ANISOTROPIC THERMOPOWER OF THE ORGANIC METAL, β-(BEDT-TTF)$_2$I$_3$

K. Mortensen*

Physics Department, Risø National Laboratory, DK-4000 Roskilde, Denmark

and

J.M. Williams[†] and H.H. Wang

Chemistry and Material Science and Technology Division, Argonne National Laboratory, Argonne,
Illinois 60439, USA

The thermopower of the ambient pressure organic superconductor β-(BEDT-TTF)$_2$I$_3$ has been studied. Measurements performed on, respectively, crystals of needle formed morphology and on flake-like crystals with hexagon shape showed equal thermopower results. S was measured along the a-axis as well as along the b'-axis. Marked anisotropy is observed in the entire temperature region studied. The temperature dependence, as represented by dS/dT, is, however, nearly isotropic. On the basis of an analysis of anisotropic thermopower we attribute the isotropic part of S to a term depending on the band-properties and the anisotropic part of S to the scattering mechanism. The analysis yields transfer integrals of the order of 0.12 eV along both the a- and b'-axes.

1. INTRODUCTION

RECENTLY, the β-phase of (BEDT-TTF)$_2$I$_3$ (or "(ET)$_2$-I$_3$") derived from bis-ethylenedithio-tetrafulvalene [1] has been shown to exhibit novel physical properties including ambient pressure superconductivity [2–4] and unusual superstructure formation [4, 5]. At ambient temperature the salt is triclinic with space-group $P\bar{1}$ [5, 6]. The structure has a two-dimensional "corrugated sheet" network of relatively short S–S interaction distances in the ab-plane [4, 5]. This indicates that β-(ET)$_2$I$_3$ is likely a two- or quasi-two-dimensional conductor.

In this paper we present thermopower results, derived from studies made in two perpendicular directions within the conducting ab-plane of single crystals of β-(ET)$_2$I$_3$ [7, 8]. The thermopower exhibits unusual characteristics by being markedly anisotropic, even with opposite sign of the two components in most of the temperature region studied, and still the relative T dependence, as determined by dS/dT, is nearly exactly isotropic.

2. EXPERIMENTAL

Flake-like crystals of the β-phase of (ET)$_2$I$_3$ crystals were grown by electrochemical oxidation of ET [Fig. 1(a)] at a constant temperature of 23.4°C in the presence of (n–Bu$_4$N)I$_3$ as the supporting electrolyte and 1,1,2-trichloroethane (TCE) as the solvent. The characteristic morphology is of a clearly distorted hexagon as is shown in Fig. 1(b). Typical dimensions within the ab-plane were 0.5 mm and the thickness of the crystals was of the order of 0.02 mm. Crystals from the same batch has been shown to superconducting below 1.4–1.5 K [3, 5]. Needle-like crystals of β-(ET)$_2$I$_3$ [Fig. 1(b)] were obtained using benzonitrile as solvent. Typical a-axis lengths were 1 mm and dimensions along b^* and c^* were 0.1 mm and 0.02 mm, respectively.

The thermopower, S, was measured by use of the conventional slow a.c.-technique. S was measured against that of pure gold and the reference thermocouples were of the chromel–Au, 0.07 at.% Fe type. All data were corrected for the thermopower of gold. Typical temperature gradients were 0.2 K.

The measured electrical potential, ΔV, was parallel to the applied thermal gradient, ΔT, as two 25 μm diam. gold wires provided both the electrical and the thermal contacts to the sample. Aquadag was used for

(a)

BEDT-TTF or ET

(b)   **(BEDT-TTF)₂I₃**

Fig. 1. (a) The BEDT-TTF molecule. (b) Morphology of the single crystal samples studied.

Fig. 2. Thermopower along the a-axis and along the b'-axis vs temperature, for β-(BEDT-TTF)₂I₃. Open symbols are results obtained on needle-shaped crystals. Closed symbols are results obtained on flake-like distorted hexagon crystals.

contacting and resulted in contact resistances of the order of $10\,\Omega$ (Silver paint contacts caused highly resistive connections due to the Ag—I chemical reaction).

The thermopower of the needle-shaped crystals was measured along the needle axis, which is the crystallographic a-axis [Fig. 1(b)]. On the flake-like hexagon-shaped crystals, S was measured along orientations close to both the a-axis and the transverse $b' = a \times c^*$-axes. X-ray diffraction techniques were used to determine the two orientations. The measured values $S_a = (\Delta V/\Delta T)_a$ and $S_b = (\Delta V/\Delta T)_{b'}$ are, due to the anisotropy of the crystal, really heat resistivity and orientational weighted sums of the thermopower components along the principal orientations. In accordance with the other approaches needed for the analysis made below, and the accuracy of the determined orientations, we will though neglect this difficulty and attribute S_a and S_b to principal thermopower components.

3. RESULTS AND DISCUSSION

The experimental thermopower results of β-(ET)₂I₃ are shown in Fig. 2. It appears that the stacking axis parameter, S_a, of the two kinds of morphologies are equal except for a minor deviation in a region below 100 K, thereby suggesting that the electronic properties are unaffected of the factors which are decisive in determination of crystal morphology. The thermopower tensor, as represented by S_a and S_b, is, moreover, seen
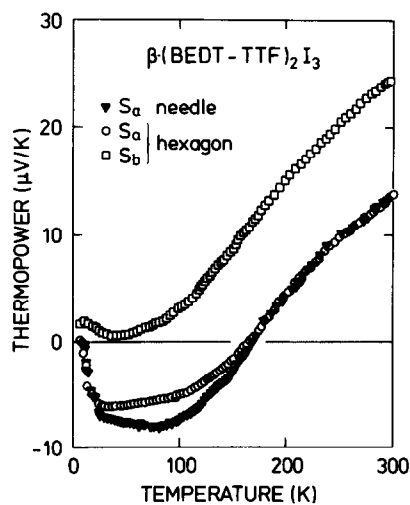
to be distinctly anisotropic in the entire T-region studied, i.e. 7–300 K. Below approximately 170 K the two components even have opposite sign. Still, however, the slope dS/dT is not only qualitatively similar for the two components in the whole T-region but also in magnitude nearly equal except for the lowest T.

At high temperature both components of the thermopower show linear S vs T relationships with positive slopes and negative intersects. Close to 200 K there are, though, small but distinct changes in slope of S vs T. At $T \simeq 130$ K a gradual cross-over in the characteristics of $S(T)$ are observed, as the slope of both components of $S(T)$ decreases. At $T \simeq 30$ K a relatively sharp change in sign of dS/dT is observed, most dramatically seen in S_b, but in S_a it is also significant.

3.1. High temperature region

The overall similarity between the two components of dS/dT suggests that it is physically meaningful to separate the ab-plane thermopower into

$$S(T) = S_1(T) + S_0, \qquad (1)$$

where S_1 is T-dependent and nearly isotropic within the plane and S_0 is anisotropic and basically T-independent except, perhaps, for the lowest temperatures. S_0 is attributed to values which at high tempratures make S_1 simply proportional to T, except for the slight changes close to 200 K.

In an attempt to discuss the high-T thermopower of β-(ET)₂I₃, we will use the general expression for the thermopower along an axis α, as given by the Mott's formula [9]

$$S_\alpha = -\frac{\pi^2}{3} \frac{k_B^2 T}{e} \sigma_\alpha^{-1} \frac{d\sigma_\alpha}{dE}\bigg|_{E_F}, \qquad (2)$$

where $\sigma_\alpha(E)$ is the electrical conductivity corresponding to the surface of energy E:

$$\sigma_\alpha(E) = \frac{e^2}{4\pi^3 \hbar^2} \int_E \left(\frac{dE}{\delta\kappa_\alpha}\right)^2 \frac{\tau(k)}{|\nabla E|} \, dA. \qquad (3)$$

The evaluation of S from equations (2) and (3) generally requires detailed knowledge on both the Fermi surface and $\tau(k)$. The expression can only, in the case of spherical Fermi surface and isotropic τ, i.e. $\sigma_\alpha \propto |\nabla E| \cdot \tau \cdot (N(E)-|\nabla E|)$, be given in the most commonly used form, written as a sum of a term depending on the band properties and a term depending on the scattering mechanism:

$$S_\alpha = -\frac{\pi^2}{3} \frac{k_B^2 T}{e} \left\{ \frac{1}{N(\nabla E)^2} \frac{d(N(\nabla E)^2)}{dE} + \frac{1}{\tau}\frac{d\tau}{dE} \right\}. \qquad (4)$$

The distinct anisotropic S measured on β-(ET)$_2$I$_3$ shows, however, that these conditions are at least not both approximately fulfilled, and accordingly equation 4 cannot be used for a discussion. It is, though, possible also in the more general case to express S_α in a way which gives some insight into, respectively, band-properties and $\tau(k)$. We will follow the basic procedure of Jan [10]. In order to calculate $\sigma_\alpha^{-1} d\sigma_\alpha/dE$, we define

$$\sigma_0(E) = \int_E \sigma(k)dA, \qquad (5)$$

with

$$\sigma(k) = (dE/dk_\alpha)^2 \cdot \tau(k)/|\nabla E|. \qquad (6)$$

We then have

$$\frac{d\sigma_\alpha}{dE} = \frac{1}{dE}\left[\int_{E+dE} \sigma(k)dA - \int_E \sigma(k)dA \right]$$

$$= \frac{1}{dE} \int [\sigma(k+dk)dA' - \sigma(k)dA], \qquad (7)$$

where

$$\sigma(k+dk) = \sigma(k) + \nabla\sigma \cdot dk, \quad dk = \nabla E \cdot dE/|\nabla E|^2,$$
$$\qquad (8)$$

and

$$dA' = dA \cdot \prod_{i=1}^{D-1}\left(1 + \frac{|dk|}{\rho_i}\right) \equiv dA \cdot \left(1 + \frac{|dk|}{\rho}\right), \qquad (9)$$

where ρ_i is the principal radii of curvature and D is the dimension of the electron gas [11]. ρ is defined by equation (9). Substituting equations (8) and (9) into equation (7) yields

$$\frac{d\sigma_0}{dE} = \int_E \left[\frac{\sigma(k)}{|\nabla E|}\frac{1}{\rho} + \frac{\nabla\sigma \cdot \nabla E}{|\nabla E|^2} \right]dA, \qquad (10)$$

ρ can be expressed in the form of k derivatives of E [12].

$$\frac{1}{\rho} = \frac{\nabla^2 E}{|\nabla E|} - \frac{1}{|\nabla E|^3} \cdot \sum_{i,j=1}^{D} \frac{d^2 E}{dk_i dk_j}\frac{dE}{dk_i}\frac{dE}{dk_j}. \qquad (11)$$

Using this expression for $1/\rho$ in equations (2) and (10) and calculating $\nabla\sigma \cdot \nabla E$ then gives a general form of the thermopower along the α-axis. It is useful to write the resulting S_α as a sum of four terms:

$$S_\alpha = S_{B1} + S_{B2} + S_{B3} + S_{SC}. \qquad (12)$$

In order to simplify the expressions for the individual terms of equation (12), we define

$$v_i \equiv \frac{dE}{dk_i}; \quad v \equiv |\nabla E| = [\Sigma v_i^2]^{1/2}, \qquad (13)$$

$$\omega_{ij} \equiv \frac{d^2 E}{dk_i dk_j}; \quad \omega_i \equiv \omega_{ii}; \quad \omega \equiv \nabla^2 E = \Sigma\omega_i, \qquad (14)$$

(i.e. the velocities are $v_i = v_i/\hbar$ and the band masses are $m_{ij}^{-1} = \omega_{ij}/\hbar^2$). This leads to

$$S_{B1} = -\frac{\pi^2}{3} \frac{k_B^2 T}{e} \int_{E_F} \frac{v_\alpha^2}{v^3}\omega\tau dA \Big/ \int_{E_F} \frac{v_\alpha^2}{v}\tau dA, \qquad (15a)$$

$$S_{B2} = -\frac{\pi^2}{3} \frac{k_B^2 T}{e} \int_{E_F} \frac{2v_\alpha^2}{v^5}$$

$$\times \Sigma v_i^2(\omega_\alpha^2 - \omega_i^2)\tau dA \Big/ \int_{E_F} \frac{v_\alpha^2}{v}\tau dA, \qquad (15b)$$

$$S_{B3} = +\frac{\pi^2}{3} \frac{k_B^2 T}{e} \int_{E_F} \frac{v_\alpha^2}{v^5}$$

$$\times \Sigma\omega_{ij}v_i v_j\tau dA \Big/ \int_{E_F} \frac{v_\alpha^2}{v}\tau dA, \qquad (15c)$$

$$S_{SC} = -\frac{\pi^2}{3} \frac{k_B^2 T}{e} \int_{E_F} \frac{v_\alpha^2}{v^3}$$

$$\times \nabla\tau \cdot \nabla E dA \Big/ \int_{E_F} \frac{v_\alpha^2}{v}\tau dA, \qquad (15d)$$

where the summations are over i and j.

For a spherical Fermi surface both S_{B2} and S_{B3} vanish. S_{B1} becomes independent of τ and is identical to the "band-term" found under more restrictive assumptions (see equation (4)). The term S_{B2} is proportional to the deviation from a spherical Fermi surface. The S_{B3} term is zero in the most simple band-models, where $d^2E/dk_i dk_j = 0$. S_{SC} gives a contribution to S_α

which is determined by the derivative of τ folded with the properties of the band.

Equation (15) shows that it is possible to have an isotropic band-contribution to S and an anisotropic scattering-contribution, namely if the Fermi surface is nearly spherical (in D dimension) and τ is anisotropic. The opposite is, however, very unlikely as the scattering term, S_{SC}, in general beyond isotropic τ also needs spherical Fermi surface, which implies that S_B is isotropic too. The separation of the experimental thermopower of β-(ET)$_2$I$_3$ into an isotropic term, S_1, and an anisotropic term S_0 (equation (1)) seems accordingly to reflect, respectively, the band-term and the scattering-term, thereby suggesting that the Fermi surface within the ab-plane is near $2D$-spherical.

Structural considerations [5], as well as theoretical band structure calculations [13], on β-(ET)$_2$I$_3$ also suggest that the electron gas is quasi-two-dimensional with almost isotropic band-properties within the ab-plane. Experimentally this has been confirmed by Jacobsen [14] who on the basis of infrared reflectivity studies, points to a bandwidth, W, which varies little within the ab-plane, with W being of the order of 0.4– 0.5 eV, and slightly larger in the "transverse" b-direction than in the direction of the stacking axis a.

In accordance with the expectations of nearly spherical Fermi surface, we will assume that we can use the expression

$$d^2E/dk_1^2 \simeq d^2E/dk_j^2 \quad \text{and} \quad d^2E/dk_idk_j \simeq 0$$

$$\text{for} \quad i \neq j, \tag{16}$$

and that

$|\nabla E|$ and $\nabla^2 E$ is approximately constant

when the transport integrals [equation (15)] are calculated. S_{SC}, which reduces to

$$S_\alpha = -\frac{\pi^2}{3} \frac{k_B^2 T}{e} \left\{ \frac{\nabla^2 E}{|\nabla E|^2} \bigg|_{k_\alpha} + \frac{1}{|\nabla E|} \frac{\int v_\alpha^2 \nabla \tau \cdot \nabla E \, dA}{\int v_\alpha^2 \rho \, dA} \right\}, \tag{17}$$

where the subscript k_α denotes that the derivatives should be calculated at the Fermi wave vector parallel to the α-direction. In the D-dimensional free electron model, the first term of equation 17 can be expressed as

$$S_{B\alpha} = -\frac{D \cdot \pi^2}{6} \frac{k_B}{e} \frac{k_B T}{E_F}. \tag{18}$$

For β-(ET)$_2$I$_3$ our approach is that the ab-plane is considered to be $2D$-orthorhombic with a $\frac{3}{4}$-filled tight binding band:

$$E(k) = 2t_a(1 - \cos k_a a) + 2t_b(1 - \cos k_b b). \tag{19}$$

To fulfil equation (16) we furthermore assume that in a region close to $\pm k_a$, the b'-axis parameters can be substituted with those of the a-axis, and vice versa. The band-term thermopower then becomes

$$S_{B\alpha} = \frac{\pi^2}{6} \frac{k_B}{e} \frac{k_B T}{t_\alpha}, \quad \alpha = a, b. \tag{20}$$

The experimental data of β-(ET)$_2$I$_3$, decomposed in accordance with equations (1) and (17) then result in transfer integrals which are both along a and b' are of the order of 0.12 eV. The good agreement between the thermopower and the optical [14] results confirms the validity of the analysis made above.

The decomposition of S leading to an anisotropic scattering term S_{SC} suggests marked anisotropy of the scattering mechanism. The origin of this is not, at present, understood. Calculations based on simple phonon scattering of electrons in organic metals generally predict that S_{SC} should give a contribution to the thermopower which both in magnitude and in T-dependence is comparable with the band term [15, 16]. Experimentally, though this has never been confirmed. On the contrary, it has been shown that in the TMTSF salts, the band term markedly dominates the stacking axis thermopower, S_b [16, 17]. Also in β-(ET)$_2$I$_3$, we find band dominance, cf. S_a. However, along the a-axis, the analysis indicates electron scattering which gives rise to a substantial negative thermopower which only varies little with temperature.

3.2. Structural transition

At $T \sim 200$ K a relatively dramatic structural change occurs, giving rise to formation of a superstructure which is incommensurate with the underlying lattice [4].

The small, but significant, change in slope of S vs T experimentally observed at $T \sim 200$ K most probably reflects this transition. In resistivity measurements one also observes a minor change in slope of R vs T [4]. Thus, it seems that the superstructure formation only affects the electronic properties very little. The small changes observed in the transport parameters may reflect a combination of a change in the bandstructure and changes in the charge carrier relaxation time.

3.3. Intermediate and low-temperature region

Below approximately 130 K the thermopower indicates a crossover in some properties (Fig. 2). Both components, S_a and S_b, exhibit an additional term $\Delta S(T)$ relative to the linear behaviour at high temperature.

Since $\Delta S(T)$ is near isotropic, it is not likely that it reflects changes in the scattering mechanism, which

according to the analysis above accounts for the anisotropic term S_0. The difference between ΔS_a and ΔS_b is of the same order of magnitude as the difference between ΔS_a of the needle-form and the flake-like crystals shown in Fig. 2. Accordingly, it may just reflect a slight sample dependence, e.g. due to different amount of impurities. Possibly, ΔS originates in the effect of phonon drag, which commonly is observed in classical metals, but never has been established in synthetic conductors. The lack of phonon-drag thermopower in previously studied organic metals may be a result of the planar Fermi surfaces. Only the very limited number of available phonons, viz., those with $q \simeq (\pm 2k_F, 0, 0)$ are namely able to drag electrons along with them. The result on S is accordingly negligible. In β-(ET)$_2$I$_3$, on the contrary, the Fermi surface is closed and a continuum spectrum of phonons is able to contribute in the drag effect. The experimental T-dependence of ΔS fits quite well the phonon-drag high-temperature $1/T$-characteristic. ΔS does, however, not exhibit a clear maximum, which should occur close to $\theta_D/5$, θ_D being the Debye temperature, and especially ΔS misses the T^3 phonon-drag behaviour at low T. These lacks in $\Delta S(T)$ behaviour may, though, not be real but can be overshadowed by other phenomena at low T.

At $T \simeq 25$ K a dramatic change is observed in $S(T)$, most marked in the S_a component, but also significant in S_b. Well below 25 K both components of the thermopower are relatively small. The relatively abrupt change in $S(T)$ at $T \simeq 25$ K suggests that a real phase transition is taking place. However, this can not be confirmed on the basis of existing data on β-(ET)$_2$I$_3$. Preliminary X-ray scattering did not indicate any structural transition at 25 K. Jacobsen et al. [14] have, on the basis of i.r. studies, given indications of $3D$ metallic behaviour at low T. The 25 K anomalous thermopower may reflect the change from high-T $2D$ to low-T $3D$ characteristics. However, the change in S seems too sharp just to reflect a $2-3D$ cross-over determined by the relative transfer integrals. According to the discussion above, it moreover appears that it first of all is the anisotropic part of S, i.e. the scattering term, which is affected by cooling to T below 25 K.

4. SUMMARY

In summary, we have shown that the thermopower components of β-(ET)$_2$I$_3$ show peculiar properties, namely nearly isotropic dS/dT behaviour, but a very anisotropic absolute value of S, even with different sign of S_a and S_b below $T = 170$ K. The experiments indicate that the electronic properties are unaffected by the factors which are decisive in determining which of the two types of crystal morphology of the crystal one obtained during electrocrystallization.

As analysis based on a new general expression for the thermopower of D-dimensional anisotropic materials indicates that the band-properties of β-(ET)$_2$I$_3$ accounts for the linear T dependence of S, whereas the scattering mechanism gives rise to a relatively large, anisotropic thermopower which varies only little with T. A simple treatment based on nearly isotropic band properties yields transfer integrals of the order of 0.12 eV.

The experimental $S(T)$ dependence shows that the dramatic structural change occurring at approximately 200 K has little influence on the electronic properties. Below $T \simeq 130$ K additional positive contribution to S appears. This may be related to the phonon-drag effect. At approximatley 25 K a marked change in S vs T indicates dramatic changes in the relaxation mechanism or perhaps a real phase transition.

REFERENCES

1. (BEDT-TTF)$_2$I$_3$ is abbreviated (ET)$_2$I$_3$ and exists in at least 5 different crystallographic phases. The β-phase presented in this work is the same as the phase marked A in Soviet literature.
2. É.B. Yagubskii, I.F. Shchegolev, V.N. Laukhin, P.A. Kanonovich, M.V. Karatsovnik, A.V. Zvarykina & L.I. Buravov, *JETP Lett.* **39**, 12 (1984).
3. G.W. Crabtree, K.D. Carlson, L.N. Hall, P.T. Copps, H.H. Wang, T.J. Emge, M.A. Beno & J.M. Williams, *Phys. Rev.* **B30**, 2958 (1984).
4. J.M. Williams et al., ICSM 1984, *Mol. Cryst. Liq. Cryst.* **119**, 347 (1985). P.C.W. Leung, T.J. Emge, M.A. Beno, H.H. Wang, J.M. Williams, V. Petricek & P. Coppens, *J. Am. Chem. Soc.* **106**, 7644 (1984).
5. J.M. Williams, T.J. Emge, H.H. Wang, M.A. Beno, P.T. Copps, L.N. Hall, K.D. Carlson & G.W. Crabtree, *Inorg. Chem.* **23**, 2558 (1984).
6. V.F. Kaminskii, T.G. Prokhorova, R.P. Shibaeva & É.B. Yagubskii, *JETP Lett.* **39**, 17 (1984); R.P. Shibaeva et al., ICSM84, *Mol. Cryst. Liq. Cryst.* **119**, 361 (1985).
7. Preliminary results on the thermopower of β-(ET)$_2$I$_3$ was presented at ICSM84 by K. Mortensen et al., *Mol. Cryst. Liq. Cryst.* **119**, 401 (1985).
8. Thermopower results on β-(ET)$_2$I$_3$ were independently presented by I. Henning et al. at ICSM84. *Mol. Cryst. Liq. Cryst.* **119**, 337 (1985).
9. See for example R.D. Barnard, *Thermoelectricity in metals and alloys*, Taylor and Francis LTD (1972).
10. J.-P. Jan, *Can. J. Phys.* **46**, 1371 (1968).
11. In classical metals D, of course, is 3. Synthetic conductors are usually treated as quasi-$1D$, i.e. $D = 1$. For β-(ET)$_2$I$_3$ we attribute D to be 2.

12. For $D = 3$, $1/\rho$ given by equation 11 is identical to "$2M$" given by Jan [10].

13. P.M. Grant, ICSM84, *Mol. Cryst. Liq. Cryst.* **119**, 385 (1985).

14. C.S. Jacobsen, J.M. Williams and H.H. Wang, *Solid State Commun.* **54**, 937 (1985).

15. E.M. Conwell, *Phys. Rev.* **B22**, 1761 (1980).

16. K. Mortensen, *Solid State Commun.* **44**, 643 (1982).

17. K. Mortensen & E.M. Engler, *Phys. Rev.* **B29**, 842 (1984).