PHYSICAL REVIEW B VOLUME 60, NUMBER 10 1 SEPTEMBER 1999-II

In-plane Hall-effect anisotropy in the organic superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br

M. A. Tanatar
Faculty of Science, Kyoto University, Kyoto 606-8502, Japan
and Institute of Surface Chemistry, National Academy of Sciences of Ukraine, 31 prospekt Nauki, 252022 Kyiv, Ukraine

V. N. Laukhin
Faculty of Science, Kyoto University, Kyoto 606-8502, Japan
and Institute for Chemical Research of Russian Academy of Sciences, Chernogolovka, MD 142432, Russia

T. Ishiguro, H. Ito, T. Kondo, and G. Saito
Faculty of Science, Kyoto University, Kyoto 606-8502, Japan

(Received 15 July 1998; revised manuscript received 28 December 1998)

Anisotropy of the Hall effect within the highly conducting plane has been measured in the organic superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. Anisotropy and magnetic field dependence nonlinearity in the Hall resistivity are found above approximately 30 K. This behavior is shown to originate from an electron sheet of the Fermi surface. The temperature at which anisotropy and nonlinearity appear correlates with the temperature at which resistivity is at its maximum. The Hall effect behavior at temperatures below about 30 K corresponds to the predictions of the semiclassical weak-field model for a two-dimensional metal. A comparison of the Hall constant predicted by the calculated band structure within this model with the experimentally determined value revealed a large discrepancy. This is discussed within the framework of a reconstruction of the Fermi surface, as recently proposed by Weiss *et al.* on the basis of Shubnikov–de Haas effect studies under pressure. [S0163-1829(99)12233-1]

INTRODUCTION

The charge transfer salts κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ and κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br [BEDT-TTF=bis(ethylene dithio)tetrathiafulvalene] are the two highest-T_C organic superconductors at ambient pressure [inductive onsets of 10.4 and 11.6 K (Ref. 1)]. The electronic structure of the κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (which we will refer to as NCS salt in the following) at low temperature is understood reasonably well. The shape of the Fermi surface, as determined from semiclassical and quantum magnetic oscillation studies, corresponds essentially to the band structure calculation.[2] A similar calculation for the κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br (which we will refer to as Br salt in the following), based on the crystal structure at room temperature,[3] predicts essentially the same Fermi surface as has been established in the NCS salt. However, experimental studies at ambient pressure show only the magnetic breakdown β orbit in very high fields.[4,5] Furthermore, several additional orbits observed under pressure[6,7] do not correspond to the calculation either. At higher temperatures both salts show a number of anomalies of electronic properties (see Ref. 8 for a useful summary of experimental results for the NCS salt). Recently we have shown that the temperatures at which the anomalies in the Br salt are observed are very close to the temperatures at which phase transformations due to ethylene ordering occur.[9] The sequence of phase transitions caused by this process includes the formation of a conformational superstructure [observed experimentally in NMR studies below around 160 K (Ref. 10)] and its transformation (in the 60 to 100 K range) towards an ordered state at low temperatures. The latter causes the superconducting properties of the Br salt to become sensitive to the thermal cycle used.[11] It is not clear, however, in what electronic state the salt exists at low temperatures. Transformation at around 60 K seems to lead to a number of electronic property anomalies in the Br salt at low temperatures: a pseudogap spin susceptibility behavior,[12] slightly reduced superconducting T_C,[13] and appearance of magnetic viscosity phenomena.[14]

Some time ago Ong[15] presented an elegant geometrical interpretation of the Hall effect in a two-dimensional metal in a weak-field semiclassical limit in terms of a scattering path length vector. The model predicts the Hall effect should be independent of direction of the current flow within the plane. It also allows a direct comparison of the Hall-effect data and the Fermi surface geometry. The aim of the present article is to study the Hall effect in the Br salt in terms of Ong's model. We shall report the results of simultaneous measurements of the anisotropy—within the highly conducting plane—of both the resistivity and of the Hall effect. This is the first observation of an in-plane Hall effect anisotropy in organic superconductors. We found that low-temperature behavior corresponds qualitatively to the predictions of Ong's model.[15] This enabled us to make a quantitative comparison between the experiment and the predictions of Ong's model with the calculated band structure. The principal deviation from the weak-field behavior appears at higher temperatures, correlating with the temperature range of superstructure phase in the ethylene ordering model.[9] We show that the deviation originates at the electron sheet of the Fermi surface.

EXPERIMENTAL

Crystals of Br salt were grown by a standard electrochemical procedure. The samples selected were rhombic

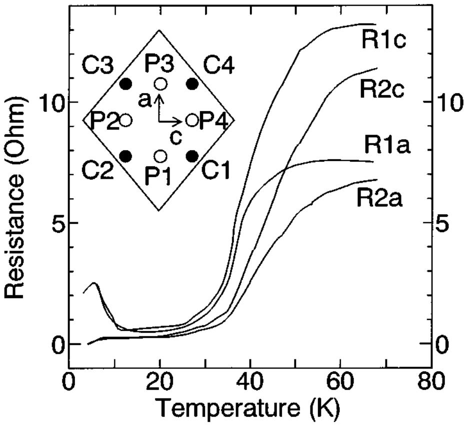

FIG. 1. Temperature dependence of resistance in the magnetic field $B = 10$ T perpendicular to the highly conducting plane in two thermal runs ($d = 0.05$ mm sample). $R1a$ and $R1c$ correspond to the measurements with current along the a and c axes in the highly conducting plane, respectively, after quenching the sample from 120 K to liquid helium temperature. $R2a$ and $R2c$ are the same for the sample annealed for 24 h at 68 K with subsequent quenching to 4.2 K. Both measurements were made on warming. Inset: a diagram of the contact arrangement on the sample.

shaped single crystals with a typical size of $1 \times 1 \times (0.02\text{–}0.11)$ mm^3. The crystal's a and c axes were found to correspond to long and short rhombus diagonals, respectively. This orientation was determined in one of the crystals by an x-ray analysis and was controlled in each crystal by the thermal probe method. After the contacts have been glued with Dotite carbon paint, the sample was locally slightly heated and the thermopower sign was determined at room temperature. By choosing several positions of the heater with respect to the sample and different contact pairs for the thermopower measurements (see inset in Fig. 1 for contact arrangement) it was easy to determine the principal directions of the thermopower anisotropy. Since the thermopower is positive for the a and negative for the c axis,[16] an unambiguous determination of the respective axes was achieved.

The rhombic shape of the samples is far from the parallel bar shape best suited for studying the Hall effect. (This shape is needed for obtaining parallel current lines.) Therefore we used an eight-probe technique[17] (inset in Fig. 1). Current contacts $C1$ to $C4$ were placed on the side surface of the sample, halfway along the rhombus sides. Potential probes were placed on the top surface of the sample, at points bisecting the sides of a rectangle formed by the current contacts. An electrical current was spread between pairs of contacts to obtain a homogeneous current distribution through the sample width. We used two configurations. In the first one, the current flowed along the a axis (between two shortened pairs $C1+C2$ and $C3+C4$). A potential drop in the sample was measured between the probes $P1$ and $P3$. The Hall voltage was measured between the probes $P2$ and $P4$. In the second case, the current flowed along the c axis (between $C2+C3$ and $C1+C4$) with the $P2$ and $P4$ probes measuring the potential drop and the $P1$ and $P3$ probes measuring the Hall voltage. We were able thus to measure in one thermal run the Hall effect as well as the resistance in both crystallographic directions.

It should be noted that these measurements do not give a quantitatively accurate resistivity anisotropy value for two directions (1 and 2) of the current flow. To establish a precise quantitative value, it is necessary to follow the general approach outlined by Montgomery.[18] Resistivity anisotropy ρ_1/ρ_2 is determined by comparing the experimentally determined value R_1/R_2 for two contact configurations, obtained by a 90° rotation of the current and potential probes (as in our case), with that of an equivalent isotropic sample. This is done by (1) calculating a ratio of resistance anisotropy R_1^i/R_2^i for an isotropic sample of equivalent shape and contact configuration as a function of its dimensions l_1 and l_2, (2) determining an l_1/l_2 ratio for the equivalent sample by comparing R_1/R_2 and R_1^i/R_2^i, (3) calculating the resistivity anisotropy by comparing the actual anisotropic sample dimensions L_1 and L_2 with l_1 and l_2, using Wasscher's scaling transformation[19] according to the formula $(\rho_1/\rho_2) = (l_1/l_2)^2/(L_1/L_2)^2$.

A solution of the problem in step (1) of this procedure—for the rhombic shape crystal with a rather complicated eight-contact configuration—is beyond our scope, so we limited ourselves to a semiquantitative determination of the measured anisotropy change with temperature and thermal cycling. To reduce geometrical correction, we transformed the rhombus into a square by elongating the rhombus c axis approximately 1.4 times. With this transformation, the resistance for the a axis decreases by 1.4 and that of the c axis increases by the same factor. All the measured resistance values were corrected in this way. This procedure essentially reduces the measured ratio, although it is fundamentally incorrect. The problem of quantitative determination of anisotropy for the Br salt was solved by Buravov *et al.*[20] using samples with more appropriate geometry, and our results predominantly agree qualitatively with the temperature dependence found in their study.

The Hall voltage was measured by effectively reversing the magnetic field direction by rotating the sample 180° in the field of a superconducting solenoid.[14] The Hall constant R_H was determined as $R_H = Vd/BI$, where V is the Hall voltage, I is the current through the sample, B is the magnetic field induction, and d is the sample thickness. We studied three crystals, 0.02, 0.05, and 0.11 mm thick. The Hall constant R_H was sample dependent and at 12 K was equal to 1.0 ($d = 0.02$ mm), 1.2 (0.05 mm), and 1.8 (0.11 mm) (in 10^{-7} m^3 C^{-1} units). For control purposes we also determined the Hall constant at 12 K using conventional five-probe geometry. Here the current flow was along the a axis and all current and potential probes were glued to the side surface of the sample.[14] Measurements were taken after performing annealing at 68 K similar to the run 2 (see below). They gave values of 1.4, 1.0, and 2 for the same samples. We found a variation of about ±10% in the measured values upon successive gluing of the contacts in the same position. The effect seems to be caused by inhomogeneity of the contact resistance in the contact area, leading to inhomogeneity of the current through sample thickness. In view of a large margin of error in determining the sample thickness (±0.005 mm) and the aforementioned irreproducibility, the degree of consistency in R_H determination between different samples seems reasonable.

The temperature dependence and the field dependence of the Hall resistance were measured in the eight-contact scheme. They were the same for all three samples below 40 K. The behavior above 40 K was qualitatively similar, though differing in respect of the magnitude of the Hall resistance for the current along the *c* axis.

RESULTS AND DISCUSSION

Long term resistance relaxation processes are typical for the Br salt. They are induced both by thermal cycling [at any temperature, although mainly at temperatures above 60 K (Refs. 9 and 21)], and by magnetic field cycling (magnetic viscosity) below 60 K.[14] Both relaxation processes produce significant noise in measurement of the Hall effect. Since the thermal instability is essentially greater than the magnetic instability, our Hall effect measurements were carried out only below 64 K. Thermal treatment of the sample between 60 and 70 K reduced the amplitude of magnetic transients, although we could not eliminate them completely. We measured the effect of thermal treatment on the resistance and the Hall constant using the same sample without any changes in the contact geometry. Our choice of thermal procedure was based on the results of Ref. 9. In the first thermal run, the sample was annealed for 3 h at 120 K and then rapidly cooled to liquid helium temperature. The Hall effect and the resistance were measured on warming to 64 K. After completing this measuring run 1, the sample was subjected to annealing at 68 K for 24 h. The state achieved after annealing was fixed by quenching to 4.2 K. Measurements were carried out upon warming (run 2). Identical measuring runs were maintained in order to avoid any possible distortion by hysteresis phenomena. Hence, any difference between the runs originates only from the preceding thermal treatment.

Figure 1 shows a temperature dependence of resistance $R(T)$ along two in-plane directions for the runs 1 and 2. The measurements were carried out in a field 10 T perpendicular to the plane in the same run as the Hall effect measurements were taken. The resistance anisotropy decreases upon cooling below 60 K and shows no detectable change upon thermal cycling. It is worth noting that in a magnetic field the resistance remains fairly constant below around 20 K in run 2, and it increases below 12 K in run 1. In run 2, the resistance starts to decrease below approximately 7 K due to incomplete suppression of the superconducting transition in the 10 T field. Therefore, to avoid complications due to the Hall effect in the mixed state, all measurements were carried out above 7 K.

Figure 2 shows a temperature dependence of the Hall resistance, as measured in the two thermal runs carried out in a constant field of 10 T. In the case of the current along the *a* axis, the Hall constant is positive and shows little dependence on temperature and thermal cycling. It increases by approximately 30% on cooling from 64 to 20 K and then decreases by about 10% when cooled to 7 K. In the case of the current along the *c* axis, R_H is negative at high temperatures and changes sign to positive at ~40–47 K. The temperature of this sign-change correlates with the position of the resistance maximum: both move to a higher temperature at almost the same rate when subjected to annealing. The Hall constant has a tendency to saturation at low temperatures (<16 K) in both directions.

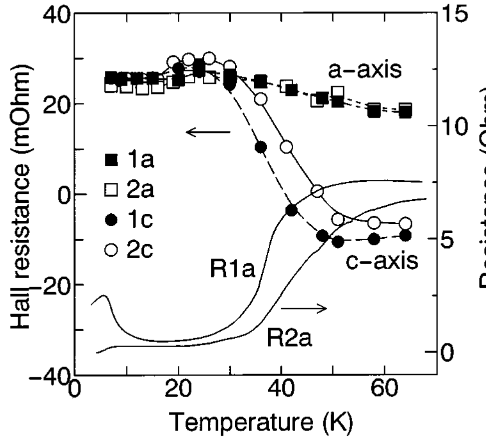

FIG. 2. Temperature dependence of the Hall resistance ($d=0.05$ mm sample) at 10 T field for current flowing along the *a* (squares) and *c* (circles) axes (solid symbols: run 1; open symbols: run 2). Temperature dependence of resistance is shown for the current in the *a* direction in the same thermal runs at 10 T field.

In Fig. 3 we show field dependence of the Hall resistance for the electrical current flowing in two directions for run 2 only, due to less noise from magnetic viscosity. At 22 K the linear field dependence of the Hall resistance is observed in both directions. At higher temperatures for the *a* direction the dependence is still linear, while in the *c* direction it is strongly nonlinear. In the latter case the dependence shows negative slope at low fields, changing to a positive slope when the field increases after passing through a broad minimum at around 5 T.

At this stage it is useful to recall the main features of weak-field Hall effect behavior in two-dimensional metals.[15] The model predicts that, as a scalar quantity, the Hall constant should be independent of the current direction in the plane and of the magnetic field. Both predictions hold, within experimental accuracy, at low temperatures. Moreover, if the resistivity at low temperatures is determined by scattering on defects, the Hall constant should be independent of both temperature and concentration of defects. Clearly, quenching the sample from the higher temperature produces a greater density of defects. We can see then, from Fig. 2, that both assumptions are fulfilled below around 20 K.

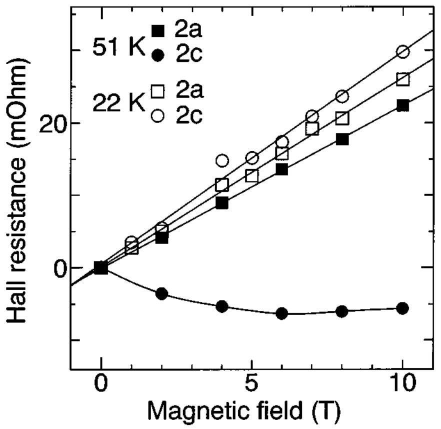

FIG. 3. Field dependence of the Hall resistance for $d=0.05$ mm sample at 51 and 22 K (run 2).

Hence, in this temperature range it is reasonable to regard the scattering path length l (Ref. 15) as a constant. In this approximation the partial Hall constant of the open electron sheets is equal to zero, and the expression for the Hall constant can be written[15] as

$$R_H=(2\pi w/e)4l_h^2/(2k_F^h l_h+k_F^e l_e)^2. \tag{1}$$

Here w is an interlayer distance, l_e and l_h are the effective electron and hole scattering lengths, and k_F^e and k_F^h their Fermi momenta. The denominator represents the square of the total conductivity as a sum of contributions of electrons σ_e and holes σ_h. (Different factors appear due to the different dimensionality of electron and hole sheets of the Fermi surface.) If we (i) neglect the electron component in the denominator, (ii) take l_h constant (similar to l_e), (iii) approximate the hole Fermi surface as a cylinder with the radius of k_F^h, so $\pi(k_F^h)^2=S_h$, where S_h is the cross-section area of the hole pocket, we obtain the following relation:

$$R_H\leqslant(2\pi^2 w/e)/S_h. \tag{2}$$

For the Br crystals, $w=b/2$. Taking $S_h=\eta S_{BZ}$ we obtain $R_H\leqslant V/4e\eta$, where V is the unit cell volume. For $V=3317\ \text{A}^3$ (Ref. 1) and $\eta\approx 0.18$, according to the band structure calculation,[3] we have $R_H\leqslant 2.9\times 10^{-8}\ \text{m}^3\,\text{C}^{-1}$. Note that both of the assumptions used in this estimation—(i) isotropic and constant scattering path, resulting in zero electron contribution to the Hall constant and (ii) the negligible partial conductivity of electron sheets—lead to an overestimation of R_H. This notwithstanding, the experimental value is at least 3 times larger. It is clear, then, that it is not possible to obtain a coincidence with the calculated Fermi surface.

We would like to point out that the anisotropy of resistivity in the salt also contradicts the band structure calculation prediction. It might be thought that the c axis should be the direction of the highest conductivity. Here, according to the band structure calculation, the contribution from the electron sheet should be dominant. Contrary to this conclusion, however, higher conductivity is found along the a axis.[20] We would expect some anisotropy of σ_h due to the anisotropy of the effective mass, leading to $\sigma_{ha}/\sigma_{hc}\approx 1.3$ to 1.5. Since the actual ratio is approximately the same,[20] the assumption of $\sigma_e\ll\sigma_h$ used in Eq. (2) seems to be reasonable. The big difference between the experimentally determined value of R_H and the calculated one can therefore be used to estimate a necessary reduction in size of the hole pocket. This value should be at least 3 times smaller than the value predicted by the band structure calculation[3] and is not far from the value of 3.8 as determined from the Shubnikov–de Haas effect in the Br salt under pressure of 8 kbar.[6] A more resent study of the Br salt under pressure has revealed three orbits,[7] thought to be caused by a reconstruction of the Fermi surface due to interaction with a superstructure in the anion layer.[22] Two of these orbits are holelike, while the third one is electronlike. The orbits are essentially smaller than the calculated size of the hole pocket. A similar reconstruction at ambient pressure could lead to an explanation of our experimental results. It is difficult, however, to make a quantitative comparison with this proposed Fermi surface change. The Hall constant in this case is the sum of contributions from three groups of carriers and hence is strongly dependent on the partial conductivity weighting factors, which are not known. Besides, the actual size of the reconstructed pockets at ambient pressure could be significantly different from that at high pressure due to a variation in superstructure gap magnitude.[14] This possibility is further indicated by the difference of the oscillation frequencies at ambient pressure and under pressure.[7]

At temperatures above around 30 K the Hall resistance does not follow weak field behavior. Nonlinear field dependence is observed in case of the current along the c axis and the Hall constant becomes anisotropic. Both these effects are related to anomalous behavior for the c axis, since the field dependence of the Hall resistance for the current along the a axis remains linear and no large changes are observed in the temperature dependence of the Hall resistance. It is worth noting that the anisotropy of the resistivity decreases in this temperature range (Fig. 1 and Ref. 20). Therefore, taking into account that the contribution of electrons is small at low temperatures, and their anomalous contribution at temperatures above the resistivity maximum disappears at low temperatures, we have to assume that the electron sheets are reconstructed at low temperature at ambient pressure as well.

This conclusion may well seem to contradict the observation of an unchanged β orbit in the Shubnikov–de Haas effect studies at ambient pressure.[4,5,7] This observation was used as an argument against Fermi surface reconstruction.[5] However, we would like to point out that the β orbit results from magnetic breakdown and can be observed even after reconstruction of the Fermi surface. The reason for the apparent lack of the other orbits at ambient pressure is unclear and deserves further study, especially in properly thermally cycled samples. It could be that it is experimentally difficult to observe low frequency oscillations in this strongly disordered material. It could, however, signify some more complicated Fermi surface reconstruction. A further possibility is that the β orbit results from a coexistence of several phases due to incomplete structural transformation

We would like to mention here that the Hall constant temperature dependence, resembling that for the c axis in the Br salt, has previously been observed in the NCS salt by Murata *et al.*[23] The direction of the current flow in their experiments corresponded to the b axis, equivalent in terms of the calculated band structure to the c axis in the Br salt. The results appear to be similar, but there is an essential difference in that there is no sign-change in their Hall constant temperature dependence. This could be because the hole pocket in the NCS salt is larger than that in the Br salt.[1] Since the high temperature behavior (above around 50 K in the NCS and 30 to 40 K in the Br salt) is similar, and since the respective temperature range matches the temperature range in which superstructure is present in the ethylene ordering model, it is tempting to relate the behavior to the presence of a superstructure (see Ref. 24 for a discussion of some possible mechanisms of this effect).

CONCLUSION

The in-plane anisotropy and the field dependence of the Hall resistance in the salt of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br at low temperatures are consistent with the weak-field behavior for two-dimensional metals. Comparing the experimentally determined Hall constant with that predicted by the calculated band structure revealed a large discrepancy. This is regarded as indicative of a reconstruction of the Fermi surface with the formation of small size pockets. Strong deviations from weak-field behavior are observed in the temperature range where ethylene superstructure exists.

ACKNOWLEDGMENTS

M.A.T. and V.N.L. acknowledge support from the Japan Society for the Promotion of Science. The work has been done under support of CREST from Japan Science and Technology Corporation and from Kyoto University Venture Business Laboratory.

---

[1] J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini, and M.-H. Whangboo, *Organic Superconductors (Including Fullerenes), Synthesis, Structure, Properties, and Theory* (Prentice Hall, Englewood Cliffs, NJ, 1992).

[2] For recent reviews see, for example, M. V. Kartsovnik and V. N. Laukhin, J. Phys. I **6**, 1753 (1996); N. Harrison, J. Caulfield, J. Singleton, P. H. Reinders, F. Herlach, W. Hayes, M. Kurmoo, and P. Day, J. Phys.: Condens. Matter **8**, 5415 (1996).

[3] U. Geiser, A. J. Schultz, H. H. Wang, D. M. Watkins, D. L. Stupka, J. M. Williams, J. E. Schirber, D. L. Overmyer, D. Jung, J. J. Novoa, and M.-H. Whangboo, Physica C **174**, 475 (1991).

[4] H. Weiss, M. V. Kartsovnik, W. Biberacher, E. Steep, A. G. M. Jansen, and N. D. Kushch, Pis'ma Zh. Eksp. Teor. Fiz. **66**, 190 (1997) [JETP Lett. **66**, 202 (1997)].

[5] C. H. Mielke, N. Harrison, D. G. Rickel, A. H. Lacerda, R. M. Vestal, and L. K. Montgomery, Phys. Rev. B **56**, R4309 (1997).

[6] M. V. Kartsovnik, G. Yu. Logvenov, H. Ito, T. Ishiguro, and G. Saito, Phys. Rev. B **52**, R15 715 (1995).

[7] H. Weiss, M. V. Kartsovnik, W. Biberacher, E. Steep, E. Balthes, A. G. M. Jansen, K. Andres, and N. D. Kushch, Phys. Rev. B **59**, 12 370 (1999).

[8] E. Demiralp and W. A. Goddard III, Phys. Rev. B **56**, 11 907 (1997).

[9] M. A. Tanatar, T. Ishiguro, T. Kondo, and G. Saito, Phys. Rev. B **59**, 3841 (1999).

[10] P. Wzietek, H. Mayaffre, D. Jerome, and S. Brazovskii, J. Phys. I **6**, 2011 (1996).

[11] W. K. Kwok, U. Welp, K. D. Carlson, G. W. Crabtree, K. G. Vandervoort, H. H. Wang, A. M. Kini, J. M. Williams, D. L. Stupka, L. K. Montgomery, and J. E. Thompson, Phys. Rev. B **42**, 8686 (1990).

[12] V. Katayev, G. Winkel, D. Khomskii, D. Wohleben, W. Crump, K. F. Tebbe, and J. Hahn, Solid State Commun. **83**, 435 (1992).

[13] A. Aburto, L. Fruchter, and C. Pasquer, Physica C **303**, 185 (1998).

[14] M. A. Tanatar, T. Ishiguro, H. Ito, M. Kubota, and G. Saito, Phys. Rev. B **55**, 12 529 (1997).

[15] N. P. Ong, Phys. Rev. B **43**, 193 (1991).

[16] R. C. Yu, J. M. Williams, H. H. Wang, J. E. Thompson, A. M. Kini, K. D. Carlson, J. Ren, M.-H. Whangbo, and P. Chaikin, Phys. Rev. B **44**, 6932 (1991).

[17] V. N. Topnikov, S. I. Pesotskii, and V. N. Laukhin, Pis'ma Zh. Eksp. Teor. Fiz. **59**, 349 (1994) [JETP Lett. **59**, 374 (1994)].

[18] H. C. Montgomery, J. Appl. Phys. **42**, 2971 (1971).

[19] J. D. Wasscher, Philips Res. Rep. **16**, 301 (1961).

[20] L. I. Buravov, N. D. Kushch, V. A. Merzhanov, M. V. Osherov, A. G. Khomenko, and E. B. Yagubskii, J. Phys. I **2**, 1257 (1992).

[21] K. Andres, H. Posselt, N. D. Kushch, M. Kund, W. Biberacher, and G. Saito, Acta Phys. Pol. A **87**, 761 (1995).

[22] Y. Nogami J. P. Pouget, T. Ishiguro, H. Ito, and G. Saito, Solid State Commun. **89**, 113 (1994).

[23] K. Murata, M. Ishibashi, Y. Honda, N. A. Fortune, M. Tokumoto, N. Kinoshita, and H. Anzai, Solid State Commun. **76**, 377 (1990).

[24] M. A. Tanatar, T. Ishiguro, H. Ito, N. D. Kushch, and E. B. Yagubskii, Synth. Met. **97**, 157 (1998).