TUNING OF MAGNETIC ORDER IN $Eu_{1-x}Ca_xB_6$*

May Chiao, G. Wigger, C. Bergemann, H.R. Ott

Laboratorium für Festkörperphysik, ETH Hönggerberg
8093 Zürich, Switzerland

S.S. Saxena

Cavendish Laboratory, University of Cambridge
Madingley Road, Cambridge CB3 0HE, UK

A.D. Bianchi, and Z. Fisk

National High Magnetic Field Laboratory, Florida State University
Tallahassee, FL 32306, USA

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We have measured the resistivity and magnetisation of several samples of the $Eu_{1-x}Ca_xB_6$ series under pressure in order to probe the evolution of itinerant electron ferromagnetism in CaB_6 from a localised moment ordered state in EuB_6. Starting with pure EuB_6, the Curie temperature T_C is reduced upon increasing x. In particular, we have investigated the magnetic field and pressure dependence of T_C, which is enhanced by both of these externally tuneable control parameters. At T_C, there is a large peak in the resistivity, which is eliminated by moderately strong magnetic fields.

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Despite the growing body of work on the hexaborides, the many and varied manifestations of magnetism in these materials are still not completely understood. While EuB_6 has localised $4f$ moments [1], La- and vacancy-doped CaB_6 display itinerant ferromagnetism with a Curie temperature of order 1000 K [2, 3]. We are interested in the evolution from one form of ferromagnetism to the other, and we present chemical and pressure tuning experimental results on the $Eu_{1-x}Ca_xB_6$ system.

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In a recent study of $Eu_{0.8}Ca_{0.2}B_6$ [4], it was observed that upon warming the charge carrier density n_c drops by nearly two orders of magnitude as the moments depolarise at T_C. Compared with EuB_6 and CaB_6, n_c in $Eu_{0.8}Ca_{0.2}B_6$ is greater than for both of them below their respective T_C's and less than for both of them above. That n_c is not between those of the parent compounds is a mystery. In an explorative pressure study we hope to clarify the nature of the magnetic interactions.

High quality single crystals were grown by the flux method. For both magnetisation and resistivity measurements, we used nonmagnetic piston-and-cylinder clamp cells with a 1:1 mixture of F70 and F77 Fluorinert as pressure medium to ensure hydrostaticity. The resistivity was measured in the standard 4-probe geometry with silver epoxy contacts. Magnetisation was measured in a small pressure cell specially designed for a Quantum Design SQUID magnetometer.

In the inset of figure 1 we display the temperature dependence of the magnetisation of a sample of pure EuB_6. At ambient pressure, the ferromagnetic transition is near 15 K. The best samples show a double transition at slightly different temperatures, but at this stage we are only concerned with the overall pressure behaviour. At 10 kbar applied pressure, the Curie temperature T_C increases to 19.5 K. This increase of 0.45 K/kbar is roughly 50% larger than the previously reported rate [5]. Most likely this difference is due to the use of a solid medium in Ref. [5], while our liquid medium provides more hydrostatic conditions. Enhanced pressure also reduces the saturation magnetisation.

Similar behaviour is observed in $Eu_{0.95}Ca_{0.05}B_6$, except T_C is strikingly less affected by pressure; the application of 8 kbar produces a small change in T_C, as shown in the main frame of figure 1. In both pure and doped EuB_6, the total magnetisation decreases with applied pressure.

In figure 2 we present the resistivity of $Eu_{0.8}Ca_{0.2}B_6$. At ambient pressure, the peak at T_C near 5 K shows a hysteresis in temperature. This hysteresis is rapidly suppressed by a magnetic field and has disappeared by 5 kOe. The peak amplitude decreases with the application of a magnetic field, which concurrently moves the maximum to higher temperatures. Such behaviour has been seen in the manganites, in which the core spins are aligned by the field such that the electrons meet less resistance as they flow from core to core via the oxygen ions [6]. However, the magnitude of the resistivity peak is much smaller in $Eu_{0.8}Ca_{0.2}B_6$ but still may have the same origin. The simplest explanation would be strong resonant scattering due to the Ca ions. Preliminary pressure measurements reveal an enhancement of T_C by 1 K in 9 kbar. Recall that in pure EuB_6, a similar pressure produces a 4 K shift in T_C.

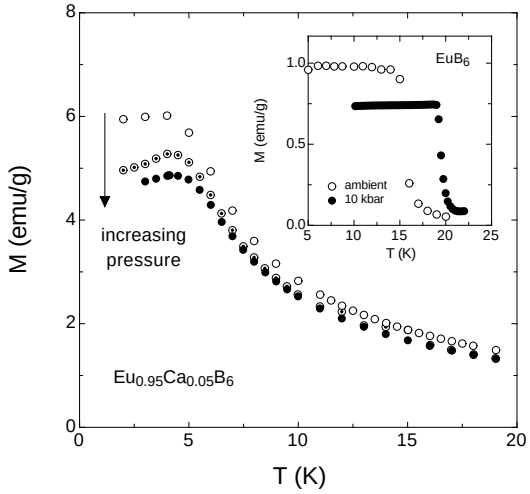

Fig. 1. Magnetisation as a function of temperature of $Eu_{0.95}Ca_{0.05}B_6$ in a field of 1 kOe. The data sets correspond to pressures from ambient up to 8 kbar. Inset: Magnetisation as a function of temperature of pure EuB_6 in a field of 50 Oe (20 times less than $Eu_{0.95}Ca_{0.05}B_6$). Open circles correspond to ambient pressure; solid circles to 10 kbar. In both cases, the moment decreases with pressure while the Curie temperature increases, although Ca-doping slows down the latter.

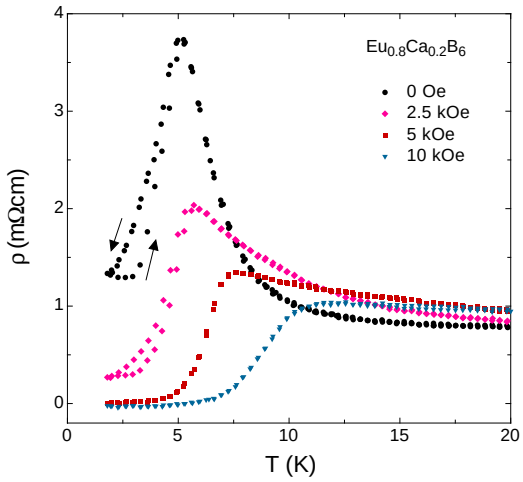

Fig. 2. Resistivity as a function of temperature for $Eu_{0.8}Ca_{0.2}B_6$ in applied magnetic fields up to 10 kOe. In zero field there is a significant hysteresis which is reduced by the magnetic field; by 5 kOe, the hysteresis is no longer observable.

There is a number of issues to be discussed, namely (1) the reduction of T_C with Ca substitution, (2) the reduction of the magnetisation with pressure, (3) the enhancement of T_C with pressure and (4) the enhancement of T_C with magnetic field. A reduction in magnetisation and an enhancement in T_C is often observed in heavy electron compounds, which is readily explained by the Doniach phase diagram describing the competing effects of the RKKY interaction and the Kondo screening of the moments. However, we are dealing with Eu, which has seven f electrons, instead of Ce or U with only two. Hence in Eu, the moment is extremely localised, prohibiting the use of the Kondo scenario to account for the reduction of the moment. From Ref. [4], we know that Ca substitution leads to an overall increase of the absolute resistivity. Let us assume that the increased resistivity is due to a reduction in charge carriers (true in the paramagnetic state, cf Ref. [4]). Then the reduced number of conduction electrons would weaken the RKKY interaction responsible for the ferromagnetism (FM), and hence the magnetic moment would be reduced. If we further assume that some exchange interaction exists between the localised Eu moments, providing antiferromagnetic (AF) coupling, pressure may then favour the AF exchange, and together with the competing FM, some canted AF or ferrimagnetic state could result, with no big change in T_C. An applied field would then align these canted spins and reduce the resistivity, which is what the data in figure 2 reflect.

Experiments to measure the charge carrier density under pressure are currently underway. We also plan to study a wider range of Ca doping.

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