



POINT - CONTACT SPECTRA OF THE ORGANIC METAL β -(BEDT-TTF) $_2$ I $_3$ *

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Abstract

The d^2U/dI^2 -characteristics of point-contacts between the organic superconductor β -(BEDT-TTF) $_2$ I $_3$ in the normal metallic state and a normal metal (copper) are measured and found to be quite similar to those of point-contacts between normal metals which are well known to be correlated with the electron phonon coupling and the phonon density of states.

1. INTRODUCTION.

The electron-phonon coupling in organic metals is of considerable importance for the understanding of the superconductivity as well as the transport properties. In contrast to "ordinary" metals, there is not yet a consensus even on the question whether the electron-phonon coupling is responsible for the superconductivity, as well as the electrical resistivity at finite temperatures /1/.

In normal metals, the electron-phonon coupling is described by the McMillan coupling constant $\alpha(\omega)$, where ω is the phonon frequency. The quantity $\alpha^2(\omega)F(\omega)$ where $F(\omega)$ is the phonon density of states can be determined experimentally as function of ω by tunneling measurements. Such measurements are most often carried out in the superconducting state (Giaever tunneling), however, they can also be carried out in the normal state, using point-contacts with a very small cross-sectional area, so that very large current-densities can be obtained without heating (Yanson tunneling). In that case, the I-U characteristics are non-linear, and the second derivative d^2U/dI^2 yields the quantity $\alpha^2(\omega)F(\omega)$, just as in Giaever tunneling. This method has been used extensively in "normal" metals, including

valence fluctuation compounds, but up to now there have been no reports of its application to organic metals.

We report here preliminary data on point-contact spectroscopy of the organic metal (and superconductor) β -(BEDT-TTF) $_2$ I $_3$.

2. EXPERIMENTAL.

Single crystals of β -(BEDT-TTF) $_2$ I $_3$ have been prepared by electrochemical methods as reported recently /2/. In this preparation using tetrahydrofuran as a solvent, α -phase and β -phase crystals of (BEDT-TTF) $_2$ I $_3$ grow simultaneously at the anode. The β -phase can be separated easily under a microscope due to the different shapes of both modifications. In addition, the β -phase crystals can also easily be identified by their ESR-linewidth /3/.

The contacts were fabricated with the "needle-anvil" method. The β -(BEDT-TTF) $_2$ I $_3$ samples, as sharp and flat single-crystals were used as needle-part of the contacts and cautiously pressed against a Cu-block in liquid He⁴. The needle axis was in the a-b plane. At the experimental minimum temperature of 1.6 K the samples still remained in the normal metallic state. The differential resistance dU/dI was measured as function of bias U with the usual lock-in technique, the d^2U/dI^2 -curves were calculated numerically from them.

*) BEDT-TTF = Bis(ethylenedithio)tetrathiofulvalene

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Theory: The resistance of a point-contact between normal metals at bias U can be written approximately as

$$R = R_s(1 + a/l(E = eU)),$$

where a is the contact-radius (typical of order 10 nm) and $l(E)$ the energy-dependent mean free path of the conduction electrons. R_s is the so-called Sharvin-resistance. In the free-electron-gas model it is expressed by

$$R_s = 4p_F/3ne^2\pi a^2 \quad (p_F \text{ is the Fermi momentum})$$

and is thus only function of the electron-density n and the contact-area πa^2 . In normal metals, R_s is assumed not to be energy (voltage)-dependent and the nonlinearities in the characteristic are thus attributed to the mean free path $l(E)$. In order to get good spectroscopic data, the ratio a/l must be $\ll 1$. Calculating $l(E)$ due to electron phonon scattering leads to the result

$$d^2U/dI^2 \sim \alpha^2 F(E = eU),$$

the Eliashberg-function of electron-phonon interaction /4,5/.

3. RESULTS.

Fig. 1 shows the dU/dI and d^2U/dI^2 -characteristics of a low-ohmic contact between β -(BEDT-TTF) $_2$ I $_3$ and Cu. The voltage is measured from Cu to the sample.

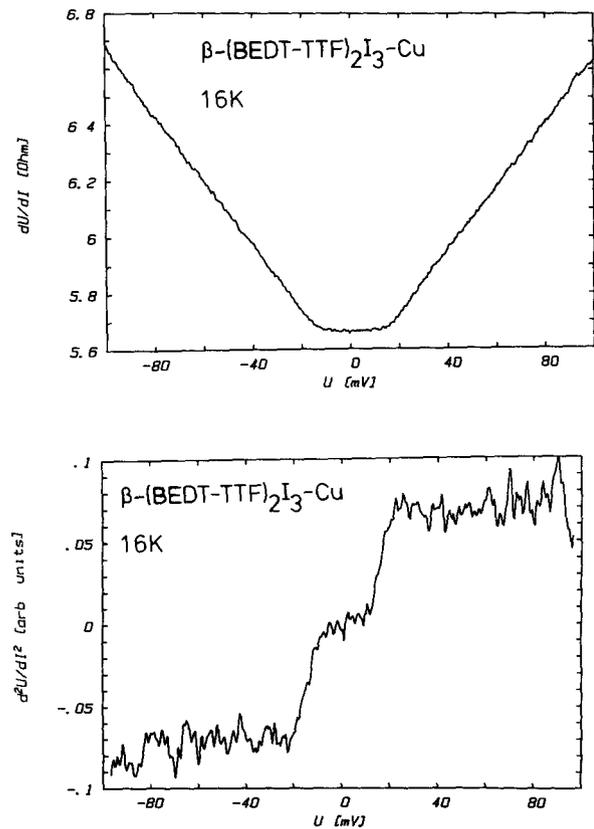


Figure 1 dU/dI and d^2U/dI^2 -characteristics of a low-ohmic contact. ($R_0 \approx 6 \Omega$)

Although the resistance is of the usual order ($\approx 6 \Omega$), we must assume that the contact-area was much larger than in normal (intermetallic) contacts, first because the characteristics show a high background (the d^2U/dI^2 -signal remains high with increasing voltage), which is also found in intermetallic point-contacts with a ratio $a/l > 1$, second because in one case we could fabricate a contact with a very high resistance (fig. 2). The low electron-density of β -(BEDT-TTF) $_2$ I $_3$ (1/100 of

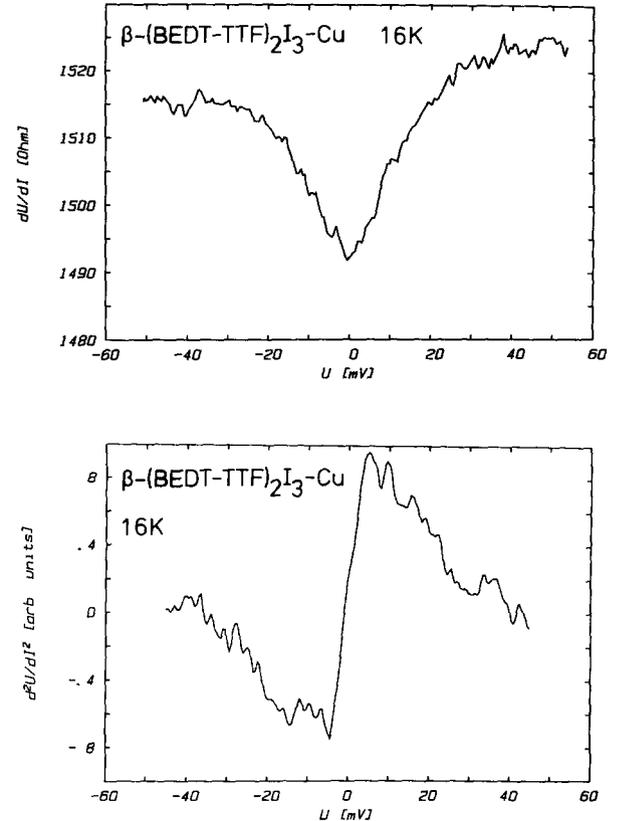


Figure 2 dU/dI and d^2U/dI^2 -characteristics of a high-ohmic contact. ($R_0 \approx 1500 \Omega$)

normal metallic n) indeed predicts a high Sharvin-resistance and the softness of the organic material accounts for the larger contact-areas in most cases. Thus we assume that only the high-ohmic contact has a usual contact-area and a ratio $a/l < 1$. With the exception of the observed asymmetry, the characteristics of this contact are quite similar to those of normal metals /4/ and therefore the d^2U/dI^2 -characteristic of fig.2 should be correlated with the electron-phonon coupling constant and the phonon density of states of β -(BEDT-TTF) $_2$ I $_3$. Our preliminary data show no detailed structure because the contact was somewhat unstable and noisy, but it shows a maximum in $\alpha^2 F$ around 5meV, a quite normal phonon energy for organic metals. An asymmetry of the I-U curve as in fig.2a is normally observed in contacts where one component has a large thermopower (e.g. intermediate-valent metals) /6/ or what is equivalent a small conduction electron bandwidth. The thermopower of the 2 dimensional metal β -

(BEDT-TTF) $_2$ I $_3$ at 300 K is orientational dependent and has values between 6 and 13 μ V/K /3/ which has to be compared with a value of 1.83 μ V/K for copper. Calculations of the bandwidth for β -(BEDT-TTF) $_2$ I $_3$ from the thermopower data depend somewhat on the assumed band-model, but it seems clear that the bandwidth is at least a factor of 10 smaller than that of copper (using an isotropic 2dim tight binding model results in a value of 0.26 eV, which is only a rough estimate /3b/).

4. DISCUSSION.

The d^2U/dI^2 -curve for the high-impedance contact yields the quantity $\alpha^2F(E)$. We see that it has a maximum at about 5 meV, drops as the energy increases towards 20 meV, and there seems to be a small maximum around 30 meV which exceeds the noise. We still cannot say whether there is structure between 5 and 20 meV. The maximum at 5 meV is due to external modes (rigid translations and librations /7/, while the weak structure at 30 meV might be due to internal ring breathing or stretching of the central double bond /8/. The data indicate that most of the electron-phonon coupling exists with the low-frequency external modes. This is consistent with resistivity data on organic metals like TTF-TCNQ, TMTSF $_2$ PF $_6$ /9,10/ which indicate that coupling with the external modes accounts well for the observed resistivity.

According to McMillan theory /11/
 $T_c = (\theta/1.45) \exp[-1.04(1+\lambda)/(1-\mu^*(1+\lambda\langle\omega\rangle/\omega_0))]$ where θ is the Debye frequency, ω_0 is the maximum phonon frequency, and

$\langle\omega\rangle = \int \alpha^2(\omega)F(\omega) d\omega / \int \alpha^2(\omega)F(\omega) \omega^{-1} d\omega$ is the average phonon frequency. For the bcc transition metals McMillan took the value $\langle\omega\rangle/\omega_0 = 0.62$; in the present case, from the d^2U/dI^2 curve (Fig. 2), we take $\theta = 20$ meV, $\langle\omega\rangle \approx 6.5$ meV, $\langle\omega^2\rangle^{1/2} \approx 7.5$ meV, $\langle\omega\rangle/\omega_0 \approx 0.3$. Assuming that $\mu^* \approx 0.1$, we obtain $\lambda = 0.4$ (for $T_c = 1$ K) and $\lambda \approx 0.7$ (for $T_c \approx 8$ K under pressure). These values of λ are rather rough. These values are not very different from those of Pb, Sn for example. In contrast, the value of λ for TMTSF $_2$ X (and TTF-TCNQ) is much lower, $\lambda \approx 0.15 - 0.2$ /10/.

We suggest that this difference in values of λ is due to the 2-d nature of the electronic band structure of β -(BEDT-TTF) $_2$ I $_3$, vs. the 1-d band structure of TMTSF $_2$ X, as manifested by the anisotropy in conductivity, which is about 10:1 in TMTSF $_2$ X salts, and about 3:1 in β -(BEDT-TTF) $_2$ I $_3$ /12/. Because of the electronic 1-d band structure of TMTSF $_2$ X, only one external phonon mode couples linearly with the electrons, namely the translation along the stack axis. The other two translational and three librational modes only couple quadratically with the electrons, and thus do not contribute to λ . Therefore λ is small. In 2-d as in β -(BEDT-TTF) $_2$ I $_3$, two translational modes, namely those in the a and b directions, and one librational mode, namely the rotation in the a-b plane, couple linearly with the electrons. (This argument is approximate, because the crystal structure is triclinic, and there is some conduction along the c-axis). The transverse translation, and the

libration, are expected to have a particularly low value of ω , as manifested by the maximum in the $\alpha^2(\omega)F(\omega)$ curve being around 4-5 meV. As a result, the contribution of these modes to λ , which is proportional to $1/\omega^2$, is particularly large. This accounts for a value of λ about 4-5 times larger than in TMTSF $_2$ X salts.

The symmetry argument, why in β -(BEDT-TTF) $_2$ I $_3$ the electrons couple linearly with the libration, is illustrated in Fig. 3.

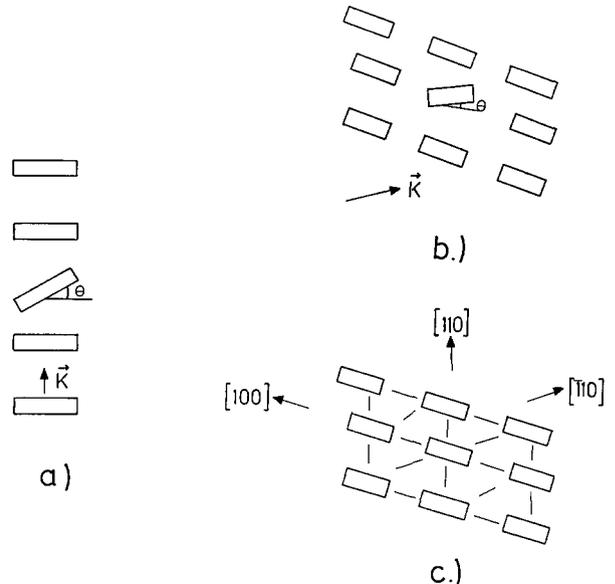


Figure 3

Illustration suggesting why in a 1-d stack (a) a libration does not couple linearly with the electrons, while in a 2-d configuration (b) a linear coupling is possible. In 1-d, the $+\theta$ and $-\theta$ rotations are equivalent as far as the electron scattering is concerned, in 2-d (b) they are not. $K = k_f - k_i$ is the change in electron momentum due to scattering. c) Stacking of molecules in β -(BEDT-TTF) $_2$ I $_3$. The short lines indicate between which molecules there is appreciable overlap (following ref. 12).

5. CONCLUSIONS.

We demonstrated that the non-linear dU/dI and d^2U/dI^2 -characteristics of point-contacts of β -(BEDT-TTF) $_2$ I $_3$ are similar to those of normal metals. This is the first time that normal-state point-contact spectroscopy on an organic metal has been reported. Work is in progress to improve the results obtained up to now.

Acknowledgements

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