Reports

Magnetic Ordering in the Rare-Earth Hexaborides

Abstract. *Magnetic ordering in the rare-earth hexaborides has been studied by a variety of methods, and a clear correlation with the presence of conduction electrons has been found.*

Matthias *et al.* have recently demonstrated that either superconductivity or antiferromagnetism occurs as the ground state of the trivalent rare-earth hexaborides (*1*). The divalent alkaline-earth hexaborides have been shown to be semiconductors with well-defined energy gaps by Johnson and Daane (*2*) who were able to make measurements on single-crystal strontium hexaboride (SrB_6). Such behavior was anticipated by the work of Longuet-Higgins and Roberts, and others (*3*). Europium hexaboride (EuB_6) is thus particularly interesting, since its lattice constant (*4*) and fine-structure x-ray absorbtion data indicate it is divalent. Heat-capacity data to be presented below, as well as measurements of the Mössbauer effect (*6*), offer convincing further evidence. Our results also suggest that EuB_6, if it could be prepared as a pure, stoichiometric phase, would be a semiconductor, which is a ferromagnet (*1*). Thus, one is led to the conclusion that magnetic rare-earth ions in the hexaboride lattice will order antiferromagnetically when they couple primarily by way of an appreciable concentration of conduction electrons (indirect exchange), and ferromagnetically as the concentration approaches zero.

It is interesting to compare both EuB_6 and gadolinium hexaboride (GdB_6) where the rare-earth configuration involves the exactly half-filled *f*-shell. Paderno *et al.* (*7*) studied their magnetic behavior above liquid nitrogen temperatures and find close to the expected effective 7.9 Bohr magnetons per ion, with Curie-Weiss intercepts of $+9°$ and $-55°$, respectively. Coles *et al.* (*8*) demonstrated by measurements of resistivity and susceptibility that GdB_6 orders antiferromagnetically at about 13°K. Our results for GdB_6 essentially confirm those of Coles *et al.*, although the sharp discontinuity in resistivity and susceptibility occurs in our samples at 18° rather than 13°K.

In contrast to all the other magnetic rare-earth hexaborides, which are metals with low-temperature resistivities of the order of 10^{-7} ohm cm and which seem to order in an antiferromagnetic manner (*9*) with no remanent moment, we find EuB_6 to be ferromagnetic below 8.5°K. The same ordering temperature was observed for two different samples of EuB_6 which had greater resistivity, by one or two orders of magnitude respectively, than GbB_6. This suggests that the ordering temperature of pure, stoichiometric (and presumably semiconducting) EuB_6 would still be 8.5°K, and that in analogy with EuO and EuSe, where the Curie temperature is also insensitive to variations in electrical conductivity caused by small deviations from stoichiometry (*10*), the ferromagnetism is due to a super-exchange mechanism not involving conduction electrons.

Our results (*11*) for the heat capacity, resistivity, and alternating-current susceptibility of EuB_6 are shown in Figs. 1 and 2. A reasonable estimate of the magnetic contribution to the heat capacity below 20°K indicates that about 80 percent of the spin entropy associated with the half-filled shell (R ln 8) per mole of EuB_6 expected for divalent Eu is accounted for. Measurements of the Mössbauer effect (*6*) confirm the onset of magnetic order below 8.5°K, and the observed isomer shift indicates the presence of divalent Eu only. The susceptibility results show that, in addition to the ferromagnetic ordering around 8.5°K, another ordering takes place at higher temperatures. The heat-capacity results show that this latter effect involves very little entropy, and it is uncertain whether it is due to the presence of a small amount of another unidentified phase or due to the onset of short-range order among the Eu^{+2} moments.

The high Debye temperatures of boron-rich compounds and their low ordering temperatures allow the magnetic phenomena to be prominently displayed in the temperature dependences of heat capacity and resistivity. The large percentage drop of the resistivity of the metallic hexaborides at their Néel temperatures (~ 100 percent) is consistent with the assumption that, in the metallic hexaborides, the ordering is due to indirect interaction by way of conduction electrons. In praesodymium hexaboride (PrB_6) a very sharp heat-capacity spike is found at 6.92°K which rises discontinuously on the high-temperature side to a maximum of 6.45 cal mol^{-1} deg^{-1}, although strangely enough only a small fraction of the expected entropy is involved. A Curie-Weiss type dependence of susceptibility upon temperature with the expected effective moment per Pr (3.56 Bohr magnetons), and an intercept of −44°K is found for the sample between 15°K and room temperature. The bulk of the entropy is therefore not removed at higher temperatures. In other cases the crystal-field splittings may be appreciable with respect to the exchange interaction, and then one can understand why the high-temperature Curie-Weiss data of Paderno (*7*) for the lighter rare earths extrapolate to higher ordering temperatures than are actually observed. For example, their intercept for cerium hexaboride (CeB_6) is −76°K, whereas we observe a Néel

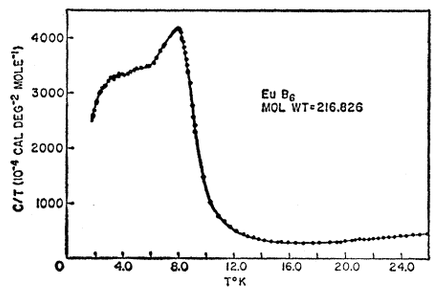

Fig. 1. Heat capacity of EuB_6.

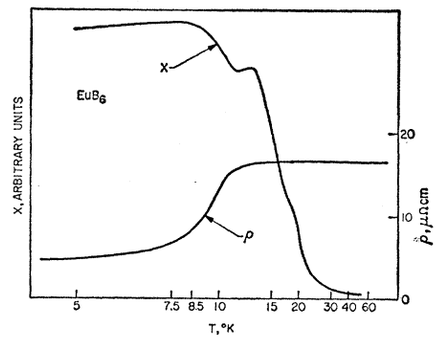

Fig. 2. Initial susceptibility (χ) and resistivity (ρ) for EuB_6.

temperature of $\lesssim$ 3.0°K. With such a low ordering temperature one might hope to break the antiferromagnetism and align the moments in an externally applied field. The results of such an experiment showed a saturation of 0.56 Bohr magnetons per Ce at 1.3°K and 50 kgauss (almost independent of field above 30 kgauss) which is in strong contrast to the paramagnetic effective moment of 2.56 Bohr magnetons expected for the trivalent Ce in the $^2F_{5/2}$ configuration, and which Paderno *et al.* find from their measurements above $\sim$ 150°K. The experiment suggests that 30 kgauss is sufficient to saturate a low-lying magnetic state which is split from the ground-state multiplet by the crystal field in the manner discussed by Jones (*12*).

In Fig. 3 we illustrate some unusual behavior of the ordering temperature of the metallic rare-earth hexaborides. The ordering temperature depends roughly upon the effective moment. We have been unable to pursue this idea further by extending the measurements to the heavier rare earths. As found by others (*13*), we were unable to prepare hexaborides of erbium (Er), thulium (Tm), and holmium (Ho), and, in fact, found no x-ray evidence for the existence of the former two. In addition, our terbium hexaboride (TbB_6) and dysprosium hexaboride (DyB_6) samples showed small quantities of phases other than the hexaboride. The work of Vainshtein *et al.* (*5*) indicates that divalent samarium (Sm) (which like trivalent Eu would have no ground-state magnetic moment) is present in appreciable amounts in SmB_6. In agreement, our SmB_6 showed no evidence of ordering above 1°K.

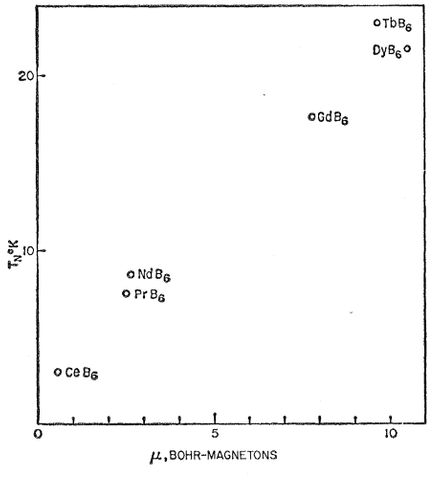

Fig. 3. Ordering temperature for antiferromagnetic hexaborides as deduced from alternating-current susceptibility and resisitivity as a function of calculated effective moment, except for cerium hexaboride where the saturated (measured) moment of low temperatures is used.

It has not yet been possible to make complete studies of variations in ordering temperature with composition. The quantitative data presented here may change somewhat if more detailed investigations on better samples are made. However, the pattern which is already emerging is likely to provide new insight and understanding of interactions between rare-earth local moments and conduction electrons.

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9. The Yb ion in our ytterbium hexaboride (YbB_6) sample is divalent as deduced from the enlarged lattice constant (4.147 Å), and previously found by others (*4*), as well as from the investigations of Vainshtein *et al.* (*5*). In agreement with this deduction and confirming the results of Paderno *et al.* our samples show no localized magnetic moment behavior at low temperatures. The earlier work of R. Benoit. *J. Chem. Phys.* **52**, 119 (1955) in which the magnetic evidence indicated the presence of trivalent Yb could not be repeated.
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11. The samples were prepared in the arc-furnace by reacting the elements during which procedure some Eu was lost by evaporation. X-ray diffraction patterns show the presence of EuB_6 and free boron. The heat capacity measurements were made by the pulse-method of F. J. Morin and J. P. Maita, *Phys. Rev.* **129**, 1115 (1963). The resistivity and susceptibility were measured using low-frequency alternating-current techniques.
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13. As might be expected from the work of G. D. Sturgeon and H. A. Eick, *Inorg. Chem.* **2**, 430 (1963) and M. Przbylska, A. H. Reddock, and G. J. Ritter, *J. Amer. Chem. Soc.* **85**, 407 (1963). Er and Tm only form dodecaborides. Similarly, although we were able to obtain evidence for HoB_6, it could not be prepared as a dominant phase.

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Erosion Rates Near Rome, Italy

Abstract. *Before man's intensive use of the land the rates of erosion near Rome, Italy, were approximately 2 to 3 centimeters per thousand years. With intensive occupation by man the rates have increased by an order of magnitude.*

Near the beginning of the Christian era, small stream valleys in the Mediterranean region began to silt up, and various works of man were buried (*1*). Such sedimentation, as well as that in larger valleys and estuaries, poses the question of the rates of production of sediment, past and present. I now report on present and past erosion rates in west-central Italy, especially north of Rome. For determination of these rates the loads carried by modern streams are used for averaging the modern rates of erosion over entire drainage basins. In addition, archeological sites provide rates over periods ranging up to 2500 years. Finally, lake cores provide estimates of the rates of erosion at two localities before the land was intensively used by man.

Table 1 gives stream data from four different gauging stations. The erosion rates derived for the drainage basins concerned vary between 9 and 73 cm/1000 years. These values take into consideration only the suspended load; if data for dissolved and bedload material were available, the values would be increased by an estimated 10 to 20 percent. The values (Table 1) are in general agreement with those from a study of erosion over all Italy (*2*).

Some archeological sites yield erosion rates over longer periods. Figure 1 illustrates one such situation; the structure served as a cistern for a Roman villa built about A.D. 150. The rough surface indicates the footings of the structure; they are made of concrete and tuff fragments originally poured into a trench. The more carefully constructed wall of bricks and shaped blocks of tuff was then built upon the footings. The soil surface at the time of construction was at the line separating the two wall textures, so that the amount of erosion here since A.D. 150 is 1.30 m. Around this structure erosion ranges between 0.60 and 1.30 m, the average rate being 50 cm/1000 years. This and six other localities are listed (Table 2), the rates of erosion varying between 20 and 100 cm/1000 years. In each of these localities man's intensive occupation of the land has always been fairly continuous.