Effect of pressure on electric transport properties of carbon-doped EuB$_6$

M. Batkova$^a$, I. Batko$^a$, E. Bauer$^b$, R. T. Khan$^b$, V. B. Filipov$^c$, E. S. Konovalova$^c$

$^a$ Institute of Experimental Physics, Slovak Academy of Sciences, Watsonova 47, 040 01 Košice, Slovakia
$^b$ Institut für Festkörperphysik, Technische Universität Wien, Wiedner Hauptstrasse 8-10, 1040 Wien, Austria
$^c$ Institute for Problems of Material Science, NASU, 252680 Kiev, Ukraine

Abstract

We report about influence of external pressure on electrical resistivity of EuB$_{5.99}$C$_{0.01}$, the compound believed to be intrinsically inhomogeneous due to fluctuation of carbon content. Our results show that the low-temperature resistivity maximum shifts to lower temperature with applied pressure, opposite to the behavior reported for stoichiometric EuB$_6$. The origin of such qualitative difference we associate with the increasing volume fraction of the phase that is not compatible with ferromagnetic ordering (originating in regions with relatively higher carbon concentration) with enhancing pressure. Our results support a recent proposition [1] that carbon-rich regions strongly influence magnetotransport properties of carbon-doped EuB$_6$, such as they play a role of “spacers”, which prevent percolation of ferromagnetic phase.

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1. Introduction

EuB$_6$ orders ferromagnetically at low temperatures and undergoes a metal-insulator phase transition [2, 3, 4]. Physical properties of this stoichiometric hexaboride are thought to be governed by magnetic polarons [4, 5, 6, 7] indicated by Raman scattering measurements [8] to appear during the cooling at about 30 K. As suggested by Sülloow et al. [4], at 15.5 K a spontaneous magnetization emerges accompanied by metalization, and magnetic polarons begin to overlap and form a conducting, ferromagnetically ordered phase that acts as a percolating, low-resistance path across the otherwise poorly conducting sample. With decreasing temperature the volume fraction of the conducting FM phase expands until the sample becomes a homogeneous conducting bulk ferromagnet at 12.6 K [4]. High-pressure measurements [8] indicate that ferromagnetic (FM) order in EuB$_6$ is driven by an RKKY interaction.

According to theoretical studies [9], both electron doping, as well as pressure enhance the FM interaction between Eu atoms. In agreement with this assumption experiments [10, 11, 8] show that increasing pressure continuously reduces the resistivity of EuB$_6$ and enhances the temperature of FM ordering.

Because of the very low number of intrinsic charge carriers ($\sim 10^{20}$ cm$^{-3}$) [12], even a slight increase in the concentration of conduction electrons drastically modifies electric and magnetic properties of this compound [1, 13, 14]. Substitution of boron by carbon increases the number of conduction electrons in the system. It seems that the prevailing effect of the additional electrons (above a certain concentration) is to produce antiferromagnetic exchange that competes with the initial FM interaction [15]. As shown by neutron diffraction studies [15], the predominant FM ordering in stoichiometric EuB$_6$ changes with increasing carbon content through a mixture of ferromagnetic and helimagnetic domains into a purely antiferromagnetic state in EuB$_{6-x}$C$_x$ with $x \geq 0.125$ [15, 13]. The helimagnetic domains are formed in carbon-rich regions, which are characterized by higher carrier density than the surrounding FM matrix [15]. Different types of magnetic order are a consequence of a distinct impact of the RKKY interaction due to distinct carrier densities [15]. The presence of the helimagnetic domains is also believed to be responsible for an additional scattering term
in the electrical resistivity below the bulk FM phase transition [1, 16].

Recently, an anomalously large negative magnetoresistance of EuB\(_{5.99}C_{0.01}\) was reported [1] and attributed to a local fluctuation in carbon content. The proposed new scenario [1] on the role of regions with increased carbon concentration has allowed to explain huge differences between the \(\rho(T)\) characteristics of pure and carbon-doped EuB\(_5\). As follows from this scenario [1], regions with charge-carrier concentration exceeding a certain threshold value, represented by the regions with correspondingly higher carbon concentration, are not compatible with the existence of magnetic polarons (and with FM state in general). Thus, in the temperature region close above the temperature of the bulk FM ordering, \(T_c = 4.3\) K, these regions act as spacers that prevent magnetic polarons to link, to form FM clusters, and eventually to percolate [1]. As a result, the percolation and the bulk FM state occur at lower temperature. According to this scenario the principal differences between the pure EuB\(_5\) and EuB\(_{5.99}C_{0.01}\) can be summarized as follows [1]: (i) While the paramagnetic state in EuB\(_5\) is homogeneous, the paramagnetic state in EuB\(_{5.99}C_{0.01}\) has to be treated as inhomogeneous, containing regions with increased carbon content and with correspondingly higher electrical conductance in comparison to the remaining matrix. (ii) The magnetic polaron phase in EuB\(_5\) can be treated as two-component system, consisting of highly conducting FM phase represented by MPs and poorly conducting paramagnetic matrix. This phase in EuB\(_{5.99}C_{0.01}\) does have three components at least: highly conducting FM phase represented by MPs, regions with lower carbon content, and carbon-rich domains. The latter, incompatible with the existence of MPs due to too high charge carriers concentration, work as “spacers”, preventing MPs to link and to form a conductive path across the sample. (iii) Finally, in the magnetically ordered state EuB\(_5\) is a homogeneous ferromagnet, 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. An important consequence of this scenario from an application point of view is that it might show a route for optimization of the magnetoresistive properties also in other spatially inhomogeneous systems with magnetic polarons, or with FM phase in general [1]. The aim of this paper is to give another experimental support that regions with increased charge-carrier concentration, not compatible with FM ordering, are responsible for huge differences between pure and carbon-doped EuB\(_5\).

2. Material and Methods

We studied single crystal EuB\(_{5.99}C_{0.01}\) with \(T_c = 4.3\) K, grown by the zone-floating method. (For more details see Ref. 1.) The electrical resistivity was measured by a standard DC four-probe method. Hydrostatic pressure conditions up to 10.3 kbar were generated by a piston-cylinder cell (liquid pressure cell). The absolute value of the pressure was determined from the superconducting transition of Pb.

3. Results and Discussion

We measured temperature dependence of the electrical resistivity between 1.6 and 300 K for three distinct values of the applied pressure: \(\sim 0, 4.4\) and 10.3 kbar. As it is evident from Fig. 1, increasing pressure has two kinds of effect on the temperature dependence of the resistivity: (i) decrease of the overall resistivity in the whole temperature interval investigated, and (ii) a shift of the resistivity maximum towards lower temperature. The former one, qualitatively similar to the observation in pure EuB\(_5\), can be simply ascribed to an increased concentration of charge carriers due to applied pressure. The latter one, however, shows an opposite tendency compared to pure EuB\(_5\) [10, 8], where the (low temperature) resistivity maximum increases upon pressure due to enhanced FM interactions caused by the increased electron concentration. A qualitative difference reflects itself also in a position of the maximum in \(d\rho/dT(T)\) (see inset in Fig. 1). While the maximum in \(d\rho/dT(T)\) for pure EuB\(_5\) shifts to higher temperatures with pressure increase [8], in the case of EuB\(_{5.99}C_{0.01}\) it

![Figure 1: External-pressure influence on the \(\rho(T)\) and \(d\rho/dT(T)\) dependences of EuB\(_{5.99}C_{0.01}\).](image)
does not change the position on temperature scale with respect to the experimental error.

Especially the opposite effect of pressure on the position of the peak in $\rho(T)$ indicates that another phenomena than those governing electrical transport properties of pure EuB$_6$ should be dominating in EuB$_{5.99}$C$_{0.01}$. This seems to be a consequence of local fluctuations in carbon content and corresponding local fluctuations in charge-carrier concentration, whereas the latter leads to the magnetic phase separation [1]. Taking into account that concentration of charge carriers is a primary parameter governing a position of the boundary between FM and non-FM regions, an increase in charge-carrier concentration due to applied external pressure shifts this boundary to the zone with lower carbon concentration. Such as spacers are defined as regions not compatible with FM ordering, external pressure in fact increases their volume and space distribution. As a consequence, conditions for a mutual interconnection of highly conductive FM regions (resulting from an overlap of magnetic polarons) close above $T_c$ become unfavourable with pressure increase. Thus, the transition from a metal-like transport ($\rho(d\rho/dT > 0)$) to a transport regime with a predominant semiconducting, nonferromagnetic phase ($\rho(d\rho/dT < 0)$, shifts towards lower temperature. In such way the scenario [1] on the spacing role of the charge-carrier-rich regions in carbon-doped EuB$_6$ yields a consistent explanation of the effect of external pressure on the electrical resistivity of EuB$_{5.99}$C$_{0.01}$.

Fig. 2 illustrates how external pressure influences the temperature dependence of the resistivity of EuB$_{5.99}$C$_{0.01}$ in the paramagnetic state, focusing on the temperature between $\sim 10$ K and $\sim 20$ K. As demonstrated previously [1, 17], a dominant contribution to the temperature dependence of the resistivity in this temperature range arises from the spin disorder scattering; the $\rho(T)$ dependence can be satisfactorily analyzed using the formula $\rho(T) = A(T)(T - \theta_C) + \rho_d$, where $A$ is a constant, parameter $\theta_C$ is the paramagnetic Curie temperature, and $\rho_d$ represents a contribution due to temperature independent scattering on defects. As can be seen from Fig. 2 external pressure lower than 4.4 kbar practically does not influence the $\theta_C$ ($\theta_C = 6.98 \pm 0.05$ K and $6.96 \pm 0.05$ K for $\sim 0$ and 4.4 kbar, respectively). At higher pressure the paramagnetic Curie temperature slightly decreases ($\theta_C = 6.38 \pm 0.05$ K), which could be also associated with the expansion of non-FM regions (spacers) and strengthened antiferromagnetic interactions inside them, consistently with the above mentioned scenario.

Of course, application of the scenario on the role of spacers requires to take into account the following aspects/limitations. (i) The volume fraction of the phase not compatible with FM ordering should be comparable to the volume fraction of the vast phase, where MPs can exist. Too high volume fraction of the phase not compatible with FM ordering would prevent the percolation process, thus only islands of FM phase would exist in the system and the percolation would not occur at all; on the other hand, too low fraction of these regions would not have any important impact on the percolation process. (ii) Characteristic dimensions of regions not compatible with FM ordering should be comparable with dimensions of MPs at temperatures close above $T_c$. If these regions were much larger than MPs, theys would only represent some "restricted regions"; but could not effectively play the role of spacers, such as MPs could easily percolate in the remaining volume of the material. On the other hand, if these regions are too small, they would not effectively prevent the percolation/overlap of significantly larger MPs.

Applying the above mentioned criteria on the case of the investigated EuB$_{5.99}$C$_{0.01}$ leads to the conclusion that the volume fraction of the charge-carrier-rich regions should be comparable to the vast material and characteristic dimensions of these regions should be of the same range as MPs close above $T_c$. Unfortunately, we have no direct evidence on the volume of regions not compatible with FM state in the investigated compound. More light into the problem should be brought e.g., by detailed neutron diffraction studies.) However, we strongly suppose a comparable volume fraction of the charge-carrier-rich regions and the vast material. (Just for illustration purposes, a consideration of the system as a mixture of EuB$_{5.995}$C$_{0.005}$ and

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Figure 2: Influence of external pressure on the $\rho(T)$ dependence.
EuB$_{5.985}$C$_{0.015}$ phase would yield a volume ratio 1:1; a mixture of EuB$_{5.97}$C$_{0.03}$ or EuB$_{5.95}$C$_{0.05}$, as the carbon-rich phase and EuB$_5$ as the carbon-poor one would provide the ratio 2:1 or 4:1, respectively.) A rough estimation of an expected size of the spacers and MPs in the studied system can be performed as follows. Estimation of an expected size of the spacers and MPs in the EuB$_5$ close above $T_C$ from Raman scattering studies [5] yields a value $a = 4.19\,\text{Å}$, where $a$ is the lattice parameter of EuB$_5$ close above the $T_C = 12\,\text{K}$ [13]. Thus, an estimated size/diameter of MPs in EuB$_5$ close above the $T_C$ is $2R \approx 16.76\,\text{Å}$. According to the neutron scattering studies reported by Tarascon et al., the size of incoherent regions present in EuB$_{5.95}$C$_{0.05}$ due to the fluctuation in carbon content is about 50 Å [15]. Supposing that carbon-rich regions in EuB$_{5.99}$C$_{0.01}$ have the same carbon concentration but adequately reduced size when comparing with EuB$_{5.95}$C$_{0.05}$, the estimated size/diameter of the spacers in the studied compound should be $\approx 29.2\,\text{Å}$, what is comparable with the above mentioned size of MPs in EuB$_5$. According to this rough estimation EuB$_{5.99}$C$_{0.01}$ can be treated within the limits of the scenario of spacers [1].

The above presented results and related discussion shed new light on an understanding of the very intriguing behavior of EuB$_{5.99}$C$_{0.01}$ system and allow to explain qualitatively different effect of pressure on the electrical characteristics of pure and carbon-doped EuB$_5$. As stated previously [1] and discussed in this paper, a major difference between the two systems is represented by the presence of the spacers, i.e., regions not compatible with FM order due to high carrier concentration, which prevent FM phase to percolate and to form an electrically conductive path along the carbon doped sample. It can be therefore concluded that both, the observed shift of the resistivity maximum to lower temperature, as well as a decrease of the paramagnetic Curie temperature upon increasing pressure, can be attributed to the expansion of the spacers upon increasing pressure. Thus the results confirm that the dominant effect of substitution of boron by carbon in EuB$_{5.99}$C$_{0.01}$, is an inhomogeneous volume distribution of carbon, causing magnetic phase separation at low temperatures, instead of (an homogeneous) increase of the charge-carrier concentration.

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