TABLE III
EQUILIBRIUM CONSTANTS AT 25° [a]

	L				
	$(CF_3)_3P$	$CH_3P(CF_3)_2$	$C_2H_5P(CF_3)_2$	$i\text{-}C_4H_9P(CF_3)_2$	$(C_2H_5)_2PCF_3$
$K_1 \rightarrow$	47	47	70	...	...
$K_1 \leftarrow$	52	...	68	...	...
ΔG_1, kcal	−2.31	−2.28	−2.51	...	...
$K_2 \rightarrow$	(1)	69	94	10	(High)
ΔG_2, kcal	...	−2.51	−2.69	−1.36	...
$K_3 \rightarrow$	(1)	2.3	4.7	0.5	13
ΔG_3, kcal	...	−0.49	−0.92	+0.41	−1.52
$K_4 = K_2/K_3$	...	30	20	20	...
ΔG_4	...	−2.02	−1.78	−1.78	...

[a] The subscripts for K and ΔG refer to equilibria 1–4. The arrows refer to forward and backward approaches to equilibrium.

(average, about ±0.3 kcal), meaning that ΔS never had more than a fairly small effect on the expression $\Delta G = \Delta H - T\Delta S$. This is a reasonable result, for eq 1–4 show no change in the number of molecules, and the reactants and products have the same numbers of bonds between the same elements, so that any change of molecular entropy would be small. Also the entropy of disproportionation, based upon the statistics of "scrambling," would be considerably smaller than would be required to change the trend of ΔH relative to ΔG. Hence it is reasonable to regard ΔG as an adequate basis for qualitative comparison of bond energies and for arguments about bond competition.

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Long-Range Magnetic Interactions in Europium Hexaborides

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Oesterreicher, Mammano, and Sienko[2] have found that $Eu(NH_3)_6$ is ferromagnetic with a Curie temperature of 5.5°K. Surprisingly, successive replacement of europium by diamagnetic ytterbium produces no change in the strength or sign of the ferromagnetic coupling, as would be expected for indirect exchange through conduction electrons. To explain the results, it has been postulated that the conduction band becomes depopulated at low temperatures due to localization of the conduction electrons in 4f or 5d orbitals. An observed increase in effective magnetic moment from 7.90 to 10.16 BM below 50°K supports this hypothesis. Because EuB_6 is also ferromagnetic with an almost identical Curie temperature (*i.e.*, 8°K), a magnetic study was undertaken in order to see if the ferromagnetic coupling in EuB_6 is also independent of dilution. The fact that EuB_6 has a fundamentally different band structure suggested that behavior might be quite different.

The crystal structure[3] of MB_6 corresponds to a primitive cubic lattice with an octahedron of boron atoms at each of the cube corners and a metal atom M at the center of the cube. The B_6 octahedra are connected to each other by covalent bonds between the neighboring boron atoms on a cube edge, so the result is a rigid-framework structure in which M atoms occupy the holes. Longuet-Higgins and Roberts[4] and, subsequently, Yamazaki[5] examined the energy-band structure and found that the boron lattice can accommodate twenty bonding electrons per B_6 octahedron with a finite energy gap between the highest bonding (valence band) and lowest antibonding orbitals (conduction band) of the crystal. In such case, when M is a divalent metal, MB_6 at zero temperature would be an insulator, since three valence electrons from each of six boron atoms plus two valence electrons from one metal atom would give just the twenty electrons needed to fill the valence set. When M is trivalent, however, the extra electron from M can only be accommodated in the conduction band; hence, $M^{III}B_6$ would be a metal. Flodmark,[6] from a more detailed calculation which took in more orbitals and interactions with more neighbors, agreed that $M^{III}B_6$ should be metallic but found that $M^{II}B_6$ might also be metallic, since there appears to be incomplete filling of conduction bands for some directions of electron transport. At present, experimental data on single-crystal conductivities are too few to justify a clear choice between the various models. The best single-crystal work, that of Johnson and Daane,[7] indicates that the alkaline earth hexaborides are semiconducting at high temperatures but may be metallic at low.

All the models are in agreement that the valence electrons of the metal atom are transferred to the boron framework. The structure can thus be considered as a simple cubic array of positive ions in a negatively charged boron network. Since, for stability, the identity of the ions appears unimportant, isomorphous dilution of magnetic rare earth ions by diamagnetic ones appears possible. In this investigation, the magnetic behavior of europium ions on dilution with diamagnetic lanthanum ions was examined.

Experimental Section

Materials.—EuB_6, LaB_6, $La_{0.50}Eu_{0.50}B_6$, and $La_{0.80}Eu_{0.20}B_6$ were prepared by heating appropriate rare earth oxide mixtures with boron at 1700°. Starting materials were 99.9% Eu_2O_3 (from Alfa Inorganics), 99.9% La_2O_3 (from Michigan Chemical Corp.), and 99.4% 60-mesh, crystalline boron (from Alfa Inorganics). The boron was heated to 100° and the rare earth oxides were heated to 1000° to remove water prior to weighing. Amounts of rare earth oxide and boron appropriate to the reaction $M_2O_3 + 15B \rightarrow 2MB_6 + {}^3/_2B_2O_2$ (where B_2O_2 subsequently goes to B_2O_3) were loaded under nitrogen into a ZrB_2 crucible, which was then enclosed in tantalum and placed in a covered recrystallized-alumina crucible on a nest of Al_2O_3 bubble insulation. Sighting holes in the alumina and tantalum covers permitted monitoring, with a calibrated pyrometer, the sample temperature to within ±20°. The reaction mixture was heated in argon for 45 min at 1700°, using an induction furnace. Outgassing was accomplished at 500°, after which the temperature was slowly raised to 1700°. Reaction began at 1500°, as could be noted by evolution of B_2O_3.

After a quench through furnace shutdown, the product was reground under nitrogen and reheated at 1700° for another 45 min. It was finally ground, washed with 1 N HCl and with water, passed through a 200-mesh sieve, and dried. X-Ray

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TABLE I

X-RAY PARAMETERS FOR HEXABORIDES (Cu Kα)

Composition	a_0, Å Obsd	a_0, Å Calcd	Composition	a_0, Å Obsd	a_0, Å Calcd
LaB_6	4.155	...	$La_{0.50}Eu_{0.50}B_6$	4.163	4.165
$La_{0.80}Eu_{0.20}B_6$	4.159	4.159	EuB_6	4.176	...

patterns, taken with a GE XRD-5 diffractometer using silicon as an internal standard, showed only a single phase, with cell dimensions as given in Table I.

Magnetic Measurements.—Magnetic susceptibilities were determined by the Gouy method over the range 1.5–300°K using the apparatus elsewhere described.[8] Samples were packed in 0.4-cm diameter silica tubes up to a height of about 20 cm, using precautions previously described to ensure uniform packing.[9] The temperature cycle was done in two stages, one using liquid nitrogen alone and the other using liquid helium. Data were reproducible to better than 1%. The magnetic field, which was varied from 300 to 6000 Oe, was calibrated with solutions of nickel chloride and with $HgCo(NCS)_4$.

Results and Discussion

Figures 1 and 2 show the observed reciprocal molar susceptibility of EuB_6, $Eu_{0.50}La_{0.50}B_6$, and $Eu_{0.20}La_{0.80}B_6$ as functions of temperature. In all three cases the slope of the linear portion indicates a Curie constant $C = 7.83$/g-atom of europium. In terms of moment, $\mu = (3kC/N)^{1/2}$, this corresponds to 7.92 BM, which compares to 7.94 BM expected for free Eu^{2+} ($4f^7$, $^8S_{7/2}$, $S = 7/2$, $L = 0$, $J = 7/2$, $g = 2$). On these graphs, data for LaB_6 would give a straight line parallel to the temperature axis corresponding to a near-zero value of the molar susceptibility. LaB_6 has a small temperature-independent paramagnetism ($\chi_m \approx 30 \times 10^{-6}$ cgsu) arising from Pauli susceptibility of an electron gas plus Van Vleck terms. In comparison with the enormous susceptibility of Eu^{2+} ($\chi_m \approx 26{,}000 \times 10^{-6}$ cgsu at 300°K), LaB_6 can be considered diamagnetic.

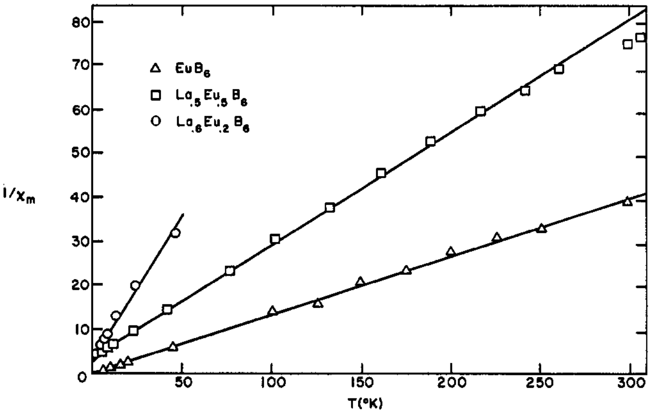

Figure 1.—Reciprocal molar susceptibility *vs.* temperature for europium hexaboride and its lanthanum-substituted isomorphs.

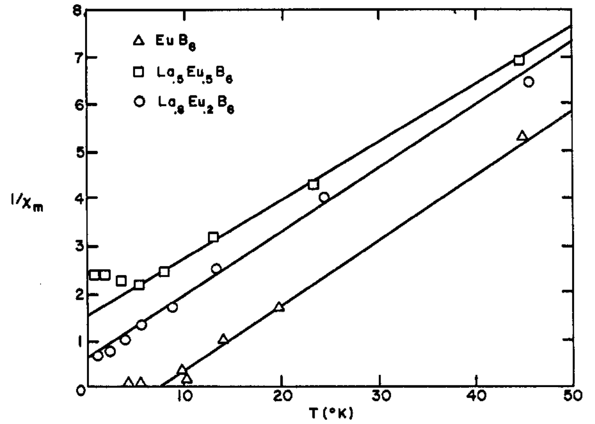

Figure 2.—Effect of lanthanum replacement on the low-temperature behavior of europium in europium hexaboride.

In agreement with Geballe, *et al.*,[10] who reported it to be ferromagnetic below 8.5°K, we find for EuB_6 a transition to ferromagnetic behavior at 8°K. This value, which is not very precise because of difficulty in measuring the huge forces involved at the low temperatures, was determined by extrapolation as a value for the Weiss constant Θ in $\chi = C/(T - \Theta)$. Also, below 8°K, behavior was typically ferromagnetic in that the susceptibility was strongly field dependent. Above 8°K, susceptibility *vs.* reciprocal field was flat to 1%. Unfortunately, forces were so large that saturation could not be attained to permit precise Curie point determination by extrapolation procedures using saturation magnetization *vs.* temperature.

As indicated in Figures 1 and 2, the behavior of $La_{0.50}Eu_{0.50}B_6$ is quite different. It shows a Néel temperature at 6°K and an extrapolated Weiss constant $\Theta = -12°$. Both Néel temperature and negative Weiss constant are characteristic of antiferromagnetic ordering. A further curious effect appears when more Eu is replaced to give $La_{0.80}Eu_{0.20}B_6$. Even at very low temperature, the magnetic behavior of $La_{0.80}Eu_{0.20}B_6$ is ideal, following a Curie law with a Weiss constant of zero.

The observed sequence on dilution—ferromagnetism, antiferromagnetism, ideal paramagnetism—suggests indirect exchange *via* conduction electrons. The observed ferromagnetism in pure EuB_6 might well be due to direct exchange between europium atoms; the observed critical temperature of 8°K is in qualitative agreement with what might be predicted from comparison with EuO. The latter is ferromagnetic with a critical temperature of 74°K. EuB_6, with six nearest europium neighbors at 4.18 Å, would be expected to have a lower critical temperature than EuO, which has twelve nearest europium neighbors at 3.64 Å. However, if the magnetic interaction in EuB_6 is by direct exchange, replacement of half the europium to give $La_{0.5}Eu_{0.5}B_6$ would be expected to reduce the critical temperature to about 4°K, still keeping the exchange interaction positive. Instead the interaction has become decidedly negative. The change in sign observed despite practically no change in lattice parameter suggests that the exchange proceeds indirectly through conduction electrons *via* the Ruderman–Kittel mechanism.[11] In the Ruderman–Kittel model, polarization of an itinerant electron changes sign in an oscillating manner as function of increasing distance from a magnetic ion and increasing wave number of the Fermi electrons. If only magnetic dilution were involved, the increase in the *average* Eu–Eu spacing in the sequence EuB_6, $Eu_{0.5}La_{0.5}B_6$, and $Eu_{0.2}La_{0.8}B_6$ would be consistent with oscillation in the sign of the magnetic interaction. However, the

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real situation is more complex than this. Europium or its diamagnetic replacement can occupy only discrete lattice sites; on dilution, there is no real increase in Eu–Eu spacing but only a decrease in the probability that a neighboring site is occupied by another europium. Hence, the observed change in sign of the magnetic interaction is probably due to the increasing electron density brought about by substituting trivalent lanthanum for divalent europium. As the population of the conduction band increases, the Fermi wave number increases, and the effect is as if the polarization wave were swept past a neighboring lattice site to oscillate the sign of the magnetic ordering interaction.

Matthias[12] has attributed the ferromagnetism observed for EuB_6 to magnetic polaron formation as predicted by Nagaev[13] for a semiconducting antiferromagnet. Unfortunately, available conductivity data and Flodmark's band calculation do not unambiguously establish that EuB_6 is nonmetallic or semiconducting. The complication in the present investigation is that dilution of EuB_6 by lanthanum substitution not only increases the average spacing between europium ions but also increases the conduction electron density. Experiments with Gd dilution and with Yb dilution to separate the two effects of changing electron density and magnetic dilution are now in progress.

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Low-Temperature Magnetic Susceptibility of Gadolinium and Terbium Tungsten Oxide Bronzes

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The metallic tungsten bronzes, M_xWO_3, are of special interest in solid-state chemistry because they are nonstoichiometric compounds in which the identity of dopant metal M and its level of concentration in the host matrix WO_3 can be varied over wide limits so as to permit study of the effect of electron concentration on physical properties.[2] In particular, when M is a rare earth element, one has a magnetic bronze, in which the interaction of conduction electrons and magnetic moments can be investigated. When x is large enough, the tungsten bronzes are approximately cubic with a unit cell in which there are W atoms at cube corners, O atoms near midpoints of cube edges, and fractional occupancy by M atoms of the cube center position. The metallic properties are ascribed to transfer of valence electrons from the M atoms to conduction bands made of W 5d t_{2g} orbitals with admixture of O p_π character.[3]

Ostertag[4] was the first to prepare tungsten bronzes in which the M atoms were rare earth metal atoms. For both europium and gadolinium he found that the structures were cubic over the range $0.085 < x < 0.18$. Subsequent work[5] showed that the resistivity was small, increased linearly with rising temperature, and had a temperature coefficient comparable to that of a metal. Attempts in this laboratory to measure Hall voltages on these crystals have proved unsuccessful, partly because of the odd pyramidal shape of the crystals; however, it seems almost certain that each rare earth atom contributes three electrons to the conduction band. Magnetic susceptibility measurements, in the range 77–300°K, had led Ostertag to conclude that the rare earth ions are indeed triply charged.

Ostertag[6] has also succeeded in making a uranium–tungsten bronze, and he has measured its magnetic susceptibility to a much lower temperature, down to 4.2°K. Although behavior above 60°K is Curie–Weiss ($\chi = C/(T - \Theta)$), with an extrapolated Weiss temperature $\Theta = -170°$, a clear minimum was also observed in the reciprocal susceptibility *vs.* temperature corresponding to a Néel temperature of about 30°K. Dilution of the uranium with diamagnetic thorium did not change the magnetic parameters, so it was assumed that the magnetic coupling was due to indirect exchange through conduction electrons. The current investigation was undertaken to see if similar indirect exchange might also occur at very low temperatures in the rare earth–tungsten bronzes. Gadolinium was chosen because of its high, spin-only magnetic moment; terbium was also investigated to see if there is an effect of an f-orbital component.

Experimental Section

Materials.—$Gd_{0.15}WO_3$ and $Tb_{0.15}WO_3$ were prepared by solid-state reaction according to the method of Ostertag.[4] A mixture composed of rare earth metal oxide, tungsten trioxide, and tungsten metal was ground in a ball mill under a nitrogen atmosphere for 8 hr. It was then heated under argon at 1100° for 24 hr, quenched, reground, and reheated. X-Ray diffraction patterns showed only the cubic tungsten bronze phase present. Starting materials were 99.9% Gd_2O_3 from American Potash and Chemical Co., "Specpure" Tb_4O_7 from Johnson Matthey Co., and highest purity W and WO_3 from Fisher Chemical Co.

Measurements.—Magnetic susceptibilities were measured over the range 1.5–300°K using the Gouy method with the apparatus previously described.[7] Samples were packed in 0.4-cm diameter silica tubes up to a height of about 20 cm. The temperature cycle was done in two stages, one using liquid nitrogen alone and the other using liquid helium. Data on descending and ascending temperature were reproducible to better than 1%. Magnetic field was varied from 300 to 2000 Oe at each temperature. Except at the very lowest temperature, plots of succeptibility *vs.*

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