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Crystal Growth and Magnetic Susceptibility of Some Rare-Earth Compounds

Part 2 *Magnetic Susceptibility Measurements on a Number of Rare-Earth Compounds*

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Magnetic susceptibility measurements have been carried out on five series of rare-earth compounds using an ac mutual inductance technique. The compounds satisfy the general formulae $RNbO_4$, R_3NbO_7, R_2TiO_5, $R_2Ti_2O_7$, or $RAlO_3$ where R is a rare-earth ion. The measurements were mainly carried out in the helium range 1 to 4.2° K, and the results analysed in terms of the general Van Vleck formula $\chi = C/(T + \theta) + \alpha$. Many of the compounds were observed to undergo antiferromagnetic transitions, and in some cases showed evidence of extremely anisotropic behaviour above the Néel temperature.

1. Introduction

The first step in the investigation of the magnetic properties of new rare-earth compounds is usually the measurement of the magnetic susceptibility, since this gives a direct indication of the presence or otherwise of magnetically interesting behaviour. This paper reports a set of such measurements made on five series of rare-earth compounds. The preparation of these compounds and the determination of their structures are reported in Part I of this paper, except for the aluminates which are described in [1]. Reference should be made to these papers for details of the purity, stoichiometry, and morphology of the specimens, most of which were either powders or small crystals.

As with many other ionic rare-earth compounds, the temperature range of interest for most of the present series is 1 to 10° K. Susceptibility measurements were therefore made on all the compounds in the liquid helium range, 1 to 4.2° K, together with either a single measurement at the normal boiling point of liquid hydrogen, 20.4° K, or in some cases a set of measurements in the liquid hydrogen range, 14 to 20° K. A mutual inductance method described previously [2] was used for all the measurements. This method has the advantage of high systematic accuracy, so that relatively small departures from monotonic variation of susceptibility with temperature are usually significant.

Magnetic susceptibility measurements are a useful preliminary for the following reasons. In ionic compounds of the type reported on here, the electrostatic environment of the rare-earth site in the crystal produces a splitting of the L, S, J ground state of the free rare-earth ion into a maximum of $2J + 1$ magnetic energy levels, the exact number depending on the symmetry of the site. For the Gd^{3+} ion, which has a $^8S_{7/2}$ ground state, these energy splittings are very small, so that at the temperature of our experiments we can expect that the magnetic properties of the ion are those of an 8-fold degenerate state. For the other ions the splittings are such that at the temperatures of our measurements only the lowest energy level is appreciably populated. Then the susceptibility measurements give at least some idea as to (i) which of these levels lies lowest and therefore dominates the low temperature behaviour, (ii) how far it is separated in energy from the nearest excited levels, and (iii) how strong the magnetic interaction is between the rare-earth ions. These features may be demonstrated more specifically by considering the different terms in the theoretical expression for the magnetic susceptibility. We assume that the temperature is so low that only the lowest energy level is appreciably populated, and this level is doubly degenerate (this is strictly true only if the rare-earth ion has an odd number of unpaired $4f$ electrons). Then the general Van Vleck expression for the magnetic susceptibility [3] takes the form:

$$\chi = \mathrm{C}/(T + \theta) + \alpha$$

Here C is the molar Curie constant, and for a doublet is equal to $\mathrm{N}g^2\beta^2/4\mathrm{k}$, where N is Avogadro's number, β is the Bohr magneton, and k is Boltzmann's constant. g is the magnetic g-factor; for rare-earth ions it may have any value between zero and twenty, and is usually anisotropic with respect to crystallographic direction. As our measurements were made on powder specimens, they gave a mean square value of the g-factor.

θ is the Weiss constant, and is a function of the total magnetic interaction between the ions. On a molecular field approximation, the interaction is expressed as an effective internal field, H_i, proportional to the magnetisation ($H = \lambda M$), and the Weiss constant θ is proportional to $\lambda\mathrm{C}$ and is therefore a measure of λ, the interaction parameter.

α is the Van Vleck temperature-independent term. It depends on the energy difference between the ground and excited energy levels through the matrix elements of the magnetic field operator $\beta H \cdot (L + 2S)$:

$$\alpha = 2\mathrm{N} \sum_\mathrm{j} \frac{|<\mathrm{i}\,|\,L + 2S\,|\,\mathrm{j}>|^2}{E_\mathrm{j} - E_\mathrm{i}},$$

Here $<\mathrm{i}\,|$ is the ground level, and $<\mathrm{j}\,|$ is any one of the excited states of the rare-earth ion. α therefore gives some measure of the separation of the excited energy levels from the ground level.

In the general case, there may be departures from the above expression for the susceptibility for a number of reasons. As the temperature rises, low-lying excited energy levels may become populated, while at low temperatures, where T is of the order of θ, there may be departures from the behaviour predicted by the simple molecular field theory of the interactions. In addition, for those ions with an even number of unpaired $4f$ electrons (Pr^{3+}, Tb^{3+}, and Ho^{3+}) doublet states are not strictly degenerate, and the small splittings of the lowest doublet may become noticeable at the lowest temperatures, the susceptibility then tending to a temperature-independent value. Nevertheless, the expression above does in many cases provide a useful description of the observed behaviour.

Finally, in estimating the Néel temperatures for those compounds which undergo transition to antiferromagnetism, we give here the temperature corresponding to the point of maximum positive slope on the plot of susceptibility against temperature, rather than the temperature at which the susceptibility is a maximum, since most theories of the ordering process relate the former temperature rather than the latter to the true transition temperature. Subsequent specific heat measurements on three of the compounds [4] agree with this interpretation.

2. Results

Table I lists results on all the series. All the susceptibility measurements were corrected for the demagnetising field of the specimen, and the results given are appropriate to a spherically shaped sample. The results have been analysed in terms of the Curie-Weiss-Van Vleck formula above. However, this does not imply that the analysis can necessarily be regarded as meaningful but rather that it provides an empirical fit to the data. In most cases the analysis is based on measurements in the helium range together with a single high temperature point at 20.4° K. This is clearly insufficient if the susceptibility rises to a maximum in the upper part of the helium range; in such cases the liquid helium measurements have been supplemented by measurements over the whole liquid hydrogen range (14 to 20.4° K). Measurements were made on at least two samples of each compound; where an average of the results on two different samples would be misleading both results are given.

3. Discussion of Results

3.1. Rare-Earth Ortho-Niobates, $\mathrm{RNbO_4}$

The results are shown in fig. 1. The Curie constant C = 8.0 for the gadolinium compound indicates stoichiometry correct to within 2%, since the theoretical value is 7.9. Although the results of the terbium and dysprosium compounds at the higher temperatures have been fitted to Curie-Weiss formulae, these cannot be taken seriously, since in each case the Weiss θ is too large for the Curie-Weiss law to be rigorously applicable in the temperature range of the measurements, and in addition, one would expect a temperature-independent term from the many excited states of each ion. In each case it is evident that the interactions between the ions are dominating the behaviour. The susceptibility of the holmium compound appears to have reached a maximum at 1° K. The gadolinium and neodymium compounds have been investigated at higher temperatures by Wang and Gravel [5]. Our results are in agreement with theirs on the gadolinium compound but differ from theirs on the neodymium compound, which they find to undergo a transition to antiferromagnetism at about 25° K.

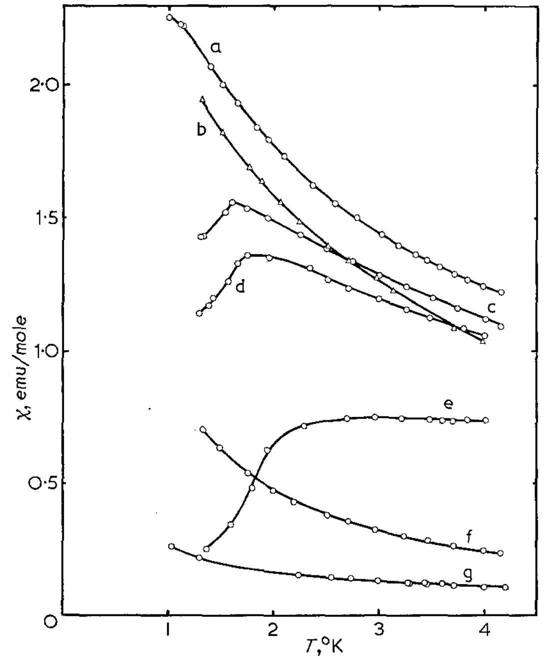

Figure 1 The magnetic susceptibility as a function of temperature for the series $RNbO_4$. (a) $HoNbO_4$; (b) $ErNbO_4$; (c) $DyNbO_4$; (d) $GdNbO_4$; (e) $TbNbO_4$; (f) $YbNbO_4$; (g) $NdNbO_4$.

3.2. Rare-Earth Niobates, R_3NbO_7

The results are shown in fig. 2. The chemical analysis of the gadolinium compound is referred to in Part I. Its susceptibility appears to have reached a maximum at the lower limit of our temperature range, indicating a transition at a slightly lower temperature. Once again, the Curie-Weiss laws to which the results on the dysprosium and holmium compounds have been fitted must be regarded simply as empirical formulae. However, it is perhaps worth noting that in each case the very large value of the Curie constant C suggests that the ground doublet state is characterised by very nearly the highest value of J_z which is available to each ion (i.e. for Dy^{3+}: $J_z = 15/2$; for Ho^{3+}: $J_z = 8$). This in turn suggests that the electrostatic environment of each ion has strongly axial symmetry, splitting the energy levels into doublets which can be characterised closely as $\pm J_z$, with the highest value of J_z giving the lowest level. The large value of the Curie constant cannot be due to incorrect stoichiometry as the nominal amount of 75 mole % R_2O_3 is at the high end of

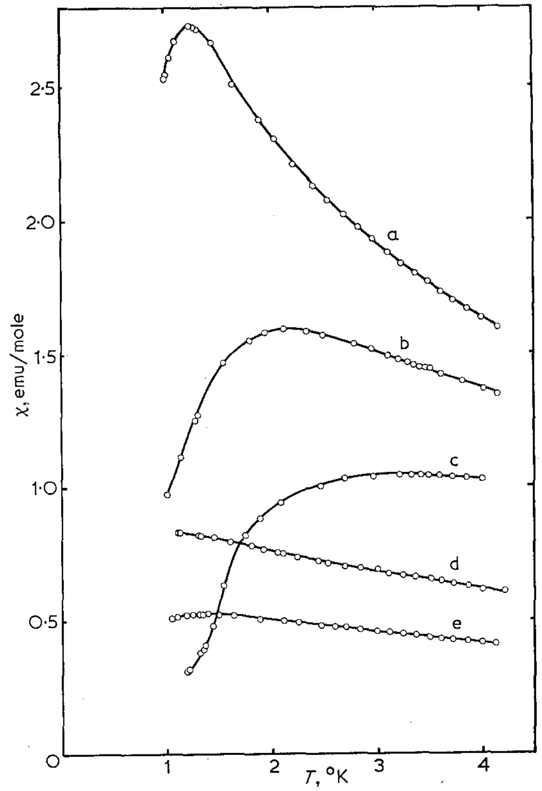

Figure 2 The magnetic susceptibility as a function of temperature for the series R_3NbO_7 and R_2TiO_5. (a) Ho_3NbO_7; (b) Dy_3NbO_7; (c) Dy_2TiO_5; (d) Gd_3NbO_7; (e) Gd_2TiO_5.

the allowed range of stoichiometry (65 to 75 mole %).

3.3. Rare-Earth Titanates, R_2TiO_5

These results are also shown in fig. 2. Although for a number of different specimens of the gadolinium compound the Curie constant C differed appreciably because of non-stoichiometry, in each case the susceptibility passed through a maximum at 1.25 °K. The dysprosium compound clearly undergoes an antiferromagnetic transition.

3.4. Rare-Earth Titanates, $R_2Ti_2O_7$

The results are shown in fig. 3. Once again, different samples of the gadolinium compound had values of the Curie constant C differing by as much as 20%, and we refer to Part I for data regarding the variation in rare-earth content. Even so the observed behaviour is unusual for a gadolinium compound in its temperature-independence below 4° K. This behaviour may indicate the possibility of magnetic ordering just below 1° K, being not dissimilar to that of potassium chloro-iridate [6] above its ordering point of 2.8° K. The susceptibilities of the dysprosium and holmium compounds are interesting in two respects: firstly, both very nearly obey the simple Curie law, $\chi = C/T$, and secondly, the value of the Curie constant C corresponds within 1% to the maximum theoretically available for a doublet level for Dy^{3+} or Ho^{3+} ions in their respective L, S, J ground states. Further investigation would be needed to confirm this, both because of the uncertainty as to stoichiometry and because of the certainty that for both ions there are low-lying energy states, so that the empirical Curie-Weiss law cannot be taken too seriously.

3.5. Rare-Earth Ortho-Aluminates, $RAlO_3$

The results are shown in fig. 4. The susceptibility of the gadolinium compound agrees well with the average of the results obtained along the three principal crystallographic directions in measurements on single crystals [7]. For the terbium compound, the Curie constant C = 10.7 is within 5% of the value to be expected if the ground level is the doublet $J_z = \pm 6$, already reported [8]. The antiferromagnetic transition temperatures estimated from the susceptibilities of the gadolinium, terbium, and dysprosium compounds are in agreement with those from specific heat measurements [4]. Although the susceptibility of the praseodymium compound does exhibit a small temperature dependence,

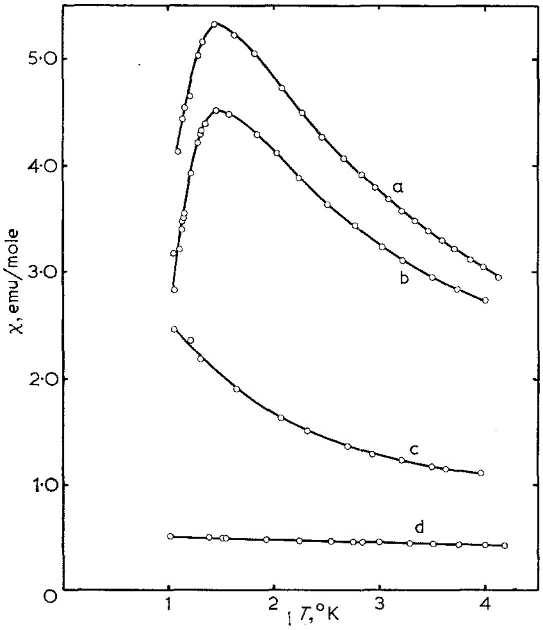

Figure 3 The magnetic susceptibility as a function of temperature for the series $R_2Ti_2O_7$. (a) $Ho_2Ti_2O_7$; (b) $Dy_2Ti_2O_7$; (c) $Tb_2Ti_2O_7$; (d) $Gd_2Ti_2O_7$.

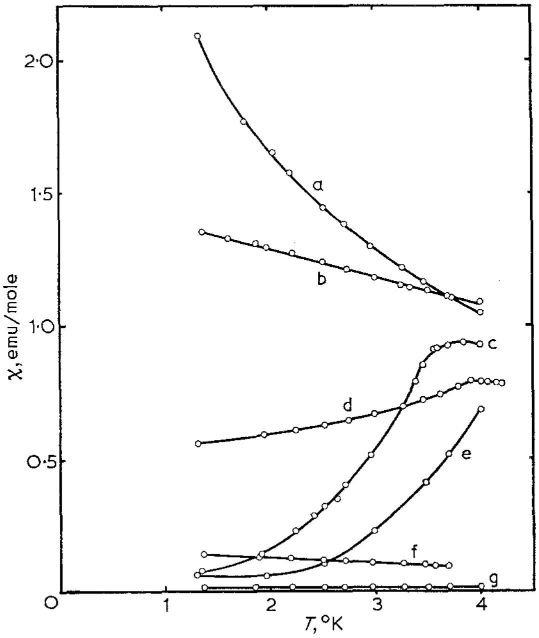

Figure 4 The magnetic susceptibility as a function of temperature for the series $RAlO_3$. (a) $ErAlO_3$; (b) $HoAlO_3$; (c) $DyAlO_3$; (d) $GdAlO_3$; (e) $TbAlO_3$; (f) $NdAlO_3$; (g) $PrAlO_3$.

TABLE I

R	T_N (° K)	Curie-Weiss Law	Remarks
$RNbO_4$			Stoichiometric
Nd	—	$0.52/(T + 1.2) + 0.006$	Small crystals
Gd	1.67	$8.0/(T + 2.5)$	„
Tb	1.82	$11.0/(T + 8.3)$	Flaky crystals
Dy (a)	1.52	$11.9/(T + 4.1)$	Large crystals
(b)	1.60	$7.4/(T + 2.7)$	„
Ho	—	$5.9/(T + 1.7) + 0.23$	Flaky crystals
Er	—	$5.4/(T + 1.4) + 0.15$	Small crystals
Yb	—	$1.1/(T + 0.073) + 0.028$	„
R_2NbO_7			Non-stoichiometric
Gd (a)	<1.0	$6.1(/T + 5.9)$	Small crystals
(b)	<1.0	$7.2/(T + 7.5)$	„
Dy	1.0	$10.9/(T + 3.7)$	„
Ho	<1.0	$10.3/(T + 2.2)$	„
R_2TiO_5			Non-stoiochimetric
Gd	—	$8.8/(T + 10)$	Fine needles
Dy	1.55	—	Platelets
$R_2Ti_2O_7$			Non-stoichiometric
Gd	—	$7.7/(T + 11.7)$	Small crystals
Tb	—	$4.5/(T + 1.2) + 0.14$	„
Dy	1.3	$12.4/(T + 0.65)$	„
Ho	1.3	$12.6/T$	Over 9 to 20.4° K
$RAlO_3$			Stoichiometric
Pr	—	χ temp.-independent	Large crystals
Nd	—	$0.65/(T + 3.2) + 0.015$	Small crystals
Gd	3.9	$7.9/(T + 5.0)$	„
Tb	4.0	$10.7/(T + 6.5)$	„
Dy	3.5	—	„
Ho	—	$11.1/(T + 5.3)$	„
Er	—	$6.8/(T + 3.4)$	Powder

the dominant feature is its very low value, suggesting that the lowest excited levels are of the order of 100 cm^{-1} above the ground level.

4. Conclusions

Many of the compounds measured become magnetically ordered at temperatures below 4° K. In all cases the ordering is antiferromagnetic. Some of the dysprosium and holmium compounds exhibit very large ground-level magnetic moments; this would be worth confirming by magnetic moment measurements. Detailed theoretical explanation of the properties in terms of the nature and position of the excited levels is severely hampered by the low crystallographic symmetry of the rare-earth sites in all the materials, and in some cases by the variation in stoichiometry. The problem of the energy level splittings produced by the crystalline electric field is not really amenable to solution at present.

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