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Ferromagnetism in Gadolinium Trichloride

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Susceptibility and magnetization measurements have been made on single crystals of $GdCl_3$ in the temperature range 1.5 to 20°K. The results indicate that this substance becomes ferromagnetically ordered at 2.2°K. Measurements were made on a number of differently shaped samples, both parallel and perpendicular to the crystallographic *c*-axis, in order to establish the direction of ferromagnetic alinement and to verify that the susceptibility in this direction is $1/N$, (N is the demagnetizing factor), as expected for a spontaneously magnetic material in which the domains can move freelly. To exclude the possibility that the ordering is ferri- rather than truly ferro-magnetic magnetization measurements were made in fields large enough to remove the domains, but small compared with the internal ordering fields. The results extrapolated to $T=0°K$ show that the spontaneous moment is at least 80% of the predicted 7 μ_B/ion, the discrepancy being tentatively ascribed to zero-point disorder produced by the relatively large dipolar interactions. Magnetic dipole interactions also account satisfactorily for the observed anisotropy as deduced from magnetization measurements made with fields perpendicular to the 'easy' axis.

Introduction

In the course of a search for magnetic materials whose low temperature properties are dominated by magnetic dipole interactions, we have made susceptibility and magnetization measurements on single crystals of $GdCl_3$, which show that this substance becomes ordered ferromagnetically at 2.20°K. This temperature is considerably higher than was expected on the basis of magnetic dipole forces alone, and from a detailed analysis of the results we conclude that there exists, in addition, an isotropic exchange interaction which favours the ferromagnetic alinement. We believe this to be the first known case of an insulating rare earth compound which becomes ferromagnetic through exchange forces, and in several respects it differs appreciably from other recently discovered non-conductors which become ferromagnetic at low temperatures (*e.g.* Dy $(C_2H_5SO_4)_3 \cdot 9H_2O$[1], $CrBr_3$[2], EuO[3]). The simple hexagonal crystal structure[4] and the isotropic nature of the Gd^{3+} ion in this structure[5] makes this a particularly convenient system for a close comparison between theory and experiment, while the low transition temperature makes it possible to influence its magnetic and thermal properties appreciably by the application of small magnetic fields.

Experiments and theory

Crystals of three different shapes (a thin needle, sphere and flat disk) were grown from the melt in quartz containers[6], in which they were kept throughout the experiments to avoid decomposition by moisture in the air. The hexagonal *c*-axis was in each case parallel to the axis of the sample. Susceptibility measurements were made in the ranges 20°−14°K and 4.2°−1.5°K using an a.c. inductance method[7]. Results for the 'needle' sample are shown in Fig. 1. We may note two main features. (i) In the hydrogen range a Curie-Weiss law is obeyed with a ferromagnetic $\theta \sim 2°K$. (ii) There is a sharp discontinuity in the susceptibility at 2.20°K, below which χ remains practically constant both parallel and perpendicular to the axis. These results strongly suggest a transition to a ferromagnetic state at 2.2°K. If this is so, we would expect χ(per cc) in the 'easy' direction of alinement to be equal to $1/N$, where N is the demagnetizing factor for the given sample shape. Measurements on the three samples are shown in Fig. 2.

The results, summarized in Table I, show good agreement with $1/N$ for the case of $\chi_{\parallel}$. We conclude that $GdCl_3$ is indeed spontaneously magnetic below 2.2°K, with an 'easy' axis which coincides with the *c*-axis of the

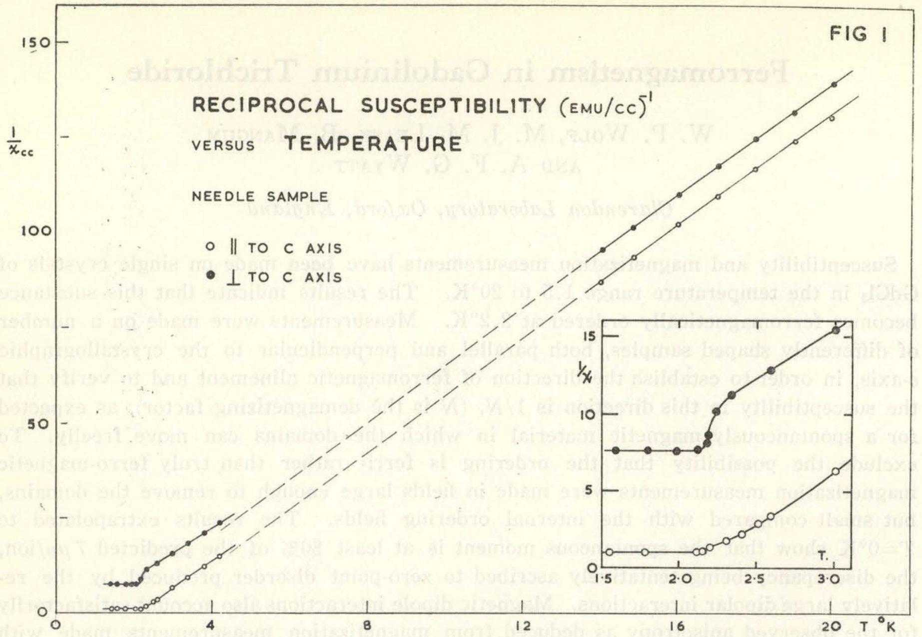

Fig. 1. Reciprocal susceptibility, measured parallel and perpendicular to the crystal *c*-axis, versus temperature for a needle shaped sample (approximating to a 4:1 ellipsoid).

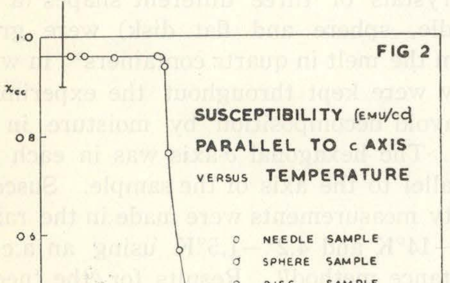

Fig. 2. Susceptibility measured parallel to *c*-axis for three samples of different shapes, showing that $\chi_{\|}$ is independent of temperature below 2.20°K at values close to $1/N$.

crystal.

Table I also shows the measured Curie-Weiss constants, (θ_{expt}), and these may be compared with the values calculated on the basis of magnetic dipole-dipole interaction (θ_{dip})[8]. It can be seen that there are large differences between θ_{expt} and θ_{dip}, but we may note that within experimental error the differences are independent of both sample shape and direction. It seems reasonable to conclude that the extra contribution to θ arises from isotropic exchange, but with the unusual feature that θ_{exch} has a ferromagnetic sign. It may be that this is an instance of 'direct' rather than 'super'-exchange. The relative positions of nearest and next-nearest neighbour are shown in Fig. 3, and it can be seen that for either kind of exchange mechanism the interaction is likely to be largest for the two nearest neighbours along the *c*-axis. If for simplicity, we neglect the effect of all other neighbours we can interpret the value of $\theta_{\text{exch}}=1.65$°K in terms of a nearest neighbour exchange constant $J_{nn}/k=-0.16$°K (defined by $\mathscr{H}_{nn}=+J_{nn}S_i\cdot S_{i+1}$). The equivalent exchange field is $8200(M/M_0)$ oersted.

To exclude the possibility that the ordering is ferrimagnetic and due to basically antiferromagnetic interactions, we measured the magnetization in fields large enough to remove the magnetic domains, $(H_0>NM)$, but small enough not to affect the type of order. The results for the 'needle' sample are shown in Fig. 4 and 5. It can be seen that, as $T\to0$°K,

Table I: Summary of Results

Susceptibility:

Sample	Direction of c-axis	N	$1/\chi(T>2.2°\mathrm{K})$		θ_{expt}**	θ_{dip}	θ_{exch}
			Expt.	Calc.			
Needle	// to H_0	1.0 ± 0.1*	1.04	1.0	2.3	+0.8	1.5
	$\perp$ to H_0	5.8 ± 0.5*	7.70	10.3	1.3	−0.4	1.7
Sphere	// to H_0	4.2 ± 0.5*	4.55	4.2	2.1	+0.4	1.7
	$\perp$ to H_0	4.2 ± 0.5*	7.30	8.7	1.6	−0.2	1.8
Disc	// to H_0	6.0 ± 1.0*	5.65	6.0	1.8	+0.2	1.6
	$\perp$ to H_0	3.3 ± 0.5*	5.56	7.8	1.8	−0.1	1.8

* estimated errors due to uncertainty in shape.

** estimated experimental error $\pm0.2°$K.

Weighted mean value of θ_{exch} $1.6_5\pm0.1_5$°K

Equivalent exchange field 8200 (M/M_0) oersted.

Curie Temperature: 2.20°K.

Magnetic Moment: Measured at $T=1.5°$K, $H_i=500$ Oe: 475 emu/cc=5.0 μ_B/ion. Calculated moment for complete ferromagnetic alinement=668 emu/cc=7.0μ_B/ion.

Anisotropy Energy (for infinite single domain).

Estimated from a. c. $\chi\perp$ $(H_0\sim10$ oersted$)=0.5\mathrm{x}10^6$ $(M/M_0)^2\sin^2\psi$ergs/cc.

Estimated from $(\partial M/\partial H_o)$ for $H_0>500$ oe$=0.8_5\mathrm{x}10^6$ $(M/M_0)^2\sin^2\psi$ergs/cc.

Calculated to first order for magnetic dipole coupling$=1.0\mathrm{x}10^6(M/M_0)^2\sin^2\psi$ergs/cc.

Equivalent anisotropy field, $2K_1/M=3000$ (M/M_0) oersted.

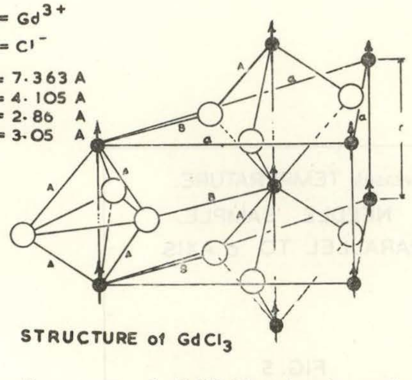

Fig. 3. Structure of $GdCl_3$⁽⁴⁾, showing relative positions of nearest and next-nearest neighbours and possible 'super'-exchange linkages through Cl^- ions.

M tends to a value sufficiently close to the theoretical moment corresponding to complete ferromagnetic alinement (M_0=668 gauss) to rule out all simple ferrimagnetic structures. The small apparent discrepancy between the observed and calculated moments, and also the relatively large field dependence which persists down to the lowest temperatures, may be connected with zero-point effects arising from the comparatively large dipole coupling, part of which does not commute with an isotropic exchange interaction.[9] An attempt to estimate this effect quantitatively is now in progress. Other possibilities include canted or long range spiral sublattice structures, but these as well as complex ferrimagnetic arrangements seem unlikely in view of the extremely simple and symmetrical crystal structure.

The anisotropy in the ordered state can generally be accounted for by three mechanisms: anisotropic exchange, crystal field effects and magnetic dipole coupling. The first two of these are very likely to be small for this substance whose magnetic ions are all in S-states, and this is supported by the high temperature susceptibility measurements and paramagnetic resonance measurements on dilute Gd^{3+} in isomorphous $LaCl_3$[5]. Dipolar interactions on the other hand will be unusually large, since the individual ionic moments are big and the crystal structure is very far from cubic. Using a first order molecular field treatment we find for the dipolar anisotropy energy (of an infinite single domain)

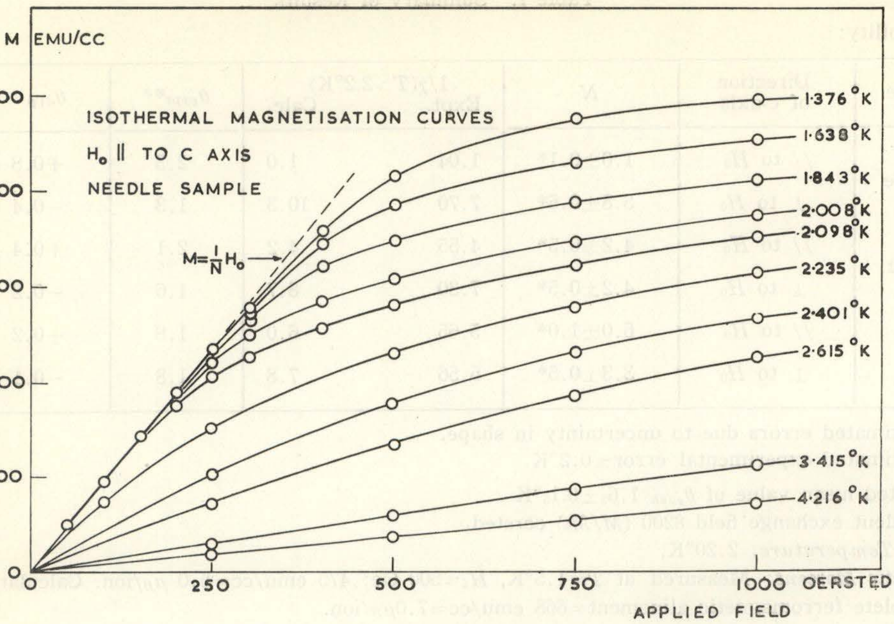

Fig. 4. Isothermal magnetization curves for the 'needle' sample parallel to the c-axis. Note that below 2.2°K all curves start initially superimposed on the straight line $M=H_0/N$. The points at which the curves break away from this line correspond to the intrinsic magnetization at the particular temperature (i. e. M_s for $H_i=0$). In practice these points are best determined by plotting M against H_0-$NM=H_i$, and extrapolating the linear parts of the curves to $H_i=0$.

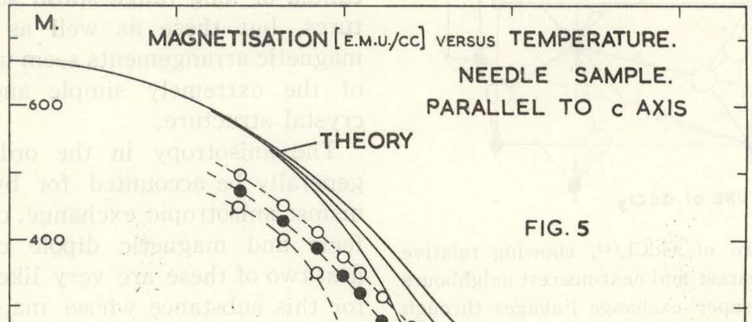

Fig. 5. Magnetization parallel to c-axis versus temperature for two fields large enough to remove domains. H_0=1000 oersted (○) and H_0=750 oersted (●), and the intrinsic domain magnetization (H_i=0) estimated by extrapolation from figure 4. Theoretical curves based on molecular field approximation using high temperature Weiss constants.

$$F_A{}^1=+1.0\times10^6(M/M_0)^2\sin^2\Psi\ \text{ergs/cc}$$
$$=K_1{}^1\sin^2\Psi \qquad (1)$$

where Ψ is the angle between the c-axis and the magnetization M. The sign of this correctly explains the observed 'easy' axis, and we can use the value of $K_1{}^1$ to estimate the moment induced by a field applied perpendicularly to the axis. If we neglect higher order anisotropy terms, and minimize the free energy including applied and demagnetizing fields we find

$$\chi_\perp=M_\perp/H_0=1/(2K_1/M^2+N_\perp) \qquad (2)$$

which is independent of field and temperature, very much as observed, (see Fig. 6 and 1). Values of $\chi_\perp$ calculated for the three sample shapes are shown in Table 1. The agreement with experiment is quite reasonable, especially in view of the crudeness of the theory and the fact that it contains no adjustable constants. Inclusion of second order terms, which are quite important since the dipole coupling is comparable with the exchange, will generally improve the agreement. Moreover we may note a slight curvature at low fields in the $M_\perp$ versus H_0 curves (Fig. 6) which is unexplained, but which implies from a practical point of view that the value of K_1 deduced from equation 2 will depend somewhat on H_0. If the low field curvature is spurious (*e.g.* due to misalinement), the most reliable estimate of K_1 would be given by the gradient $(\partial M_\perp/\partial H_0)$ for $H_0>500$ oe, which is much more independent of T and H than the low field a.c. $\chi_\perp$. This leads to $K_1=0.8_5\times10^6$ ergs/cc, in even closer agreement with the theory. We may conclude that it seems most likely that the entire anisotropy can be accounted for by magnetic dipole coupling.

With the same first order molecular field approximation as above, but including now also the isotropic exchange estimated from the Curie-Weiss constants, we can similarly calculate the moment parallel to the axis, both in zero field and in a field large enough to remove the domains. The results are shown in Fig. 5, and it can be seen that the agreement is again quite reasonable. The predicted Curie point is 2.6°K compared with the observed 2.20°K. The close agreement with so crude a theory seems surprising, but it is probably explained in part by the fact that nearly 40% of the molecular field arises from long range dipolar forces, for which a molecular field is probably a fairly reasonable approximation. The results shown in Fig. 5 demonstrate clearly the large magnetic effects which can be produced in this substance by the application of quite modest fields, and

FIG. 6

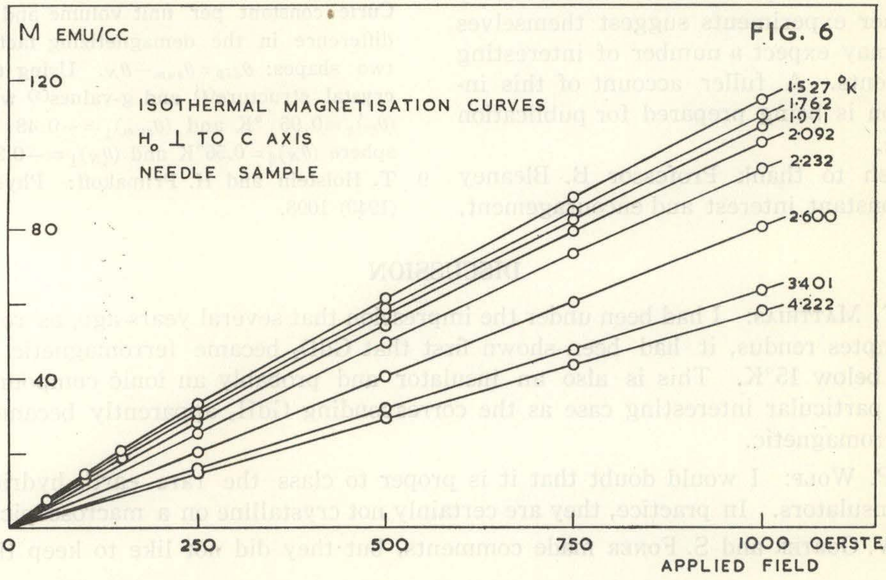

Fig. 6. Isothermal magnetization curves for 'needle' sample perpendicular to c-axis, showing the general linearity and close coincidence of all the curves for temperatures below 2.2°K (cf. equation 2). Note especially the constancy of $(\partial M/\partial H_0)$ above $H_0=500$ oersted.

they suggest that marked change in the thermal properties should also be produced by similar magnetic fields. Measurements of these effects are now in progress.

There remain several unexplained effects. Preliminary microwave resonance experiments have shown a complex absorption spectrum, but this may have been connected with the considerable difficulties of preparing a suitable sample. The a.c. susceptibility measurements indicate strong relaxation effects, with characteristic times in the millisecond region, which give rise to large shape and temperature dependent out-of-phase components in $\chi_\perp$ at 175 c/s, even though no hysteresis or remanence ($>0.001\,M_0$) could be detected in the magnetization curves. It is clear that the nature of the domains in this material is quite different from that in more normal cases.

Conclusion

Our preliminary measurements have shown that $GdCl_3$ is in many respects a most unusual substance. It belongs to the so far very small class of ferromagnetic insulators, and most of its bulk properties are well explained by a simple model based on the molecular field theory involving only isotropic ferromagnetic exchange and magnetic dipole interactions. Many refinements to the theory and further experiments suggest themselves and one may expect a number of interesting developments. A fuller account of this investigation is being prepared for publication elsewhere.

We wish to thank Professor B. Bleaney for his constant interest and encouragement, and Professor C.A. Hutchison, Jr. for valuable advice on the preparation of samples. This work was supported in part by the Electronics Research Directorate, A.F.C.R.L., through the European Office, Aerospace Research, U.S. Air Force, and it was carried out during the tenure of a Pressed Steel Fellowship by M.J.M.L., a National Science Fellowship by B.M., and a D.S.I.R. Studentship by A.F.G.W., all of which are gratefully acknowledged.

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8 In practice θ_{dip} is calculated most simply by performing a numerical summation over lattice points for a very long but relatively thin shape, and allowing for the actual shape by a demagnetizing term $\theta_N=(\Delta N)c$, where c is the Curie constant per unit volume and ΔN is the difference in the demagnetizing factors for the two shapes: $\theta_{dip}=\theta_{sum}-\theta_N$. Using the known crystal structure(4) and g-values(5) we find (θ_∞) $(\theta_\infty)_\parallel=0.96$ °K and $(\theta_{sum})_\perp=-0.48$ °K; for a sphere $(\theta_N)_\parallel=0.56$°K and $(\theta_N)_\perp=-0.28$°K.

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DISCUSSION

B. T. MATTHIAS: I had been under the impression that several years ago, as reported in Comptes rendus, it had been shown first that GdD_2 became ferromagnetic somewhere below 15°K. This is also an insulator and probably an ionic compound. It was a particular interesting case as the corresponding GdH_2 apparently became only antiferromagnetic.

W. P. WOLF: I would doubt that it is proper to class the rare earth hydrides as ionic insulators. In practice, they are certainly not crystalline on a macroscopic scale.

E. W. GORTER and S. FONER made comments, but they did not like to keep them.