

Anomalous Seebeck effect in the vicinity of the magnetic phase transition in $\text{ET}_2\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}_{1-x}\text{Br}_x$ ($0 \leq x < 0.5$), where it is bis(ethylenedithio)tetrathiafulvalene

M. A. Tanatar, V. S. Yefanov, and V. V. Dyakin

Institute of Surface Chemistry, Ukrainian AS, Kiev 252650, Ukraine

V. A. Bondarenko

Institute of Semiconductors, Ukrainian AS, Kiev 252650, Ukraine

N. D. Kushch and E. B. Yagubskii

Institute of Chemical Physics, Russian AS, Chernogolovka 142432, Russia

(Submitted 12 April 1994)

Pis'ma Zh. Eksp. Teor. Fiz. **59**, No. 10, 682–686 (25 May 1994)

The temperature dependences of the a axis in-plane resistivity and of the thermopower S along the a and c axes were measured for the single crystals $\text{ET}_2\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}_{1-x}\text{Br}_x$ ($0 \leq x < 0.5$). The most interesting feature of the S -vs- T curves is that for both in-plane directions the magnitude of S starts to decrease at nearly 35 K and reaches zero at nearly 20 K. This behavior is related to the magnetic phase transition in the salt and is attributed tentatively to the magnetic polaron formation.

We have recently shown that thermopower S -vs-temperature dependences for $\text{ET}_2\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}_{1-x}\text{Br}_x$ salts ($x=0.2-0.5$) reveal a phase transition at 20–25 K to a nearly zero S state.^{1,2} This behavior was assumed to be due to the sliding spin density wave (SDW) transport. Welp *et al.* have shown that the transition is accompanied by the appearance of a weak ferromagnetism.³ The aim of this paper is to present some results of thermopower studies in a pure ($x=0$) chloride salt and in chloride-bromide solid solutions ($x < 0.5$) and to discuss briefly the thermopower behavior in relation to the weak ferromagnetism of the compound.

Single crystals with the shape of a perfect rhombus and of sufficient size along the short diagonal c direction were selected for thermopower studies. Chloride crystals were shown to suffer strongly from occasional bromide contamination.⁴ The real bromide content was determined in each crystal by means of an electron probe microanalysis (EPMA). Three samples of sufficient size were selected: two bromine-free samples (samples 1 and 2) and a third crystal (sample 3), which was shown to have $x=0.4$. Unfortunately, we found that the EPMA analysis of the $x=0.5$ compound overestimates by $\sim 20\%$ the bromine content compared with the structural analysis data. Taking this fact into account, we found that the real bromide content in the crystal studied in the preceding papers^{1,2} is 0.4 ± 0.1 , not 0.5, as was claimed there. The resistivity R was studied in the same crystals along the a direction.

Figure 1 shows $\log R$ -vs- $1/T$ curves for all three samples. For the pure samples 1 and 2, the R -vs- T curves show a slight increase of R upon cooling to nearly 50 K, followed by accelerated increase of an activation type with an activation energy E_a of

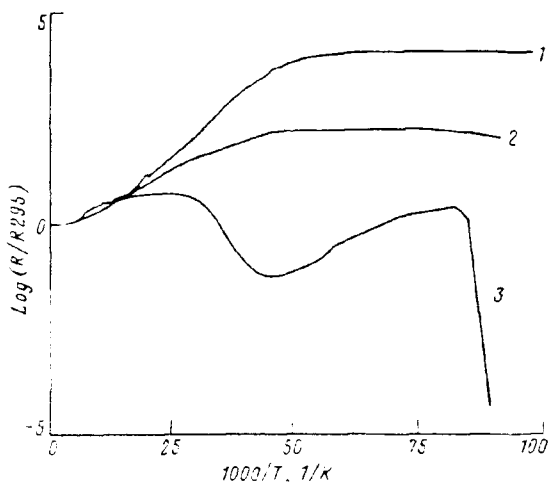


FIG. 1. R -vs- T dependences for $\text{ET}_2\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}_{1-x}\text{Br}_x$ crystals (1, 2— $x=0$; 3— $x=0.4$) at ambient pressure along the a axis.

200-250 K. Both E_a and the width of the interval in which it is observed depend on the sample perfection. At lower temperatures, the curves flatten out at nearly 30 K and even show a decrease in R on further cooling (sample 1). In sample 2, a trace of the resistive superconducting transition (SC) is seen at 12.5 K. The curve for sample 3 shows slight increase in R on cooling from 300 to 40 K of the same type as in the pure samples, a hump at 40 K, a large decrease to 25 K, an increase on further cooling below 25 K, and a SC transition at 12.5 K.

The S -vs- T behavior is shown in Fig. 2. At room temperature for all three samples S is positive for the a direction and negative for the c direction. For the a axis S_a is slightly temperature dependent at $T > 100$ K, changes sign at 50–70 K depending on the sample, and decreases sharply in magnitude starting at approximately 35 K. At nearly 20 K, S_a becomes smaller than an experimentally resolved value (on the order of $0.5 \mu\text{V}/\text{K}$) at this temperature for the two pure samples 1 and 2. It becomes positive for sample 3 ($\approx 1.5 \mu\text{V}/\text{K}$), but decreases with further cooling and becomes zero at the SC transition near 12 K. For the c direction, S_c is negative and increases in magnitude with cooling in 300 to 40-K intervals approximately as $1/T$. Below 35 K, the S_c decreases sharply and goes to zero in pure samples 1 and 2 below 20 K, but remains negative ($\approx -1 \mu\text{V}/\text{K}$) in sample 3 until the SC transition.

As a starting point of the discussion we recall the calculated band structure of the chloride and bromide salts.⁵ According to the calculation, the Fermi surface (FS) of the compounds is multiply connected and consists of two parts. A closed hole part is centered at the x point and the warped open sheets separate electron states which are located along the MZ line of the Brillouin zone (Fig. 3). Evidently, S_a and S_c are determined by carriers of both types (the electron and hole contributions are dominant in the c and a directions, respectively) in accordance with the experiment. However, contrary to this calculation, transport is of an activation type, and below a definite temperature S_a becomes negative, showing a decrease in the hole contribution, probably because of the hole density decrease. Worth noting is that electrons are also captured as a result of cooling, as can be

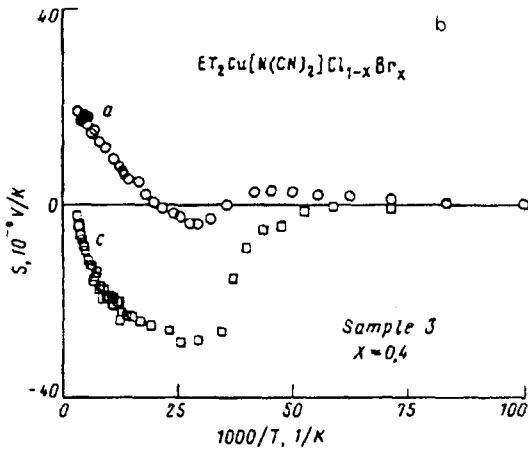
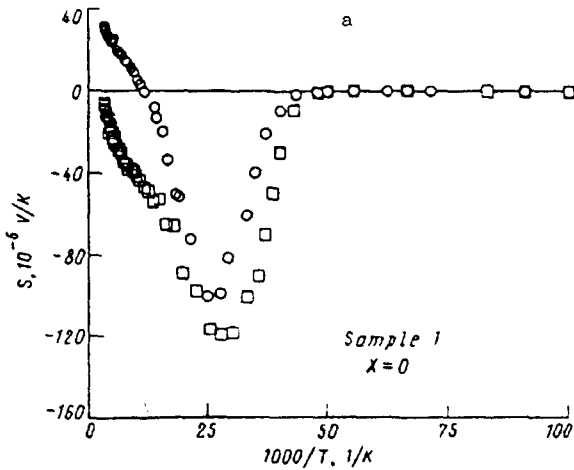


FIG. 2. Thermopower-vs-temperature curves for a and c directions in the highly conducting plane of $\text{ET}_2\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}_{1-x}\text{Br}_x$ samples 1 and 3. Sample numbers are the same as in Fig. 1.

seen from the typical $S_c \sim 1/T$ dependence for the c axis, where the electron contribution is dominating.

The most prominent feature of the S -vs- T curves is the sharp drop in the value of S_a and S_c , starting at approximately 35 K. First of all, it should be noted that the behavior of S_a at low temperatures depends strongly on the sample quality. Its minimum value is very sensitive to the bromine content¹ and sample perfection, while the position of the peak moves to lower temperatures for the less-perfect samples. The same is true for S_c ; however, its magnitude and the minimum position are less sensitive to imperfections.

Three points on the S -vs- T behavior should be specially noted.

1. $S(T)$ becomes zero below 20 K in both in-plane directions a and c , although the electron and hole contributions here are quite different. Therefore, the behavior may not be attributable to a compensation.

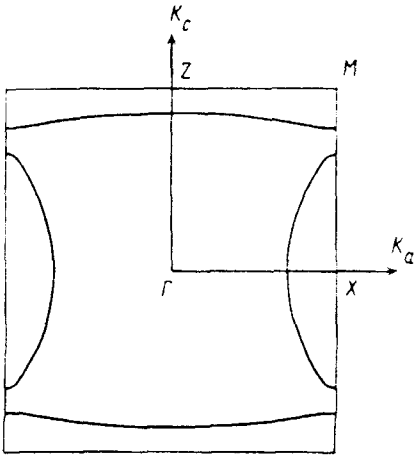


FIG. 3. Schematic diagram of the Fermi surface of salt.⁵

2. S_a and S_c are zero in samples of different quality with different values of the thermopower before the drop, i.e., in the samples with very different defect concentrations. Therefore, the behavior is not related to the change in the conductivity mechanism, say, from the band to the impurity or the hopping ones. If the change were the case, the decrease of the S in more disordered samples should begin at higher temperatures, i.e., it would not be observed.

3. Although it is difficult to ascertain that $S \equiv 0$ below 20 K, due to the calibration problem, it is important to note that in sample 2, with the SC inclusions, there is no drop of the S at the 12-K SC transition, indicating that S is already zero.

These results, taken collectively, allow us to state that zero S value is an intrinsic property of a phase, which is realized in the salt below 20 K, and the process of its vanishing starts at nearly 35 K.

In general, zero thermopower value, if it is not the result of compensation, suggests collective carrier transport without entropy.⁶ Three possibilities have been mentioned in the literature to obtain *intrinsically* zero S value.⁶ The most common one is the presence of SC inclusions in the samples. In the temperature interval of interest this possibility may be ruled out by ESR¹ and by the results of a magnetization study.³ The second study involves transport in the quantum Hall effect regime. In our opinion, there is no reason to use the model here. The third possibility is a sliding charge or spin density wave (CDW or SDW) transport. Evidently, this case is of special interest in view of the Argonne's group claim⁷ of the SDW formation at nearly 45 K. However, account must be taken of the fact that due to a special form of the FS in this system, with the presence of a one-dimensional (1D) electron sheet, where the SDW may be formed, and a 2D hole cylinder which is not influenced by the SDW formation, two carrier types should be considered. The first one participates in the conductivity as the SDW condensate, while the second one participates as single particle excitations. To obtain a zero S value in the compound, the conductivity of the sliding SDW should be considerably larger than that of the single particles. This can be obtained if the SDW is not pinned. In this case its conductivity should be very large,⁸ as would be evident in the R -vs- T dependences.

However, as is evident from these dependences (Fig. 1), the probable SDW formation at about 45 K causes the conductivity to decrease and is not clearly revealed on the S -vs- T curve. On the other hand, if the SDW conductivity is not large, but the carriers from the FS cylinders are trapped and do not participate in the transport, then upon cooling the single-particle contribution to the conductivity becomes unimportant, and at nearly the same temperatures on the S -vs- T and the R -vs- T curves the SDW contribution should become dominant. This is likely to be the case for sample 2; notice the shelf on the R -vs- T dependence below 30 K. However, the temperature of this change in the conductivity mechanism would then depend on the sample (i.e., the R value), which is unlikely to be the case. Moreover, it is unclear, why the SDW should be isotropic in the conduction plane. It is unlikely therefore, that the SDW transport could explain the results.

The proximity of the zero S state to the magnetic transition temperature³ makes it attractive to relate the decrease of S to the spin entropy quenching at the transition. The contribution of spin entropy can add a term on the order of $60 \mu\text{V/K}$ (Ref. 6). However, the drop for the c direction in samples 1 and 2 is even larger than this value. The drop may be larger if the magnetic order leads to some electronic spectrum transformations, as in a magnetic semiconductor CdCr_2Se_4 , where a considerable decrease of S in the vicinity of the magnetic transition was observed⁹ especially for a p -type doped material. Calculations of the Seebeck effect in this case in a magnetic polaron model have shown that S can change markedly at the magnetic transition.¹⁰ The drop of the thermopower in the salts may thus be related to the magnetic transition in the salts. It is known that magnetic correlations exist well above the magnetic transition.¹¹ Therefore, the decrease may start by itself well above the transition, which is the case. In addition, the width of the temperature interval in which the correlations exist should decrease in the samples with a higher carrier density, which is the case for sample 3 with $x=0.4$. However, it is not clear, why there should exist zero S state.

We would like to discuss now this behavior. In our opinion, it may be due to the aforementioned peculiar character of the electron spectrum; specifically, the presence of the 1D and 2D features. In conventional 1D compounds, where the FS consists of two plane sheets only, the SDW is formed due to a decrease in electron energy. In the simple case of the half-filled band, this leads to the antiferromagnetic spin order. The situation is different in the compounds under study. Because of the presence of the closed hole part of the FS, there appears an additional contribution to the electron energy which is attributable to the conduction band splitting in the magnetic field. In antiferromagnetic materials this leads to the formation of the ferrons—ferromagnetically ordered regions near the free carriers.¹¹ Because of the local character of this particle, this effect destroys the SDW magnetic order. However, it is possible to restore both energy gains if the SDW acquires new magnetic order. The typical features of this magnetic order should be the $2k_f$ wave vector of the SDW and the magnetic order of the weak ferromagnetic type, observed in the salt.³ However, the SDW order imposes some limitations on the magnetic polaron movement in this case and it becomes collective in the origin. Specifically, this ordered magnetic polaron formation may account for the zero S value observed in the experiments.

This picture should be very sensitive to the hole density. When it is increased, the antiferromagnetic spin order in the SDW state may be transformed into a more complex

magnetic order, which is likely to be the case for the $\text{ET}_2\text{MHg}(\text{SCN})_4$ compounds.^{1,2} Upon further increase, the SDW state may become unstable.

To test the model, further investigations, especially of the R and S behavior in the magnetic field, are needed.

The research described in this publication was made possible, in part, by grant No. P2U-0137-0925 from the International Science Foundation. The authors thank Prof. I. F. Schegolev for stimulating discussions in the process of this work and for the critical reading of the manuscript.

¹V. A. Bondarenko, Yu. V. Sushko, V. I. Barchuk *et al.*, *Synth. Metals* **55–57**, 2386 (1993).

²V. A. Bondarenko, M. A. Tanatar, V. S. Yefanov *et al.*, *Synth. Metals* **55–57**, 2391 (1993).

³U. Welp, S. Fleshler, W. K. Kwok *et al.*, *Phys. Rev. Lett.* **69**, 840 (1992).

⁴Yu. V. Sushko, H. Ito, T. Ishiguro *et al.*, *Solid State Commun.* **87**, 997 (1993).

⁵U. U. Geiser, A. J. Shultz, H. H. Wang *et al.*, *Physica C* **17**, 475 (1991).

⁶P. M. Chaikin, in *Organic Superconductivity*, ed. V. Z. Kresin and W. A. Little, Plenum Press, New York, 1990, p. 101.

⁷H. H. Wang *et al.*, *Mater. Res. Soc. Symp. Proc.* **247**, 471 (1992).

⁸L. P. Gor'kov, *Usp. Fiz. Nauk.* **144**, 381 (1984).

⁹H. W. Lehman, *Phys. Rev.* **163**, 488 (1967).

¹⁰A. Yanase, *Solid State Commun.* **9**, 2111 (1971).

¹¹E. L. Nagaev, *Usp. Fiz. Nauk* **117**, 437 (1975).

¹²M. V. Kartsovnik, A. E. Kovalcv, V. N. Laukhin, and S. I. Pesotskii, *J. Phys. I. France* **2**, 223 (1992).

Published in English in the original Russian journal. Reproduced here with stylistic changes by the Translations Editor.