Point contact spectroscopy of the electron-phonon interaction in the layered conductor beta -

(bis(ethylenedithio)tetrathiofulvalene)$_2$I$_3$

Point contact spectroscopy of the electron–phonon interaction in the layered conductor β-(bis(ethylenedithio)tetrathiofulvalene)₂I₃

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Abstract. A theory of point contact (PC) spectroscopy of the electron–phonon interaction in layered conductors with a quasi-two-dimensional energy spectrum of charge carriers is developed. The predicted anisotropy of the PC spectra is observed on heterocontacts of Cu and the organic metal β-(BEDT-TTF)₂I₃. Two types of PC spectrum are revealed, which correspond to different orientations of the contact axis. The spectra measured on contacts with the current flow in the plane of the organic molecule layer display features caused by the interaction between the electrons and intramolecular vibrations. The spectra of the samples with the axis perpendicular to the BEDT-TTF layers have maxima reflecting the predominating contribution of the I₃⁻ anions in the processes of energy relaxation of the current carriers in such PCs.

1. Introduction

Investigation of the interaction between current carriers and molecular vibrations in conducting organic materials is of basic importance to understanding the peculiarities of transport processes in this class of compounds and the nature of the superconducting state in some of them. Among the known organic superconductors, compounds based on the bis(ethylenedithio)tetrathiofulvalene (BEDT-TTF) complexes are of a great interest. The crystals of this ion-radical salt with certain anions show superconducting properties with T_c ranging from 1.5 to 12.4 K. The iodine compound β-(BEDT-TTF)₂I₃, belonging to this group of conductors, with the critical temperature $T_c \simeq 1.5$ K and a metallic type of conductivity above T_c was the object of our study.

Unlike traditional metals, the β-(BEDT-TTF)₂I₃ crystals have a layered structure [1] with a set of organic molecule layers and iodine atoms between them. The bonds between the cation radicals are much stronger in the layer than between the neighbouring planes, which pre-determines considerable anisotropy of the physical properties of these crystals, e.g. the conductivities along and perpendicular to the organic molecule layers may differ by hundreds [2]. This undoubtedly affects the electrical characteristics of the point contacts (PCs) with this organic conductor.

Information on the structure of the vibrational spectrum of a metal can be derived directly from studies of the electron–phonon interaction (EPI) function by the PC spectroscopy method [3–5]. A contact of small size (a PC), formed between two electrodes in liquid helium by

means of a special device, is used as the source of information in this case. Among the other methods of contact formation the shift technique and the 'needle–anvil' method [3,5] are the most widely used. 'Needle–anvil' type of PCs are obtained as a result of pressing a sharp electrode on a flat electrode. When using the shift technique, one must touch the edges or side surfaces of electrodes and shift them while a small contact between the electrodes is obtained. When the contact experiences an electric current flow, the relaxation of non-equilibrium electrons on phonons in the constricted area is the origin of the non-linear addition to the contact resistance. As a result, the current–voltage (I–V) characteristic of the contact experiences singularities which are due to the EPI. The second derivative of the I–V characteristics becomes proportional to the EPI function of the metal studied. The main contribution to the non-linear conductivity of the contact is from the relatively small metal area in the contact axis direction [5]. This allows one to obtain the anisotropy of PC spectra by means of orientation of the contact axis along different crystallographic directions.

According to [6], the EPI function of β-(BEDT-TTF)$_2$I$_3$ has maxima at 1, 4 and 15 meV, while optical studies [7] show the existence of vibrational modes even at higher energies. With this ambiguity of results [6,7], it is topical to obtain new independent data.

Here we study the second derivatives of the I–V characteristics (PC spectra) of Cu-β-(BEDT-TTF)$_2$I$_3$ heterocontacts (section 3). It was found that the anisotropy of the elastic and electron properties of an organic conductor causes the essential dependence of its PS spectrum type on the orientation of the contact axis with respect to the high-conductivity planes. The existing theory of PC spectroscopy [8,9] is not always adequate for describing the above situation, which requires special consideration (section 2).

2. Theory

The observation of quantum galvanomagnetic effects in layered conductors [10–13] indicated that their kinetic and thermodynamic characteristics may be described in terms of quasi-particles—conduction electrons with a quasi-two-dimensional energy spectrum ε_p (see, e.g., [14]) given by

$$\varepsilon_p = \sum_{n=1}^{\infty} \varepsilon_n(p_{\parallel}) \cos(n\pi p_{\perp} b) \tag{1}$$

where $p_{\parallel}$ and $p_{\perp}$ are the components of the electron quasi-momentum parallel and perpendicular to the layers; $b^{-1} = |\alpha_1 \times \alpha_2|/\alpha_1(\alpha_2 \times \alpha_3)$; α_i are the basic vectors of the crystalline lattice (α_1 and α_2 are in the layer plane).

The coefficient ε_n rapidly decreases with increasing n. This allows the sum over n to be reduced to the first two terms in the theoretical study of the electron transport in such conductors, which corresponds to the result obtained in the tight-binding approximation. Subsequently, to avoid awkward calculations, we employ the simplified model with $\varepsilon_0 = p_{\parallel}^2/2m$ and $\varepsilon_1 = $ constant, which is often used to calculate the kinetics of layered metals [14–16].

The method of PC spectroscopy is based on a study of the EPI-related non-linearities in the I–V characteristics of PCs whose diameters d are much smaller than the electron energy relaxation length λ_ε ($= \min(l_{ep}, \sqrt{l_{ep}l_i})$; l_{ep} and l_i are the characteristic mean free path with respect to the electron collisions of phonons and impurities, respectively). We discuss below the so-called diffusion mode of current flow ($d \gg l_i$), which apparently corresponds to the experimental situation. In this case the conducting properties of the PC are characterized by

the electrical conductivity tensor σ_{ik} independent of the coordinates. At weak EPI ($d \ll l_\varepsilon$) and low excess energies eV (compared with the Fermi energy ε_F) of the carriers, the second voltage derivative of the I–V characteristic of the PC (the PC spectrum) is proportional to the EPI function $G_{pc}(eV)$ at low temperatures [5, 6]

$$\frac{1}{R(0)}\frac{dR}{dV}(V) = \frac{32ed}{3\pi V_F}G_{pc}(eV) \tag{2}$$

where

$$G_{pc}(\omega) = \sum_\alpha \frac{1}{(2\pi)^3\langle 1\rangle}\left(\langle W_{p-p',\alpha}K(p,p')\delta(\omega - \omega_{p-p',\alpha})\rangle\right)$$

$$\langle\ldots\rangle = \int_{\varepsilon_p=\varepsilon_F}\frac{dS_p}{v}\ldots \qquad v_F = \sqrt{\frac{2\varepsilon_F}{m}}. \tag{3}$$

Equation (2) contains the summation over the phonon spectrum branches α and integration over the momenta p and p' on the open Fermi surface $S_p = S_F$ within the Brillouin zone; $\omega_{q,\alpha}$ is the phonon frequency, $W_{q,\alpha}$ is the squared modulus of the EPI matrix element, $v = \partial\varepsilon_p/\partial p$ is the electron velocity, $v = |v|$ and $\hbar = 1$.

The EPI function $G_{pc}(\omega)$ of the PC differs from the thermodynamic EPI function in the presence of the contact-geometry-dependent form factor under the integral

$$K(p,p') = \frac{3\pi l_i}{32d}\left[\int d^3r\left((v-v')\frac{\partial\Phi}{\partial r}\right)^2\right]\bigg/\left(\langle v_z^2\rangle\int_{S_c}dS\frac{\partial\Phi}{\partial z}v\right) \tag{4}$$

where $\Phi(r)$ is the electric field potential, the z axis is normal to the orifice plane ρ_c, $l_i = v_F\tau_i$ and τ_i is the characteristic time of the elastic relaxation of the charge carriers.

The distribution of the electric potential in the metal may be found from the continuity equation

$$\sigma_{ik}\frac{\partial^2\Phi}{\partial x_i\partial x_k} = 0 \tag{5}$$

with the boundary conditions

$$n_i\sigma_{ik}\frac{\partial\Phi}{\partial x_k}\bigg|_{r=r_s} = 0 \qquad \Phi(r\to\infty) = \tfrac{1}{2}V\theta(z). \tag{6}$$

In equations (5) and (6), σ_{ik} is the tensor of the electrical conductivity; n_i are the components of the vector normal to the surface of the sample at the point r_s.

Let us consider a PC shaped as an orifice with $r^2 = x^2 + y^2 \leqslant \tfrac{1}{4}d^2$ in the impenetrable partition. We also assume that the z axis of the contact either coincides with the axis of the corrugated cylinder of the Fermi surface ($p_\perp \parallel z$) or is strictly perpendicular to it ($p_\perp \perp z$). In such geometry the conductivity tensor of the metal obeying the law of carrier dispersion (1) is diagonal, i.e. $\sigma_{ik} = \sigma_{ii}\delta_{ik}$, and condition (6) of zero current through the boundary ($z = 0$; $r > \tfrac{1}{2}d$) reduces the electric field component perpendicular to the boundary to zero ($E_z = -\partial\Phi/\partial z = 0$ at $z = 0$ and $r > \tfrac{1}{2}d$). In the $x_i' = x_i\sqrt{\sigma_{ii}}$ coordinates, which transform equation (5) into the Laplace equation, the contact has the shape of an ellipse at

arbitrary σ_{ii}. While solving the boundary problem (7) and (8), the exchange to the general ellipsoidal coordinates ξ, η, ζ is convenient:

$$(x')^2 = \frac{(a^2 + \xi)(a^2 + \eta)(a^2 + \zeta)}{(a^2 - b^2)a^2}$$

$$(y')^2 = \frac{(b^2 + \xi)(b^2 + \eta)(b^2 + \zeta)}{(b^2 - a^2)b^2} \qquad (z')^2 = \frac{\xi \eta \zeta}{a^2 b^2}$$

$$-a^2 \leqslant \zeta \leqslant -b^2 \qquad -b^2 \leqslant \eta \leqslant 0 \qquad \xi \geqslant 0 \tag{7}$$

$$\begin{bmatrix} a \\ b \end{bmatrix} = \begin{bmatrix} \max \\ \min \end{bmatrix} \left\{ \frac{d}{2\sqrt{\sigma_{xx}}}; \frac{d}{2\sqrt{\sigma_{yy}}} \right\}.$$

Using this, we have

$$\Phi(r) = \tfrac{1}{2}V \left[\theta(z) - 1 - \frac{1}{2K(k)} \operatorname{sgn}(z) F \left(\tan^{-1} \left(\frac{a}{\sqrt{\xi}} \right), k \right) \right] \tag{8}$$

where $F(\Phi, k)$ and $K(k)$ are the incomplete and complete first-order elliptic integrals, respectively; $k^2 = 1 - b^2/a^2$.

With the functions $\Phi(r)$ known, the contact resistance $R(0)$ can readily be calculated:

$$R^{-1}(0) = -\frac{1}{V}\sigma_{zz} \int ds \, \frac{\partial \Phi}{\partial z} = \pi \sqrt{\sigma_{xx}\sigma_{yy}\sigma_{zz}} a K^{-1}(k) \tag{9}$$

$$R^{-1}(0) = \begin{cases} d\sqrt{\sigma_\perp \sigma_\parallel} & \sigma_{zz} = \sigma_\perp \\ \pi d\sigma_\parallel \ln^{-1}(\sigma_\parallel/\sigma_\perp) & \sigma_{zz} = \sigma_\parallel \qquad \sigma_\parallel/\sigma_\perp \gg 1 \end{cases} \tag{10}$$

where

$$\sigma_\perp = \frac{e^2 \tau_i m \pi^2 \varepsilon_1^2 b}{(2\pi)^3} \qquad \sigma_\parallel = \frac{e^2 \tau_i \varepsilon_F}{\pi^2} \left(1 - \frac{\varepsilon_1}{\varepsilon_F} \right).$$

$R(0)$ is dependent both on the electroconductivity along the contact axis and on the conducting properties of the sample perpendicular to this axis. This is connected with the three-dimensional spread of the electric current in the vicinity of the PC. It should be noted that at $\sigma_{zz} = \sigma_\parallel$ and $\sigma_\parallel/\sigma_\perp \to \infty$ (strictly two-dimensional conductivity) the resistance (12) contains the logarithmic divergence. In this case the sample size D must be taken into account, and at $\sigma_\parallel/\sigma_\perp \gg D/d \gg 1$ the resistance $R(0) \propto (\sigma_\parallel d)^{-1} \ln(D/d)$. The form factor $K(p, p')$ in $G_{pc}(eV)$ is then

$$K(p, p') = \frac{3l_t}{128d} K^{-1} \left(\sqrt{1 - \frac{1}{\lambda}} \right) \frac{1}{\langle v_z^2 \rangle} \times \left((v_x - v_x')^2 \frac{\sigma_{zz}}{\sigma_{xx}} \frac{1}{\lambda - 1} I_1(\lambda) \right.$$

$$\left. + (v_y - v_y')^2 \frac{\sigma_{zz}}{\sigma_{yy}} \frac{\lambda}{\lambda - 1} I_2(\lambda) + (v_z - v_z')^2 I_3(\lambda) \right) \tag{11}$$

where

$$\lambda = a^2/b^2 \qquad I_1(\lambda) = \hat{F}\{f(\lambda)\} \qquad I_2(\lambda) = \hat{F}\{f^{-1}(\lambda)\}$$

$$\hat{F}\{f\} = \int_1^\lambda d\zeta \int_0^1 d\eta \int_0^\infty d\xi \, \frac{\zeta - \eta}{(\xi + \eta)(\xi + \zeta)} \left(\frac{\xi}{\zeta \eta} \right)^{1/2} f(\zeta, \eta, \xi)$$

$$f(\zeta, \eta, \xi; \lambda) = \left(\frac{(\lambda - \eta)(\lambda - \zeta)(\xi + 1)}{(1 - \eta)(\zeta - 1)(\xi + \lambda)} \right)^{1/2}$$

$$I_3(\lambda) = 4\pi \sqrt{\lambda} K \left(\sqrt{1 - \frac{1}{\lambda}} \right) - \frac{1}{\lambda - 1} [I_1(\lambda) + \lambda I_2(\lambda)].$$

The latter equation follows from the harmonicity of the function $\Phi(r)$ and the boundary conditions (6).

When the contact axis is perpendicular to the planes with high electrical conductivity $(\lambda = i, \sigma_{zz} = \sigma_\perp; \sigma_{xx} = \sigma_{yy} = \sigma_\parallel)$, equation (11) takes the form

$$K(p, p') = \frac{3l_i}{32d} \left(\frac{1}{p_F^2} (p_\parallel - p_\parallel')^2 + 8\pi [\sin(\pi p_\perp b) - \sin(\pi p_\perp' b)]^2 \right) \tag{12}$$

$$p_F = \sqrt{2m\varepsilon_F}$$

i.e. at $\varepsilon_1 \ll \varepsilon_F$ the PC spectrum (2) intensity is independent of ε_1 and the contributions of electron–phonon scattering on changing the carrier velocities along and across the layers are of the same order of magnitude.

If the contact axis is parallel to the layers $(\sigma_{zz} = \sigma_{yy} = \sigma_\parallel; \sigma_{xx} = \sigma_\perp)$, the quasi-two-dimensionality of current flow causes the predominating contribution to the PC spectrum of the electron scattering that mainly changes the tangential component of the momentum:

$$K(p, p') = \frac{3\pi l_i}{32dp_F^2} ((p_y - p_y')^2 + 2(p_z - p_z')^2) \qquad \frac{\sigma_\perp}{\sigma_\parallel} \ll 1. \tag{13}$$

The important difference of the function $K(p, p)$ and the analogous function for an isotropic metal [9] contains multipliers highly dependent on the contact orientation, before the terms $(p_i - p_i')^2$. This anisotropy of the K-factor has a very clear physical meaning. The PC spectroscopy method is based on investigation of the I–V characteristics of the contacts. The conducting properties of the contact between layered conductors are extremely sensitive to the orientation of the contact axis with respect to layers with high charge carrier mobility. This is one of the main causes of the anisotropy of the PC spectra of the EPI, determined by the non-linear part of the resistance. Note that another possible reason for the observed PC spectra anisotropy is the anisotropy of the phonon excitation spectrum, theoretical studies of the latter being an independent problem.

Thus, the changes in the intensity of the PC spectra obtained for layered metals with contact axes of different orientations permit us to separate unambiguously the lines corresponding to the electron relaxation at two-dimensional phonon modes whose existence in layered metals was predicted theoretically [17].

The above theory refers to homocontacts between layered metals, while the experiments discussed below were made on β-(BEDT-TTF)₂I₃ at $V \leqslant 100$ mV [18]. The use of a highly thermoconductive electrode permits us to obtain samples with spectral properties in a wide range of voltages. The PC spectrum of the heterocontact contains additive contributions of the contacting metals. The mutual influence of the metals comes to emergence of the multipliers, which are independent of the electron momentum in the case of a dirty metal contact $(l_i \ll d)$ in the form factor $K(p, p')$.

3. Experiment

The theoretical results obtained are in good agreement with the data from experiments on Cu-β-(BEDT-TTF)₂I₃ heterocontacts oriented along and perpendicular to the layers of organic molecules. The experiments were carried out at a temperature $T = 4.2$ K. The second derivatives of the I–V characteristics $d^2V/dI^2(V)$ were measured. The experimental technique used in our work provided reliable PCs of desired orientation. Hence

the probability of formation of contacts of intermediate type was highly improbable, and spectra essentially different from the curves discussed below were never observed in our experiments. More than 40 reliably reproducible PC spectra of the contacts oriented along or perpendicular to the layers of organic molecules were obtained.

Typical dependences are shown in figure 1 for each contact orientation studied. Curve 1 is for samples with current flow in the plane of the organic molecule layers. This direction was achieved using the shift technique with special geometry bringing the electrodes into contact (cf [18]). The contacts were formed at the point where the copper electrode surface and the side face of the β-(BEDT-TTF)$_2$I$_3$ crystal touched. Spectra of the first type (curve 1) have features caused by the scattering processes in both copper and the organic metal. It is typical for the contacts discussed to have a low-frequency maximum at 17–18 meV in the I–V second derivatives, which corresponds to the EPI in copper [19]. At higher energies, some features of the vibrational spectrum of the organic metal are observed. The peculiarity of the lowest frequency at 54–55 meV was first reported in [19]. Also the PC spectra of this type have maxima at 103, 134 and 145 meV (the measurements were carried out up to 150–160 meV). As comparison of the PC data and the optical reflection and absorption spectra shows [18], the above maxima have a vibron nature and have the high electron–vibration interaction constants. It should be noted that the vibron bands are polarized along the direction of conductivity of β-(BEDT-TTF)$_2$I$_3$, i.e. in the a–b plane taking into account its characteristic anisotropy of the conducting properties.
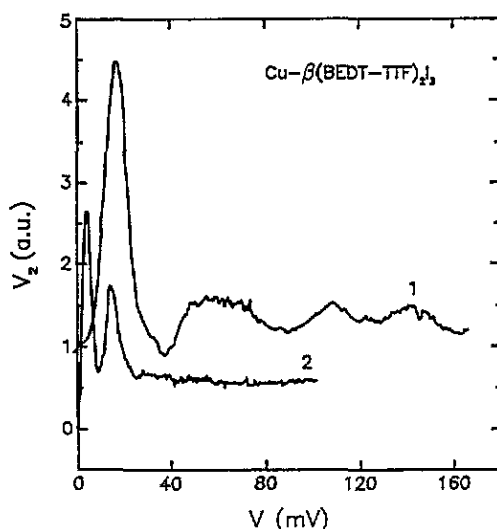

Figure 1. PC spectra of the heterocontacts of an organic conductor, typical of different orientations of contacts axis (a.u., arbitrary units): curve 1, contact axis in the plane of the layers of organic molecules; curve 2, contact axis perpendicular to the layers of organic molecules.

Contacts of another type were formed by touching the β-(BEDT-TTF)$_2$I$_3$ plane with a copper needle point. Their preferential orientation was along the c^* axis of the organic crystal, i.e. perpendicular to the layers of organic molecules. The PC spectra of these samples differ considerably from the dependences of the first type. It should be noted that, in addition to scattering anisotropy, the PC spectra along the c^* axis are influenced by the difference between the Fermi electron velocities in the contacting metals, which in this case

can amount to three to four orders of magnitude. As a result, the $d^2V/dI^2(V)$-dependences of these samples show no features related to EPI in copper (curve 2).

PC spectra of the second type have maxima at 4 and 15 meV. They do not show the high-frequency features which are pronounced in curve 1. The spectra boundaries are at about 27–30 meV. The $d^2V/dI^2(V)$-dependences for contacts of this orientation are similar to those in [6]. The maxima at 4 and 15 meV in spectra of the second type can be accounted for by vibrations in the anion (as in [6]). The maxima discussed correlate well with the 30 and 120 cm^{-1} bands in the Raman spectrum of this compound [20], which are due to the librational mode of I_3^- and the symmetric stretching vibrations of the iodine atoms. Proceeding from the conclusion in [20], the bands may be ascribed to asymmetric stretching vibrations and to symmetric atom vibrations in I_3^-, respectively. The latter vibration is, however, active in the Raman spectrum and shows up in IR measurements probably owing to the deviation of the anion from the linear and symmetrical shape in the crystal. It is quite probable also that with this completely symmetrical vibration the dipole moment may be due to redistribution of the electron density between the donor and the acceptor caused by the shift of the I_3^- atoms from their equilibrium positions.

The absence of components contributed by intramolecular vibrations of the donor in PC spectra of the second type is quite reasonable assuming that the charge-transfer direction in such samples is normal to the BEDT-TTF layers. Indeed, theory [21] does not anticipate the strong interaction between the molecule vibrations and the electron transition if they occur within the same plane. A much larger contribution is expected from the linear anions I_3^- nearly normal to BEDT-TTF, which was just observed in our experiment.

4. Conclusion

Thus, the non-linear electrical conductivity of the PC between layered conductors is extremely sensitive to the orientation of the contacting crystals. Because of the three-dimensional current flow, the resistance is dependent on the metal conductivity both along and across the contact axis as distinct from the bulk samples. The PC spectra of EPI in layered conductors are essentially anisotropic. The results of our studies revealed that two types of PC spectrum are observed in the organic–metal crystal β-(BEDT-TTF)₂I₃. PC spectra of the first type corresponding to carrier transfer in the a–b plane have pronounced features caused by the interaction between the current carriers and the intramolecular vibrations of the donor. The spectra measured on the contact with the axis perpendicular to the BEDT-TTF layers have maxima related to the I_3^- anions and no maxima which might be ascribed to the intramolecular vibrations of the donor.

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