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Anomalous Behavior of the Thermoelectric Power in the Vicinity of the Superconducting Transition in the Organic Superconductors $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ and $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br

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Abstract. — The in-plane thermoelectric power (TEP) of the layered organic superconductors $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ and $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br has been studied in the vicinity of the superconducting transition under magnetic field. Below the transition temperature, an anomalous non-monotonic behavior of the TEP is found in the $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ salt: instead of a gradual monotonic decrease, the TEP shows a prominent sign-change before vanishing. Similar, although less pronounced features have been found in the other compound. The change in sign of the TEP is explained in terms of the two-fluid counterflow model, assuming a predominant role of one of the two anisotropic bands (namely, the electron-like one) in the superconducting pairing.

1. Introduction

Layered organic superconductors (OSC’s) of the $\kappa$-(BEDT-TTF)$_2$X family with anions $X = $ Cu(NCS)$_2$ and Cu[N(CN)$_2$]Br synthesized on the basis of the bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) organic donor molecule with the superconducting transition temperatures $T_c \sim 10$-11 K manifest a number of similarities with high-temperature cuprates (HTSC’s). Like the HTSC’s, due to the layered structure and a small coherence length the role of the flux flow effects in the transport properties of the OSC’s cannot be neglected [1]. In spite of the high two-dimensionality of these superconductors, the anisotropy of the electronic bands in the conducting plane is of great importance in transport properties and superconducting pairing.

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For instance, the normal-state thermoelectric power (TEP) of both salts has different signs with respect to crystallographic directions in the conducting plane due to the anisotropic two-band nature of the conducting system [2, 3]; their Fermi surfaces (FS) consist of open electron-like sheets and a closed hole-like cylinder. The presence of two types of carriers in these OSC's raises a fundamental question about their relative contribution into the superconducting pairing.

Normally, the metallic thermoelectric power is associated with the diffusion of the normal carriers under a temperature gradient. In the mixed state, (below the superconducting transition temperature under magnetic fields $H > H_{c1}$, where $H_{c1}$ is the first critical field) the TEP is ascribed to the flux motion [4]. The mixed state TEP in the different HTSC's has been studied in detail recently [5] and is described by the two-fluid counterflow model proposed in reference [4] without detail consideration of the FS peculiarities. On the other hand, the mixed state TEP data are lacking for the organic superconductors, in which the FS is known very well due to numerous magnetooscillation studies.

In this paper we report the study of the TEP of the organic superconductors, $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ and $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, in the vicinity of $T_c$ at different magnetic fields applied perpendicular and parallel to the conducting planes.

2. Experimental

Several high quality single crystals of $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ and $\kappa$-(BEDT-TTF)$_2$Cu [N(CN)$_2$]Br salt were used. By means of the X-ray analysis of these samples, the main crystallographic axes have been determined; no twins or other defects were detected. The longitudinal thermoelectric voltage, $V_x$, was measured in the $x$-direction using a steady-state method with a temperature gradient in the same direction. The temperature gradient was applied using a small heater which was in a good thermal contact with one crystal edge via a small amount of Apiezon vacuum grease. The other sample edge was anchored with a copper block, whose temperature was controlled independently. The temperature difference was determined in zero magnetic field using a Au/Fe-chromel differential thermocouple mounted in the vicinity of the sample sides. Experiments in the magnetic fields were carried out with a constant temperature difference in the sample, $\Delta T \sim 0.2$ K, produced by a d.c. current, which corresponds to the heat power $\sim 10^{-4}$ W. The thermoelectric power (TEP) was calculated as $S = -V_x/\Delta T$. The experiments were carried out in magnetic fields up to 2 T, perpendicular or parallel to the 2D (highly-conducting) planes. We evaluated the wire contribution in the thermoelectric voltage versus temperature and subtracted it from the experimental data. The dependence of this contribution on magnetic field up to 2 T was negligibly small.

3. Results

The in-plane TEP of the $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ single crystal n° 1 in the $b$- and the $c$-crystallographic directions at different magnetic fields perpendicular to the $b$-$c$ plane is shown in Figures 1a and b, respectively. The similar results on the in-plane negative TEP obtained on a different crystal n° 2 are shown in Figure 2. The in-plane TEP of the crystal n° 1 along the $b$-axis at several magnetic fields parallel to the conducting plane is shown in Figure 3a. The anomalous temperature dependence including the change in sign of the negative (electron-like) TEP, presented in Figures 1a, 2, and 3a does not depend on the orientation of the magnetic field. This sign change behavior was reproduced by use of different experimental setups (at Kyoto University (Fig. 1) and Institute of Solid State Physics (Fig. 2)) on different $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ crystals. The TEP is very sensitive to temperature under rather low magnetic field, following the field dependence of the superconducting resistive transition.
Fig. 1. — a) In-plane negative thermoelectric power (TEP) in the $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ (crystal no. 1) along the b-axis versus $T$ at different magnetic fields. b) Positive TEP in the $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ along the c-axis versus $T$. c) In-plane resistance of the $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ salt versus $T$. Magnetic field (a) 0; (b) 0.05 T; (c) 0.1 T; (d) 0.2 T; (e) 0.5 T; (f) 1 T; (g) 2 T is perpendicular to the conducting $bc$-plane.
Fig. 1. — (Continued)

Fig. 2. — In-plane negative thermoelectric power (TEP) in the κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (crystal n° 2) along the $b$-axis versus $T$ at different magnetic fields (a) 0; b) 0.05 T; c) 0.1 T; d) 0.2 T; e) 0.5 T; f) 1 T; g) 2 T).
Fig. 3. — a) Negative thermoelectric power (TEP) in the $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ (crystal n° 1) along the $b$-axis versus $T$ at different magnetic fields (a) 0; b) 0.1 T; c) 0.5 T; d) 1 T; e) 2 T) applied parallel to the conducting plane. The curves are offset for clarity. Distance between ticks corresponds to $5 \times 10^{-6}$ V/K. The dashed lines show the zero voltage level. The vertical mark corresponds to the TEP of 5 $\mu$V/K. b) In-plane resistance versus $T$ at magnetic fields (a) 0; d) 1 T; e) 2 T) parallel to the conducting plane.
Fig. 4. — a) Negative thermoelectric power (TEP) in the \(\kappa\)-(BEDT-TTF)\(_2\)Cu[N(CN)]\(_2\)Br (crystal n° 1) along the c-axis at different magnetic fields (a) 0; b) 0.1 T; c) 0.5 T; d) 1 T; e) 2 T) applied parallel to the conducting plane. The TEP sign-anomaly below \(T_c\) is ascribed to the low quality of the crystal.

The temperature broadening of the TEP transition under magnetic field corresponds to that for the resistive transition presented as Figures 1c and 3b. These facts indicate the flux flow origin of the TEP below \(T_c\). Besides the main peak giving the sign-change, a smaller shoulder has been detected in the TEP in the high temperature side for low field. This shoulder is very sensitive to the remanent field and disappeared in the applied magnetic field higher than \(\sim 0.05\) T. The peak in the TEP and the sign anomaly of the negative TEP in the mixed state were always observed in the \(\kappa\)-(BEDT-TTF)\(_2\)Cu(NCS)\(_2\) crystals.

An anomalous behavior similar to the \(\kappa\)-(BEDT-TTF)\(_2\)Cu(NCS)\(_2\), although less pronounced, has been generally observed in the \(\kappa\)-(BEDT-TTF)\(_2\)Cu[N(CN)]\(_2\)Br crystal n° 1 (see Fig. 4). The good quality \(\kappa\)-(BEDT-TTF)\(_2\)Cu[N(CN)]\(_2\)Br crystal n° 2 exhibited no sign-change anomaly along the c-axis (Fig. 5a). The sign and the value of the normal state TEP in the different crystallographic directions are in agreement with reference [2].

4. Discussion

In general, the sign change of the TEP comes from the different temperature dependencies of the normal state TEP contributions. However, the present sign-anomaly is ascribable to the superconductivity of these compounds. In order to understand the origin of the anomalous behavior of the mixed state TEP in the two-band organic superconductors, we apply the two-fluid counterflow model to an anisotropic two-band superconductor. The counterflow scheme is shown in Figure 6. The thermal diffusion normal current of the unbound quasiparticles due to both hole- and electron-like bands, \(J_{nh} = -L_h \cdot \nabla T\), and \(J_{ne} = L_e \cdot \nabla T\), respectively, is
Fig. 5. — a) In-plane negative thermoelectric power (TEP) in the $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br (crystal no 2) along the c-axis versus $T$ at different magnetic fields. b) In-plane positive TEP in the $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br along the a-axis versus $T$. c) In-plane resistance of the $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br salt versus $T$. Magnetic field (a) 0; (b) 0.05 T; (c) 0.1 T; (d) 0.2 T; (e) 0.5 T; (f) 1 T; (g) 2 T) is perpendicular to the conducting a-c-plane.
Fig. 5. — (Continued)

Fig. 6. — Effective forces acting on a magnetic flux line in the counterflow model. a) The case of the temperature gradient applied in the e-direction. \( v_{ne,ah} \) is drift velocity and \( J_{ne,ah,} \) is normal current of the electron- and hole-like normal carriers, respectively. \( J_s = -J_{ne,ah} \) is a counterflowing supercurrent. \( F_T = J_s \times \Phi \) is the driving force, which is opposite in the case of the hole- and electron-like carriers transport, correspondingly.

compensated by a counterflowing supercurrent, \( J_s = -(J_{nh} + J_{ne}) = (L_{h} - L_{e}) \cdot \nabla T \), where \( L_{h,e} = S_{h,e} \cdot \sigma_{h,e} \) is the thermoelectric coefficient, \( S_{h,e} \) is the thermoelectric power and \( \sigma_{h,e} \) is the electrical conductivity for the hole- and electron-like band, denoted by index h or e, respectively. This supercurrent consists of two terms: the first term is due to the thermal diffusion of holes and the second term is due to electrons. Generally, each of the terms depends on temperature at a constant magnetic field. The expression for the expected longitudinal electric field component, \( E_z \), can be derived from the force-balance equation. If the pinning is neglected, it can be written as,

\[
J_s \times \Phi_0 + \eta u = 0,
\]
where $\Phi_0$ is a vector representing the flux, $\Phi_0 = \hbar c/2e$ is flux quantum, $\eta = \Phi_0 B/\rho_{\eta}(T, H)$ is the viscosity coefficient, $B$ is the magnetic induction in the sample, $\mathbf{u}$ is the vortex velocity, and $\rho_{\eta}(T, H)$ is the flux flow resistivity. Using the relation $\mathbf{E} = \mathbf{B} \times \mathbf{u}$, we obtain the expression for the TEP in the mixed state as,

$$S(T, H) = \frac{E_z}{\nabla T} = \rho_{\eta}(T, H)[L_h(T) - L_e(T)].$$  (2)

The TEP is determined by the superposition of the two band contributions which are, in anisotropic case, dependent on the mutual orientation of the temperature gradient and crystal axes. The general expression for the TEP in the two-band model is given by $S = (S_1 \cdot \sigma_1 + S_2 \cdot \sigma_2)/(\sigma_1 + \sigma_2)$ [6], where $S_1$ and $\sigma_1$ are the TEP and the conductivity of the first band respectively and $S_2$ and $\sigma_2$ are those for the second band. There are two temperature dependent terms in this expression, which are responsible for the observed anomaly. The resulting TEP depends on the value of $L_h$, $L_e$ as well as on $\rho_{\eta}$. If both bands have the same temperature dependence of the carrier mobility and equally contribute to the superconducting pairing, then it is natural to propose the same temperature dependencies of $L_h$, $L_e$ in the superconductivity transition region. As a result, we get the conventional monotonic decrease of the TEP from its normal state value to zero as a temperature decreases, like in the one-band superconductor.

A different result will be obtained, if the two bands play different roles in superconducting pairing. Let us suppose that one band is intrinsically normal, while the other one is superconducting. In this case one term in equation (2) decreases very rapidly at the superconducting transition, whereas the other term changes only slightly in the same temperature interval. This may lead to the sign change of the TEP. Assuming that only the electron-like band is superconducting, our experimental results can be qualitatively explained in this way. The negative TEP is due to the electron contribution, $-L_e(T)$, which, as is shown in Figure 1a, decreases very rapidly in the vicinity of the superconducting transition. At a definite temperature the term $L_e(T)$ becomes smaller than the hole contribution $L_h(T)$ which is less temperature dependent; this results in the sign change of the total TEP determined by equation (2). The behavior of the positive TEP (along the c-axis), with a maximum below $T_c$, is explained in the same way. In other words, the negative TEP changes its sign to the positive below $T_c$ due to the change of the direction of the flux motion, which is governed by the counterflow supercurrent (see Figs. 6a, b). In the vicinity of $T_c$, the supercurrent in the frame of the counterflow model is controlled by the thermal diffusion of both the electron- and hole-like normal carriers respectively in the e- and h-crystal directions. As the temperature decreases, the normal current of the carriers responsible for the superconductivity decreases rapidly and the supercurrent changes the direction due to the dominant role of the other sign carriers, which are still normal. Thus, both negative and positive TEP behaviors can be explained taking into account the anisotropic nature of the conducting system in these compounds and assuming a predominant role of the electron-like band in the superconducting pairing. This conclusion is in an agreement with recent Nernst effect data [7]. In reference [8] the superconductivity in the organic superconductors is proposed to be based on the hole-like carriers. Their conclusion is based on the agreement between superconducting pair concentration estimated via the muon-spin-relaxation London penetration depth with the hole concentration. However, we should note that the conclusion is based on the numerical estimation of the carrier number from simple band calculations, where uncertainties can not be ruled out.

The sign-anomaly of the TEP was generally observed in the both studied compounds. The smaller magnitude of the sign-change anomaly in the $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br salt can be understood taking into account the difference in the in-plane anisotropy of the conducting bands. Indeed, recent magnetoresistance studies [9] have revealed the FS cylinder to have a
much smaller cross-section in this compound than in the \( \kappa-(\text{BEDT-TTF})_2\text{Cu(NCS)}_2 \) salt. On the other hand, the presence of the magnetic breakdown oscillations evidences the FS consisting of a pair of slightly corrugated open sheets and a cylinder strongly elongated in the direction perpendicular to the sheets, as argued in reference [10]. Therefore, both corresponding bands can be regarded as highly anisotropic and even quasi-one-dimensional from the viewpoint of the transport contribution. In this situation, if one applies the temperature gradient exactly perpendicular to the electron-like sheet, the contribution of the hole-like band will be negligible and no sign change of the TEP will be observed below \( T_c \). This is likely the case shown in Figure 5a. To obtain the sign change anomaly, one has to somewhat tilt the gradient direction from the crystallographic axis (and/or to take the low quality sample with mosaic structure and defects, the case of Fig. 4). Of course, the above consideration is somewhat oversimplified, and does not pretend to quantitatively describe the effect. From this consideration a definite conclusion can be made that electron-like band plays a predominant role in the superconducting pairing, although this does not mean that hole-like band gives absolutely no contribution to the superconductivity.

5. Conclusions

We have measured TEP in the two-band organic superconductors \( \kappa-(\text{BEDT-TTF})_2\text{Cu(NCS)}_2 \) and \( \kappa-(\text{BEDT-TTF})_2\text{Cu[N(CN)}_2\text{]Br} \) in the vicinity of the critical temperature, at different magnetic fields. An anomalous behavior with the sign reversal has been found for the negative TEP and attributed to the dominant role of the electron-like band into the superconducting pairing.

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