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Unusual magnetism of hexaborides

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Abstract

Various recent experimental investigations have revealed unusual magnetic properties of hexaborides with divalent cations M^{2+}. EuB_6 is ferromagnetic below 16 K and its low-temperature properties show remarkable similarities to those of manganese oxides, exhibiting the phenomenon of colossal magnetoresistance. Close to the phase transition as well as far below the ordering temperature, EuB_6 exhibits anomalous features, that are briefly discussed. Alkaline-earth hexaborides are close to a metal–insulator transition and it has been found that, in a narrow range of electron doping, an itinerant-type of ferromagnetic order, stable up to temperatures of the order of 600–900 K, is established. This remarkable phenomenon is suspected to be due to the peculiar electronic band structure of these materials. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Weak ferromagnetism; Hexaborides; Phase separation

1. Introduction

Hexaborides are binary compounds, crystallizing with a simple cubic structure, which may be synthesized both with di- and trivalent metal cations, of the alkaline-earth and rare-earth series, respectively [1]. Until recently, most experimental investigations have been concentrated on rare-earth hexaborides. In spite of their simple chemical and structural configuration, these hexaborides have proven to exhibit a variety of physical properties. First, we mention LaB_6, a fairly simple metal with a transition to superconductivity at very low temperature [2] and a rather low work function, favourable for applications in coherent electron sources. Next, SmB_6 is a notorious intermediate valent compound [3] where, with decreasing temperature, the formation of a gap in the electronic excitation spectrum [4] leads to a ground state with a low electrical conductivity, whose exact nature is still a matter of debate. Finally we recall that EuB_6 has been

known to order magnetically at low temperatures [5], suggesting a divalent configuration of the Eu ions. The transition into the magnetically ordered state is accompanied by a sizeable reduction of the electrical resisitivity by two to three orders of magnitude [6]. In addition large negative magnetoresistance effects have been observed below liquid nitrogen temperatures [6]. Because of these similarities with transition metal oxides [7], the magnetism of EuB_6, due to the local 4f electron moments of the Eu ions, deserves further attention.

More recent experimental work on hexaborides with cations of the alkaline-earth series (Ca, Sr, Ba) probing electrical transport properties [8] has shown, that these materials are at the border separating semi-metals from insulators. This was indeed confirmed by band structure calculations which revealed a very peculiar configuration of the electronic excitation spectrum of these compounds [9]. The calculations indicate that the valence- and the conduction band are well separated by a sizeable gap in most parts of the momentum space, except for a tiny region around the X points of the Brillouin zone, where a faint overlap, depending on the interatomic distance between B ions in the crystal structure, may

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been identified. It has turned out that this situation leads to rather unexpected magnetic features of these materials [10], as will be outlined in greater detail below.

2. Ferromagnetism of EuB$_6$

As indicated by various experimental results, the magnetic order of this compound is due to the ferromagnetic alignment of localized Eu 4f electron moments. According to recent neutron-scattering experiments [11], the zero-temperature moment is 7 μ_B/Eu ion, as expected for the divalent configuration of Eu. Specific heat $C_p(T)$ experiments [12,13] reveal the corresponding molar entropy release of $R \ln 15$ below the Curie temperature T_C and, at the same time, they indicate the occurrence of two-phase transitions with onsets at 16 and 14.5 K, respectively. The above-mentioned reduction of the electrical resisitivity below T_C is at least partially due to a substantial increase of the density of itinerant charge electrons, as revealed by optical reflectivity [12] and Hall effect measurements [14]. A concomitant decrease of the effective mass of the itinerant charge carriers adds, via an enhancement of their mobility, to the observed decrease of the electrical resistivity [14]. The temperature dependence of the magnetization [11] is far from being of mean field type; neither is the shape of the specific heat anomaly [12,13]. It may be that the temperature dependence of the alignment of the local magnetic moments is the result of the interplay of the spontaneous magnetization and the concomitant change of the electronic excitation spectrum, i.e., the increasing number of conduction electrons with increasing magnetization and hence internal magnetic field.

Another more recent microscopic probing of the magnetically ordered state by ^{153}Eu NMR experiments [15] has identified an additional and rather unexpected complication of the situation. The main result may be seen in Fig. 1, where the essential part of the NMR signal of the ^{153}Eu nuclei at low temperatures is displayed. It may be seen that, below about 2 K, next to the single resonance signal A observed at elevated temperatures, a second signal B develops at lower external magnetic fields, with growing intensity as the temperature decreases. Since the internal magnetic field at the Eu nuclei is of the order of 30 T, external magnetic fields of the order of 1 T should not substantially alter the intrinsic features of the ordered state. Measurements of the spin–spin relaxation time T_2 have been used to show that these two signals are to be interpreted as being due to a phase separation phenomenon, leading the coexistence of two magnetically and electronically distinct phases in the ferromagnetic state of EuB$_6$, well below T_C. The temperature dependence of the relative B signal intensity is shown in Fig. 2.

The magnetic field and temperature dependences of T_2 are quite different in phase A and phase B. For
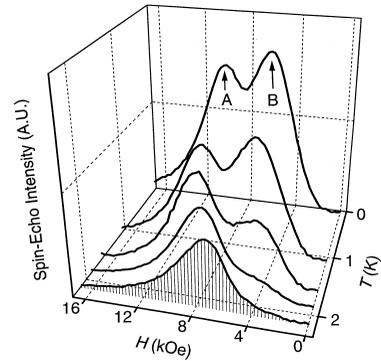

Fig. 1. Low-Temperature ^{153}Eu NMR spectra of EuB$_6$ at a fixed frequency of 156.36 MHz. Note the gradual enhancement of peak B with decreasing temperature.
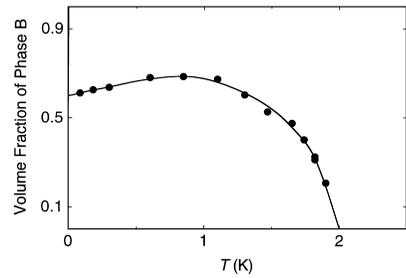

Fig. 2. Temperature dependence of the relative integrated intensity of signal B shown in Fig. 1. The solid line is to guide the eye.

instance, at a fixed magnetic field, T_2 in phase A is practically constant below 2 K whereas in phase B, T_2^{-1}, the spin–spin relaxation rate, increases with increasing slope towards the phase boundary, i.e., with increasing temperature. This phase separation is not significantly manifest in the temperature dependence of other physical properties, such as the electrical conductivity or the thermal conductivity [16], confirming the results of the NMR experiments which suggest that the hyperfine fields of the A and the B phase at the Eu nuclei are almost the same and that it is mainly the interaction of the nuclear spins with the electronic environment which is different in the two phases. A rather abrupt change in the $C_p(T)/T$ ratio well below T_C may be another manifestation of the phenomenon [12,13] but this has not been confirmed yet.

The appearance of a phase separation phenomenon in the magnetically ordered state of EuB$_6$ is quite surprising and may have its roots in the peculiar electronic energy spectrum of this type of materials mentioned in the introduction. The similarities of the phenomena observed in the magnetic- and transport properties of EuB$_6$ with those previously reported for manganese oxides where ferromagnetic order, concomitant with a drastic increase

of the electrical conductivity in the ordered state, strong magnetoresisistance effects in the temperature range of the transition and, in some cases, phase separation [17], are quite striking. It does not seem obvious that these seemingly similar physical properties of the two types of materials share any common origin, except that in both cases the localized magnetic moments are embedded in an environment with a low concentration of itinerant charge carriers, the density of which is substantially enhanced below the ferromagnetic transition temperature.

3. Magnetism of $M_{1-x}^{2+}La_xB_6$ (M = Ca,Sr,Ba)

The temperature dependence of the electrical resisitivity $\rho(T)$ of the binary compounds CaB_6 and SrB_6 indicates that these two materials are very close to a metal-insulator transition. As an example we show $\rho(T)$ of Ca-rich CaB_6 below room temperature in Fig. 3 [18]. The Ca-rich starting composition for the synthesis of the single-crystalline samples is intended to minimize vacancies in the M^{2+} sublattice which may contribute to a self-doping of itinerant charge carriers. An initially positive slope $\partial\rho/\partial T$ just below room temperature is followed by a minimum in $\rho(T)$ and after a subsequent increase of the resistivity by almost four orders of magnitude, not quite obvious in Fig. 3, $\rho(T)$ tends to saturate at low temperatures at a level of $15\,\Omega\,cm$, indicating the presence of a very low number of itinerant charge carriers. Rather unexpectedly but as observed before in SrB_6 [8], the resistivity loses about 30% of its value below $0.5\,K$ and varies proportional to T^3 below $0.1\,K$. This feature is not yet explained but it is accompanied by anomalies in the temperature dependences of the specific heat [8] and, at least in the case of SrB_6, of the NMR spin-lattice relaxation rate [19].

Substitutions of the divalent alkaline-earth ions with trivalent rare-earth (RE) elements at the level of the order of 1 at.% induce a metallic behaviour with an order of magnitude lowering of the absolute value of the resisitivity at room temperature and a positive $\partial\rho/\partial T$ over most of the temperature regime below 300 K [20]. This indicates that the extra electron of the RE^{3+} ions is added to the itinerant charge carrier reservoir. More surprising is that this type of doping with La^{3+} at a level of 0.1 at.% leads to a very unexpected field dependence of the low-temperature magnetization $M(H)$ of, e.g., $Ca_{1-x}La_xB_6$, very clearly exhibiting the hysteresis-curve features of a ferromagnet. The saturation moment has been found to be very sensitive to the number of added charge carriers. Both these features, first identified in La-doped CaB_6 [10], may be seen in Fig. 4. The sharp decrease of the saturation moment per added charge carrier for $x > 0.005$ indicates that the observation of this ferromagnetic behaviour cannot simply be traced back to a trivial impurity effect.
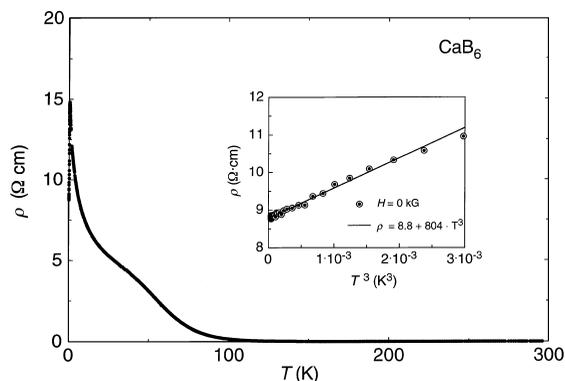

Fig. 3. Temperature dependence of the electrical resistivity of stoichiometric CaB_6. The inset is an expanded view of the data at very low temperatures.
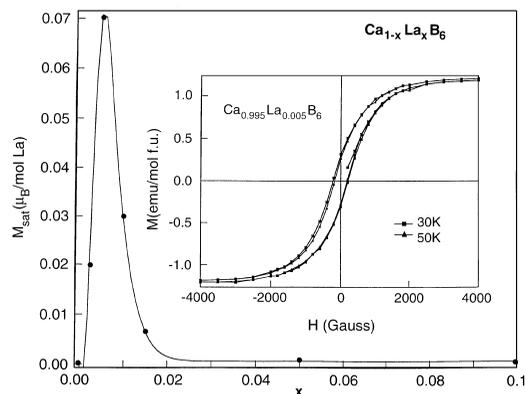

Fig. 4. Concentration x dependence of the saturation magnetic moment per charge carrier for $Ca_{1-x}La_xB_6$. The inset displays $M(H)$ curves of $Ca_{0.995}La_{0.005}B_6$ at two temperatures.

Even more surprising, however, is the stability of this ferromagnetic state. Measurements of $M(T)$ in a fixed external magnetic field revealed a Curie temperature T_C of 600 K for $Ca_{0.995}La_{0.00}YB_6$. This is to be compared with a Fermi temperature of the order of 700 K that is calculated by considering the La-induced extra charge carrier density. Because of the obvious lack of localized magnetic moments in these alloys, the ferromagnetism must almost inevitably be ascribed to a, at least partial, polarization of the Fermi surface, i.e., a spontaneous magnetic order provided by itinerant charge carriers. That this instability of the conduction electron system occurs on an energy scale that is comparable with its Fermi energy is another amazing result of this study.

In Fig. 5 we display $M(T)$ of nominal $Ca_{0.99}La_{0.01}B_6$, for which the ordered magnetic moment per added charge carrier has been calculated to be approximately $0.02\,\mu_B/La$ atom, substantially less than for the material with 0.5% La doping. It may be seen that in spite of this
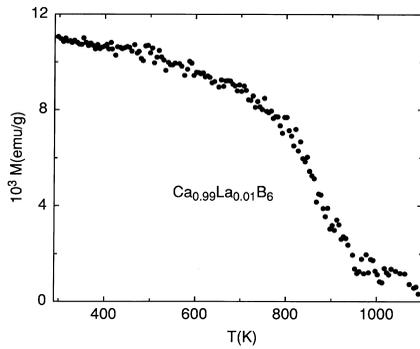
Fig. 5. Temperature dependence of the magnetization of $Ca_{0.99}La_{0.01}B_6$ above room temperature.

substantial reduction of the induced moment, the Curie temperature is of the order of 900 K. This seems to indicate that the usually observed scaling between the ordering temperature and the ordered moment is not obeyed in this case.

Preliminary experimental data reveal that ferromagnetic order with very low values of the saturation moment also develops in the binary compounds CaB_6 and SrB_6, again with amazingly high Curie temperatures of the order of 800 K. It is suspected that in these materials, for which a doping level of the order of 10^{-4} per unit cell has been estimated, the itinerant charge carriers are due to self-doping invoked by vacancies, most likely on the sublattice of the alkaline-earth ions. Experiments to verify this conjecture and aiming at avoiding the self doping are under way.

4. Discussion

As demonstrated above, we are facing two very different phenomena of magnetic order in hexaborides with divalent cations. The divalent rare-earth ions Eu^{2+} carry a local moment of several Bohr magnetons, while for the La-doped alkaline-earth hexaborides no source of local moments may be identified. Ferromagnetic order among the local Eu^{2+} moments sets in below 16 K and is, at least partially, mediated by the interaction between the local moments and the conduction electrons, whose density changes substantially from the high-temperature paramagnetic to the low-temperature ferromagnetic phase.

The weak ferromagnetism carried by the itinerant electron system up to temperatures of almost 1000 K in the "non-magnetic" alkaline-earth hexaborides is, of course, of much less obvious origin. Very early discussions of correlation effects in low-density electron gases and the possible onset of ferromagnetism in such systems are due to Bloch [21] and Wigner [22]. Later it has been argued

that, by considering all possible interactions, the physical realization and actual observation of this phenomenon in real solids would be rather unlikely [23]. Nevertheless, subsequent numerical calculations [24], in part of very recent origin [25], seem to indicate that this possibility may still be a viable route to explain the observations described above.

A quite different approach is offered by considering more seriously the particular electronic band-structure features briefly mentioned above. These considerations imply that the formation of stable excitons between electrons and holes in the overlap region around the X point of the Brillouin zone is very likely and that the observed ferromagnetism is a possible ground state of this exciton subsystem. The formation of excitons and the consequences on physical properties have theoretically been studied extensively 30 years ago by various authors [26–28]. These ideas have now been taken up in recent work [29–31] in attempts to identify the weak ferromagnetism of the hexaborides as a physical realization of the mentioned exciton formation, a very exciting possibility indeed. Whether the resulting new type of magnetic order is an adequate basis for explaining the experimental data needs further work, in both experimental and theoretical investigations.

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