Evidence for magnetic phase separation in colossal magnetoresistance compound
EuB$_{5.99}$C$_{0.01}$

I. Batko$^a$, M. Batkova$^{a,*}$, V. H. Tran$^b$, U. Keiderling$^c$, V. B. Filipov$^d$

$^a$Institute of Experimental Physics, Slovak Academy of Sciences, Watsonova 47, 040 01 Košice, Slovakia
$^b$Polish Academy of Sciences, Institute of Low Temperature and Structure Research, 50-422 Wroclaw, Poland
$^c$Helmholtz Zentrum Berlin, D-14109 Berlin, Germany
$^d$Institute for Problems of Material Science, NASU, 252680 Kiev, Ukraine

Abstract

EuB$_{5.99}$C$_{0.01}$ is a low-carrier density ferromagnet that is believed to be intrinsically inhomogeneous due to fluctuations of carbon content. In accordance with our previous studies, electric transport of EuB$_{5.99}$C$_{0.01}$ close above temperature of the bulk ferromagnetic (FM) ordering is governed by magnetic polarons. Carbon-rich regions are incompatible with FM phase and therefore they act as spacers preventing magnetic polarons to link, to form FM clusters, and eventually to percolate and establish a (homogeneous) bulk FM state in this compound, what consequently causes additional (magneto)resistance increase. Below the temperature of the bulk FM ordering, carbon-rich regions give rise to helimagnetic domains, which are responsible for an additional scattering term in the electrical resistivity. Unfortunately, there has not been provided any direct evidence for magnetic phase separation in EuB$_{5.99}$C$_{0.01}$ yet. Here reported results of electrical, heat capacity, Hall resistivity and small-angle neutron scattering studies bring evidence for formation of mixed magnetic structure, and provide consistent support for the previously proposed scenario of the magnetoresistance enhancement in EuB$_{5.99}$C$_{0.01}$.

Keywords: magnetically ordered materials, electronic transport, phase transitions, colossal magnetoresistance

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1. Introduction

EuB$_6$ is a rare example of low carrier density hexaboride that orders ferromagnetically at low temperatures via two consecutive phase transitions [1]. Physical properties of this system are thought to be governed by magnetic polarons (MPs) [2, 3, 4, 5, 6]. As indicated by Raman-scattering measurements [2], MPs have set in at about 30 K when cooling EuB$_6$ from a higher temperature. According to Süllo et al. [5], the magnetic phase transition at 15.5 K represents emergence of spontaneous magnetization accompanied with metalization. At this temperature MPs begin to overlap and form a conducting, ferromagnetically ordered phase that acts as a percolating, low-resistance path across the otherwise poorly conducting sample [5, 6]. With decreasing temperature the volume fraction of this conducting ferromagnetic (FM) phase expands until the sample becomes a homogeneous conducting bulk ferromagnet at 12.6 K [3].

High-pressure measurements indicate that the FM order is driven by an RKKY interaction between the localized Eu moments and the very dilute pocket of conduction electrons arising from a semi-metallic band overlap [7]. Due to a very low number of intrinsic charge carriers, $10^{20}$ cm$^{-3}$ [8], the system is very sensitive even to a slight change in concentration of conduction electrons, e. g. due to change in chemical composition or in impurity concentration [5, 10]. A substitution of boron by carbon in EuB$_6$ increases number of conduction electrons in the conduction band of EuB$_6$ [11], thus EuB$_{6-x}$C$_x$ carbide borides behave as degenerate semiconductors, in which both, carrier concentration, and antiferromagnetic interaction increase with increasing carbon content [11]. As it was shown by neutron diffraction studies, EuB$_6$ behaves like a simple ferromagnet, whereas EuB$_{5.80}$C$_{0.20}$ has an incommensurate
spiral structure \[11\,12\], and the magnetic structure of intermediate EuB\(_{5.99}\)C\(_{0.01}\) can be described as a mixture of FM and helimagnetic (HM) domains \[11\,12\]. Appearance of the HM domains is associated with local increase of carbon concentration in the material. Size of these incoherent regions is estimated to be about 5 nm \[12\]. The presence of the HM domains formed in carbon-rich regions due to distinct impact of the RKKY interaction because of distinct carrier density \[12\] is believed to be responsible for an additional scattering term in the electrical resistivity \[13\].

Electric, magnetic, and heat capacity studies of EuB\(_{5.99}\)C\(_{0.01}\) support the hypothesis that the dominant scattering process in this material at temperatures below the bulk magnetic transition, \(T_C \approx 4.3\) K \[14\], has its origin in the mixed magnetic structure \[11\,14\,15\]. The anomalous transport properties of the EuB\(_{5.99}\)C\(_{0.01}\) can be satisfactorily explained assuming the presence of MPs \[14\]. It has been proposed that carbon-rich regions act as spacers, which prohibit formation of a conducting, ferromagnetically ordered path across the sample. As a consequence, the system persists in a poorly conducting state down to lower temperatures. Due to the extended temperature interval, in which the resistivity increases upon cooling, an additional resistivity increase is observed, resulting in the higher value of the resistivity maximum. Such a scenario, assuming the presence of MPs, allows also to explain why the resistivity maximum of the EuB\(_{5.99}\)C\(_{0.01}\) \((\approx 390\,\Omega\cdot\text{cm at } \approx 5\,\text{K})\) is larger than that of the stoichiometric EuB\(_6\) \((\approx 350\,\mu\Omega\cdot\text{cm at } 15\,\text{K})\), although the EuB\(_{5.99}\)C\(_{0.01}\) is about four times better conductor at room temperature, having \(\rho(300\,\text{K}) \approx 180\,\mu\Omega\cdot\text{cm}\), than the EuB\(_6\) with \(\rho(300\,\text{K}) \approx 730\,\mu\Omega\cdot\text{cm}\). An important consequence of this scenario \[14\] is that it might show a route for an optimization of magnetoresistive properties also in other spatially inhomogeneous systems with magnetic polarons or with FM phase in general \[14\]. Unfortunately, there has not been provided any direct evidence for magnetic phase separation in EuB\(_{5.99}\)C\(_{0.01}\) yet. The purpose of this paper is to bring experimental support for the presence of magnetic phase separation phenomena in EuB\(_{5.99}\)C\(_{0.01}\) based on performed Hall-effect, heat-capacity, and small angle neutron scattering (SANS) studies.

2. Material and Methods

All samples studied in this work were cut from the same single crystal grown by means of the zone floating used in our previous studies \[13\,14\,15\]. The resistance, Hall resistance, heat capacity, and magnetization were measured in Physical Property Measurement System and Magnetic Property Measurement System (Quantum Design, USA). SANS measurements were carried out at the V4 instrument at Helmholtz-Zentrum Berlin.

3. Results and Discussion

Hall resistivity \((R_{HH})\) and magnetization \((M)\) measurements were performed in the temperature range of \(2 - 300\,\text{K}\) and in magnetic fields up to \(5\,\text{T}\). The temperature dependences of \(R_{HH}\), and \(1/M\) measured at the magnetic field of \(B = 5\,\text{T}\) are shown in Fig.1

![Figure 1: Temperature dependence of the Hall resistivity \((R_{HH})\) for EuB\(_{5.99}\)C\(_{0.01}\) measured at 5 T in the temperature range 2 - 300 K. Inset shows the corresponding inverse magnetic susceptibility for the same value of magnetic field.](image)

Hall resistivity in magnetic conductors can be expressed as \(R_{HH} = R_0 + 4\pi R_S M / B\), where \(R_0\) and \(R_S\) are the ordinary and anomalous Hall coefficients, respectively \[16\]. Therefore, \(R_0\) and \(R_S\) can be accurately determined when combining both, the Hall resistivity and magnetization data. Our analysis shows that neither \(R_S\) nor \(R_0\) changes with temperature in the temperature range of \(80 - 300\,\text{K}\) (see Fig.2). However, \(R_S\) was found to change significantly at lower temperatures, especially around the temperature of the FM ordering, \(T_C = 4.3\,\text{K}\) \[13\], where it exhibits an extremum as typically observed in magnetic materials. Comparison of \(R_S(T)\) to the \(\rho(T)\) dependence (see Fig.2) reveals that processes governing electric transport in region of the resistivity maximum are adequately sensed in the anomalous term of the Hall resistivity. On the other hand, there is only weak change of \(R_0\) in the whole temperature range. The value of \(R_0\) at room temperature corresponds to the electron concentration of
3.3x10^{20} \text{ cm}^{-3}, which is approximately 3-times greater than 1.2x10^{20} \text{ cm}^{-3} reported for the stoichiometric EuB_{6}. Such a temperature dependence of R_{0} coincides with our expectations. As showed in our previous studies of optical reflectivity of EuB_{5.99}C_{0.01}, the plasma edge frequency value, \omega_{p} = (ne^{2}/\varepsilon_{0}m_{e})^{1/2} (here n is the electron concentration, e is the electron charge, \varepsilon_{0} is the vacuum permittivity, and m_{e} is the electron mass) has been found to be almost constant between 4.5 and 30 K [13]. The finding infers that the electron concentration n does not change substantially in the whole temperature range studied [13]. Thus, the Hall resistivity data obtained in this work bring an independent proof that strong temperature dependence of the electrical resistivity of EuB_{5.99}C_{0.01} in the vicinity and close above the temperature of the bulk FM ordering (see Fig.2b) is not a consequence of changes in electron concentration, but it is a result of scattering processes, presumably due to magnetic phase separation.

Heat capacity, C_{p}, of EuB_{5.99}C_{0.01} and the isostructural non-magnetic compound LaB_{6} was measured in the temperature range 0.35 – 20 K. The phonon contribution, C_{ph}, for EuB_{5.99}C_{0.01} was estimated from the heat capacity of LaB_{6}. As can be seen in Fig. 3 the (C_{p} - C_{ph})/T dependence of the studied system shows a broadened continuous decrease in the temperature region between 5 and 15 K, i.e. above the temperature of the bulk ferromagnetic ordering. This decrease can be ascribed to a short range magnetic ordering. A clear evidence of the FM order appears as local maximum in the (C_{p} - C_{ph})/T curve at 4.3 K. It is remarkable that (C_{p} - C_{ph})/T goes through a knee around 2.5 K, implying the crystal electric field splitting of energy levels of the Eu^{2+} ions. (C_{p} - C_{ph})/T drops rapidly with further decreasing temperature, but finally attains a rather huge (C_{p} - C_{ph})/T value of \approx 0.5 \text{ Jmol}^{-1}\text{K}^{-2} at 0.35 K. Due to the nearby FM order transition, this value cannot be taken as an electronic specific heat coefficient. However, as temperature approaches 20 K, (C_{p} - C_{ph})/T dependence becomes constant, which thus represents the electronic specific heat only. Thus, for purposes of our analysis we have estimated the coefficient \gamma to be the value (C_{p} - C_{ph})/T at 20 K (see Fig. 3). Such estimation yields a \gamma value of \approx 0.1 \text{ Jmol}^{-1}\text{K}^{-2}. In combination with the low charge-carrier concentration n \approx 3.3x10^{20} \text{ cm}^{-3}, the enhanced electronic specific heat could be associated either with (i) an anomalously large effective mass of the electrons \propto 190 m_{e} (like in heavy fermions) or (ii) a strong disorder of the system. Because of the nature of the system and according to SANS measurements discussed below we prefer the latter case.
Magnetic contribution to the heat capacity, \( C_m \), is assumed to be \( C_m = C_p - C_{ph} - \gamma T \). The temperature dependence of the magnetic entropy, \( S_m(T) = \int_0^{20k} C_m(T) dT \), was calculated and shown in the inset of Fig. 1. As can be seen the magnetic entropy of the EuB\(_{6}\) of Fig. 3 observed also for the stoichiometric EuB\(_{6}\) is comparable to the theoretical entropy of the magnetic ordering of Eu\(^{2+}\) ions. A similar reduction in \( S_m \) was observed also for the stoichiometric EuB\(_{6}\)\[3\].

Small-angle neutron scattering (SANS) experiments were performed at temperatures between 2 and 30 K with the aim to provide direct evidence for presence of magnetic phase separation in the temperature range of 2 - 7 K. Considering the physical state at 30 K as a reference paramagnetic state without magnetic phase separation\[2\] we focused on evolution of magnetic state in the mentioned temperature interval. The SANS measurements were performed for scattering vectors Q from the interval of 0.3 – 3.4 nm\(^{-1}\). Supposing the simplest case of scattering due to spherical objects, such interval enables to detect objects having size/diameter between 1.8 and 20 nm. Here should be noted that our earlier size estimation of the “spacers” in EuB\(_{5.99}C_{0.01}\) has provided the value 2.9 nm \[15\].

The usual way for the interpretation of the scattered neutron intensity \( I(Q) \) would be: (1) correction of the data for experimental parameters like sample transmission, background scattering and local detector efficiencies, and then (2) calculation of a particle size distribution, the scattering of which would produce just this corrected scattered neutron intensity. The structural changes in the sample as a function of the varied experimental parameter (in this case the temperature) would then become directly obvious when the different particle size distributions are compared. However, the studied sample was prepared from natural boron, which contains approximately 20% of highly neutron-absorptive isotope of \(^{10}\)B. This lead to an extremely low neutron transmission of the sample of less than 1%. As a consequence, the intensity scattered from the sample itself was so low and noisy that it was not possible to perform the usual data correction procedure to separate the actual sample scattering from the background contributions. We even noticed that the scattered intensity was sensitive to very small displacements of the unit of sample holder plus sample in the beam, indicating that the scattering contribution from the sample holder was even higher than the contribution from the sample. Therefore, we chose the following alternative way to conduct and interpret the experiment:

Measurements at all temperatures were done without moving the sample inbetween. Since no separate background scattering could be measured, all scattering intensities remain a mixture of sample and background scattering. This means that no calculation of explicit size disributions is possible, and only qualitative interpretation can be done directly on the scattering curves. These interpretations are based on the fact that particles with a diameter \( d \) produce a scattering contribution in the range order of \( Q \approx 2\pi/d \). From the known properties of the used cryomagnet we could assume that the background contribution would not change within the investigated temperature range. To eliminate the very large contribution of the background, we considered the relative change of the intensities \( |I(Q)|_T - |I(Q)|_{30\,K} \)/\( |I(Q)|_{30\,K} \). Since we know that at \( T = 30 \) K none of the expected scattering objects should be present, this relative comparison of the scattering at a temperature \( T \) and at the reference temperature \( T = 30 \) K will extract the very small intensity contribution added by those objects. To reduce the noise further, we divided the investigated \( Q \) range into only 6 intervals, so that each interval was an average over approximately 9 detector cells. This of course significantly reduces the \( Q \) resolution and therefore the sensitivity of the experiment to small changes in the number and size of the scattering objects. However, this approach is sufficient to detect the qualitative results, that are discussed in the following. This way averaged \( |I(Q)|_T - |I(Q)|_{30\,K} \)/\( |I(Q)|_{30\,K} \) dependences for temperatures 2 K, 4 K, 6 K, and 7 K are shown in Fig. 4.

As can be seen in Fig. 4 temperature changes in the vicinity of the temperature of the resistivity maximum (\( \approx 6 \) K) reveal clear evolution in the \( |I(Q)|_T - |I(Q)|_{30\,K} \)/\( |I(Q)|_{30\,K} \) dependences, which can be explained taking into account differences between the EuB\(_{5.99}C_{0.01}\) and the EuB\(_{6}\)\[14\]. Let us summarize the most essential differences here. (i) While the paramagnetic state in EuB\(_{6}\) is homogeneous, the paramagnetic state in EuB\(_{5.99}C_{0.01}\) is inhomogeneous, containing regions of increased carbon content that are characterized by correspondingly higher electrical conductance in comparison to the remaining matrix \[14\]. (ii) The magnetic polaron phase in EuB\(_{6}\) can be treated as a two-component system consisting of poorly conductive paramagnetic matrix and highly conductive FM phase represented by MPs \[3\], whereas this phase in EuB\(_{5.99}C_{0.01}\) has three components at least: less conductive regions with lower carbon content, highly conductive FM phase represented by MPs (formed in less conductive regions with lower carbon content), and more conductive carbon-rich domains. The latter, incompatible with the existence of MPs due to too high charge...
carrier concentration, play role of spacers that prevent MPs to link and to form a highly conductive path across the sample [6] [14]. (iii) Finally, magnetically ordered state in EuB$_5$ is a homogeneous ferromagnet [8], while EuB$_{5.99}$C$_{0.01}$ can be treated as two-component system consisting of FM matrix and HM domains formed in the carbon-rich regions [14]. Here should be mentioned that the mixed magnetic phase of EuB$_{5.99}$C$_{0.01}$ is expected to be a reason for anomalously high resistivity, which at temperatures as low as 50 mK is even greater than the room temperature resistivity [13].

Taking into account the picture of EuB$_{5.99}$C$_{0.01}$ sketched above and the electrical resistivity behaviour, one could expect that fraction of FM phase in this compound near above 7.5 K is still very small, such as volume of this phase is still not sufficient to change semiconducting behaviour of the $\rho(T)$ dependence $[d^2\rho(T)/dT<0]$. (7.5 K is the position of the inflection point in the $\rho(T)$ dependence, as can be seen in Fig. [2b]). However, volume of the FM phase should rapidly increase at lower temperatures approaching $T_M$, and consequently $T_C$. Under this assumption, the $(I(Q)|_{T=7.5 K} - I(Q)|_{T=30 K})/I(Q)|_{T=30 K}$ dependence shown in Fig. [4] can indicate that scattering at this temperature is a consequence (i) of increasing the number of MPs and/or (ii) HM domains that are formed in regions of higher carbon content (spacers) already at this temperature. Because of very similar diagram of scattered intensities at 4 K and 2 K, the latter case is preferred, and only minor amount of small FM-volumes (MPs) is believed to contribute to neutron scattering at this temperature, predominantly at highest $Q$-values. As can be seen in the Fig. [4] maximal relative change in the neutron scattering intensity in the temperature region between 30 K and 7 K is observed for the interval of $Q$ with the centre slightly above 2 nm$^{-1}$. This corresponds to neutron scattering on spherical objects with diameter 3 nm. Such result is in excellent agreement with our earlier estimation that dimension of the spacers should be around 2.9 nm [14]. Temperature decrease to 6 K is expected to be accompanied by rapidly increasing proportion of the FM phase, because the $\rho(T)$ dependence in the vicinity of 6 K clearly tends to reach maximum, which is believed to be a consequence of formation, growth, and linking of MPs. Indeed, such picture adequately explains the rapid increase of scattering intensity in the whole investigated $Q$-range after cooling the sample from 7 K to 6 K. Thus, the relative increase of neutron scattering observed at 6 K, $(I(Q)|_{T=6 K} - I(Q)|_{T=30 K})/I(Q)|_{T=30 K}$ dependence, can be associated with volume increase of the FM regions at cooling. Such conclusion moreover correlates with the above discussed heat capacity studies indicating high disorder of the system and presence of short range ordering above the temperature of the bulk FM ordering. The observed increase of scattering intensities for highest $Q$ (smallest particles) can be associated with the fact that there were formed new MPs, and/or many MPs, which were too small to contribute to
neutron scattering at 7 K have grown in size enough to be detectable at 6 K. Analogously, according to growing and linking of MPs with decreasing temperature, the MPs detected at 7 K contribute to neutron scattering at highest values of $Q$ than it is at 6 K. Further decrease of temperature causes further grow of volumes filled with FM objects, which merge at the temperature of the bulk FM ordering, $T_C = 4.3$ K [14]. It is therefore naturally expected that scattering on individual FM objects should almost vanish at 4 K, and only objects non-compatible with FM ordering (HM domains) should still contribute to scattering. Indeed, comparison of $(I(Q)|_{6 \text{ K}} - I(Q)|_{30 \text{ K}})/I(Q)|_{30 \text{ K}}$ dependence with that observed for 6 K and 7 K is in excellent agreement with such a picture. Thus the neutron scattering observed at 4 K is believed to be predominantly associated with scattering on HM domains formed in regions with higher carbon content. As evident from Fig. 4, further cooling down to 2 K does not have any significant impact on $(I(Q)|_{T} - I(Q)|_{30 \text{ K}})/I(Q)|_{30 \text{ K}}$ dependence. The observed minor changes can be a consequence of minor redistribution of FM and HM phase with decreasing temperature.

In summary, the obtained Hall resistivity data bring direct proof that strong temperature dependence of the electrical resistivity of EuB$_{5.99}$C$_{0.01}$ in the vicinity and close above the temperature of the bulk FM ordering (see Fig. 2) is not a consequence of changes in electron concentration. As follows from indications for short-range magnetic ordering of performed heat capacity studies and evidence for formation/disappearance of nanometer-sized “objects” at temperatures above and below the temperature of resistivity maximum as provided by SANS studies, such resistivity behaviour can be adequately explained by disorder of material due to magnetic phase separation. In this sense the above presented results bring evidence about mixed magnetic structure in EuB$_{5.99}$C$_{0.01}$ and provide another support for our previous proposition that carbon rich regions play role of “spacers”, which are crucial in preventing percolation of MPs and formation of the bulk FM state [14]. Indeed, it seems that just spacers are responsible for high disorder, extremely high residual resistivity, short-range magnetic ordering of the system above the $T_C$, and in general, they are the main reason for huge differences in $\rho(T)$ behaviour between the EuB$_{5.99}$C$_{0.01}$ and the stoichiometric EuB$_6$.

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**References**

[1] L. Degiorgi, E. Felder, H. R. Ott, J. L. Sarrao, Z. Fisk, Phys. Rev. Lett. 79 (1997) 5134.
[2] C. S. Snow, S. L. Cooper, D. P. Young, Z. Fisk, A. Comment, and J.-P. Ansermet, Phys. Rev. B 64 (2001) 174412.
[3] S. Süllo, I. Prasad, M. C. Aronson, S. Bogdanovich, J. L. Sarrao, Z. Fisk, Phys. Rev. B 62 (2000) 11626.
[4] M. J. Calderón, L. G. L. Wegener, P. B. Littlewood, Phys. Rev. B 70 (2004) 092408.
[5] U. Yu, B. I. Min, Phys. Rev. B 74 (2006) 094413.
[6] M. B., A. Amyan, J. Brandenburg, J. Müller, P. Xiong, S. von Molnár, Z. Fisk, Phys. Rev. B 86, (2012) 184425.
[7] J. C. Cooley, M. C. Aronson, J. L. Sarrao, Z. Fisk, Phys. Rev. B 56 (22) (1997) 14541.
[8] M. C. Aronson, J. L. Sarrao, Z. Fisk, M. Whitton, B. L. Brandt, Phys. Rev. B 59 (1999) 4720.
[9] M. Kasaya, J. M. Tarascon, J. Etourneau, P. Hagenmuller, Mat. Res. Bull. 13 (1978) 751.
[10] S. von Molnar, J. M. Tarascon, J. Etourneau, J. Appl. Phys. 52 (1981) 2158.
[11] J. Etourneau and P. Hagenmuller, Philos. Mag. B 52 (1985) 589.
[12] J. M. Tarascon, J. L. Soubeyroux, J. Etourneau, R. Georges, J. M. D. Coey, O. Massenet, Solid State Commun. 37 (1981) 133.
[13] I. Bafko, M. Bafkova, K. Flachbart, D. Macko, Y. B. P. E. S. Konovalova, J. Magnetism and Magn. Mat. 140 (1995) 1177–1178.
[14] M. Batkova, I. Batko, K. Flachbart, Z. Janú, K. Jurek, J. Kováč, M. Reiffers, V. Sechovský, N. Shitsevalova, E. Šantavá, J. Šebek, Phys. Rev. B 78 (2008) 224414–1.
[15] M. Batkova, I. Batko, E. Bauer, R.T. Khan, V.B. Filipov, E.S. Konovalova, Solid State Commun. 150 (2010) 652.
[16] C.M. Hurd, The Hall Effect in Metals and Alloys, Plenum Press, New York, 1972.
[17] X. Zhang, L. Yu, S. von Molnár, Z. Fisk, P. Xiong, Phys. Rev. Lett. 103 (2009) 106602.