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An observation of electron phase transition in SmB_6 at low temperatures ☆

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Abstract

In order to reveal the nature of the ground state of archetypal intermediate-valence compound SmB_6, a comprehensive study of its transport and magnetic properties was carried out on high-quality single crystals at temperatures of 1.8–300 K in magnetic fields up to 7 T. A drastic enhancement of negative magnetoresistance was observed below 14 K, with the maximum absolute value of $\Delta\rho/\rho B^2 \sim 2.2\times10^{-3}\,T^{-2}$ at $T\approx5.2$ K. This effect seems to be attributable to anomalous magnetic scattering of many-body (exciton–polaronic) complexes induced by fast valence fluctuations on Sm sites. The observed anomalies of magnetotransport, thermoelectric and magnetic characteristics are discussed in terms of electron phase transition to the coherent state of interacting many-body complexes occurring at $T^*\sim5$ K.

Keywords: Intermediate valence; Heavy fermions; Exciton–polaronic complexes

The problem of intermediate valence [1] in some rare-earth compounds has attracted considerable attention from the condensed matter community during the last four decades [2,3]. One of the most typical representatives of these materials is samarium hexaboride, which was found to have the intermediate valence of samarium ions $\upsilon\sim2.6$ [2,4]. In spite of 40 years of investigating SmB_6, the ground state of this narrow-gap ($E_g\approx20$ meV) semiconductor remains unclear. The commonly used approach, which describes this compound in terms of Kondo insulating state [5], contradicts numerous experiments (see, e.g., [6–8]). To explain the anomalous low-temperature magnetic excitations observed in inelastic neutron spectra of SmB_6 [7], the authors of [9] suggested a formation of exciton–polaronic complexes induced by soft valence fluctuations on Sm-sites.

Recent studies of optical conductivity [10], charge transport [11,12] and low-frequency dielectric permittivity [11] performed on high-quality single crystals of SmB_6 have favored an explanation in terms of the formation of many-body (exciton–polaronic) complexes at $T<15$ K. It has also been shown that many-body states forming in the indirect gap are strongly influenced by anisotropic polaronic contributions to the binding energy $E_p\approx0.5$–3 meV, depending on the crystallographic direction in the SmB_6 matrix [12]. Besides, a whole number of anomalies has been observed in the physical properties of SmB_6 in the vicinity of $T^*\sim5$ K [8,10–16]. The most exotic feature is a zeroing of the Seebeck coefficient ($S=0$), which is observed for some crystallographic directions at $T<3$ K and is probably an indication of inherent coherence in this strongly correlated electron system [10]. This unusual behavior of $S(T)$ is also accompanied by saturation of low-temperature resistivity and the Hall coefficient to the values of $\rho\sim10$–100 Ω cm

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and $R_H \sim 10^2$–$10^3\,cm^3/C$, respectively [3,8,11,13], as well as by anomalies in thermal dilatation [14], elastic modulus [15] and NMR spectra [16]. It should be especially noted that the low-temperature "metallization" with the saturation of transport characteristics, which does not qualitatively depend on defect concentration, cannot be explained in terms of hopping transport through an impurity band [8,17].

To shed more light on this puzzling behavior observed in this intermediate-valence compound below $T^* \sim 5\,K$, a detailed study of transport and magnetic properties has been carried out on single crystals of SmB_6 in a wide range of temperatures (1.8–30 K) and magnetic fields (up to 7 T). The details of sample preparation and characterization are given in [18]. To allow for the possible influence of "induced anisotropy" [12] the measurements were performed for single crystals cut from one ingot along various crystallographic directions in one (110) plane. Special attention was paid to the chemical etching of the sample's surface to exclude any parasitic contribution from surface defects, which could be induced by sparkling cutting and abrasive polishing. Owing to careful preparation and the high quality of the single crystals we were able to observe very high residual resistivity ratios ($RRR = \rho(2\,K)/\rho(300\,K) > 1.2 \times 10^5$) for all samples under investigation. Note that the temperature dependence of resistivity $\rho(T)$ is well consistent with the data obtained for other single crystals of SmB_6 [3–5,13–16]. The measurements of charge transport were made with the standard four-probe technique in helium cryostat equipped with a 7 T superconducting magnet. Precision measurements of magnetic susceptibility were carried out on SmB_6 single crystals with a SQUID magnetometer in magnetic fields up to 0.2 T at temperatures between 4.2 and 300 K.

The experimental data of magnetoresistance $\Delta\rho/\rho = f(B)$ presented in Fig. 1 are typical of all the samples under investigation. Fig. 1 clearly shows that a reduction in temperature to below 15 K results in a drastic increase of negative magnetoresistance $\Delta\rho/\rho \sim -B^2$ up to a maximum absolute value of $T_{max} \approx 5.2\,K$ (Fig. 1). It is interesting to note here that the decline in negative magnetoresistance observed below T_{max} is accompanied by the onset of a negative linear contribution to $\Delta\rho/\rho$, predominantly in the low field region $B < 2\,T$ at $T < 4.2\,K$ (Fig. 1). This correlates with the data of [12], where strongly anisotropic behavior of the linear term $\Delta\rho/\rho \sim -B$ was reported and discussed in detail. At the same time, the small positive magnetoresistance observed at $T > 4.2\,K$ for all samples under investigation (Fig. 1) was found to result from a small error in the CERNOX thermometer ($\Delta T < 0.01\,K$) in the presence of weak magnetic fields $B < 2\,T$ [19].

The temperature dependence of magnetic susceptibility $\chi(T)$ measured along the <100> direction is shown in Fig. 2. The data obtained agree very well with the results of previous investigations [4,18]. We found only weak (~6%) anisotropy of magnetic properties for magnetic fields applied along the <100> and <111> directions. This magnetic anisotropy is temperature independent and seems to arise from the uncertainty in determining geometrical factors. It should be especially noted that no distinct anomaly was detected in the vicinity of T^*. However, it was also found that the low temperature magnetic susceptibility of SmB_6 significantly deviates from Curie-like behavior

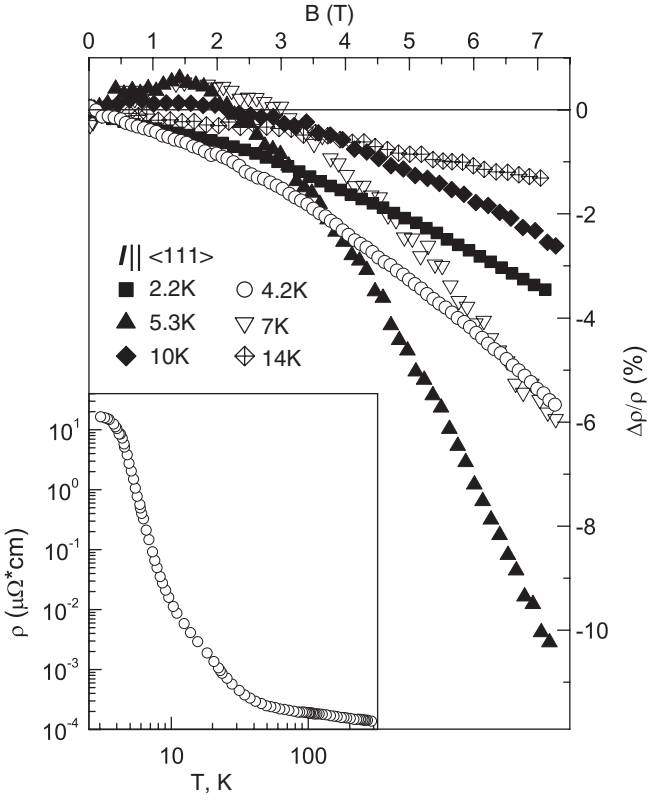

Fig. 1. Magnetoresistance of SmB_6 measured for currents applied in the <111> crystallographic direction at various temperatures. The inset shows the temperature dependence of resistivity measured for the same sample of SmB_6.

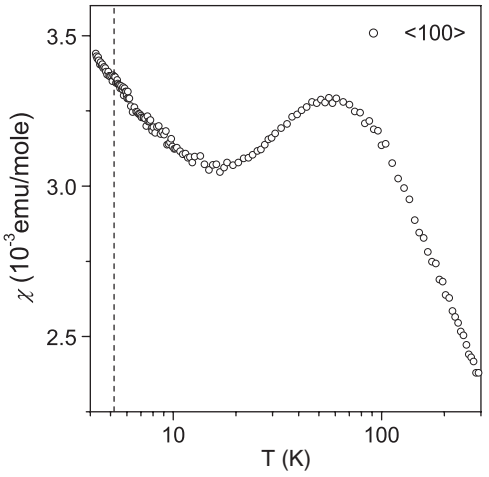

Fig. 2. Temperature dependence of magnetic susceptibility of SmB_6 as measured in magnetic fields applied along <100> axis. The dotted line shows the temperature of transition into the coherent state $T^* \sim 5\,K$.

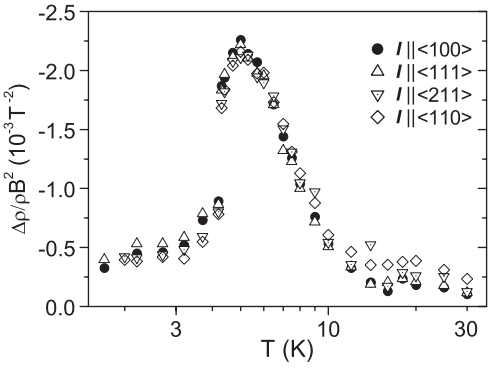

Fig. 3. Temperature dependencies of $\Delta\rho/\rho B^2$ as estimated for various crystallographic directions in the [110] plane.

thus excluding any explanation in terms of magnetic impurities as proposed in [18].

For a quantitative characterization of the negative magnetoresistance in SmB_6, the data of Fig. 1 were used to calculate the temperature dependencies of parameter $\Delta\rho/\rho B^2$ for all samples under investigation. To exclude any influence of anisotropic linear contributions to magnetoresistance $\Delta\rho/\rho \sim B$ [12], the quadratic term $\Delta\rho/\rho B^2$ was estimated for the upper limit of the magnetic field ($B > 5$ T). Fig. 3 shows that the pronounced anomaly of $\Delta\rho/\rho B^2$ reaches its maximum absolute value of $2.2 \times 10^{-3}\,\mathrm{T}^{-2}$ at $T_{max} \approx 5.2$ K. Note that no anisotropy of the quadratic component $\Delta\rho/\rho B^2$ was observed for the upper limit of the magnetic field in the vicinity of T_{max} within experimental accuracy. However, some anisotropic features, which were evident below T_{max} (e.g., the largest effect for the current applied in the $<100>$ direction in comparison with that of $<110>$, see Fig. 3), are well consistent with the low-temperature anisotropy of charge transport in SmB_6 as reported in [12].

It should be especially noted that the anomalous increase in negative magnetoresistance, which was for the first time observed in our study, cannot be explained in terms of the Kondo-insulating model [5]. In Kondo insulators the application of magnetic field should strongly reduce the forbidden gap due to Zeemann splitting of the excited triplet state [5], and thus lead to a reduction in resistivity as described by the activation law $\rho = \rho_0 \exp(\Delta(H)/2k_B T)$. However, preliminary measurements of the Hall effect carried out in our study revealed no change in activation energy. So the observed anomaly in magnetoresistance cannot be explained by the Kondo-insulating model with the gap which is independent of magnetic fields up to 7 T. In this case, Iosida's model [20], which takes into account the effects of *s–d* exchange interaction, seems to be the most appropriate for describing the anomalous magnetic scattering of charge carriers in the SmB_6 matrix. The same approach was taken to explain the anomalous magnetotransport properties of cerium intermetallides [21]. This approach [20] allowed us to calculate the local susceptibility in the vicinity of the charge carrier $\chi_{loc} = \left(-\Delta\rho/\rho B^2\right)^{-1/2}$ (Fig. 4). For SmB_6, local susceptibility seems to characterize the internal magnetic field and magnetic scattering of short-range (<10 Å) exciton–polaronic complexes resulting from fast valence fluctuations on Sm-sites. This approach also explains why in the presence of a low effective concentration of exciton–polaronic complexes ($n \sim 10^{17}$–$10^{18}\,\mathrm{cm}^{-3}$) [11,12] no features in bulk magnetic susceptibility of SmB_6 at T^* (Fig. 2) could be observed. In contrast, an increase of magnetic scattering in the vicinity of T^* is accompanied by a drastic reduction in relaxation time from $\tau(10\,\mathrm{K}) \sim 2 \times 10^{-12}$ s to $\tau(2\,\mathrm{K}) \sim 4.2 \times 10^{-13}$ s (Fig. 4) as estimated from Hall mobility data within the framework of the simple expression $\mu H = e\tau/m^*$ and the effective mass value $m^* \sim 30 m_0$ [12,14]. Allowing for anomalies in transport [3,11,12], thermodynamic [14,22], elastic [15] and noise [23] properties as well as unusual features in neutron scattering [7], Raman [6] and NMR [16] spectra, this reduction in relaxation time values (which correspond to the characteristic frequency of valence fluctuations ($\sim 10^{12}$–$10^{13}\,\mathrm{s}^{-1}$ [3])) seems to indicate the onset of a low-temperature coherent state in the low-density ($\sim 10^{17}$–$10^{18}\,\mathrm{cm}^{-3}$) system of interacting exciton–polaronic complexes below $T^* \sim 5$ K. Taking into account that the Coulomb attraction between the itinerant d electrons and localized f holes induces a built-in coherence between these electronic states [24]—thus leading to the break-down of inversion symmetry and the onset of electronic ferroelectricity [25]—the reported enhancement of magnetic scattering as well as the other anomalies of physical properties of SmB_6 seem to be explained in terms of an electron phase transition occurring

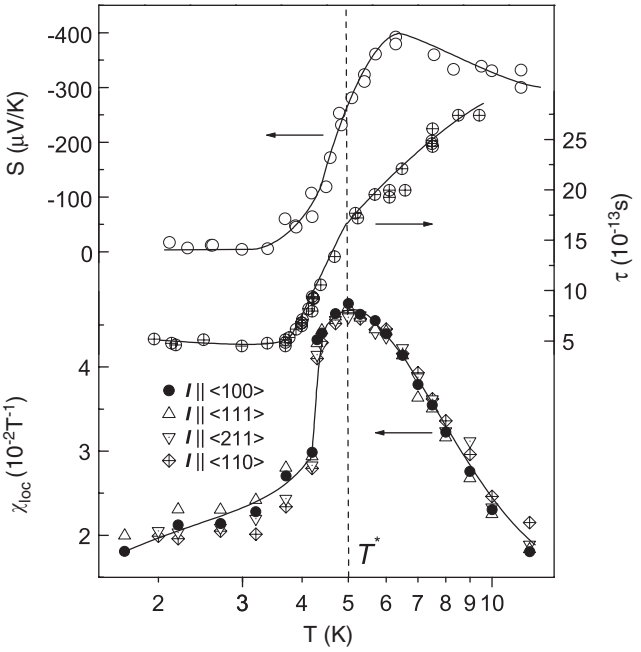

Fig. 4. Temperature variation of local susceptibility χ_{loc} (see text), relaxation time τ and Seeebeck coefficient S observed in SmB_6 in the vicinity of $T^* \sim 5$ K. Solid lines are just guides for the eye.

in this intermediate valence compound at $T^{*}\sim 5$ K. However, the absence of a theoretical model which could provide an adequate quantitative explanation of the anomalies observed for temperature dependencies of bulk and local susceptibility, relaxation time and Seebeck coefficient (Fig. 4), will make it necessary to carry out a more detailed analysis to discover the nature of this unusual coherent state in SmB_6.

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References

[1] D.L. Khomskii, Sov. Phys. Usp. 22 (1979) 879.
[2] E.E. Vainstein, S.M. Blokhin, Yu.B. Paderno, Sov. Phys. Sol. St. 6 (1965) 281.
[3] P. Wachter, in: K.A. Gschneidner Jr., L. Eyring, G.H. Lander, G.R. Choppin (Eds.), Handbook on the Physics and Chemistry of Rare Earths, Elsevier, British Vancouver, Amsterdam, 1994.
[4] R.L. Cohen, M. Eibschütz, K.W. West, Phys. Rev. Lett. 24 (1970) 383–386.
[5] G. Aeppli, Z. Fisk, Comm. Cond. Mater. Phys. 16 (1992) 155.
[6] P. Nyhus, S.L. Cooper, Z. Fisk, J. Sarrao, Phys. Rev. B 55 (1997) 12488.
[7] P.A. Alekseev, J.-M. Mignot, J. Rossat-Mignod, V.N. Lazukov, I.P. Sadikov, E.S. Konovalova, Yu.B. Pademo, J. Phys.: Condens. Matter 7 (1995) 289.
[8] N.E. Sluchanko, A.A. Volkov, V.V. Glushkov, B.P. Gorshunov, S.V. Demishev, M.V. Kondrin, A.A. Pronin, N.A. Samarin, Y. Bruynseraede, V.V. Moshchalkov, S. Kunii, JETP 88 (1999) 533.
[9] K. Kikoin, A. Mishchenko, J. Phys.: Condens. Matter 7 (1995) 307.
[10] B. Gorshunov, N. Sluchanko, A. Volkov, M. Dressel, G. Knebel, A. Loidi, Phys. Rev. B 59 (1999) 1808.
[11] N.E. Sluchanko, V.V. Glushkov, B.P. Gorshunov, S.V. Demishev, M.V. Kondrin, A.A. Pronin, A.A. Volkov, A.K. Savchenko, G. Gruner, Y. Bruynseraede, V.V. Moshchalkov, S. Kunii, Phys. Rev. B 61 (2000) 9906.
[12] N.E. Sluchanko, V.V. Glushkov, S.V. Demishev, A.A. Pronin, A.A. Volkov, M.V. Kondrin, A.K. Savchenko, S. Kunii, Phys. Rev. B 64 (2001) 153103.
[13] J.C. Cooley, M.C. Aronson, Z. Fisk, P.C. Canfield, Phys. Rev. Lett. 74 (1995) 1629.
[14] D. Mandrus, J.L. Sarrao, A. Lacerda, A. Migliori, J.D. Thompson, Z. Fisk, Phys. Rev. B 49 (1994) 16809.
[15] S. Nakamura, T. Goto, M. Kasaya, S. Kunii, J. Phys. Soc. Japan 60 (1991) 4311.
[16] O. Pena, M. Lysak, D.E. MacLaughlin, Z. Fisk, Solid State Commun. 40 (1981) 539.
[17] S. Curnoe, K.A. Kikoin, Phys. Rev. B 61 (2000) 15714.
[18] K. Flachbart, S. Gabani, T. Herrmannsdorfer, E. Konovalova, Y. Paderno, V. Pavlik, Physica B 284–288 (2000) 1353.
[19] B.L. Brandt, D.W. Liu, L.G. Rubin, Rev. Sci. Instr. 70 (1999) 104.
[20] K. Yosida, Phys. Rev. 107 (1957) 396.
[21] N.E. Sluchanko, A.V. Bogach, G.S. Burkhanov, O.D. Chistyakov, V.V. Glushkov, S.V. Demishev, N.A. Samarin, D.N. Sluchanko, Physica B 359–361 (2005) 308.
[22] S. Gabani, K. Flachbart, E. Konovalova, M. Orendac, Y. Paderno, V. Pavlik, J. Sebek, Solid State Commun. 117 (2001) 641.
[23] V. Glushkov, N. Sluchanko, M. Ignatov, S. Demishev, S. Safonov, A. Savchenko, V. Fillipov, Yu. Paderno, S. Kunii, Acta Phys. Pol. B 34 (2003) 1097.
[24] S.H. Liu, Phys. Rev. B 37 (1988) 3542.
[25] T. Portengen, Th. Ostreich, L.J. Sham, Phys. Rev. B 54 (1996) 17452.