1. Introduction

Intricate relationship between semimetal–metal transition at \( T_{\text{M}} \approx 12.5–15.6 \) K and ferromagnetic ordering below the Curie temperature \( T_{\text{C}} \approx 9–13.9 \) K in \( \text{EuB}_6 \) [1–3] attracts the attention of researchers to this compound. Studying the Ca-doped system seems to be a real challenge to shed light on the unusual properties of \( \text{EuB}_6 \) [4–6]. The dilution of Eu sublattice by nonmagnetic calcium suppresses long range magnetic order at \( x_c \approx 0.7 \) enhancing colossal magnetoresistance (CMR) effect [4]. However, recent magnetooptical studies of \( \text{Eu}_{1-x} \text{Ca}_x \text{B}_6 \) [6] favor a disorder driven metal–insulator transition (MIT) at \( x_{\text{MIT}} \approx 0.4 \) earlier predicted for calcium concentration well below \( x_c \) [7]. In this respect a detailed study of \( \text{Eu}_{1-x} \text{Ca}_x \text{B}_6 \) \( (x \approx x_{\text{MIT}}) \) seems to be of great importance for understanding the origin of CMR in this strongly correlated electron system.

In this paper we report on the study of transport, magnetic and thermal properties of \( \text{Eu}_{1-x} \text{Ca}_x \text{B}_6(0 \leq x \leq 0.244) \) carried out at temperatures 1.8–300 K in magnetic fields up to 8 T. The single crystals have been grown by the crucible-less inductive zone melting in argon gas atmosphere. X-ray and scanning electron microscopy (SEM) analysis used to control the quality of the samples showed the samples being homogeneous within \( \pm 0.5 \) at.\% \( \text{Ca} \) (\( \Delta x \approx 0.005 \)). The experimental setup for resistivity and Hall effect is described in Ref. [8]. Quantum Design PPMS-9 and MPMS-5 systems were used to measure specific heat and magnetization. Zero field ac magnetic susceptibility at frequency 1 kHz was detected using excitation field \( \approx 1 \) Oe.

2. Results and discussion

The temperature dependences of resistivity \( \rho \) for Ca doped system are presented in Fig. 1. The values of the Curie temperature \( T_{\text{C}} \) identified from sharp bends on \( \rho(T) \) are found to diminish from \( T_{\text{C}} = 13.9 \) K for \( x = 0 \) to \( T_{\text{C}} = 4.4 \) K for \( x = 0.244 \) (inset in Fig. 1), the \( T_{\text{C}}(x) \) dependence agreeing rather well with that of Refs. [4, 5]. Ca doping is shown to induce a crossover from “metallic” \( (\text{EuB}_6) \) to “insulating” \( (\text{Eu}_{0.756}\text{Ca}_{0.244}\text{B}_6) \) behaviour of \( \rho(T) \) data (Fig. 1) favouring disorder driven MIT at

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approximately constant. Let us note that the amplitude of CMR effect for \( x = 0.244 \) increases to \( \Delta = (\rho(0) - \rho(H))/\rho(H) \approx 7 \times 10^5 \) in magnetic field \( H = 8 \) T (Fig. 1). At \( x \approx x_{\text{MIT}} \) the absolute value of \( \rho \) is very sensitive to Ca content. Indeed, the comparison of \( x = 0.152 \) and \( x = 0.155 \) data (Fig. 1) shows that at \( T \approx 16 \) K the values of \( \rho(T) \) differ by about two orders of magnitude while \( T_C \) stays approximately constant.

Fig. 2. Temperature behavior of (a) resistivity \( \rho(T) \) and the amplitude of CMR effect \( \Delta = (\rho(0) - \rho(H))/\rho(H) \) for \( H = 1 \) T, (b) static \( \chi(T) \) and ac \( \chi_{\text{AC}}(T) \) magnetic susceptibilities and (c) molar heat capacity \( C(T) \) and magnetic entropy \( S(T) \) per Eu\(^{2+} \) ion measured for two samples of Eu\(_{0.845}\)Ca\(_{0.155}\)B\(_6\) (see text). Solid line in part (b) presents the Curie–Weiss fit.

To shed more light on the influence of Ca doping on resistivity in vicinity of MIT, we studied transport and magnetic properties of two samples cut from the same single crystal Eu\(_{0.845}\)Ca\(_{0.155}\)B\(_6\) (referred to as 1 and 2 in Fig. 2). The \( \rho(T) \) dependences agree very well below \( T_C \) and at \( T > T^* \approx 30 \) K (Fig. 2a). In these intervals the effective concentration of charge carriers \( n_{\text{eff}} \) estimated from the Hall effect equals \( n_{\text{eff}} \approx 1.8 \times 10^{20} \) cm\(^{-3}\) for \( T < T_C \) and to \( n_{\text{eff}} \approx 4.1 \times 10^{18} \) cm\(^{-3}\) for \( T > T^* \). On the contrary, clear distinction of \( \rho(T) \) values was established for these two samples at temperatures \( T_C < T < T^* \) (Fig. 2a). Let us note that the same temperature range is characterized by the large CMR effect in moderate magnetic field (\( \Delta(H = 1 \) T) \( \approx 400 \), solid line in Fig. 2a). Besides, below \( T^* \) the magnetic susceptibility \( \chi(T) \) deviates from high temperature Curie–Weiss law with effective moment \( \mu_{\text{eff}} \) (Eu\(^{2+}\)) \( \approx 7.81 \) \( \mu_B \) to larger values (Fig. 2b). Finally, a clear distinction between the static \( \chi \) and zero field ac \( \chi_{\text{AC}} \) magnetic susceptibility (Fig. 2b) is observed at \( T \approx 10 \) K where a wide maximum is detected on \( \chi_{\text{AC}}(T) \) curve.

To explain the observed discrepancy we analysed heat capacity \( C(T) \) data measured below 80 K (Fig. 2c). The calculation of magnetic contribution to \( C(T) \) by subtracting phonon part of LaB\(_6\) shows that considerable amount (\( \approx 30\% \)) of magnetic entropy releases in the range \( T_C < T < T^* \) (Fig. 2c). In our opinion, this effect should be ascribed to short-range magnetic ordering occurring in paramagnetic state at \( T > T_C \). So both the enhancement of low field CMR effect (Fig. 2a) and the anomalies of magnetic susceptibility (Fig. 2b) observed for \( x = 0.155 \) compound in the range \( T_C \leq T \leq T^* \) could be associated with the formation of magnetic phase separated state induced by Ca disorder.

3. Conclusion

To summarize, the anomalous behaviour of transport, magnetic and thermal properties of Eu\(_{1-x}\)Ca\(_x\)B\(_6\) found at \( x \approx x_{\text{MIT}} \) suggests short range magnetic ordering occurring at intermediate temperatures \( T_C < T < T^* \). The related magnetic phase separated state, which is sensitive to small variation of \( x \), seems to be a main reason for the different behaviour of \( \rho(T) \) and \( \chi(T) \) (Fig. 2a,b) observed below 30 K in Ca doped EuB\(_6\).

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