

## Magnetic dipole interactions in dysprosium ethyl sulphate

### II. Magnetic and thermal properties between 1 °K and the Curie point†

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The thermal and magnetic properties of dysprosium ethyl sulphate have been measured in the temperature range from 1 °K down to its Curie temperature of  $0.13 \pm 0.01$  °K. Because of the extreme anisotropy of the spectroscopic splitting factor ( $g_{\parallel} = 10.8$ ,  $g_{\perp} = 0$ ) and the fact that magnetic dipole interaction between the ions predominates the system behaves like an Ising model. This fact allows the calculation of the magnetic and thermal properties of the system in a simple manner and good agreement is obtained with experiment. The particular properties of this salt also allow the measurement of its specific heat by each of the three methods (electrical heating, X-ray heating and relaxation heating) which may be employed at temperatures below 1 °K and excellent agreement is obtained.

#### 1. INTRODUCTION

In a previous paper (Cooke, Edmonds, McKim & Wolf 1959) (to be referred to as 'I') the properties of dysprosium ethyl sulphate in the temperature range 20 to 1 °K were reported. It was shown that in this salt the dysprosium ion is magnetically highly anisotropic, having a spectroscopic splitting factor  $g_{\parallel} = 10.8$  parallel to the crystal axis and  $g_{\perp} = 0$ . These values furnish the reason for a further study of the salt at temperatures below 1 °K. Because  $g_{\parallel}$  is so large the magnetic dipole-dipole coupling between the ions is unusually large; it was shown in I that the magnetic contribution to the specific heat and the departure of the susceptibility from Curie's law are accounted for by this interaction, exchange and other interactions between the ions being negligible. The energy of the magnetic interactions is of the order  $kT_{\text{int.}}$  with  $T_{\text{int.}}$  about 0.1 °K, and we may therefore expect there will be an ordering of the magnetic ions at a temperature near 0.1 °K. Because  $g_{\perp}$  is zero, the moment of a magnetic ion can be treated as a scalar, and the system closely resembles the Ising model of a magnetic substance. The theoretical treatment of the interactions is therefore particularly simple, and a close comparison of theory and experiment is possible.

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In this paper we deal with the properties of the salt down to a temperature of  $0.13^{\circ}\text{K}$ .<sup>†</sup> Below this temperature the salt becomes ordered ferromagnetically due to the magnetic dipole interaction (Cooke, Edmonds, Finn & Wolf 1959). An account of work on the salt below the Curie temperature is given in the following paper (Cooke *et al.* 1968).

## 2. THE MAGNETIC TEMPERATURE SCALE BELOW $1^{\circ}\text{K}$

Below  $1^{\circ}\text{K}$  it is not possible to measure the absolute temperature by a direct method, and it is usual in experiments on magnetic specimens to make measurements against an arbitrary scale of temperature  $T^*$  based on the magnetic susceptibility of the specimen, and then to convert the results to the absolute temperature scale  $T$  after a thermodynamic determination of the relation of  $T^*$  to  $T$ . For a salt which obeys Curie's law,  $\chi = \lambda/T$ , in the helium range, the simplest definition of  $T^*$  is to put  $T^* = \lambda/\chi$ . However, the susceptibility of dysprosium ethyl sulphate departs appreciably from Curie's law at temperatures above  $1^{\circ}\text{K}$ , and we were therefore obliged to define  $T^*$  in a more complicated way. We assume that in the liquid helium range of temperatures the magnetic susceptibility per unit volume,  $\chi$ , measured with a field along the crystal axis, follows a law

$$\chi = (\lambda/T)(1 + \Delta/T),$$

where  $\lambda$  is the Curie constant per unit volume and  $\Delta$  is a constant. The form of this expression and the value of  $\Delta$  can be justified on theoretical grounds (see discussion later); the experiments reported in I show that it accurately represents the behaviour of the salt in the liquid helium temperature range. For example, for a spherical specimen we find a fit with  $\Delta = 0.135^{\circ}\text{K}$ . If we define  $T^* = \lambda/\chi$ , it then follows that in the helium range,  $T^*$  is not equal to  $T$ , but to  $T/(1 + \Delta/T)$ . The magnetic thermometer is therefore calibrated by measuring the susceptibility of the specimen at different temperatures in the helium range, and plotting susceptibility in arbitrary units (the mutual inductance units of our Hartshorn bridge) against  $T/(1 + \Delta/T)$ , giving a straight line whose slope measures the Curie constant  $\lambda$  in the same units. Below  $1^{\circ}\text{K}$  the value of  $T^*$  is then obtained from the susceptibility, measured in terms of the change of inductance  $\Delta M$  due to the specimen, by the relation  $T^* = \lambda/\Delta M$ .

Two points must be noted about the definition of  $T^*$ . The susceptibility was measured by an alternating field method, by measuring the effect of the specimen on the mutual inductance of a coil system. At temperatures below  $1^{\circ}\text{K}$  the susceptibility,  $\chi$ , in an alternating field contains components in and out of phase with the applied field,  $\chi = \chi' - i\chi''$ . The determination of  $T^*$  from the change of mutual inductance implies that  $T^*$  is defined from the value of  $\chi'$  alone, the value of  $\chi''$ , the out-of-phase component being determined separately from its effect on the

<sup>†</sup> A preliminary account of some of this work was given at the seventh International Conference on Low Temperature Physics and Chemistry, Toronto (Cooke *et al.* 1960) and at the International Conference on Magnetism and Crystallography, Kyoto (Cooke *et al.* 1962).

resistive balance of our Hartshorn bridge. Secondly, for any particular specimen the value of  $\chi$  and hence of  $T^*$  will depend on the shape of the specimen, because of demagnetizing effects. For an ellipsoidal specimen measured in a field parallel to one of its axes the field within the specimen,  $H_1$ , is related to the applied field  $H_0$  by the relation

$$H_1 = H_0 - DM,$$

where  $D$  is the classical demagnetizing factor and  $M$  is the magnetic moment per unit volume. Hence

$$T_{\text{measured}}^* = \frac{\lambda}{\chi_{\text{measured}}} = \frac{\lambda H_0}{M} = \frac{\lambda H_1}{M} + \lambda D.$$

At a given absolute temperature, values of  $T^*$  measured on two differently shaped specimens differ therefore by a constant amount,  $\lambda(D_1 - D_2)$ . In all the results given, we have converted the values of  $T^*$  measured on ellipsoidal specimens to the corresponding value for a spherical specimen.

### 3. THE EXPERIMENTS

#### (a) Specific heat measurements

The three most commonly used methods of specific heat measurement below 1 °K employ (i) electrical heating, (ii) heating by absorption of  $\gamma$ -rays and (iii) absorption of heat from an applied sinusoidal magnetic field. Owing to the particular properties of this salt it was possible to employ in turn each one of these methods over the same temperature range. Such a direct comparison of the three methods has not previously been reported.

#### (i) Electrical heating

For this method the specimen consisted of two single crystal hemispheres of the salt, attached one on either side of a thin (0.004 in.) silver foil, using Apiezon J oil to make good thermal contact. The heater coil, a 100 Ω length of 47 s.w.g. Eureka wire wound directly on the silver strip, was also impregnated with J oil to ensure good contact. The leads to the coil were coated with a superconducting layer of soft solder, so that no potential drop occurred across them and no heat was developed in them during heating of the coil and specimen. The silver foil was divided into strips along its length to minimize the effect of eddy currents induced by the alternating magnetic field used to measure the susceptibility of the sphere. In this manner  $C^* = dQ/dT^*$ , the specific heat measured on the  $T^*$  scale, was obtained as a function of  $T^*$ . The heat capacity of the heating coil and the silver foil was negligible in the temperature range of the experiments (below 0.5 °K).

#### (ii) $\gamma$ -ray Heating

In these experiments the specimen consisted of a sphere made by pressing together the two single crystal hemispheres with a little Apiezon J oil between them. It was held between two thin Perspex rings and suspended in the cryostat by fine cotton threads. The  $\gamma$ -rays were emitted by two  $\frac{1}{2}$ Ci  $^{60}\text{Co}$  sources arranged at the ends

of two swinging arms so that they could be raised rapidly into positions on either side of the specimen sphere and some 5 cm from it. Locating stops ensured that the sources always returned to the same positions and the time of heating was measured by an electric clock actuated by a mercury switch attached to one arm. The rate of heat absorption by the specimen was assumed to be constant, say  $Q_0$  ergs/second. The value of  $Q_0$  was obtained by normalizing the resultant curve of  $C^*$  against  $T^*$  to that obtained by electrical heating at one particular value of  $T^*$  ( $T^* = 0.4^\circ$ ).

### (iii) Relaxation heating

The specimen for these experiments was that used for the  $\gamma$ -ray method. At temperatures in the neighbourhood of a cooperative anomaly the magnetization in an alternating field has a component out of phase with the field, so that energy is absorbed. If we write

$$\chi = \chi' - i\chi''$$

the rate of absorption of energy by the salt is given by

$$dQ/dT = \frac{1}{2}h_0^2\omega\chi'',$$

where  $\omega$  is the angular frequency and  $h_0$  is the amplitude of the applied sinusoidal magnetic field. With a measured value of  $h_0$  the rate of heating was observed as a function of  $T^*$ . At intervals the value of  $h_0$  was dropped to a very much smaller value and the rate of rise of temperature observed. From a knowledge of the rate immediately before and after changing  $h_0$  the amount of stray background heating could be deduced and allowed for. The value of  $h_0$  was calculated from a measurement of the current in the coil and the geometry of the coil (63 Oe/A).  $\chi''$  was measured directly by the potentiometer of the Hartshorn bridge; if the resistance required to balance the out of phase susceptibility of the specimen is  $\Delta R$  and the mutual inductance required to balance the in phase susceptibility is  $\Delta M$ , at an angular frequency  $\omega$ , then

$$\chi''/\chi' = \Delta R/\omega\Delta M.$$

In general the frequency used was 175 c/s, and the field  $h_0$  was between 0.6 and 8 Oe, different values being used at different temperatures, since  $\chi''$  varies rapidly with temperature.

The values of  $C^*$  obtained by these three methods agree well over the whole temperature range. The results are plotted against  $T^*$  in figure 1. It is worth emphasizing the good agreement between the three methods when applied to the same specimen, since in the past there has been some discussion as to the validity of the  $\gamma$ -ray method of heating in specific heat work, and the question has been raised whether the discrepancies between results on the same substance obtained in different laboratories might be due to uncertainties in this method of heating (de Klerk, Steenland & Gorter 1948, 1950; Platzman 1953; reply by Kurti & Simon 1953).

### (b) Entropy measurements

The entropy of the sample as a function of  $T^*$  was measured in the standard manner, as first described by Kurti & Simon (1935). The specimen was magnetized at a known temperature  $T_i$  near 1 °K and a known magnetic field  $H_0$ . The specimen was then thermally isolated from the cryostat and the field was lowered steadily.



The readings were then extrapolated back in time to give the value of  $T^*$  at the instant the field became zero. Since the entropy is conserved in a reversible adiabatic demagnetization, the entropy at this point corresponds to that in the initial field  $H_i$  at temperature  $T_i$ , which could be calculated. By repeating this procedure using different values of the initial field  $H_0$ , a plot of  $S$  as a function of  $T^*$  could be constructed. In calculating the entropy change on magnetization, it has to be remembered that because of the strong interionic forces, the applied magnetic field does not correspond to that experienced by an ion within the crystal. This effect is allowed for by the calculation given in appendix 1. The plot of  $S$  as a function of  $T^*$  is given in figure 2.

A point of interest noted during these measurements was that immediately on switching off the magnetic field the rate of temperature rise, as measured by the susceptibility, was very rapid, but in a time of about  $\frac{1}{2}$  min decayed to a much smaller rate that was thereafter maintained. Such behaviour is always to be expected to some extent, owing to the fact that residual gas in the cryostat takes a finite time to condense on the specimen. However, the initial fast heating was independent of the length of time for which the cryostat was evacuated before demagnetization, which suggests that it is associated with a relaxation time for attainment of equilibrium within the specimen.

### (c) $T-T^*$ determination

To measure  $T^*$  as a function of  $T$  we used the method employed by Meyer (1959) for his work on praseodymium ethyl sulphate. This consists in essence of measuring simultaneously the values of  $T^*$  for two specimens in good thermal contact. The  $T-T^*$  relation being known for one specimen, that for the other is obtained by a simple comparison. For the second salt we used cerium magnesium nitrate which is known from theoretical considerations and from experiment (Cooke, Duffus & Wolf 1953; Daniels & Robinson 1953) to obey a simple Curie law down to a temperature of a few millidegrees, so that  $T^* = T$ . To measure the susceptibilities independently these specimens were separated by some 20 cm, the upper lying within one mutual inductance coil system and the lower within another. Good thermal contact was maintained by means of strips of silver foil. The spherical dysprosium salt specimen and the cylindrical cerium salt specimen were attached one half at each side of a central silver strip, as in the experiments to measure the specific heat by the electrical method. Other silver strips were laid over the two specimens and the whole was bound with thread and finally impregnated with apiezon J oil.

Cerium magnesium nitrate was chosen as the second salt not only because  $T^* = T$  but also because it has an extremely small specific heat ( $CT^2/R = 7 \times 10^{-6}$ ) and thus requires very little heat to pass along the foils to maintain thermal equilibrium. During an experiment the compound specimen was demagnetized and the value of  $T^*$  observed for each specimen as it warmed up. The thermal contact between the specimens could be checked by either heating the dysprosium salt by relaxation heating or the cerium salt by an electrical heater and observing the time for the attainment of equilibrium. The results of the measurements are shown in figure 3.

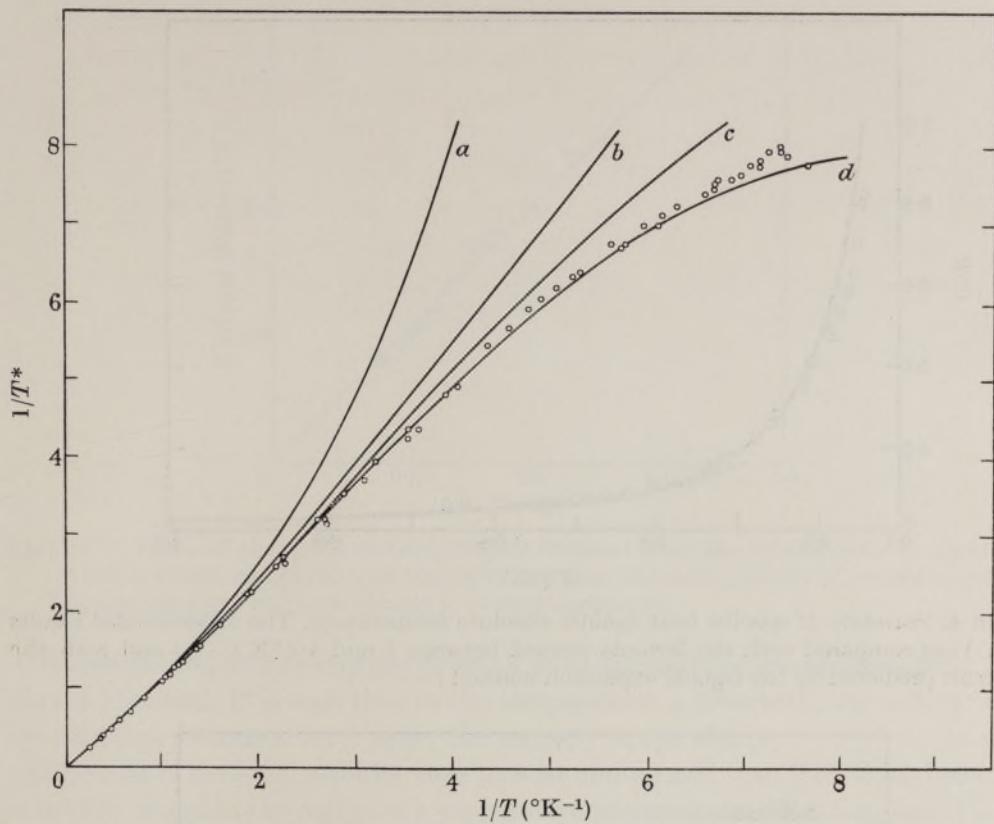


FIGURE 3. Variation of  $1/T^*$  ( $= \chi/\lambda$ ) against  $1/T$ . The points ( $\circ$ ) represent the experimental results. The curves represent the results calculated for various theoretical models. (a) Molecular field model; (b) Van Vleck expansion to second order in  $(1/T)$ ; (c) Ising model with nearest neighbour interactions in a molecular field; (d) Ising model with nearest and next nearest neighbour interactions in a molecular field.

#### (d) Analysis of data

Using the  $T-T^*$  relation, we can convert the  $C-T^*$  and the  $S-T^*$  curves to  $C-T$  and  $S-T$  curves,  $C$  being now the true specific heat. These are displayed in figures 4 and 5. The three sets of data,  $C^*$  against  $T^*$ ,  $S$  against  $T^*$ , and  $T^*$  against  $T$ , which can be measured directly are not independent. We have

$$T = \frac{dQ}{dS} = \frac{dQ/dT^*}{dS/dT^*} = \frac{C^*}{dS/dT^*},$$

which is the basis of the Kurti-Simon method of  $T-T^*$  determination (Kurti & Simon 1935). The value of  $T$  was calculated at several different values of  $T^*$  from the  $C^*-T^*$  curve and the gradient of the  $S-T^*$  curve. The value of  $T$  so obtained is plotted against the value of  $T$  obtained experimentally in our  $T-T^*$  determination (figure 6). To within the accuracy of the thermodynamic method the results are seen to agree; that is, the three sets of independently measured data are consistent.

Similar specific heat results have recently been given by Huiskamp (1966), who, by using an independent method of measuring temperatures, was able to obtain

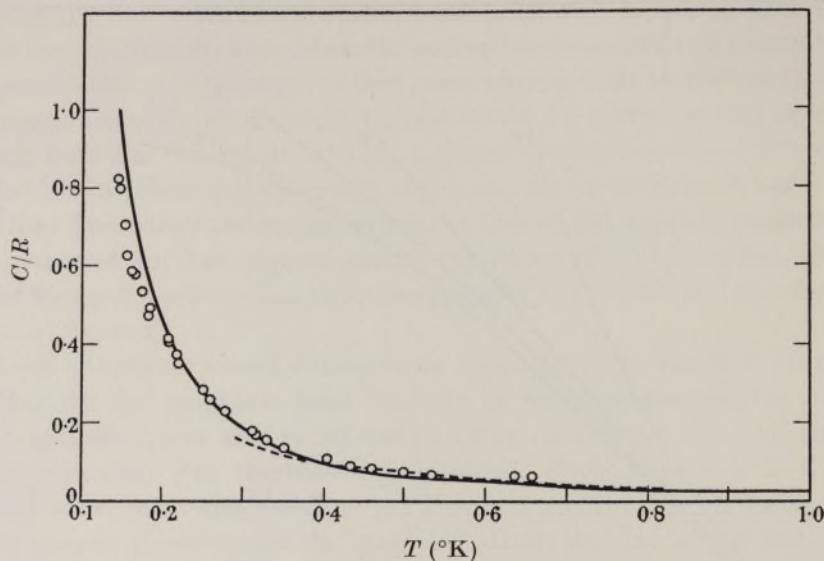


FIGURE 4. Variation of specific heat against absolute temperature. The experimental results ( $\circ$ ) are compared with the formula obeyed between 1 and  $4.2\text{ }^{\circ}\text{K}$  (----) and with the result predicted by the Oguchi expansion method (—).

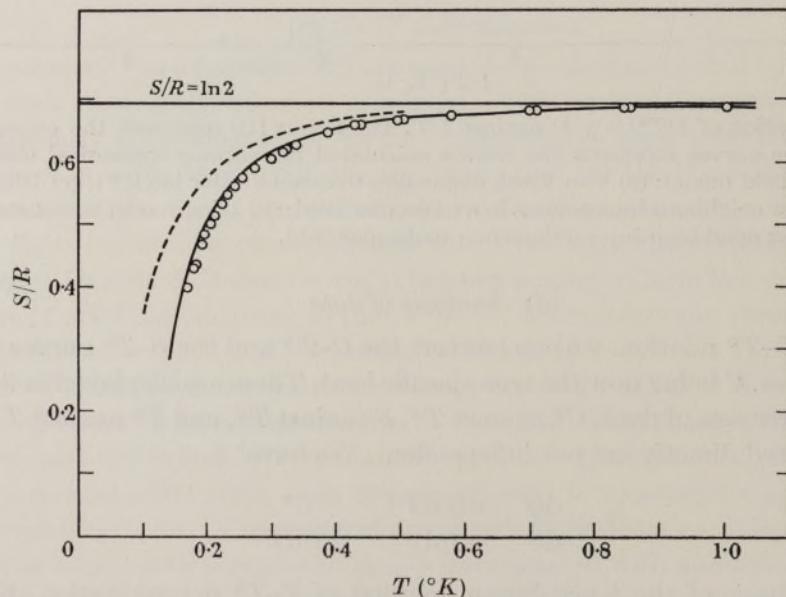


FIGURE 5. Variation of entropy against absolute temperature. The experimental results ( $\circ$ ) are compared with a model assuming non-interacting linear Ising chains (----) and with the result predicted by the Oguchi expansion method (—).

$C-T$  values down to about  $0.1\text{ }^{\circ}\text{K}$ . In the range covered by both our experiments he obtains specific heat values at a given temperature of about 15 % lower than ours, which could be accounted for if there were a difference of about 6 % in our absolute temperature scales. This would also help to account for the 10 % discrepancy between our estimates of the critical temperature.

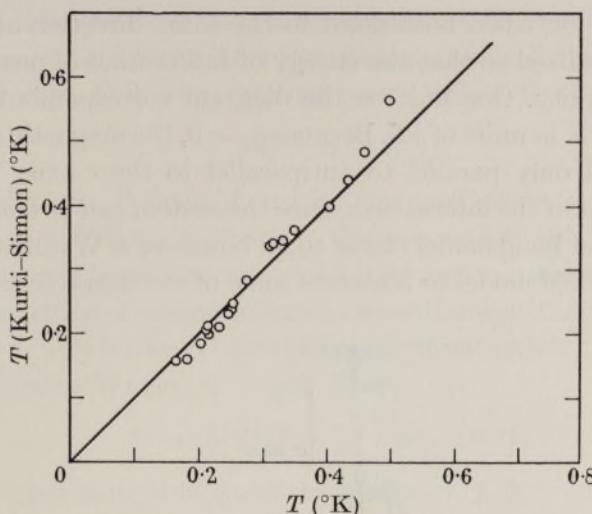


FIGURE 6. Value of the absolute temperature deduced from the thermodynamic method of Kurti & Simon compared with that obtained from the susceptibility of cerium magnesium nitrate. Straight line corresponds to perfect agreement.

Before dealing with the results in detail let us discuss briefly the general form of the curves obtained. It is seen that as the temperature is lowered towards  $0\cdot13\text{ }^{\circ}\text{K}$  the specific heat becomes very large, the entropy drops sharply and  $\chi'$  the in-phase component of the susceptibility rises to a maximum and then falls. Such behaviour is usually found in the region of a cooperative phenomenon. This conclusion is supported by the fact that as the temperature was lowered in the vicinity of  $0\cdot13\text{ }^{\circ}\text{K}$ ,  $\chi''$ , the out-of-phase component of the susceptibility became rapidly larger. When the coupling forces between magnetic ions become sufficiently large their magnetic moments tend to become ordered in some definite array and thus are restrained from responding instantaneously to an impressed magnetic field. The resulting phase lag between the induced magnetic moment and the primary field leads to an increase in  $\chi''$ . As the temperature is further diminished increasing numbers of ions become ordered. This effect gradually outweighs that of the decreased disturbance from the thermal motion, so that  $\chi'$  passes through a maximum value and finally decreases. The marked drop in entropy and rise of specific heat reflect the onset of order. We would therefore say that in the vicinity of  $0\cdot13\text{ }^{\circ}\text{K}$  there is a cooperative anomaly leading to an ordered array of the ionic magnetic moments. In the following paper, which deals with the behaviour of this substance below the susceptibility maximum, we present the evidence that the ordered state is ferromagnetic.

#### 4. THEORY

##### *Introduction*

The crystal structure of the rare earth ethyl sulphates has been determined by Ketelaar (1937). Figure 7 shows how the dysprosium ions are disposed in the lattice. Knowing their relative positions and *g*-values we can calculate the strength of the magnetic dipole-dipole coupling between any two ions. The number in round brackets against an ion in figure 7 indicates the relative energy of interaction of this

ion with the central ion when both point in the same direction along the *c*-axis. The values are normalized so that the energy of interaction of nearest neighbours along the *c*-axis is unity. One unit on the diagram corresponds to an energy of  $0.071 \text{ cm}^{-1}$ , or  $0.104 \text{ }^{\circ}\text{K}$  in units of  $kT$ . Because  $g_{\perp} = 0$ , the magnetic moment of each ion may be directed only parallel to antiparallel to the *c*-axis. This immensely simplifies calculations of the interaction, since the system can be treated classically. Such an assembly, an Ising model (Ising 1925; Kramers & Wannier 1941) has long been used as a simplified model to illustrate some of the characteristics of cooperative phenomena.

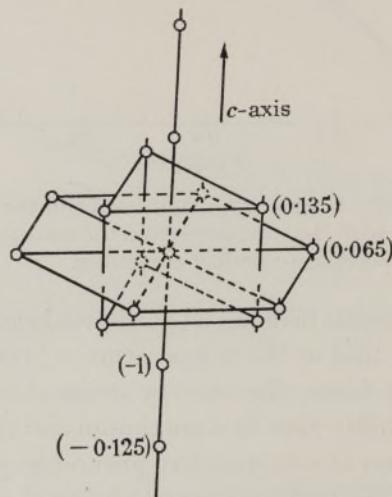


FIGURE 7. The arrangement of the dysprosium ions in the ethyl sulphate lattice. The numbers in brackets give the relative strengths of the interaction through magnetic dipole-dipole forces of that ion with the central ion.

#### *The magnetic susceptibility*

The simplest calculation we can make is a molecular field calculation, in which the actions of other ions on any one ion in the salt are represented as a change in the effective field it experiences. The mean value of such a field will be proportional to the intensity of magnetization of the material. By assuming that every ion experiences this value of the field, i.e. by ignoring all local variations, we obtain a self-consistent expression for the magnetization in a given external field. We have

$$M/H_{\text{ion}} = \lambda/T \text{ at high temperatures.}$$

Here

$M$  = magnetic moment per unit volume,

$H_{\text{ion}}$  = field experienced by a magnetic ion.

$H_{\text{ion}} = H_0 + H_D + H_M$ ,

where

$H_0$  = applied field,

$H_D$  = demagnetizing field due to surface effects in a finite sample,

$H_M$  = molecular field due to interactions with all the other ions in the sample.

For an ellipsoid magnetized along a principal axis,  $H_D$  is uniform throughout the specimen and  $= -DM$ , where  $D$  is the demagnetizing factor determined by the shape of the ellipsoid. Following Lorentz (1916) we put

$$H_M = H' + H'',$$

where  $H'$  = field due to the neighbouring ions lying within a sphere centred on the ion considered, and  $H''$  is the field due to the ions outside this sphere. Provided the radius of the sphere is large compared with the interionic distance,  $H''$  can be found by replacing the lattice of magnetic ions by a continuum. Then  $H'' = \frac{4}{3}\pi M$ . Lorentz showed that for a cubic lattice  $H' = 0$ . However, this does not hold for the hexagonal ethyl sulphate lattice. We put  $H' = pM$ . Then

$$M = (\lambda/T)[H_0 + (p + \frac{4}{3}\pi - D)M].$$

Hence the measured susceptibility of the specimen,  $\chi$ , is

$$\chi = \frac{M}{H_0} = \frac{\lambda}{T - \lambda(p + \frac{4}{3}\pi - D)}. \quad (1)$$

For a sphere,  $D = \frac{4}{3}\pi$ , and then

$$\chi_{\text{sphere}} = \frac{\lambda}{T - \lambda p} = \frac{\lambda}{T - \theta}.$$

The value of  $\lambda$ , the Curie constant per unit volume of dysprosium ethyl sulphate, is 0.0308. The value of  $p$  can be calculated from the lattice sum for magnetic dipole interaction

$$L = \sum_j \left( \frac{3z_j^2}{r_j^5} - \frac{1}{r_j^3} \right),$$

where  $r_j$  = distance from the central ion to the  $j$ th ion, and  $z_j$  = coordinate of the  $j$ th ion along the  $c$ -axis of the crystal relative to the central ion. This sum has been calculated by Daniels (1953) who obtained  $L = 18.7a^{-3}$  for a sphere for radius  $a\sqrt{10}$ . We have computed the more accurate value of  $L = 19.3a^{-3}$  for a sphere summing over more than 36 000 nearest neighbours. Using this value we obtain

$$p = L/(\text{number of ions/cm}^3) = 4.21$$

and

$$\theta = \lambda p = 0.130 \text{ } ^\circ\text{K}.$$

Since we define  $T^* = \lambda/\chi_{\text{sphere}}$ , we have  $T^* = T - \theta$ . This expression is compared with the experimental results in figure 3. It can be seen that while it is adequate at higher temperatures, it fails badly at lower temperatures.

#### *The series expansion method*

This general method has been used extensively for various magnetic problems in a form given by Van Vleck (1937). The partition function  $Z$  for an assembly of ions coupled by magnetic dipole or other interactions is

$$Z = \text{trace} [\exp(-W/kT)],$$

where  $W$  represents the energy matrix of the whole assembly. This can be expanded in powers of  $W$

$$Z = \text{trace} [1 - W/kT + \frac{1}{2}(W/kT)^2 - \dots].$$

The advantage of the method lies in the fact that the trace of any power of  $W$  is independent of the representation chosen, so that it is not necessary to find the individual eigenvalues of  $W$ . Its disadvantage is that the computation of the higher terms is difficult, so that its usefulness is limited to comparatively high temperatures where the series converges rapidly, and the first few terms suffice. The method has been applied to the ethyl sulphates by Daniels (1953). If we put

$$Z = 2^N \left( 1 + \frac{A}{T} + \frac{B}{T^2} + \frac{C}{T^3} + \frac{D}{T^4} + \dots \right)$$

then  $\chi_{\text{sphere}} = \lim_{H \rightarrow 0} \left\{ \frac{k}{H} \left[ \frac{1}{T} \frac{\partial B}{\partial H} + \frac{1}{T^2} \frac{\partial C}{\partial H} + \frac{1}{T^3} \frac{\partial (D - \frac{1}{2}B^2)}{\partial H} \right] \right\}.$

(It can be shown that  $A \equiv 0$ ). Writing

$$\chi_{\text{sphere}} = \frac{\lambda}{T} \left( 1 + \frac{\Delta_1}{T} + \frac{\Delta_2}{T^2} + \dots \right);$$

we have  $\Delta_1 = \frac{g^2 \beta^2}{4k} \sum_j \frac{3z_{ij}^2 - r_{ij}^2}{r_{ij}^5},$

which is identical to the Curie-Weiss  $\theta$  calculated above for the molecular field model

$$\Delta_1 = \theta = 0.130 \text{ } ^\circ\text{K}.$$

The expression for  $\Delta_2$  becomes

$$\Delta_2 = \frac{(\bar{P})^2 - \bar{P}^2}{k^2},$$

where  $\bar{P} = \frac{g^2 \beta^2}{4} \sum_j \frac{3z_{ij}^2 - r_{ij}^2}{r_{ij}^5}$

and  $\bar{P}^2 = \frac{g^4 \beta^4}{16} \sum_j \left[ \frac{3z_{ij}^2 - r_{ij}^2}{r_{ij}^5} \right]^2.$

Using the values of these lattice sums given in Daniels's paper we obtain

$$\Delta_2 = -0.008 \text{ } (^\circ\text{K})^2,$$

so that finally we obtain

$$\chi_{\text{sphere}} = (\lambda/T) \left( 1 + \frac{0.130}{T} - \frac{0.008}{T^2} + \dots \right). \quad (2)$$

It will be seen that as far as terms in  $1/T^2$ , the molecular field and Van Vleck methods give the same result. However the inclusion of the next term in the expansion brings the Van Vleck method closer to the experimental results at low temperatures (figure 3).

#### *The Ising model*

As shown in figure 7, by far the strongest coupling between ions in this salt is that between nearest neighbours along the *c*-axis (1 unit), while that between next nearest neighbours along this axis (0.125 unit) is almost as strong as the strongest coupling of a given ion with any ion not on its own *c*-axis (0.135 unit). This suggests

that a calculation which takes account exactly of the interactions of neighbouring ions forming a chain along the direction of the *c*-axis but treats the interactions of other ions only approximately may be more profitable than one which treats only a few near neighbours. We construct then a model of Ising chains in the direction of the *c*-axis with interactions between nearest neighbours in the chains, and we represent the coupling between the chains by a molecular field acting on an ion in a given chain, due to all the ions save its two nearest neighbours. Similar calculations using this general method have been given by Stout & Chisholm (1962) and by Marsh (1966).

The partition function per ion in a one-dimensional Ising chain with nearest neighbour interactions has been calculated exactly by Kramers & Wannier (1941)

$$Z_1 = e^K \cosh C + (e^{2K} \sinh^2 C + e^{-2K})^{\frac{1}{2}},$$

where  $C = \mu H/kT$  ( $\mu$  = magnetic moment per ion);  $K = E/kT$  ( $E$  = energy of interaction of two nearest neighbours pointing in the same direction).

The value of  $K$  for magnetic dipole interaction is given by

$$K = \frac{2\mu^2}{c^3} \frac{1}{kT},$$

which for our system gives  $K = 0.104/T$ .

If there are  $N$  ions per unit volume the average magnetic moment per unit volume is given by

$$\begin{aligned} \langle M \rangle &= NkT \partial \ln Z_1 / \partial H \\ &= N\mu \frac{\sinh C}{(\sinh^2 C + e^{-4K})^{\frac{1}{2}}}. \end{aligned}$$

Now take

$$H = H_0 + p' \langle M \rangle,$$

where  $H_0$  is the externally applied magnetic field and  $p' \langle M \rangle$  is the molecular field due to all ions except the two nearest. Then with some manipulation we have for the magnetic susceptibility per unit volume,

$$\begin{aligned} \chi &= \lim_{H_0 \rightarrow 0} \frac{\langle M \rangle}{H_0} \\ &= \frac{\lambda}{Te^{-2K} - p'\lambda}, \end{aligned} \tag{3}$$

where  $\lambda = N\mu^2/k$ , the Curie constant per unit volume. Now  $p'$  is given by

$$p' = \sum_j \left( \frac{3z_{ij}^2}{r_{ij}^5} - \frac{1}{r_{ij}^3} \right),$$

where the summation is taken over all the ions in the vicinity of the *i*th ion except its two immediate neighbours on the same Ising chain. We may obtain the value of  $p'$  by subtracting the contribution  $p_{nn} = 6.77$  from the two nearest neighbour ions so that for a spherical specimen

$$p' = 4.21 - 6.77 = -2.56$$

Substituting for  $p'$ ,  $\lambda$  and  $K$  we obtain

$$\chi_{\text{sphere}} = \frac{\lambda}{T e^{-2K} + 0.078},$$

or

$$T^* = T e^{-0.208/T} + 0.078 \text{ } ^\circ\text{K}.$$

This theoretical prediction is compared with experiment in figure 3. The agreement is seen to be good, the maximum discrepancy between theory and experiment of some 10 mdeg occurring in the region of the cooperative phenomenon. We may expect a method relying on statistical averaging, such as the molecular field method, to break down here, since in the neighbourhood of a cooperative effect local ordering may cause the magnetic environment of a particular ion to differ markedly from the mean.

It is possible, by using the partition function of a one-dimensional Ising chain with nearest and next nearest neighbour interactions derived by Montroll (1941) and introducing the effect of a small external field along the chain as a perturbation, to obtain even better agreement with experiment (Edmonds 1958), (figure 3). However, because of the ponderous mathematics involved and the fact that no further physical insight into the problem is gained, the details of the calculation are omitted here. The agreement with experiment of both approximations is good enough to give confidence in the model of loosely coupled Ising chains along the *c*-axis.

#### *The entropy and specific heat*

The defect of the molecular field model is that it takes no account of interactions within the group of ions giving rise to the molecular field. These interactions have only a second-order effect on the magnetic susceptibility, but they have a first-order effect on the entropy and specific heat, since it is just these interactions which produce the local ordering responsible for the fall of entropy which occurs even above the temperature of a cooperative anomaly. It follows that the semi-molecular field treatment given above, while successful in dealing with the magnetic susceptibility, cannot be applied to a calculation of the entropy and specific heat in zero field. We are indebted to Dr B. R. Heap for a calculation of the partition function by a method taking into account the interaction of each ion with eighteen near neighbours (those shown in figure 7 together with the next neighbours along the *c*-axis). The calculation, which is based on the Oguchi expansion method (Oguchi 1951) is set out in the appendix to this paper contributed by Dr Heap. Before the result of this calculation can be compared with experiment it is necessary to take into account the effect of nuclear hyperfine interaction. Two of the stable isotopes of dysprosium,  $^{161}\text{Dy}$  and  $^{163}\text{Dy}$ , have nuclear spin ( $I = \frac{5}{2}$  in each case) and hence have nuclear magnetic moments. As  $g_{\perp} = 0$ , the magnetic field due to an electronic moment at its nucleus will always be parallel or antiparallel to the crystalline *c*-axis, so that a nucleus having a magnetic moment can exist in one of six quantized states characterized by the quantum number  $I_z$  which may take values  $\pm \frac{5}{2}, \pm \frac{3}{2}, \pm \frac{1}{2}$ . (We have taken the *z*-axis along the *c*-axis of the crystal.) Associated with this multiplicity of nuclear energy states is a nuclear entropy, which must be taken into account when considering the determination of the  $S-T^*$  curve.

On the application of a magnetic field at 1 °K a calculable quantity of electronic entropy is extracted, (it can readily be shown that no appreciable nuclear entropy is extracted), but during the demagnetization, when the total entropy of the system remains constant, it is no longer true to say that the electronic contribution to this total remains constant. In fact as the temperature falls during demagnetization the amount of entropy associated with the nuclear system falls, so that the electronic entropy must rise. When zero field is reached, the total entropy extracted by magnetization at 1 °K must be regarded as having been used partly to lower the entropy of the electronic system and partly that of the nuclear system, the proportion extracted from each depending on the final temperature reached and on the interactions between the two systems. However, in this particular case, with  $g_{\perp} = 0$  the problem can be solved exactly, for it can be shown (Edmonds 1958; Mattis & Wolf 1966) that the values of the entropy associated with the two systems are simply additive; that is, the partition function factorizes so that  $Z_{\text{total}} = Z_{\text{electronic}} Z_{\text{nuclear}}$ . Physically, the simplicity of this particular case arises from the fact that the nuclear entropy depends only on even powers of the hyperfine interaction Hamiltonian  $\mathcal{H} = S_z A I_z$ , so that the two possible states of the electronic moment are equivalent. That is, the entropy of the nuclear system is independent of the state of polarization of the electronic moments and hence independent of the effect of an applied magnetic field on the electronic moments. The nuclear contribution to the specific heat or the entropy may be calculated exactly, as in I (p. 253). We find that to a sufficient approximation it is given by

$$C_n T^2/R = 9.5 \times 10^{-4}.$$

Allowing for this contribution, the calculated entropy and specific heat curves are compared with the experimental values in figures 4 and 5. The agreement is seen to be excellent.

## 5. CONCLUSIONS

The close agreement between the experiments and calculations described in this paper have shown that dysprosium ethyl sulphate is an unusually simple magnetic system in some respects. It is found that magnetic dipole coupling between the Dy<sup>3+</sup> ions accounts quite adequately for all the observed interaction effects, which because of the extreme anisotropy of the electronic splitting factor may be expressed in terms of a sum of Ising model interactions  $\sum_{i>j} P_{ij} S'_{zi} S'_{zj}$  between effective spins with  $S' = \frac{1}{2}$ . For any particular pair of neighbouring ions the interaction is thus specified by a single constant  $P_{ij}$  which is determined completely by the lattice parameters and the principal electronic splitting factor.

Such an interaction is of course not restricted to nearest neighbours alone and it is therefore not possible to make direct comparisons with any of the available Ising model calculations which in almost all cases have considered only nearest neighbours. However, because of the particular structure of the ethyl sulphates the magnetic dipole interaction with each of the two nearest neighbours along the hexagonal axis is more than seven times stronger than any of the other interactions,

and it is therefore possible to take account of the more distant neighbours using various approximations. Two of the simplest approximations are discussed in the present paper but it seems clear that more refined theoretical calculations on this particular system would be both straightforward and worthwhile.

Long-range magnetic dipole interactions are of course present in all real systems, but it would seem particularly advantageous to study their effect in a situation in which the anisotropy is so strong that only the simple scalar part of the interaction is effective. All contributions to the total Hamiltonian then commute and all observable properties can thus be calculated classically. For example, the formation of domains under these conditions can be calculated from simple dipole lattice sums as shown in the following paper, in which we also discuss several of the other properties of dysprosium ethyl sulphate below its ferromagnetic Curie temperature at 0.13 °K. One might hope that the simple Ising-like form of the interaction Hamiltonian in highly anisotropic systems such as this one might ultimately lead to a better quantitative understanding of all the various effects resulting from long range character of the magnetic dipole interactions.

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## APPENDIX I

This appendix evaluates the initial entropy of dysprosium ethyl sulphate in an external field  $H_0$  and at a temperature  $T_i$  account being taken of the magnetic dipolar interaction on the basis of various models.

### (A) Molecular field model

As discussed in the text we may write

$$H_{\text{ion}} = H_0 + (p + \frac{4}{3}\pi - D) M \dots, \quad (\text{i})$$

where  $M$  is the magnetic moment per unit volume. Also

$$\chi = \lambda/(T - \theta) \quad \text{where} \quad \theta = (p + \frac{4}{3}\pi - D)\lambda \dots. \quad (\text{ii})$$

As we have a simple magnetic doublet occupied at the temperatures  $T_i$  of interest we may write

$$M = n\mu \tanh(\mu H_{\text{ion}}/kT),$$

where  $n$  is number of ions per unit volume and  $\mu$  is their magnetic moment.

Assuming that  $(p + \frac{4}{3}\pi - D) M \ll H_0$  we may expand  $M$  as

$$M = M|_{H=H_0} + \left. \frac{\partial M}{\partial H} \right|_{H=H_0} (H_{\text{ion}} - H_0) + O(H_{\text{ion}} - H_0)^2 \dots, \quad (\text{iii})$$

and substituting for  $(H_{\text{ion}} - H_0)$  from (i) and using (ii) we have

$$M = n\mu \tanh \frac{1}{2}x \left\{ 1 + \frac{\theta}{T} \operatorname{sech}^2 \frac{1}{2}x \right\} + O\left(\frac{\theta^2}{T^2}\right) \dots, \quad (\text{iv})$$

where

$$\frac{1}{2}x = \mu H_0/kT.$$

Thus the magnetization per mole is given by

$$M_0 = N\mu \tanh \frac{1}{2}x \left\{ 1 + \frac{\theta}{T} \operatorname{sech}^2 \frac{1}{2}x \right\} + O\left(\frac{\theta^2}{T^2}\right) \dots, \quad (\text{v})$$

where  $N$  is the Avogadro number.

The first-order correction to the entropy of magnetization may be found in a similar manner. If  $S_0$  is the entropy in the absence of any interionic coupling (Hull & Hull 1941) while  $S_1$  is the entropy with such coupling on a molecular field model then

$$S_1 = S_0 + \left. \frac{\partial S}{\partial H} \right|_{H=H_0} (H_{\text{ion}} - H_0) + O(H_{\text{ion}} - H_0)^2.$$

Using the Maxwell relation  $\left( \frac{\partial S}{\partial H_0} \right)_T = \left( \frac{\partial M}{\partial T} \right)_{H_0}$

and equation (v) we obtain for the entropy  $S_1$

$$S_1/R = S_0/R - \left( \frac{\theta}{T} \right) \left( \frac{1}{2}x \right) \operatorname{sech}^2 \left( \frac{1}{2}x \right) \tanh \left( \frac{1}{2}x \right) + O\left(\frac{\theta^2}{T^2}\right).$$

#### (B) Ising chain model with nearest neighbour interactions and a molecular field representing the effect of all other ions

As discussed in the text the partition function for the Ising chain with nearest neighbour interactions in an external magnetic field (Kramers & Wannier, 1941) is given by

$$Z = e^K \cosh C + (e^{2K} \sinh^2 C + e^{-2K})^{\frac{1}{2}}.$$

Hence the entropy per mole  $S_2$  is given by

$$\begin{aligned} \frac{S_2}{R} &= \ln Z + \frac{T}{Z} \left( \frac{\partial Z}{\partial T} \right)_H \\ &= \ln Z - \frac{1}{Z} \left\{ e^K (K \cosh C + C \sinh C) \right. \\ &\quad \left. - \frac{e^{2K} (K \sinh^2 C + C \sinh C \cosh C) - K e^{-2K}}{(e^{2K} \sinh^2 C + e^{-2K})^{\frac{1}{2}}} \right\} \dots \end{aligned} \quad (\text{vi})$$

In  $C = \mu H/kT$  the field  $H$  may be written on a molecular field approximation as

$$H = H_0 + (p' + \frac{4}{3}\pi - D) M \dots, \quad (\text{vii})$$

where the lattice sum  $p'$  is taken over all ions in the given sphere except for the two nearest neighbour ions to the central ion, as discussed in the text. The two nearest neighbour interactions have been included exactly in the Ising model. Using equation (iv) to calculate  $M$  we may thus find  $C$  for any given  $H_0$  and  $T_i$  and substituting in (vi) find the entropy of magnetization for the Ising chain model.

## APPENDIX II. THE EXPANSION METHOD

BY B. R. HEAP

This method is used to calculate the partition function of an assembly of interacting ions by treating the strongest nearest neighbour interactions exactly and the weaker interactions with more distant neighbours as an approximation. It is based upon the high temperature expansion method developed by Oguchi (1951) for the Ising ferromagnet.

If we associate an operator  $\sigma$  with each spin such that  $\sigma = \pm 1$  depending on whether the spin points up or down the crystalline axis, the energy of interaction between two spins,  $i$  and  $j$  can be written as

$$-J_{ij}\sigma_i\sigma_j,$$

where  $-J_{ij}$  is the energy of interaction of two parallel spins at  $i$  and  $j$ . Then the partition function for the assembly is

$$Z = z^N = \sum_{\substack{\text{all} \\ \sigma' s = \pm 1}} [\exp \{ \beta \sum_{\text{pairs}} J_{ij} \sigma_i \sigma_j \}]$$

where  $z$  is the partition function for one ion,  $\beta = 1/kT$ ,  $N$  = number of ions in the crystal. This partition function can be factorized to give

$$z^N = \sum_{\substack{\text{all} \\ \sigma' s = \pm 1}} [ \prod_{\text{pairs}} \exp (\beta J_{ij} \sigma_i \sigma_j) ].$$

Since all of the  $\sigma$ 's =  $\pm 1$  we have

$$\cosh (\sigma_i \sigma_j \beta J_{ij}) = \cosh \beta J_{ij}$$

and

$$\sinh (\sigma_i \sigma_j \beta J_{ij}) = \sigma_i \sigma_j \sinh \beta J_{ij},$$

so that we can rewrite this partition function as

$$z^N = \sum_{\substack{\text{all} \\ \sigma' s = \pm 1}} [ \prod_{\text{pairs}} \cosh \beta J_{ij} \{ 1 + \sigma_i \sigma_j \tanh \beta J_{ij} \} ].$$

Since we are to consider interactions between the  $i$ th ion and its 18 nearest neighbours, we restrict our attention to the following interactions:

$J_1$  between the  $i$ th ion and the 1st neighbour in the same chain,

$J_2$  between the  $i$ th ion and the 2nd neighbour in the same chain,

$J_3$  between the  $i$ th ion and the 3rd neighbour in the same chain,

$J'$  between the  $i$ th ion and the nearest neighbours in the adjacent chains,

$J''$  between the  $i$ th ion and the nearest neighbours in the next adjacent chains.

The values of these interactions, normalized so that  $J_1 = 1$  are (in absolute units  $J_1 = k \times 0.104 \text{ } ^\circ\text{K}$ )

$$J_1 = 1, \quad J_2 = 0.125$$

$$J_3 = 0.037, \quad J' = -0.134,$$

$$J'' = -0.065.$$

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If we neglect all other interactions, the partition function is

$$\begin{aligned} z^N = & (\cosh \beta J_1)^N (\cosh \beta J_2)^N (\cosh \beta J_3)^N (\cosh \beta J')^{3N} (\cosh \beta J'')^{3N} \\ & \times \sum_{\substack{\text{all} \\ \sigma_s = \pm 1}} \left\{ \prod_r [(1 + \sigma_r \sigma_{r+1} t_1) (1 + \sigma_r \sigma_{r+2} t_2) (1 + \sigma_r \sigma_{r+3} t_3) \right. \\ & \left. \times (1 + \sigma_r \sigma_{r+1} t') (1 + \sigma_r \sigma_{r''} t'')] \right\} \dots, \end{aligned} \quad (1)$$

where  $t_1 = \tanh \beta J_1$ , etc., and the positions  $r, r+1$ , etc., of the ions are shown in figure 8. This is a side view of figure 7.

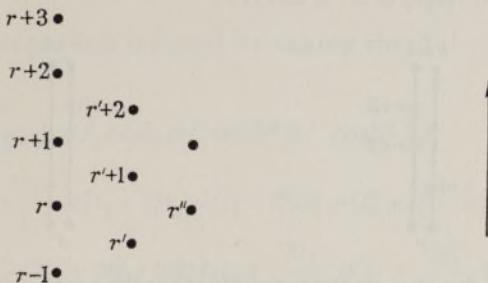


FIGURE 8. Side view of the hexagonal Dy ethyl sulphate space lattice. The circles represent the sites of the *Dy* ions. The labelling scheme for the lattice sites is shown.

It should be explained that, in factorizing out the terms  $\cosh \beta J_2$ , etc., in (1), it has to be remembered that, although each ion has two interactions of types  $J_1, J_2, J_3$  and six of types  $J', J''$ , the summation is over pairs.

We now wish to expand the partition function (1) so that, while the largest interaction is included exactly, the others are included to second order only. This is equivalent to expanding (1) in powers of  $t_2, t_3, t', t''$  {which are  $\ll 1$ }, up to second order, but including all powers of  $t_1$ , i.e.

$$\begin{aligned} & \text{terms like } t_1^n t_2 t_3 \text{ are included for all } n; \\ & \text{terms like } t_1^n (t')^2 t_3 \text{ are not included.} \end{aligned}$$

Although at first sight this seems a hopeless task, only certain combinations of the  $t$ 's are allowed and this simplifies the matter considerably. The reason for this becomes clear when some examples are considered.

Consider the coefficient of  $t_1^3 t_2 t_3$ . From (1) it is

$$\sum_{\substack{\text{all} \\ \sigma_s = \pm 1}} \left[ \sum_{\substack{i+j=k \\ l, m}} (\sigma_i \sigma_{i+1}) (\sigma_j \sigma_{j+1}) (\sigma_k \sigma_{k+1}) (\sigma_l \sigma_{l+2}) (\sigma_m \sigma_{m+3}) \right] \dots \quad (2)$$

On summing over all the possible values ( $\pm 1$ ) of all of the  $\sigma$ 's, it can be seen that each term in the sum  $\sum_{\substack{i+j=k \\ l, m}}$  will be zero unless each  $\sigma_r \{r = i, j, k, l, m\}$  appears an even number of times. In order to find the number of non-zero terms, we use a geometrical method.

With each pair of spins  $\sigma_i \sigma_{i+1}$  we associate a line joining the points  $i$  and  $i+1$ ; with each pair  $\sigma_l \sigma_{l+2}$ , we associate a line joining  $l$  and  $l+2$ , etc. Thus we see the only non-vanishing terms in (2) are those which correspond to a closed graph on the

lattice; for such a graph, each  $\sigma_r$  must be counted an even number of times. The value of the coefficient (2) of  $t_1^3 t_2 t_3$  will be given by the number of different closed graphs that can be drawn on the lattice obeying the rule under the second summation sign. At one particular lattice point  $r$ , two such graphs can be drawn and they are shown in figure 9. For clarity, the paths away from the starting point  $r$  and the return are shown separated although in fact they are collinear. As we can choose our starting point  $r$  in  $N$  ways, there will be  $2 \times N$  different graphs of this type that can be drawn on the lattice. Further, as each  $\sigma$  can take two values, there is another factor of  $2^N$ . Hence the coefficient of  $t_1^3 t_2 t_3$  is  $2^N \times 2 \times N$ .

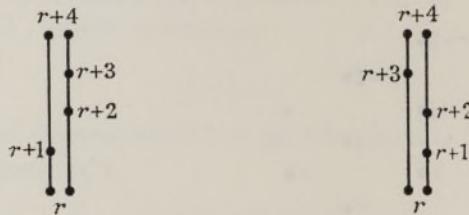


FIGURE 9. Lattice graphs for evaluating the coefficient of  $t_1^3 t_2 t_3$ .

It should be added here that a term such as  $t_1^n t_2 t_3$  with  $n > 2 + 3$  does not appear in the expansion of (1) since we cannot draw a *closed* lattice graph.

In the calculation of the coefficient of  $t_1^3 t_2 t_3$ , we drew our lattice graph on one chain. As a second and final example, we shall consider one where the lattice graph embraces more than one chain, e.g. consider the coefficient of  $(t_1)^3 (t')^2$ . From the expansion of (1) it is

$$\sum_{\substack{\text{all} \\ \sigma' s = \pm 1}} \left[ \sum_{\substack{i+j+k \\ l+m}} (\sigma_i \sigma_{i+1}) (\sigma_j \sigma_{j+1}) (\sigma_k \sigma_{k+1}) (\sigma_l \sigma_{l+1}) (\sigma_m \sigma_{m+1}) \right].$$

The corresponding lattice graph is shown in figure 10. Because of the three-dimensional nature of the lattice, the lattice graph in figure 10 is in reality three graphs.

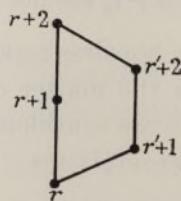


FIGURE 10. Lattice graph for evaluating the coefficient of  $t_1^3 (t')^2$ .

Hence there are three unique graphs that can be associated with each lattice point  $r$  and the coefficient of  $t_1^3 (t')^2$  is

$$3 \times N \times 2^N,$$

where the factor of  $N \times 2^N$  appears as before. It can be seen that the requirement that the lattice graph be closed is met by any term of the form  $(t_1)^n (t')^2$  where  $n = 1, 2, \dots, \infty$  and that the coefficient of all of these terms is the same as that of  $t_1^3 (t')^2$ . Terms such as  $t_1^n t'$  are inadmissible since they cannot satisfy the closure condition.

When this type of analysis has been carried out for all the permissible terms in the expansion of (1), we find

$$\begin{aligned} z^N = & 2^N (\cosh \beta J_1)^N (\cosh \beta J_2)^N (\cosh \beta J_3)^N (\cosh \beta J')^{3N} (\cosh \beta J'')^{3N} \\ & \times \left\{ 1 + Nt_1^2 t_2 + Nt_1^2 t_2^2 + \frac{1}{2} N(N-3) t_1^4 t_2^2 + Nt_1^3 t_3 \right. \\ & + Nt_1^2 t_3^2 + Nt_1^4 t_3^2 + \frac{1}{2} N(N-5) t_1^6 t_3^2 + 2Nt_1 t_2 t_3 \\ & \left. + 2Nt_1^3 t_2 t_3 + N(N-4) t_1^5 t_2 t_3 + 3N \sum_{n=1}^{\infty} t_1^n (t')^2 + 3N \sum_{n=1}^{\infty} t_1^{2n} (t'')^2 \right\} \dots \quad (3) \end{aligned}$$

The partition function per ion is found by taking the  $N$ th root of (3) and is, by the binomial theorem

$$\begin{aligned} Z = & 2 \cosh \beta J_1 \cosh \beta J_2 \cosh \beta J_3 \cosh^3 \beta J' \cosh^3 \beta J'' \\ & \times \left\{ 1 + t_1^2 t_2 + t_1^3 t_3 + (t_1^2 - t_1^4) t_2^2 + (t_1^2 + t_1^4 - 2t_1^6) t_3^2 \right. \\ & \left. + (2t_1 + 2t_1^3 - 3t_1^5) t_2 t_3 + \frac{3t_1}{1-t_1} (t')^2 + \frac{3t_1^2}{1-t_1^2} (t'')^2 \right\} \dots \quad (4) \end{aligned}$$

to second order in  $t_2, t_3, t'', t'$ .

From this partition function, the entropy and specific heat may be found from the formulae

$$\frac{s}{k} = \ln z - \beta \frac{\partial}{\partial \beta} \ln z$$

$$\text{and } \frac{c}{k} = -\beta \frac{\partial}{\partial \beta} \left( \frac{s}{k} \right).$$

As a check on the above analysis, if we put all of the  $J$ 's equal to zero except  $J_1$ , (4) becomes

$$z = 2 \cosh \beta J_1,$$

which is the partition function for an Ising chain with nearest neighbour interactions only.

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