A giant enhancement of CMR in Eu$_{0.6}$Ca$_{0.4}$B$_6$

V V Glushkov$^{1,2,6}$, M A Anisimov$^2$, A V Bogach$^1$, O A Churkin$^3$, S V Demishev$^{1,2}$, V B Filipov$^4$, K Flachbart$^5$, A V Kuznetsov$^{3,1}$, A V Levchenko$^4$, N Yu Shitsevalova$^4$, N E Sluchanko$^1$

$^1$A.M.Prokhorov General Physics Institute of RAS, 38, Vavilov str., Moscow 119991 Russia
$^2$Moscow Institute of Physics and Technology, 9, Institutskii per., Dolgoprudny, Moscow Region 141700 Russia
$^3$Moscow Engineering Physics Institute, 31, Kashirskoe Shosse, Moscow 115409 Russia
$^4$I. Frantsevich Institute for Problems of Materials Science NAS, 3, Krzhyzhanovsky str., Kiev 03680 Ukraine
$^5$Centre of Low Temperature Physics, IEP SAS and IPS FS UPJS, Kosice SK-04001 Slovakia

E-mail: glushkov@lt.gpi.ru

Abstract. The transport and magnetic properties of Eu$_{0.6}$Ca$_{0.4}$B$_6$ single crystals have been studied at temperatures 1.8-300 K in magnetic fields up to 80 kOe. It was found that lowering of temperature results in a drastic increase of magnetoresistance up to the values of $\rho(0)/\rho(H) \approx 7 \times 10^5$ detected below 6K. The Hall and Seebeck effect measurements showed that colossal magnetoresistance (CMR) observed in Eu$_{0.6}$Ca$_{0.4}$B$_6$ is accompanied by a crossover from hole-like to electron-like regime of charge transport induced by applied magnetic field. Hall mobility values $\mu_H \approx 200-350$ cm$^2$/V*s estimated for the high conductive state of Eu$_{0.6}$Ca$_{0.4}$B$_6$ in the presence of strong substitutional disorder were proved to be comparable with these ones measured for undoped EuB$_6$. The anomalous behaviour of transport and magnetic parameters is discussed in terms of metal-insulator transition earlier predicted for this low carrier density system within double exchange model by V M Pereira et al., Phys. Rev. Lett. 93 147202 (2004).

1. Introduction
The intricate interplay between ferromagnetism and electronic transport, which results in the effect of colossal magnetoresistance (CMR) in divalent hexaboride EuB$_6$, stimulates permanent interest to this compound [1,2]. A new intriguing challenge is provided by the study of doped system Eu$_{1-x}$Ca$_x$B$_6$, in which the dilution of Eu$^{2+}$ sublattice by nonmagnetic calcium fully suppresses ferromagnetic ordering.

6 Corresponding author

© 2010 IOP Publishing Ltd
at europium content (1-x)~0.3 corresponding to percolation limit for cubic lattice [3]. However, the conclusion that the magnetic percolation effects are exceptionally responsible for the CMR enhancement in Eu1-xCaxB6 [3] doesn’t agree with the scenario of disorder driven metal-insulator transition (MIT), which was recently predicted for calcium concentration xMIT<xc [4] and observed in experiments far from the percolation limit at xMIT~0.3–0.4 [5, 6]. In this respect a comprehensive study of transport and magnetic properties of Eu1-xCaxB6 compounds in the critical region x~xMIT seems to be important for elucidating the physical mechanisms of CMR in this strongly correlated electron system.

2. Experimental details
The high quality single crystals of substitutional solid solutions Eu1-xCaxB6 have been grown for various nominal calcium concentrations x by the crucible-less inductive zone melting in argon gas atmosphere. X-ray and SEM analysis were used to control the quality of the samples under investigation. The real concentration of calcium in solid solutions was found to be smaller than nominal one, however, the crystals under investigation estimated from SEM analysis was proved to be homogeneous within ±1 at.% Ca (Δx~0.01). The precise determination of Ca content by SEM using EuB6 and CaB6 standards is in progress and will be discussed elsewhere. The experimental set-up for resistivity, Hall effect and thermopower has been described in detail in Ref. [7]. SQUID magnetometer was used to measure the temperature dependences of magnetization in steady magnetic fields H=9-130 Oe.

3. Results and discussion
The temperature dependences of transport and magnetic properties, measured on single crystals with nominal concentrations x = 0 and x = 0.4, are shown in Fig. 1. The decrease of Curie temperature estimated from the data (from Tc=13.9 K for x = 0 to Tc=4.4 K for x = 0.4) agrees well with the previous reports [3, 5]. Zero field data of resistivity ρ(T) (Fig.1a) clearly demonstrate the change from “metallic” (EuB6) to “insulating” (Eu0.6Ca0.4B6) behaviour favouring to disorder driven MIT at xMIT~0.3 [5, 6]. The thermopower data show the change of negative electron-like Seebeck coefficient S<0 observed in EuB6, to positive hole-like one (S>0) found in Eu0.6Ca0.4B6 (Fig.1b) pointing to a pronounced variation of electronic density-of-states at Fermi level induced by Ca doping. Moreover, Ca doping reduces both effective magnetic moment per Eu²⁺ ion and paramagnetic Curie temperature (from μeff=8.01μB/Eu and Θ~17.1 K in EuB6 to μeff=7.3μB/Eu and Θ~8.6 K in Eu0.6Ca0.4B6) estimated from the Curie-Weiss behaviour of magnetic susceptibility χ(T)=μeff²/(T-Θ) (Fig.1c).

Magnetic field strongly affects on the resistivity of Eu0.6Ca0.4B6 resulting in a huge decrease of its absolute value. The most prominent changes of ρ are observed at liquid helium temperatures, where
resistivity falls from zero field values $\rho \sim 300 \Omega \cdot \text{cm}$ down to $\rho \sim 340 \ \mu\Omega \cdot \text{cm}$ detected at $H=70 \ \text{kOe}$ (Fig.1a). The set of isothermal magnetoresistance $\rho(H)/\rho(0)$ also demonstrates an anomalous enhancement of CMR effect below 40 K, which achieves the largest value of $\rho(0)/\rho(H) \sim 7 \times 10^5$ at temperatures $T \sim 6 \ \text{K}$. Note also that an appreciable deviation of zero field $\chi(T)$ dependence from Curie-Weiss behaviour is observed in the temperature interval corresponding to the CMR enhancement (Fig.1c). In our opinion, this correlation between transport and magnetic characteristics seems to reflect the change of effective exchange mechanism between Eu$^{2+}$ ions induced by a gradual onset of the low temperature “insulating” state of Eu$^{2+}$.

The field dependences of Hall resistivity $\rho_{H}(H)$ measured on Eu$_{0.6}$Ca$_{0.4}$B$_{6}$ single crystal at $T<60\ \text{K}$ are shown in Fig.2b. At $T>15\ \text{K}$ Hall coefficient $R_{H}=\rho_{H}/H$, which stays approximately constant in low enough magnetic fields $H<20 \ \text{kOe}$, is characterized by the positive values $R_{H} \sim +0.5 \ \text{cm}^2/\text{C}$ corresponding to the reduced charge carriers’ concentration $\sim 9 \times 10^{12}$ states/cell. In this temperature range the positive Hall effect ($R_{H}>0$) is in good agreement with the positive Seebeck coefficient ($S>0$) found in this study (see Fig.1b). Below 40K the increase of applied magnetic field induces a gradual transition from low-field positive $\rho_{H}$ values to high-field negative ones (Fig.2b), the magnetic field of Hall effect sign inversion decreasing from $H_{\text{inv}} \sim 80 \ \text{kOe}$ at $H_{\text{inv}} \sim 26 \ \text{kOe}$ at $T=16 \ \text{K}$. It is interesting to note that the $H_{\text{inv}}$ values for Hall effect data agree very well with the characteristic fields of a kink-like features observed in magnetoresistance curves $\rho(H)$ (indicated by arrows in Fig.2a).

The correlation of charge transport parameters allows concluding that the giant enhancement of CMR effect observed in Eu$_{0.6}$Ca$_{0.4}$B$_{6}$ should be explained in terms of crossover between hole-like and electron-like regimes of charge transport induced by applied magnetic field. This conclusion is also supported by the magnetic field and temperature evolution of Hall mobility $\mu_{H}=R_{H}/\rho$ estimated from the data of Fig.2. In low magnetic fields the temperature lowering in the range 20-200K results in a pronounced field independent decrease ($\sim 10$ times) of Hall mobility values (see $\mu_{H}(T)$ data for $H=10 \ \text{kOe}$ in Fig.3). On the contrary, the increase of magnetic field at $T<40\ \text{K}$ induces not only the sign inversion of Hall effect but also the significant elevation of $\mu_{H}$ absolute values. For example, at $T=16 \ \text{K}$ Hall mobility changes from $\mu_{H} \sim 2 \ \text{cm}^2/(\text{V} \cdot \text{s})$ ($H<H_{\text{inv}} \sim 26 \ \text{kOe}$) to $\mu_{H} \sim 350 \ \text{cm}^2/(\text{V} \cdot \text{s})$ ($H>H_{\text{inv}}$). The onset of ferromagnetic state below Curie temperature $T=4.55 \ \text{K}$ reduces slightly the absolute value of Hall mobility to $\mu_{H} \sim 200 \ \text{cm}^2/(\text{V} \cdot \text{s})$, which is almost field independent in this temperature interval (Fig.3).

The value of $\mu_{H}(20\ \text{K}) \sim 350 \ \text{cm}^2/(\text{V} \cdot \text{s})$ found in this study for Eu$_{0.6}$Ca$_{0.4}$B$_{6}$ (Fig.3) turns out to be comparable with the values of Hall mobility $\mu_{H} \sim (400-800) \ \text{cm}^2/(\text{V} \cdot \text{s})$ characterizing the paramagnetic
state of undoped EuB$_6$ in temperature interval 20 K$\leq$T$<$80 K[9]. This observation can hardly be explained in the presence of the strong substitution disorder of Ca-doped EuB$_6$ matrix. Allowing for the values of charge carriers relaxation rate $\Gamma_1=\hbar/\tau=18$-40 cm$^{-1}$ ($\tau$ - the relaxation time of charge carriers) [8] the estimations of electrons’ effective mass $m_{\text{eff}}=e\tau/\mu_H$ provide rather large values of $m_{\text{eff}}=(4.3$–13)$m_0$ ($m_0$ – free electron mass) for temperature interval 4.2-20 K. In our opinion, the noticeable renormalization of effective mass favours the spin polaronic nature of charge carriers in this strongly correlated electron system [9].

![Figure 3. Temperature dependences of Hall mobility $\mu_H(T)=R_H/\rho$ measured for Eu$_{0.6}$Ca$_{0.4}$B$_6$ single crystal at $H=10$ and 70 kOe. Note different scales of vertical axes in upper and lower panels. Solid lines for the data are drawn to guide for eye.](image)

Finally, the comprehensive study of transport and magnetic properties of substitutional solid solution Eu$_{0.6}$Ca$_{0.4}$B$_6$ corresponding to the dielectric side of concentration driven MIT [4] allowed to detect the anomalous enhancement of CMR up to values of $\rho(0)/\rho(70$ kOe)$\approx7\times10^5$ found below 6 K. However, the crossover from hole-like to electron-like regime of charge transport induced by magnetic field at helium and intermediate temperatures seems to have no adequate explanation in terms of double exchange approach [4] and requires further investigations of this CMR system.

4. Acknowledgements

This work was supported by RFBR projects 05-08-33463 and 07-02-90903 and RAS program “Strongly correlated electrons in semiconductors, metals, superconductors and magnetic materials”.

References

[1] Süllow S, Prasad I, Aronson M C, Sarrao J L, Fisk Z, Hristova D, Lacerda A H, Hundley M F, Vigliante A and Gibbs D 1998 Phys. Rev. B 57 5860A
[2] Zhang X, von Molnár S, Fisk Z and Xiong P 2008 Phys Rev Lett 100 167001
[3] Wigger G A, Beeli C, Felder E, Ott H R, Bianchi A D and Fisk Z 2004 Phys. Rev. Lett. 93 147203
[4] Pereira V M, Lopes dos Santos J M B, Castro E V and Castro Neto A H 2004 Phys. Rev. Lett. 93 147202
[5] Caimi G, Perucchi A, Degiorgi L, Ott H R , Pereira V M, Castro Neto A H, Bianchi A D and Fisk Z 2006 Phys. Rev. Lett. 96 016403
[6] Glushkov V V, Anisimov M A, Bogach A V, Demishev S V, Samarim N A, Kuznetsov A V, Dukhnenko A V, Levchenko A V, Shitsevalova N Yu, Flachbart K and Sluchankh N E 2009 Sol. St. Phen., 152-153 307
[7] Sluchankh N E, Bogach A V, Glushkov V V, Demishev S V, Ignatov M I, Samarim N A, Burkhano G S and Chistyakov O D 2004 JETP 98 793
[8] Perucchi A, Caimi G, Ott H R, Degiorgi L, Bianchi A D and Fisk Z 2004 Phys. Rev. Lett. 92 067401
[9] Glushkov V, Bogach A, Demishev S, Gon’kov K, Ignatov M, Khayrullin Eu, Samarim N, Shubin A, Shitsevalova N, Flachbart K, and Sluchankh N 2008 Physica B 403 820