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Long-Range Ordering in Magnetically Diluted Europium Hexaboride*

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Magnetic susceptibilities of the compounds $Eu_xYb_{1-x}B_6$ have been measured by the Faraday method over the range 1.7–300 K. The susceptibilities follow a Curie–Weiss law with an effective magnetic moment of 8 μ_B per europium. Weiss constants are 8.8, 7.0, 4.9, 3.6, 2.0, 0.0, and 0.0 ± 0.3 K for x values of 1.0, 0.8, 0.6, 0.4, 0.3, 0.2, and 0.1, respectively. Corresponding ferromagnetic Curie temperatures are 8.4, 7.1, 4.6, 1.5, 0.0, 0.0, and 0.0 ± 0.2 K. Comparison of the change in Curie temperature with that expected by various theories of magnetic dilution suggests that the exchange mechanism involves nearest-neighbor interactions only.

Introduction

Europium hexaboride is unique among the rare earth hexaborides in being ferromagnetic. The other hexaborides display antiferromagnetism or, in the cases where the rare-earth ion does not possess a localized moment, a small temperature-independent paramagnetism. Special features of the hexaboride structure make it attractive for studying the mechanism of magnetic coupling between rare-earth ions. This paper reports an investigation of interactions between europium ions as a function of magnetic dilution.

The MB_6 structure (*1*) can be described by a cubic unit cell in which octahedra of boron atoms occupy corner positions and the metal atom M, the body center. The apexes of the boron octahedra lie on the cubic edges, and the B–B distances between adjacent octahedra are very similar to the B–B distances within the octahedra. The result is an infinite, three-dimensional, covalently bonded array of boron atoms, the interstices of which form a simple cubic array of metal atom sites.

Longuet-Higgins and Roberts (*2*) as well as Flodmark (*3*) have made molecular-orbital and band calculations for MB_6; the results are not in complete accord but they suggest that the boron framework has an incompletely filled valence band corresponding to two hole states per B_6 formula-unit. The function of the M atom is to provide one or more electrons to occupy these hole states and, if in excess, conduction band states beyond the forbidden gap. The experimental data on electrical conductivity, although fragmentary and uncertain because most of the measurements have been made on powders, suggest that MB_6 is an insulator or semiconductor when M is divalent (e.g., CaB_6) (*4*) but a metal when M is trivalent (e.g., LaB_6) (*5*). This difference in electrical properties appears to be at the root of the explanation for the two different kinds of magnetic ordering observed for the rare-earth hexaborides. EuB_6, which is ferromagnetic, contains the divalent cation Eu^{2+} ($4f^7, {}^8S_{7/2}$) and is an insulator or semiconductor; GdB_6, which is antiferromagnetic, contains the trivalent cation Gd^{3+} ($4f^7, {}^8S_{7/2}$) and is a metal. The antiferromagnetic ordering of GdB_6, as in the case of the rare-earth metals, can be accounted for by the Ruderman–Kittel (*6*) theory of indirect exchange via conduction electrons. The ferromagnetic ordering of EuB_6 may be attributed to the fact that the itinerant-electron polarization wave remains positive even at very large distances when conduction electron density is lower than that corresponding to degenerate statistics (*7*) or, as suggested by Matthias (*8*), to formation of magnetic polarons (*9*).

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Shannon and Sienko (*10*) have shown for europium hexaboride that replacement of 50% of the europium by lanthanum produces a change from ferromagnetic behavior (Curie temperature = 8 K) to antiferromagnetic behavior (Néel point = 6 K); replacement of 80% of the europium by lanthanum gives an ideal paramagnet with no evidence of ordering down to 1.5 K. Unfortunately, replacement of europium by lanthanum varies two parameters at the same time—it decreases the concentration of magnetic ions but also increases the conduction electron density. This work was undertaken to separate the two effects and to look directly at the magnetic dilution effect alone. Ytterbium apparently exists in YbB_6 as the ion $\text{Yb}^{2+}(4f^{14}, {}^1S_0)$; as such it is diamagnetic (*11*) but, being divalent, it can be substituted for Eu^{2+} in EuB_6 without changing the conduction electron density. Neshpor and Samsonov (*12*) have pointed out that so long as the metal atom in MB_6 is large and has relatively low ionization potentials, its actual identity has no influence on site occupancy. It is quite probable, therefore, that in the compounds $\text{Eu}_x\text{Yb}_{1-x}\text{B}_6$ the europium and ytterbium ions are distributed at random over the array of simple cubic sites. The near-identity of the ionic radii of Yb^{2+} and Eu^{2+} makes ytterbium an ideal diluent for the europium.

Experimental Part

The compounds were prepared by mixing the rare earth sesquioxides and boron in proportions determined from the equation

$$x\text{Eu}_2\text{O}_3 + (1-x)\text{Yb}_2\text{O}_3 + 15\text{B} \rightarrow 2\text{Eu}_x\text{Yb}_{1-x}\text{B}_6 + \tfrac{3}{2}\text{B}_2\text{O}_2$$

together with a 5% excess of boron as suggested by Meerson and Mamedov (*13*). The oxides, obtained from Alfa Inorganics, were 99.9% pure in the rare-earth element. The crystalline boron, obtained from Alfa Inorganics or Eagle–Picher Industries, ranged from 99.9% to 99.999% pure, respectively; there was no discernible effect on magnetic properties due to change in the degree of purity.

The mixtures were heated under argon in a zirconium diboride crucible. The temperature, obtained by rf induction heating, was 1800°C. After a first heat for 15 min, the samples were remixed and reheated for another 15 min. Products were analyzed by X-ray diffractometry and emission spectroscopy.

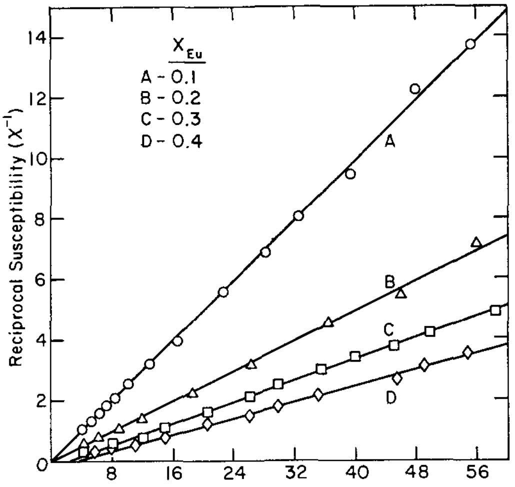

FIG. 1.

The magnetic susceptibilities were measured by the Faraday method, using the apparatus and procedure elsewhere described (*14*). Temperatures ranged from 1.7 to 300 K; at each temperature, the susceptibility was determined at several different fields. In those cases where a field dependence was observed at temperatures ten degrees and more above the Curie temperature, the susceptibilities were plotted versus reciprocal field and extrapolated to infinite field. All the χ vs H^{-1} plots were linear, so it was believed that any field dependence observed was due to ferromagnetic impurities and the extrapolation gave a valid paramagnetic susceptibility.

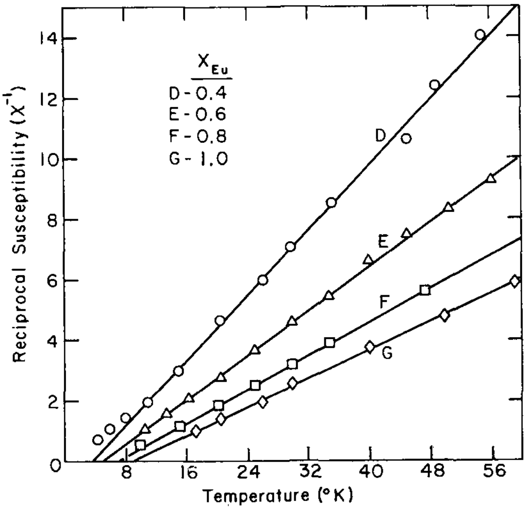

FIG. 2.

TABLE I

Magnetic Parameters of Hexaborides $Eu_xYb_{1-x}B_6$

Value of x	Gram susceptibility at 300 K (in 10^{-6} units)	Weiss constant θ_W (K)	Effective moment μ_{eff} (μ_B)	Curie temperature θ_C (K)
1.00 ± 0.01		8.8 ± 0.3		8.4 ± 0.2
0.80	108 ± 5	7.0	8.3 ± 0.2	7.1
0.60	78	4.9	8.2	4.6
0.40	49	3.6	8.1	1.5
0.30	40	2.0	8.3	0.0
0.20	27	0.0	8.6	0.0
0.10	12	0.0	8.3	0.0

Results

Figures 1 and 2 show the course of the reciprocal susceptibility as a function of temperature for the various europium-containing hexaborides. Because the masses of the samples were too small to be determined precisely, the results are presented on arbitrary scales of susceptibility, which are not the same in Figs. 1 and 2. This

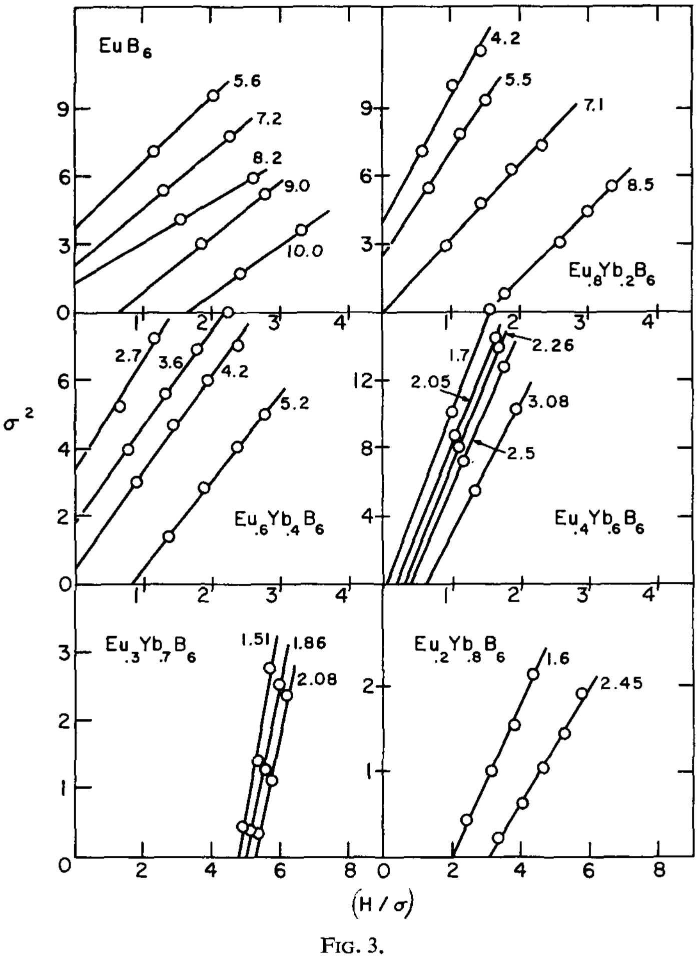

FIG. 3.

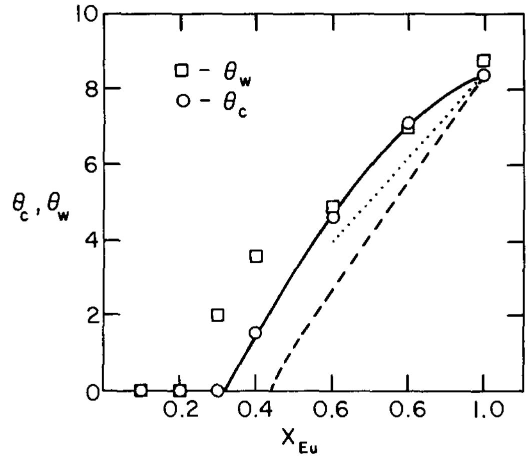

FIG. 4.

affects the value for the slope C but not for the intercept θ_W in the Curie–Weiss representation $\chi = C/(T - \theta_W)$. Gram susceptibilities, χ_g, were determined as precisely as possible at room temperature; these, along with Weiss constants θ_W and effective magnetic moments μ_{eff} per europium ion, are reported in Table I.

Isotherms of the second power of the magnetization (σ^2) versus the reciprocal susceptibility ($\chi^{-1} = H/\sigma$) were used to determine the Curie temperature (θ_C) of the ferromagnetic transition. These plots are illustrated in Fig. 3. The method, which is based on the molecular field model of magnetism as discussed by Kouvel and Fisher (*15*), fixes the Curie temperature by the isotherm which extrapolates through the origin. The Curie temperatures so determined are listed in Table I. Since, at very low fields, the σ/H dependence probably changes from cubic to quartic, the Curie temperatures given in Table I are possibly slightly overestimated.

Figure 4 shows the dependence of the derived Weiss constant and the Curie temperature on the concentration of europium as expressed by x_{Eu}, the mole fraction of metal that is europium. The only significant deviations between the critical parameters are at the concentrations $x_{\text{Eu}} = 0.3$, 0.4. These deviations are reasonable, however, if one recognizes that short-range effects (represented by the Weiss constant) can be appreciable at these concentrations while the long-range order (represented by the Curie temperature) need not be.

Discussion

In order to interpret the above results, they can be compared with those predicted by the various theoretical models for magnetic interactions. A most important result obtained from the various theoretical treatments is the minimum or critical concentration of paramagnetic ions at which an ordered ground state is stable. Because a basic assumption of these theories is that the exchange interaction is between nearest neighbors only, the underlying condition of an ordered state is that a certain number of the paramagnetic ions be continuously connected in an infinite cluster. This infinite cluster is realized when at least one paramagnetic ion on one crystal surface is connected to at least one on all the other surfaces. The number of paramagnetic ions in this cluster is only a small percentage of those present at the critical concentration (*16*, *17*).

Table II shows how the various theories compare in their predictions to the result of this work. As can be seen, the results of the present investigation cannot distinguish between the various theories except to exclude the spin-wave treatment of Murray, which predicts a lower

TABLE II

CRITICAL CONCENTRATION (FRACTION OF METAL IONS THAT ARE PARAMAGNETIC) FOR ORDERING IN S. C. LATTICE AS PREDICTED BY VARIOUS THEORIES

Critical concentration	Theory	Reference
0.28	Domb and Sykes	*Phys. Rev.* **122**, 77 (1961).
0.30	Elliott and Heap	*Proc. Roy. Soc.* **A265**, 264 (1962).
0.325 ± 0.023	Frisch et al.	*Phys. Rev.* **124**, 102 (1961)
0.33	$2/Z$	
0.33	Charap	*Phys. Rev.* **126**, 1393 (1962).
>0.44	Murray	*Proc. Phys. Soc.* **89**, 111 (1966).
>0.30; <0.40 ≈0.33		This work

limit of 0.44 for the critical concentration in a simple cubic array. A question has been recently raised about the validity of the Murray result in that one of the terms in the Murray expression was apparently not evaluated (*18*).

A second theoretical prediction concerns the initial decrease of the Curie temperature with magnetic dilution. Figure 4 shows some of the predictions as compared with the results of this work. The dashed curve is as predicted by the Murray spin-wave treatment. The dotted curve follows from the calculations of Morgan and Rushbrooke (*19*), assuming isotropic Heisenberg interaction and counting clusters containing up to five magnetic ions. Except that none would be expected for *S*-state Eu^{2+}, anisotropy would tend to raise the critical parameters above those predicted for a pure Heisenberg interaction.

If one discounts the Murray spin-wave results, then the present work suggests that in EuB_6 the magnetic results can probably be explained by an exchange mechanism that primarily involves interactions between nearest neighbors.

Acknowledgment

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