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Antiferromagnetic coupling in ytterbium-diluted dysprosium hexaborides*

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A series of dysprosium hexaborides in which dysprosium was progressively replaced by ytterbium have been prepared by high temperature reaction between elemental boron and rare earth oxide. Magnetic susceptibility measurements have been performed by the Faraday method over the range $1.6-300^{\circ}$ K. In the interval $63-300^{\circ}$ K, the susceptibilities follow Curie–Weiss laws with an effective moment per dysprosium of 10.6 ± 0.3 Bohr magnetons. The Weiss constants are relatively small, having values of -21.5, -18.5, -14.0, -11.5, and -7.5° K in Dy_xYb_{1-x}B₆ at x = 1, 0.8, 0.6, 0.4, and 0.2, respectively. Below 60° K, the materials show antiferromagnetism; Néel temperatures were observed to decrease in the sequence 21, 16, 8, and 2° K for the first four of the above compositions. Interpretation of results via statistical analysis of two, three, and greater-than-three clusters indicates that when isolated magnetic ions are corrected for, the residual magnetism corresponds to a constant exchange energy J, independent of conduction electron concentration. There is no direct evidence that indirect exchange plays a role in the magnetic interaction.

INTRODUCTION

The metal hexaborides are of interest as possible vehicles for studying the influence of electron density on the magnitude and direction of conduction-electronmediated indirect exchange. The MB₆ structure is a very rigid one containing a simple cubic array of M atoms in a covalently bonded boron-atom network.¹ The unit cell, describable as a cube with an octahedron of boron atoms at each corner and a metal atom M in the body center, corresponds in the zone scheme to two electron holes per B_e unit and two electrons per M atom needed to fill the holes.² If M is trivalent instead of divalent, the third valence electron goes into a second zone which, being only partially filled, constitutes a conduction band. Because of the rigidity of the covalently bonded boron network, the MB₆ structure is not expected to deform much when divalent M^{II} is successively replaced by trivalent M^{III} or vice versa. By proper choice of the ratio M^{II}/M^{III} , the conduction electron density can be manipulated; by choosing M to be a magnetic ion, the interaction of itinerant electrons with magnetic dipoles can be investigated. Hulliger has recently called attention to the wide variety of technological materials that might be so produced.³

In the alloys of the rare earth metals, cooperative ordering of the magnetic moments, as reflected in the Curie-Weiss constants and occasional appearance of Néel temperatures, shows a characteristic oscillation between ferromagnetism and antiferromagnetism as well as in the strength of the coupling interaction. The theoretical interpretation of this, generally called the RKKY interaction, ⁴ is based on the fact that polarization of an itinerant electron changes sign in an oscillating manner as a function of increasing distance from a magnetic ion and increasing wavenumber of the Fermi electrons. In a preliminary work, Shannon and Sienko⁵ investigated the magnetic effect of successive substitution of lanthanum for europium in EuB₆. They found in the sequence EuB₆, Eu_{0.5}La_{0.5}B₆, Eu_{0.2}La_{0.8}B₆ oscillation from ferromagnetism to antiferromagnetism to almost-ideal Curie paramagnetism, corresponding

not only to changing sign of the magnetic interaction but also to decreasing magnitude of the interaction as the average distance between the magnetic ions was increased. Similar results were later found by Mercurio et al.⁶ and likewise attributed to RKKY interaction. It was not clear, however, whether the observed effect was due to increasing conduction electron density (arising from substitution of trivalent La for divalent Eu) or to increasing magnetic dilution (arising from substitution of diamagnetic La³⁺ for paramagnetic Eu^{2*}). Subsequent work disclosed the effect of these two variables separately. For a series of ytterbiumdiluted europium hexaborides wherein divalent, diamagnetic Yb²⁺ (4 f^{14} , ${}^{1}S_{0}$) replaced paramagnetic Eu²⁺ $(4f^7, {}^8S_{7/2})$, Krause and Sienko⁷ found, in the absence of conduction electrons, a normal magnetic dilution effect, i.e., a simple monotonic decrease in Curie ordering temperatures as would be expected on the basis of direct exchange between nearest neighbors only. To study the effect of electron density alone, Ross, Thomas, and Sienko⁸ investigated gadoliniumdiluted europium hexaboride, wherein trivalent Gd³⁺ $(4f^{7}, {}^{\theta}S_{7/2})$ was substituted for Eu²⁺ $(4f^{7}, {}^{\theta}S_{7/2})$; with magnetism of the ion constant but electron density increasing, they found for $Gd_xEu_{1-x}B_6$ (0 < $x \le 0.10$) a smooth monotonic decline from a ferromagnetic Weiss constant for x = 0 to an antiferromagnetic one for x = 0.10, just as would be expected for a pure RKKY interaction.

Actually, these findings of smoothly varying interaction temperatures may be somewhat deceptive. Occupancy of lattice sites is on a discrete basis, and the actual distance between magnetic ions is not continuously variable but increases stepwise in conformity with lattice periodicity. One might ask, therefore, whether there is any evidence that the magnetic interaction constants indeed change stepwise, or barring that, that there is but a single interaction constant characteristic of a pair of ions separated by the nearest-neighbor lattice spacing. Also, so far as changing electron density is concerned, it may not be true that arguments based on simple free-electron calculations actually hold for MB_6 . Mössbauer measurements⁹ suggest that the conduction-electron density in MB_6 is essentially free of *s*-type character. In such case, the Fermi wave vector is probably greater than calculated on a free-electron basis, and the resulting RKKY exchange integral might in fact be negligible.

In order to cast more light on this problem of magnetic exchange in conducting compounds, the present investigation of $Dy_x Yb_{1-x}B_6$ was undertaken. Dysprosium was picked as the magnetic ion because it has a very large magnetic moment $(Dy^{3*}, 4f^9, {}^6H_{15/2}, \mu = 10.63 \mu_B)$ and because it has an orbital contribution (L=5), a feature missing in the other cases so far studied. Throughout the following it is assumed that ytterbium remains Yb^{2*} ($4f^{14}$, diamagnetic), as it apparently is in YbB_8 .

EXPERIMENTAL

Preparation of samples. The compounds were prepared by rf induction heating of mixtures of elemental boron with rare earth sesquioxides as determined by the equation

$$x Dy_2 O_3 + (1 - x) Yb_2 O_3 + 15B - 2Dy_x Yb_{1-x} B_6 + \frac{3}{2}B_2 O_2$$

except for a 5% excess of boron, as suggested by Meerson and Mamedov.¹⁰ The oxides were obtained from Alfa Inorganics and were 99.9% pure in the rare earth element; the crystalline boron, obtained from Eagle-Picher Industries, was 99.999% pure. The mixtures under argon were heated to about 1800 °C in a zirconium



FIG. 1. Reciprocal magnetic susceptibility (in arbitrary units) per mole of dysprosium in $Dy_x Yb_{1-x}B_6$ as a function of temperature in the high-temperature region.

TABLE I. Weiss constants (θ), Neel tempera-
tures (T_N) , and effective moments (μ_{eff}) for
nexaborides of composition $Dy_{x}Yb_{1-x}B_{6}$.

<u>x</u>	θ(° K)	<i>Т_N</i> (°К)	$\mu_{eff}(\mu_B)$
1.00	-21.5 ± 0.5	21 ± 1.5	10.3 ± 0.3
0.80	-18.5	16	10.2 ± 0.3
0.60	-14.0	8	10.6 ± 0.2
0.40	-11.5(-13) ^a	$2(7)^{a}$	10.8 ± 0.2
0.20	$-7.5(-13)^{a}$	$0(7)^{a}$	10.8 ± 0.1

^aResult obtained after subtracting out correction for isolated magnetic ions.

diboride crucible. After a first heat for 15 min, the samples were remixed and reheated for another 15 min. Product analysis was by x-ray diffractometry and emission spectroscopy.

Magnetic measurements. Magnetic susceptibilities were measured over the range 1.6-300 °K using the Faraday method with Spectrosil quartz buckets and Cahn-Electrobalance force recording, as described elsewhere.¹¹ The temperature was monitored by conventional carbon resistor and GaAs diode techniques. Generally, at least four magnetic fields in the range 2-12 kG were applied at each temperature. Fields were calibrated using Pt and HgCo(NCS)₄.

Results. Figure 1 shows the high-temperature results for the reciprocal susceptibility of $Dy_{r}Yb_{1-r}B_{6}$ as a function of temperature at various Dy/Yb ratios. In all the samples, in the liquid nitrogen temperature range and above (i.e., 63-300 °K), the reciprocal susceptibility was strictly proportional to temperature and could be represented by a Curie-Weiss law of the type $\chi^{-1} = (T - \theta)/C$. Because they were negligibly small and approximately cancelled each other, no corrections were applied either for the diamagnetism of the rare earth ions and the boron network or for the Pauli paramagnetism of the electron gas. Table I shows the values of the Weiss constant θ as determined by extrapolating the high-temperature portions of the respective χ^{-1} vs T curves to $\chi^{-1} = 0$. As can be seen, all the values of θ are negative, corresponding to an antiferromagnetic interaction, and there is practically a straight-line dependence between θ and x in $Dy_x Yb_{1-x}B_{\theta}$.

Figure 2 shows the low-temperature behavior of $Dy_x Yb_{1-x}B_6$ presented as plots of molar susceptibility as a function of temperature. There is clear indication of a Néel temperature, with a value of 21 °K for DyB_6 , which moves to lower temperatures as Yb replaces Dy (see Table I). The Néel temperatures have been determined in a rather subjective manner as either the temperature of the susceptibility maximum or, lacking a reasonably sharp maximum, the temperature of greatest curvature in a $1/\chi$ vs T plot.

DISCUSSION

In the RKKY mechanism for long range exchange interaction through the conduction electrons, the sign of the exchange integral J between magnetic ions at positions \mathbf{R}_i and \mathbf{R}_j oscillates according to



FIG. 2. Magnetic susceptibility (in arbitrary units) per mole of dysprosium in $Dy_x Yb_{1-x}B_6$ as a function of temperature in the low-temperature region.

$$J \sim \frac{\sin y - y \cos y}{v^4}$$

where $y = 2k_F(\mathbf{R}_i - \mathbf{R}_i)$ and k_F is the Fermi wave vector. For an isotropic conduction band $k_F = (3\pi^2 N/V)^{1/3}$, where N/V is the number of conduction electrons per unit volume. Ignoring the very small contraction of the lattice (less than 1%) on replacing Dy for Yb, we find $k_F \sim x^{1/3}$, where x is the mole fraction of M in MB₆ that is dysprosium. If we assumed that the dysprosium atoms were uniformly distributed in a continuously contracting simple cubic network, then (\mathbf{R}_i) $-\mathbf{R}_{i}$) would be proportional to $x^{-1/3}$. The net result would be no change in the RKKY parameter y as Dy is substituted for Yb-i.e., no oscillation in the sign of the exchange integral J. In fact, y and J would be constant at 6,188 and -0.00427, respectively, as calculated for pure DyB₆ ($a_0 = 4.10 \times 10^{-8}$ cm, $k_F = 7.55 \times 10^{7}$ cm⁻¹). Since DyB_6 is antiferromagnetic, showing not only a negative Weiss constant θ but even a Néel temperature $T_N = 21$ °K (see Table I), one might expect ytterbium-substituted DyB₆ to remain antiferromagnetic at all concentrations of ytterbium. However, the above situation is unrealistic. So long as metal atoms are confined to a single specific site in each unit cell, the distance between magnetic ions in different unit cells cannot be continously varied but must progress in jumps, corresponding to whether the next site is occupied or vacant. In other words, we have to sum over a set of discrete interaction distances, the above equation being better written as

$$J \sim \sum_{\mathbf{R}_{i} \neq \mathbf{R}_{j}} \frac{\sin y - y \cos y}{y^{4}}$$

Although we associate no special significance to the actual signs or magnitudes obtained (since the assump-

tion of an isotropic conduction band, i.e., a perfectly spherical Fermi surface, is probably not justified), we can calculate a composite exchange integral by summing over the successive sets of neighbors in a simple cubic array. The results obtained by summations through the seventh set of neighbors are shown in Table II. The calculations have been carried out under the following assumptions: (1) The lattice parameter a_0 contracts linearly with x from the 4.14 \times 10⁻⁸ cm that is characteristic of YbB₆ to 4.10×10^{-8} cm for DyB₆. (2) The number of interaction sites is 6 at a_0 , 12 at $\sqrt{2a_0}$, 8 at $\sqrt{3}a_0$, 6 at $2a_0$, 24 at $\sqrt{5}a_0$, 24 at $\sqrt{6}a_0$, and 12 at $\sqrt{8a_0}$. At each successive distance the fraction of sites actually occupied by dysprosium is just equal to x. (4) Each dysprosium atom contributes but one free electron to the conduction band.

As can be seen from Table II, there is indeed a change of sign in the net interaction constant as the concentration of dysprosium is diminished; at the least, there is a change in the magnitude of the exchange integral. At face value, it would appear that the antiferromagnetism should peak at x = 0.6 and that there should be ferromagnetism at x = 0.2. In fact, the experimental behavior shows no ferromagnetism (there is no field dependence of the susceptibility) and the apparent antiferromagnetism as judged by θ or T_N decreases regularly as the dysprosium concentration diminishes.

The persistence of the negative Weiss constant and the unmistakable Néel inversion clearly suggest antiferromagnetic exchange between neighboring dysprosium atoms, regardless of conduction electron density. In order to appreciate the exchange more fully, we have analyzed the results in terms of statistics of small clusters. For the compositions x = 0.4 and x= 0.2, we have calculated the probable number of "isolated" dysprosium ions (i.e., with no near-neighbor dysprosium), the number that occur in pairs, in clusters of three, and so forth. For the isolated dysprosium ions, we have assumed a Curie law behavior and subtracted the corresponding susceptibilities from the observed values. The surprising result for the "corrected" susceptibility is Curie-Weiss behavior with a constant interaction parameter (same θ as for x = 0.6) and a constant Néel temperature (same T_N as for x = 0.6). We take this to mean that once the isolated ions are corrected for, the behavior of the system is largely decided by the interaction between a pair of dysprosium ions, independent of whether the pair exists as an isolated pair or as part of a larger cluster. That this

TABLE II. RKKY parameters as calculated for hexaborides of composition $Dy_xYb_{1-x}B_6$ by lattice summation.

Mole fraction	Fermi wavenumber $k_F \times 10^{-7} \text{ (cm}^{-1})$	Exchange integral $\sum (\sin y - y \cos y)/y^4$
1.0	7.546	-0.00887
0.8	6.992	-0.0202
0.6	6.326	-0.0266
0.4	5.529	-0.0119
0.2	4.379	+0.0124

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cannot be precisely true can be seen from the fact that for x > 0.6, θ and T_N increase with dysprosium concentration as would be expected for a normal increase in the number of Dy-Dy interactions. One possible explanation would be enhanced clustering at low values of x; another would be special features in the electronic band structure. Perkins, Armstrong, and Breeze¹² have recently reported a new LCAO band structure calculation on the hexaborides of Ca, Sr, Ba, and La. Unfortunately, even for LaB_6 , their basis set did not include the d orbitals, so the results have only limited quantitative validity. Of interest here is to note that their calculated Fermi surface intersects three bands with relatively little s character and is multiply connected through k space. The result suggests conduction electrons with a range of Fermi velocities, which complicates the above calculation in which a spherical Fermi surface is assumed.

In the RKKY interaction, the exchange interaction is between spins S. For a rare earth ion such as dysprosium, where the state is specified by the total angular momentum J, it is necessary to correct for the orbital moment and have the projection of S on J. This amounts to replacing S by $(g_J - 1) J$, which leads to the so-called deGennes factor $(g_J - 1)^2 J(J+1)$ in the expression for the interaction energy. For Dy³⁺, the deGennes factor is 7.07; for Yb²⁺, it is zero. Using a mean value \overline{G} , obtained by weighting G_{D_T} with the mole fraction x of Dy in Dy_xYb_{1-x}B₆, we find that the observed Néel temperatures do not follow a $T_N \propto \overline{G}^{2/3}$ relation as has been observed for alloy systems in which indirect exchange is generally assumed.¹³

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