



# Electronic transport and thermal properties of $\text{CaB}_6$ and $\text{Eu}_{1-x}\text{Ca}_x\text{B}_6$

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## Abstract

By substituting Ca for Eu in  $\text{EuB}_6$ , a local-moment ferromagnet, the transition temperature of 16 K for the binary compound, is lowered substantially with increasing  $x$ . In spite of the divalency of both Eu and Ca, significant changes in the electronic properties are indicated by changes in the temperature and magnetic-field dependences of the electrical resistivity, particularly at low temperatures. For pure  $\text{CaB}_6$  similar anomalies in the resistivity and the specific heat at very low temperatures as previously observed for  $\text{SrB}_6$ , have been identified. Most of these properties most likely originate in the particular electronic structure of these hexaborides. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Hexaborides; Resistivity; Specific heat

## 1. Introduction

The  $\text{Eu}_{1-x}\text{Ca}_x\text{B}_6$  series of compounds shows remarkable features, with at one end  $\text{EuB}_6$ , a local-moment ferromagnet, and at the other end  $\text{CaB}_6$ , a high  $T_C$  weak ferromagnet [1]. With the aim of acquiring additional informations on this series of compounds we first studied a metal-rich  $\text{CaB}_6$  sample. Hexaborides have the tendency to become boron-rich by the formation of metal vacancies, but they are essentially stoichiometric at the metal-rich phase boundary. The flux-growth synthesis of stoichiometric single crystals was therefore started with a mixture containing an extra amount  $\delta$  of Ca. Furthermore, we studied  $\text{Eu}_{0.8}\text{Ca}_{0.2}\text{B}_6$  [2] and  $\text{Eu}_{0.9}\text{Ca}_{0.1}\text{B}_6$  samples in order to explore the changes in the electronic properties and the weakening of the local-moment ferromagnetism when replacing Eu by Ca ions.

## 2. Results and discussion

In Fig. 1 we show  $\rho(T)$ , the resistivity of  $\text{Ca}_{1+\delta}\text{B}_6$  as a function of the temperature. Qualitatively the same features as for  $\text{SrB}_6$  [3] have been observed. However, the order of magnitude of the resistivity variation as function of temperature is much larger. The resistivity first drops by 8% from 300 K down to 230 K, but then increases by about four orders of magnitude between 230 and 1 K. Below 0.4 K a reduction of about 40% of the resistivity is observed. As for  $\text{SrB}_6$  [3],  $\rho(T)$  varies as  $T^3$  for  $T \rightarrow 0$  K (inset of Fig. 1). The application of an external magnetic field of about 1 T suppresses the decrease of the resistivity below 0.4 K.

In Fig. 2 we present our specific heat data of  $\text{Ca}_{1+\delta}\text{B}_6$ . At low temperatures we observe an excess specific heat with a maximum at 0.3 K, similar to what has previously been observed for  $\text{SrB}_6$  [3]. It may be noticed that the local maxima of the specific heat and of the resistivity are situated at approximately the same temperature.

Because of the divalency of both Eu and Ca, no large changes in the electronic structure are expected when replacing Eu by Ca ions. However, resistivity and magnetoresistance measurements show significant changes in the electronic properties of  $\text{Eu}_{1-x}\text{Ca}_x\text{B}_6$  compounds,

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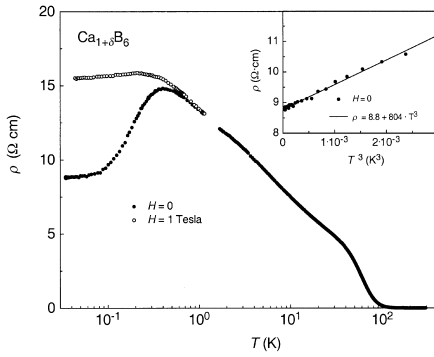


Fig. 1. Resistivity of  $\text{Ca}_{1+\delta}\text{B}_6$  as function of the temperature between 35 mK and 300 K.

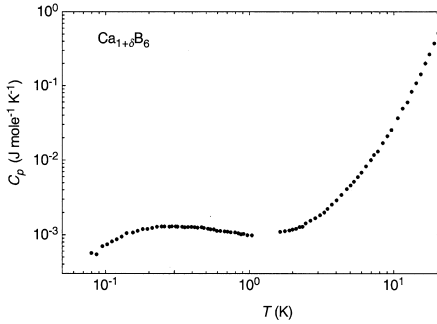


Fig. 2. Specific heat measurement of  $\text{Ca}_{1+\delta}\text{B}_6$  as function of the temperature between 80 mK and 20 K.

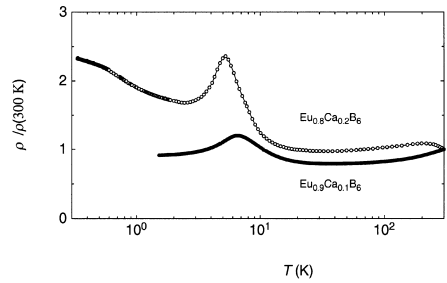


Fig. 3. Resistivity of  $\text{Eu}_{1-x}\text{Ca}_x\text{B}_6$  as function of the temperature with  $x = 0.2$  [2] and  $x = 0.1$ .

particularly at low temperatures. In Fig. 3 we show the resistivity of  $\text{Eu}_{1-x}\text{Ca}_x\text{B}_6$  samples as a function of temperature. It may be seen, that the ferromagnetic transition of 16 K of the binary compound  $\text{EuB}_6$ , is lowered substantially with increasing  $x$ . The sample with  $x = 0.1$  exhibits a resistivity maximum, which is associated with the onset of ferromagnetic order, at about 6.6 K, whereas the sample with  $x = 0.2$  [2] exhibits a maximum in resistivity at about 5.3 K.

**References**

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