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Demagnetization Experiments on Substances with Large Magnetic Dipole Interactions

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The properties of some rare earth salts are strongly influenced by magnetic dipole interaction between the rare earth ions, which at sufficiently low temperatures produces an ordered state, which may be ferromagnetic or antiferromagnetic. An account is given of experiments on dysprosium ethyl sulphate, which undergoes a transition to ferromagnetism at a temperature of 0.13°K. The magnetic properties of the substance above and below the transition are compared with those calculated on different theoretical models.

At sufficiently low temperatures any paramagnetic will show departures from ideal behaviour because of interactions between the magnetic ions. Normally the dominant effect is exchange interaction; even in substances in which the magnetic ions are relatively far apart and are separated by intervening atoms, indirect exchange is usually more powerful than magnetic dipole interaction¹⁾. However in compounds of the rare earths, in which the magnetic electrons belong to the inner 4 f group, exchange interaction is weak, and there is good experimental evidence that in the hydrated salts such as the ethyl sulphates and double nitrates, magnetic dipole interaction is the predominant effect, and suffices to account for the observed interaction contribution to the specific heat and the departure of the susceptibility from Curie's law²⁾. By experiments on compounds of rare earths belonging to the second half of the series, in which the ionic moments are very large, it is possible to study the effects of magnetic dipole interaction at temperatures where the interaction energy is of the same order of magnitude as kT, and so may be expected to produce an ordered state. If the crystal structure is known, the interaction forces are then known exactly, and it is possible to compare the observed behaviour with that calculated by different theoretical methods, and so to assess the merits of the different models used. Such precision is not possible when exchange interaction is important, since then the magnitude and symmetry of the forces have to be considered as adjustable elements in the calculation.

A complication arises from the fact that magnetic dipole forces are long range, and hence it is necessary to take account of interactions between relatively distant neighbours. Lorentz showed that for a magnetized system of cubic symmetry the interaction field due to neighbours within a sphere surrounding a given ion averages to zero. From this point of view the rare earth ethyl sulphates form a specially interesting series, since the lattice of magnetic ions is hexagonal³⁾, and the internal field due to near neighbours is large⁴). The best example for study is dysprosium ethyl sulphate, in which the crystalline electric field splits the ${}^{6}H_{15/2}$ free ion ground state in such a way as to produce a doublet ground level with a very large g-value (10.8) parallel to the symmetry axis of the crystal and a very small g-value perpendicular to it





 $(\approx 0)^{5}$. This enormously simplifies theoretical calculation, since the magnetic moments can be considered as scalar quantities which can point either up or down along the symmetry axis, exactly as in the classical Ising model. Fig. 1 shows the dysprosium ion lattice. It can readily be seen that the greatest interaction is that between nearest neighbours along the symmetry axis, and favours parallel alinement. The experiments described below lead us to believe that at a temperature of 0.13°K the magnetic dipole interaction forces bring about a transition to ferromagnetism. The experimental results are compared with theoretical calculations of different degrees of approximation.

The experiments can conveniently be considered in two parts, above and below the transition point. Those above the Curie point consist of measurements of the specific heat, entropy and susceptibility as functions of temperature. The chief problem is of course the determination of the temperature. For the specific heat and entropy measurements the magnetic susceptibility, measured by an alternating field method at 175 c/s, was used as the thermometric parameter, and the results converted to absolute temperatures from the susceptibility—temperature measurements. For this two methods were used. At higher temperatures (>0.2°K) the temperature was measured from the susceptibility of a sample of cerium magnesium nitrate kept in thermal contact with a spherical specimen of dysprosium ethyl sulphate by strips of silver to which they were both attached6). At lower temperatures this method gave inadequate heat contact, and a concentric shell technique⁷⁾ was used in which the magnetic susceptibility of a sphere of dysprosium ethyl sulphate was compared with that of a surrounding sphere of chromic methylammonium alum⁸⁾. This method was also used below the Curie point. The specific heat measurements were made using three different methods of heating, electrical heating, relaxation heating and gamma ray heating. All three agreed excellently together. The entropy measurements were made by adiabatic demagnetizations from known fields. and temperatures at which the entropy of the specimen could be calculated. The three different types of experiment are not of course independent; checks made by calculating the absolute temperature corresponding to a given susceptibility from the specific heat curve and the slope of the entropy curve showed that they were internally consistent.

The chief interest of these measurements lies in the opportunity they offer to com-







Fig. 3. Experimental and theoretical values for the entropy of dysprosium ethyl sulphate as a function of temperature.

pare theory and experiment, and so to test the validity of the assumption that magnetic dipole forces are the only important interactions between the ions.

Fig. 2 shows the observed variation of magnetic susceptibility plotted against 1/T, together with different theoretical curves. The first is a simple molecular field model, giving a Curie-Weiss law. The next is the result of the Van Vleck⁹⁾ expansion of the interaction Hamiltonian, taken to terms in $1/T^{3}$, that is, to give one more term than the molecular field model. The third is based on a model in which the interaction of an ion with its nearest neighbours is taken into account exactly by the Ising chain partition function of Kramers and Wannier¹⁰, while the interaction with other neighbours is represented by a molecular field. The last is a similar calculation in which the Ising chain method is used to calculate the interaction of nearest and next rearest neighbours along the chain¹¹⁾, other interactions being represented by a molecular field. It can be seen that these successive stages of approximation approach more and more closely to the experimental results, giving us confidence that only mathematical elaboration separates us from exact agreement. This remark also applies to the other results. Fig. 3 shows the entropy variation in zero external field, compared first with the Ising chain model with nearest neighbour interactions, as above, and then with the result of a calculation based on the Oguchi expansion method¹²⁾ which takes into account interaction with 18 nearest neighbours. This calculation represents the experimental results very closely indeed. (It must be noted that in comparing the experimental and theoretical curves, allowance must be made for the entropy arising from the nuclear hyperfine splitting of the electronic levels of Dy¹⁶¹ and Dy¹⁶³.¹³⁾ This however is small, and can be calculated exactly).

The experiments below the transition point consist of similar measurements of entropy and susceptibility against temperature. Here however the susceptibility is strongly dependent on the frequency of the alternating field used for the measurement, and to obtain a full picture of the behaviour



Figure 4. Comparison of the steady field and alternating field susceptibilities of dysprosium ethyl sulphate, as a function of entropy.

of the salt it is necessary to carry out measurements in alternating fields of different frequencies, and also to measure the susceptibility in steady fields. (A ballistic galvanometer of 20 seconds period was used for this). It was found that while above the transition the steady field and alternating field susceptibilities agreed, below the transition the steady field susceptibility was independent of temperature, while the alternating field susceptibility fell with temperature. Measurements on different specimens showed that within the error of experiment the volume susceptibility in steady fields has the value 1/N, where N is the demagneting factor of the specimen. This is precisely the behaviour to be expected of a ferromagnetic substance magnetized in domains, in which the magnetization of a specimen will be such that within the specimen the applied and demagnetizing fields cancel. We therefore form the hypothesis that in this substance magnetic dipole interaction brings about ferromagnetism, at a temperature of 0.13°K. We attribute the decreasing susceptibility in alternating fields to relaxation effects.

Considering this idea in more detail, we note that the strongest interaction between ions is that between neighbours in a chain along the crystalline *c*-axis. If we consider a very long specimen, in which demagnetizing effects are very small, we may expect that the ions would tend to aline in chains along the caxis. We have then to consider the interaction between neighbouring chains. A computor calculation for such a specimen (a 70:1 ellipsoid with some 400 ions along the axis) shows that by far the strongest interaction is provided by the three nearest neighbour chains, and is in such a direction as to favour parallel alinement of neighbouring chains, i.e. a ferromagnetic system. In a short specimen, we must expect that the magnetization will break up into domains, so as to reduce the external field energy. A simple calculation based on the considerations put forward by Kittel¹⁴⁾ shows that for a specimen whose dimensions are of the order of 1 cm the domains, which will consist of long needles or sheets parallel to the c-axis, will have thicknesses of the order of 10⁻⁴ cm.

As a further test of this hypothesis, we have measured the approach of the magnetization to saturation, both above and below the Curie point. The experiments were made by measuring the differential susceptibility of a specimen in applied fields up to



Fig. 5. Adiabatic magnetization curves of dysprosium ethyl sulphate above and below the transition point (experiment).

a few hundred gauss, and integrating the results to give the magnetization. Since the experiments were made on an isolated specimen, they were necessarily made at constant entropy instead of at constant temperature. but it can be seen that there is an essential difference between the results above and below the Curie point. Below the Curie point the magnetization at first rises at a constant rate independent of the particular value of the entropy, (corresponding to a susceptibility 1/N). This continues to a critical value of the field, dependent on the entropy, above which the magnetization rapidly approaches a constant value. This is again the behaviour to be expected of a ferromagnetic. We can reproduce it qualitatively by the model in which we have Ising chain interactions between nearest neighbours along the crystal axis, with a molecular field due to all other ions. The Kramers and Wannier partition function allows the magnetization and entropy of the Ising system to be calculated exactly in a finite field. For a specimen in which demagnetizing effects are negligible, we may put this field equal to the internal field due to the spontaneous magnetization of the rest of the specimen, and so obtain self-consistent values for the magnetization and entropy as a function of temperature. This model exaggerates the

suddenness of the transition to ferromagnetism, since it is incapable of representing adequately the short range ordering which occurs above the Curie point, but at present the more refined models have not been applied to the case of finite fields. The model gives a transition at a temperature of 0.170° K and an entropy S/R=0.534, compared with experimental values $T_c=0.127\pm.005^{\circ}$ K and S/R=0.205. Applying it to calculate the isentropic magnetization curves for a finite specimen, we obtain a series of curves of the general form of the experimental magnetization curves.

The choice of dysprosium ethyl sulphate was dictated by the high magnetic moment and complete magnetic anisotropy of the ground level. Holmium and terbium ethyl sulphate have also high and anisotropic magnetic moments, but since the ground level is not a Kramers doublet, the behaviour is complicated by the zero field Jahn-Teller splitting⁶⁾ and also by the nuclear hyperfine structure of the ground level, which provides the major part of the specific heat at temperatures near 1°K. Erbium ethyl sulphate is a case of interest, since here the ground level is a Kramers doublet with a high gvalue (8.8) perpendicular to the axis, and a low value (1.5) along the axis. It therefore provides the opposite case to dysprosium



Fig. 6. Theoretical isentropic magnetization curves, for the N=2.8 ellipsoid calculated on a model of Ising chains with molecular field.

ethyl sulphate, but as yet measurements have not been carried to a sufficiently low temperature to study interaction effects.

A detailed account of this work is in course of preparation for publication elsewhere.

References

- H. A. Kramers: Physica 1 (1934) 182; W.
 Opechowski: Physica 14 (1948) 237; R. J.
 Benzie, and A. H. Cooke: Nature 164 (1949) 837; J. F. Ollom, and J. H. Van Vleck: Physica, 17 (1951) 205.
- 2 A. H. Cooke, H. J. Duffus, and W. P. Wolf: Phil. Mag. 44 (1953) 623; J. M. Daniels, and F. N. H. Robinson: Phil. Mag. 44 (1953) 630; A. H. Cooke, F. R. McKim, H. Meyer, and W. P. Wolf: Phil. Mag. 2 (1957) 928; A. H. Cooke, D. T. Edmonds, F. R. McKim, and W. P. Wolf: Proc. Roy. Soc. A252 (1959) 246; But see also C. E. Johnson, and H. Meyer:

Proc. Roy. Soc. A253 (1959) 199.

- 3 J. A. A. Ketelaar: Physica 4 (1937) 619.
- 4 J. M. Daniels: Proc. Phys. Soc. A66 (1953) 673.
- 5 A. H. Cooke, D. T. Edmonds, F. R. McKim, and W. P. Wolf: Proc. Roy. Soc. A252 246.
- 6 H. Meyer: J. Phys. Chem. Solids 9 (1959) 296.
- 7 A. H. Cooke, J. H. M. Meyer, and W. P. Wolf: Proc. Roy. Soc. A233 (1956) 536.
- 8 W. E. Gardner, and N. Kurti: Proc. Roy. Soc. A223 (1954) 542.
- 9 J. H. Van Vleck: J. Chem. Phys. 5 (1937) 320.
- 10 H. A. Kramers, and G. H. Wannier: Phys. Rev. 60 (1941) 252.
- 11 E. W. Montroll: J. Chem. Phys. 10 (1942) 68.
- 12 T. Oguchi: J. Phys. Soc. Japan 6 (1951) 31.
- 13 A. H. Cooke, and J. G. Park: Proc. Phys. Soc. A69 (1956) 282.
- 14 C. Kittel: Phys. Rev. 82 (1951) 965.

DISCUSSION

J. W. STOUT: If the interactions in dysprosium ethyl sulphate are purely magnetic dipole ones, should not the Curie temperature depend on the shape of the specimen?

A. H. COOKE: In this substance, the largest interaction is that between nearest neighbours along the crystal axis. If we postulate that its ions aline in chains, we find that for a large specimen in which demagnetization effects are small, its interaction between neighbouring chains is such as to produce ferromagnetic (parallel) ordering of the chains. Considering now a short specimen, we find that it will break up into long thin domains along its crystal axis. The energy of its domain walls is small, so that the number of domains formed can be large, the width of individual domains being of the order 10^{-4} cm in a specimen whose dimensions are of order 1 cm. Hence its Curie point will be independent of the shape of the specimen.

W. C. MARSHALL: Would Dr. Wolf please explain how, in dysprosuim ethyl sulphate, the domain wall can have no width and yet simultaneously have very little energy?

W. P. WoLF: If the domain walls are parallel to the *c*-axis, as would seem to be reasonable, only interactions between ions which are in different chains are involved, and these are small. Moreover the energy of interaction is further reduced by the partial cancellation of the dipolar fields when the chains become ordered. The field acting from one chain on another, then falls off much more rapidly than $1/r^3$. Under these conditions there is only a narrow region between the domains in which the magnetization is different from that in the bulk material, and the energy involved is very low.

R. KUBO: In connection with Professor Stout's question about the long range dipolar forces, I would like to ask Dr. Wolf, if it is not effective to determine the size or shape of the domains? How are these determined?

W. P. WoLF: The Curie point will not depend on the sample shape because of the domains which are formed. Due to the nature of the interactions and the geometry of the lattice the domain wall energy is very low, so that the domains will be very thin whatever the sample shape or temperature. The properties of such thin domains are then independent of their precise configuration.