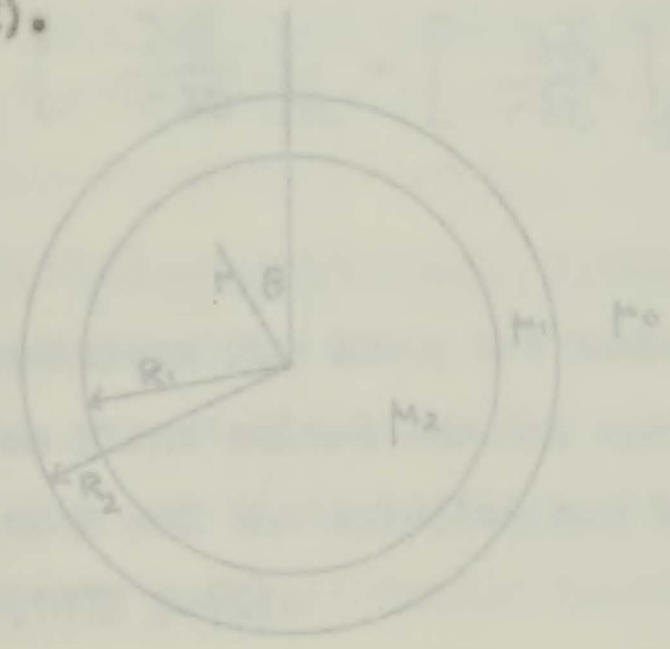
Thus in the region where Curie's law is obeyed ($T > 0.05^\circ\text{K}$) the entropy and specific heat both follow a $\frac{1}{T^2}$ law to very good accuracy ($\sim 1\%$).

6. Conclusion

This method of calculating macroscopic quantities from the spin hamiltonian can be used in all cases where the energy levels are well defined and the state of the ion can be represented by an exact hamiltonian. In cases where the interactions between the ions are considerable and the energy levels are broadened, account must be taken of the interaction forces in setting up the hamiltonian. For pure magnetic dipole-dipole forces this is done by including a term of the form of eq. 6.12, but for exchange forces no general theory has yet been worked out. The contribution

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to the $\frac{1}{2}$ part of the specific heat and entropy from the interactions is additive to that from the nuclear effects but in higher terms cross products occur (Daniels, 1953). These cross products are however very small when, as in the case of Nd Mg Nitrate, the hyperfine splittings are much larger than the interaction energies. The calculations based on considering the two effects separately are then valid until the interactions energies become comparable with kT ($\sim 0.01^\circ K$).



We can show that the potentials which satisfy Laplace's equation are of the form

$$\Phi_1 = \sum a_n r^n \cos \theta \quad (1)$$

for the inner sphere,

$$\Phi_2 = \sum b_n r^{-n-1} \cos \theta + \sum c_n r^n \cos \theta \quad (2)$$

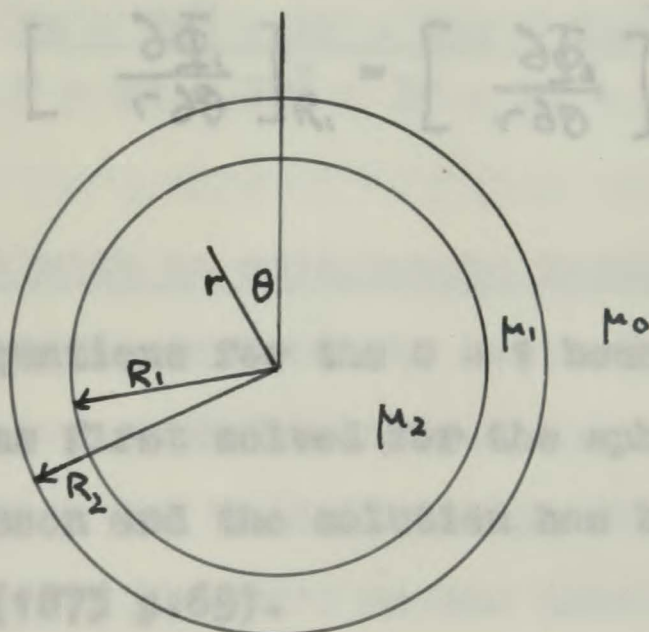
III.1

for the shell; and APPENDIX III.

THE DEMAGNETIZING CORRECTION FOR TWO CONCENTRIC SPHERES

1. Isotropic shell with an isotropic kernel

Let us consider first the case of an isotropic sphere of permeability μ_0 , surrounded by an isotropic shell of permeability μ_1 , in a magnetic field H_0 .



From eq.(3) it will be seen that in the region of space outside the specimen the effect of the concentric spheres

We can show that the potentials which satisfy Laplace's equation are of the form

the constants in the general case we find that

$$\Phi_2 = a_2 r \cos \theta \quad (1)$$

for the inner sphere,

$$\Phi_1 = a_1 r \cos \theta + b_1 \frac{\cos \theta}{r^2} \quad (2)$$

....(4)

III.2

for the shell, and introduce the following condition:

$$\Phi_0 = -H_0 r \cos \theta + b_0 \frac{\cos \theta}{r^2} \quad (3)$$

for the space outside the specimen.

The 4 constants a_0, a_1, b_1, b_2 are determined by the boundary conditions

$$\left[\mu_1 \frac{\partial \Phi_1}{\partial r} \right]_{R_1} = \left[\mu_2 \frac{\partial \Phi_2}{\partial r} \right]_{R_1}$$

$$\left[\frac{\partial \Phi_1}{r \partial \theta} \right]_{R_1} = \left[\frac{\partial \Phi_2}{r \partial \theta} \right]_{R_1}$$

... (5)

with two similar equations for the 0 - 1 boundary.

The problem was first solved for the spherical case $\mu_0 = \mu_2 = 1$ by Poisson and the solution has been given in detail by Maxwell (1873 p.65).

From eq.(3) it will be seen that in the region of space outside the specimen the effect of the concentric spheres is exactly equivalent to a dipole whose strength is equal to b_0 . Carrying out the differentiations and solving for the constants in the general case we find that

$$b_0 = \frac{-H_0 R_2^3 \left[(\mu_1 - \mu_0)(\mu_2 + 2\mu_1) + \left(\frac{R_1}{R_2}\right)^3 (\mu_0 + \mu_1)(\mu_2 - \mu_1) \right]}{(2\mu_0 + \mu_1)(\mu_2 + 2\mu_1) + 2\left(\frac{R_1}{R_2}\right)^3 (\mu_0 - \mu_1)(\mu_1 - \mu_2)}$$

....(4)

III.3

In order to simplify this expression we put $\mu_0 = 1$ and introduce the following quantities:

$$x = \mu_1 - 1 = 4\pi \chi_1$$

$$y = \mu_2 - 1 = 4\pi \chi_2$$

$$n = \frac{R_1^3}{R_2^3} \quad (\text{see p. 8.14})$$

$$b = b_0$$

where μ is now the permeability tensor. If H_0 is parallel to one of the principal axes of μ then the tensor reduces

$$\frac{b}{H_0 R_2^3} = \frac{3x + 2x^2 + xy - 3nx - 2nx^2 + 3ny + 2nxy}{9 + 9x + 2x^2 + 3y + xy - 2nx^2 + 2nxy} \quad \dots (5)$$

2. Isotropic shell with an anisotropic kernel

Equation (5) was derived on the basis that x and y are isotropic. In our case this is not so: in one direction y is comparable with x but in a direction at right angles y is practically zero. However, we can show that equation (5) still holds in the case of an anisotropic inner sphere provided the external field is applied parallel to one of the principal axes of susceptibility since the same solutions of Laplace's equation satisfy the boundary conditions in both cases.

From equation (1) we see that for the case of an isotropic sphere and shell, the field inside the inner sphere, H_2 , is uniform and parallel to H_0 , so that the

III.4

induction $\underline{B}_2$ is also parallel to $\underline{H}_0$ and equal to $\mu_2 \underline{H}_2$.

Let us assume that the internal field in the case of an anisotropic inner sphere is still uniform and parallel to $\underline{H}_0$. Then the induction $\underline{B}$ is given by

$$\underline{B}_2 = \mu \cdot \underline{H}_2$$

where μ is now the permeability tensor. If $\underline{H}_2$ is parallel to one of the principal axes of μ then the tensor reduces to a number, $\underline{B}$ and $\underline{H}$ are then parallel as in the isotropic case, and the constant connecting them is the appropriate principal value of the μ tensor. If this value is equal to μ_2 , then the boundary conditions for $\underline{B}$ and $\underline{H}$ are exactly the same as in the isotropic case and hence, by the uniqueness theorem, the same solution holds. It must be pointed out that the same argument can not be applied to the case of an anisotropic shell since the internal field in a shell is not uniform and it is thus impossible to align the shell in such a way that the principal axis is parallel to the internal field at every point.

The case of $\underline{H}_0$ not parallel to the principal axis must be considered separately. In general, we can resolve $\underline{H}_0$ into 3 components $l\underline{H}_0$, $m\underline{H}_0$ and $n\underline{H}_0$ parallel to the 3 principal axes and consider the problem as a superposition

III.5

of the 3 fields. Each component will induce a dipole moment which is a function of the susceptibility of the shell $\frac{\chi}{4\pi}$ and the appropriate principal value of y . Resolving the 2 dipole moments along the direction of H we find that

$$b_{l,m,n} = l^2 b(x, y_l) + m^2 b(x, y_m) + n^2 b(x, y_n) \quad (6)$$

Thus in the general case b transforms like a tensor of rank 2, with principal values given in terms of the principal susceptibilities of the inner sphere. However, as in the present experimental arrangement it was possible to align the spheres to within 3° we need not consider this case any further.

In order to obtain an expression for the magnetic moment of the specimen when H_0 is applied in the direction of small susceptibility of the inner sphere, we put $y = 0$ in eq. (5) and consider the problem as one of a hollow isotropic shell. The small effect ($\sim 2\%$) of the inner sphere is then calculated separately and added to the result.

This addition is however not valid when H_0 is applied in the direction in which both the sphere and the shell have a comparable magnetic moment, and in this case we have

$$\chi(\text{shell}) = \chi(\text{sphere}) \left[1 + \frac{\frac{3}{2} \chi(\text{shell})}{1 + \frac{3}{2} \chi(\text{shell}) - \frac{3}{2} \chi(\text{sphere})} \right]$$

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to consider the effect of one on the other in greater detail. This calculation is given in section 4, but first let us consider a hollow shell, of a body of standard shape (in this case a sphere). The effect is small except

3. The demagnetizing correction of a hollow isotropic shell

Putting $y = 0$ in eq. (4) we find that the magnetic moment of a hollow shell is given by

$$b(\text{shell}) = \frac{H_0 R_2^3 x(3+2x)(1-n)}{9+9x+2x^2(1-n)} \quad (7)$$

so that the effective susceptibility per unit volume

$$\chi(\text{shell}) = \frac{b(\text{shell})}{H_0 \frac{4\pi}{3} R_2^3 (1-n)} = \frac{3x(3+2x)}{4\pi [9+9x+2x^2(1-n)]} \quad (8)$$

For small x this reduces to $\frac{x}{4\pi} = \chi_1$, the susceptibility as defined in magnetostatics for an infinite needle.

Similarly we find that the effective susceptibility as measured on a sphere, $\chi(\text{sphere})$ is given by

$$\chi(\text{sphere}) = \frac{3x}{4\pi(3+x)} \quad (9)$$

so that eliminating x we get a relation between $\chi(\text{shell})$ and $\chi(\text{sphere})$ and hence $\Delta M(\text{shell})$ and $\Delta M(\text{sphere})$.

From eqs. (8) and (9) we get

$$\chi(\text{shell}) = \chi(\text{sphere}) \left[1 + \frac{\frac{2}{9} n (4\pi \chi_{sp})^2}{1 + \frac{4\pi}{3} \chi_{sp} - \frac{2}{9} n (4\pi \chi_{sp})^2} \right]$$

III.7

This correction replaces the conventional demagnetizing factor which relates the susceptibility as measured on a given specimen to that of a body of standard shape (in this case a sphere). The effect is small except at very low temperatures. Thus at 0.15°K for the specimen of manganous ammonium sulphate used

$$\chi(\text{shell}) \approx \chi(\text{shell}) [1 + 0.04]$$

so that if we define $T^*(\text{shell}) = \frac{\lambda}{\chi(\text{shell})}$, then T^* shell will be lower than T^* by 3 millidegrees at 0.15°K. In the helium range the correction is negligible.

4. The additivity correction

In order to find the absolute temperature we require to find the magnetic moment which the inner sphere of Ce Mg Nitrate would have in the absence of the outer shell. If we denote the magnetic moment of the compound specimen in the direction of maximum susceptibility by $b(\text{comp})$ then, to a first approximation, the magnetic moment of the Cerium sphere is given by $b(\text{comp}) - b(\text{shell})$. However at low temperatures, where the susceptibilities became large, the magnetic interaction between the sphere and shell must be

III.8

considered and we can write

$$b(\text{Ce}) = b(\text{comp}) - b(\text{shell}) + \delta b \quad (11)$$

where δb is a function of the susceptibilities which allows for the magnetic interaction. We can estimate the relative magnitude of δb from eq.(5). Neglecting terms in y compared with x ($y:x \approx 1:8$ in our case) we get

$$\begin{aligned} \frac{b}{b(\text{comp}) - b(\text{shell})} &= \frac{2x^2 [18 + 18x + 2x^2(1-n)] (1-n)}{[9 + 9x + 2x^2(1-n)]^2} \\ &= \frac{\delta M}{\Delta M_H - \Delta M(\text{shell})} \end{aligned} \quad (12)$$

For the "diluted" specimen of manganous ammonium sulphate used, $x = \frac{0.08}{T_0}$ so that for example at 0.15°K , $\frac{\delta b}{b_{\text{Ce}}} \approx 2\%$. In the helium range the correction is negligible. As δb must be added to the dipole moment of the sphere as calculated from $\Delta M_H - \Delta M(\text{shell})$, the temperature deduced will be lowered by a small amount.

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