Synthetic Metals, 41–43 (1991) 1885–1891

POINT CONTACT SPECTROSCOPY MEASUREMENTS ON α_t-(BEDT-TTF)$_2$I$_3$

M. Weger, A. Nowack* and D. Schweitzer**
Racah Institute of Physics, Hebrew University, Jerusalem, Israel.
*Experimentalphysik II, Universität Köln, 5000 Köln, Germany.
**3. Physikalisches Institut, Universität Stuttgart, 7000 Stuttgart, Germany

ABSTRACT

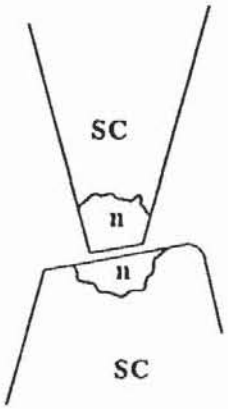
We report point-contact spectroscopy I-V data on superconducting α_t-(BEDT-TTF)$_2$I$_3$. The I-V curves show structure in 3 regions: For energies of order 0.25 meV, of about 4.5 meV and for energies of about 10 meV. No structure is observed near the BCS gap (1.3–1.4 meV). We attribute the structure at 4.5 meV to interaction with the phonon possessing this frequency which was observed independently by Raman spectroscopy, and the structure near 0.25 meV to an excitation energy considerably smaller than the BCS gap.

INTRODUCTION

The point-contact spectroscopy method was pioneered by Sharvin & Yanson [1], and described in a review article [2]. In this method, a metallic point-contact is pressed against a metal, and the non-linearity of the I-V curves is measured. We have applied this method, as well as vacuum tunneling, to various BEDT-TTF salts [3]. We found the best results are obtained when two single crystals are pressed against each other, so that the current flows in the conducting plane (fig. 1). Similar measurements have been carried out by other groups [4,5]. The theory that underlines these measurements is the Blonder-Tinkham-Klopwijk [6] theory. This theory considers a barrier between a superconducting and a normal region, which can be perfectly transmitting, resulting in Andreev reflection, or it can be insulating, resulting in Giaever tunneling, or it can be intermediate between these limits. In the case of Andreev reflection, there is a minimum in the differential resistance R= dV/dI at zero bias, and an increase by a factor of 2 at eV=Δ, where Δ is the BCS gap. In the case of Giaever tunneling, there is a maximum in R(0) (R at zero bias), and a sharp minimum at eV=Δ. Thus, as the reflectivity of the barrier increases, the zero-bias structure changes from a minimum to a maximum, the anomaly at eV=Δ changes from a discontinuity to a minimum, but the position of the anomaly doesn't change, and stays at eV=Δ, or eV= 2Δ for a s-n-s (or s-i-s) structure. The conductivity dI/dV as function of V, from the BTK paper [6] is reproduced in fig. 2.

We have previously [3] observed minima in R(0) in some cases, and maxima in others, and assigned the gap Δ to the position of the anomalies, as is the customary practice. Following the earlier measurements on β-(BEDT-TTF)$_2$IAuI and β-(BEDT-TTF)$_2$I$_3$, we employed α_t-(BEDT-TTF)$_2$I$_3$ crystals [7], which gave us much sharper structures of the I-V curves.

Elsevier Sequoia/Printed in The Netherlands



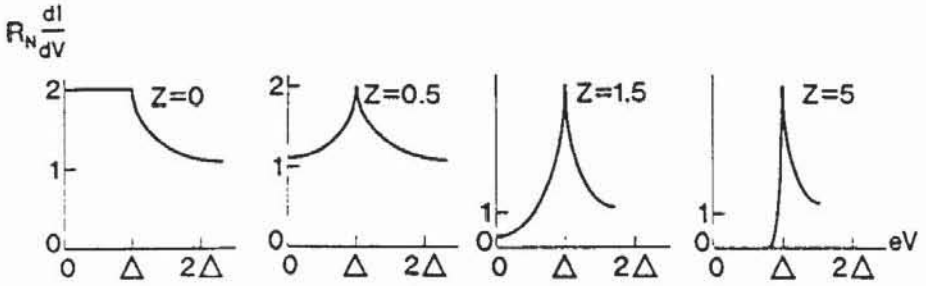


Figure 2

Figure 1 (left): Illustration of the configuration for point-contact spectroscopy. At the point of contact, we may expect a pressure of a few kbar, which renders this region normal.

Figure 2: Differential conductivity as function of voltage, reproduced from [6]. At zero bias we may have a maximum or a minimum, but the anomaly in d^2I/d^2V is always at $eV = \Delta$, where Δ is the BCS gap.

RESULTS

The previous measurements on β-(BEDT-TTF)$_2$I$_3$ (fig. 1 in ref. 3) provided us with a detailed strucutre. These measurements were conducted at T=1.6 K, which is above the transition temperature of this material. However, subsequent measurements showed [8,9] that this structure disappeares sharply at T=8-9 K, which is the value of T_c of this material under pressure. Therefore, we have to attribute the structure to regions of superconducting β-(BEDT-TTF)$_2$I$_3$ under pressure. The pressure is due to the contacts; if we apply a force of a milligram on a contact area of a radius of a few hundred Angstrom, the pressure amounts to several kbars. Under such high pressure T_c is very low, and at 1.6 K the material is normal. However, further away from the contact region, the radius is larger and the pressure drops to about 1 kbar, and there T_c = 8 K. Still further away, the pressure drops to zero and the material is normal again. Thus, for two crystals, we have four s-n interfaces and the voltage (fig. 1 of ref. 3) has to be devided by 4 to give the value of Δ. Thus, we see that we have structure at $\Delta \approx 0.25$ meV and at $\Delta \approx 4$ meV. Structure near 4 meV was also reported by Hawley et al [4] and by Saito et al [5].

Much better results can be obtained when we use α_t-(BEDT-TTF)$_2$I$_3$ crystals, for which T_c = 8 K at ambient pressure, and consequently we have only two s-n interfaces (fig. 1). Thus, to obtain Δ, we have to divide the measured voltage by a factor of 2. We show the R vs. V and dR/dI vs. V curves at T = 1.6 K in fig. 3 (a,b,c), and R vs. V curves at various temperatures in fig. 3d. We see that the structure disappears at $T = T_c$, and is thus due to the superconducting state. There is structure in 3 regions: (i) There is a minum in R at zero bias. This minimum is very sharp, about $\delta_{1/2}(0) \approx 0.25$ meV. We denote the width by δ, since we do not want to commit ourselves to say that this is the band gap Δ. The superscript (0) denotes zero bias, and the subscript 1/2 indicates that this is the width to about half the "final" value. (ii) There is a maximum in R at $\delta_M^{(1)} \approx 5.2$ meV, and a maximum in dR/dI at $\delta_{1/2}^{(1)} \approx$ 4.5 meV. (iii) There is a maximum in R at $\delta_M^{(2)} \approx 12.5$ meV, and a maximum in dR/dI at $\delta_{1/2}^{(2)} \approx 11.5$ meV. Note that these three structures are very sharp, and there is hardly any structure elsewhere.

We can now assign the structures of other BEDT-TTF salts, which are much broader, to $\delta^{(0)}$, $\delta^{(1)}$, $\delta^{(2)}$. This assignment is listed in table 1. Note that now we can understand the discrepancy between the results of Hawley et al [4], who reported a value of "Δ" ≈ 2.5 meV in β-(BEDT-TTF)$_2$IAuI, and our value of 0.7 meV in this material [3]. Our value is $\delta_M^{(0)}$, while Hawley's et al value is $\delta_{1/2}^{(1)}$

The zero-bias structures $\delta(0)$ is sometimes a maximum in R, as it should be for Giaever tunneling (fig. 3 of ref. 3), and sometimes a minimum, as it should be for Andreev reflection (fig. 3). But the width is always in the same range. We note that in one case the structure changed from a maximum to a minimum as function of temperature; namely fig. 2 of ref. [3]. At T = 0.08 K it is a maximum, while at T = 1.6 K it is a minimum. The change is gradual as function of temperature.

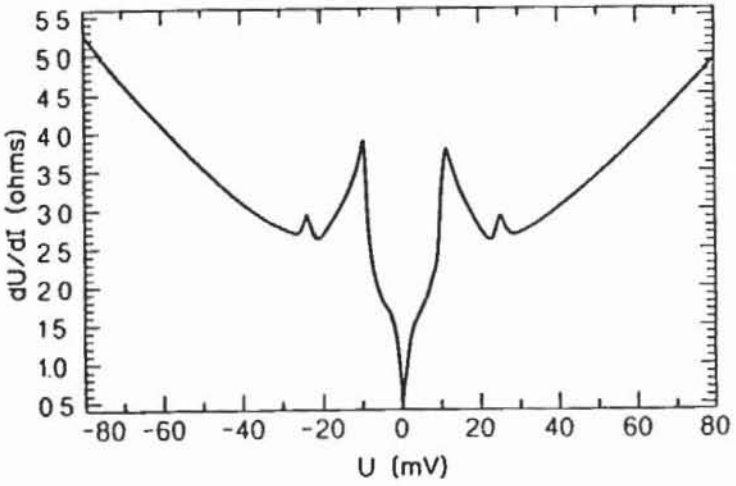


Figure 3a

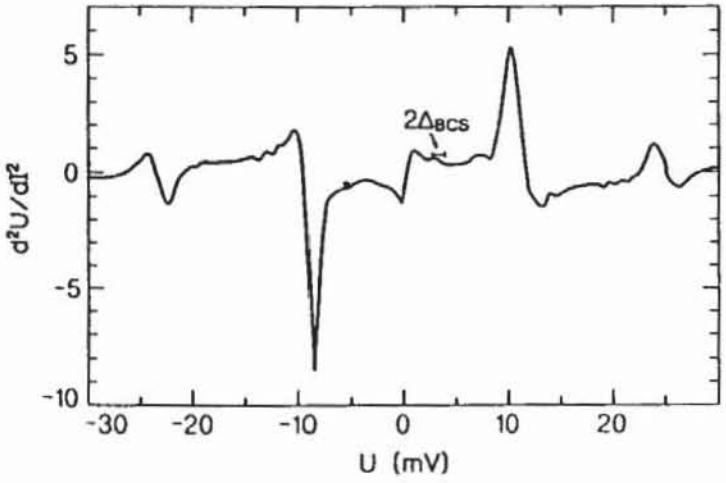
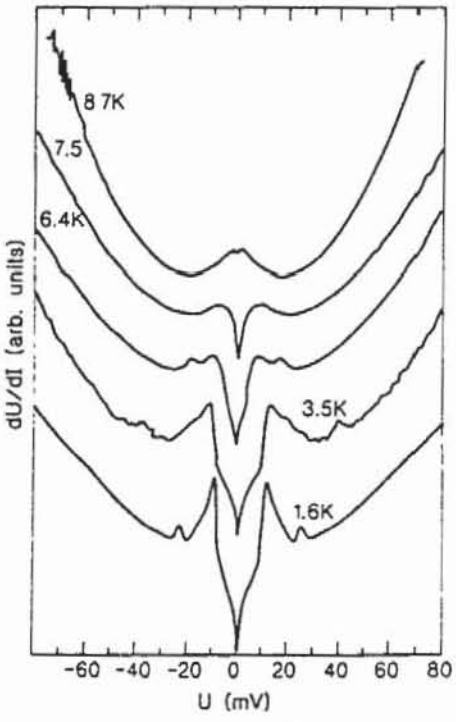


Figure 3b



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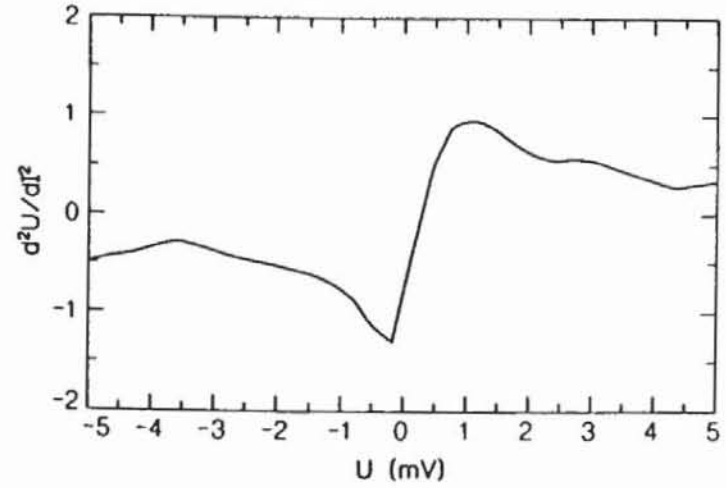

Figure 3c

Figure 3: The differential resistance dV/dI(a) and the second derivative d^2V/dI^2(b) as a function of V for α_t-(BEDT-TTF)$_2$I$_3$ at T=1.6 K. The data near zero bias are shown in (c). Figure 3d shows dV/dI vs. V curves at various temperatures.

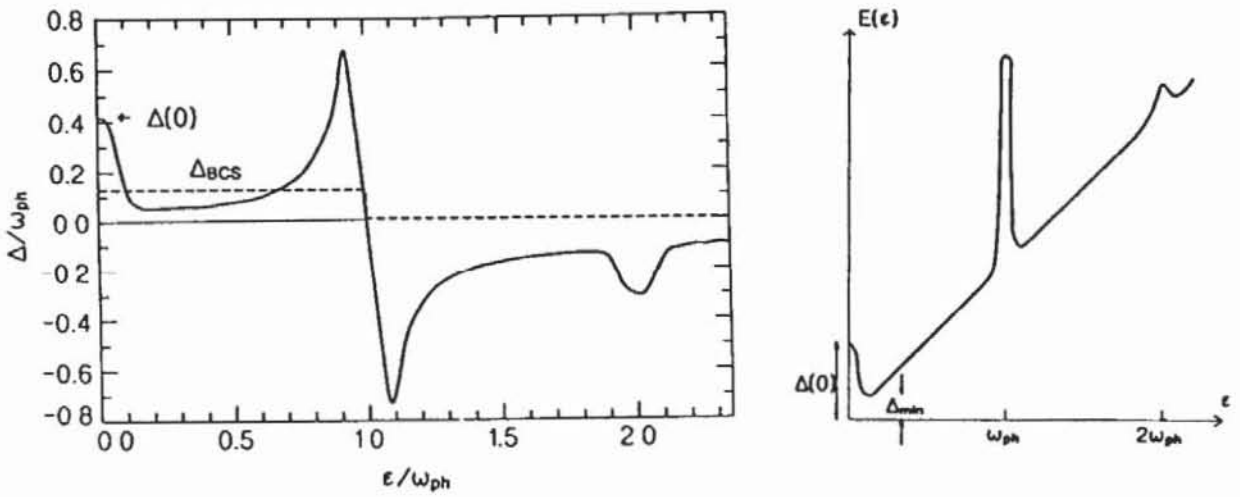

Figure 4: (a) $\Delta(\varepsilon)$ as function of the one-electron energy ε, for an Einstein spectrum, with an electron-phonon coupling constant $\lambda = 0.5$, and a "bare" Coulomb interaction $\mu = 0.4$. The conventional BCS solution is also shown. (b) The excitation energy $E(\varepsilon) = \sqrt{\varepsilon^2 + |\Delta(\varepsilon)|^2}$ as function of ε. The minimum is not at $\varepsilon = 0$ (the Fermi level) but slightly away.

Table 1: Explanation see text.

	T [K]	$\delta_T^{(0)}$ [mV]	$\delta_{1/2}^{(0)}$ [mV]	$\delta_T^{(1)}$ [mV]	$\delta_{1/2}^{(1)}$ [mV]	$\delta_T^{(2)}$ [mV]	$\delta_{1/2}^{(2)}$ [mV]	T_c [K]
β-(BEDT-TTF)$_2$I$_3$	0.08	0.5	0.21					1.35
(point contact) [3]	1.4	0.5	0.3	5.5	3.75			(?)
β-(BEDT-TTF)$_2$IAuI								
(vacuum tunneling) [3]	0.47	0.7	0.35					4.1
Hawley et al [4]	2.4			4	2.5			4.1
α_t-(BEDT-TTF)$_2$I$_3$								
(point contact)	1.4		0.25	5.2	4.5	12.5	11.5	8.0

DISCUSSION

a. Conventional interpretation.

The conventional interpretation identifies δ with the BCS gap Δ_{BCS}, which is related to the transition temperature T_c by $\Delta_{BCS} = 1.76\ T_c$ for weak coupling, and $\Delta_{BCS} \approx 2\ T_c$ for strong coupling [10]. When we attempt such an identification, we face the problem whether to identify Δ_{BCS} with $\delta^{(0)}$ or with $\delta^{(1)}$, which differ from each other by an order of magnitude. Moreover, neither $\delta^{(0)}$ nor $\delta^{(1)}$ are close to Δ_{BCS}; $\delta^{(0)}$ is 3 to 6 times smaller for the α_t-(BEDT-TTF)$_2$I$_3$; (for β-(BEDT-TTF)$_2$IAuI, $\delta_M^{(0)}$ is close to Δ_{BCS}, as we pointed out in ref. [3]. $\delta^{(1)}$ is 3-4 times bigger than Δ_{BCS}, as was already pointed out by Hawley et al [4].

When $\delta^{(0)}$ corresponds to a minimum in R(0), we may associate $\delta^{(1)}$ with Δ_{BCS}, and $\delta^{(0)}$ with a Josephson effect, or alternatively with a proximity effect in the normal region that is in contact with the superconducting region. A maximum in R(0) may be associated with

states in the barrier, a Schottky barrier, perhaps. But the rather constant value of $\delta^{(0)}$ for many crystals and the fact that it is the same whether R(0) is a minimum or a maximum, makes this interpretation tenous.

Also, if we identify $\delta^{(1)}$ with Δ_{BCS}, we have to account for the very large value of $\delta^{(1)}/T_c$. We used the Bergmann-Rainer algorithm [11] for the solution of the Eliashberg equation, and were not able to obtain such large values, for any reasonable values of λ or shape of the phonon spectrum.

It might be possible to postulate an anisotropic gap $\Delta(\Theta)$ that extends from $\delta^{(0)}$ to $\delta^{(1)}$. To account for the strong structure at $\delta^{(0)}$ and $\delta^{(1)}$, with nothing observed in between, we must postulate divergences of $d\Delta(\Theta)/d\Theta$ at (say) $\Theta = 0$ and $\Theta = \pi/2$. Such a model is artificial, and we do not see how it can be related to the band structure of these materials [12].

Alternatively, it might be possible to postulate a two-band model, like those of Suhl et al [13] and Kresin et al [14], in which one band possesses the gap $\delta^{(0)}$, and the other one the gap $\delta^{(1)}$, and T_c is in between. For such a model, the scattering matrix elements between the two bands must be extremely small, and we do not believe that this is physical.

b. Unconventional interpretation.

Raman spectra [15] of $(BEDT\text{-}TTF)_2I_3$ salts show that a phonon energy is given by 4 meV. A Raman-line at 15 meV, and its harmonic are due to stretching vibrations of the I_3, which probably do not couple strongly with the electrons on the donor molecule.

Raman data yield the frequency of just the q=0 phonon. However, the unit cell is large, therefore the Brilluoin-zone is very small, and therefore we do not expect a very large dispersion of an individual optical mode. There is a rather large number of optical branches, since there are two BET-TTF molecules per unit cell, each with 6 degrees of translational and rotational freedom, and an I_3 molecule, with 5 degrees of freedom; but only the branch at 4 meV is seen in the Raman data. Therefore, we believe that the coupling of the other branches with the electrons is not very strong. (In principle, symmetry may prohibit a mode from being Raman active, and we should look by IR whether there are other modes in that range which are IR active). In any case, the Raman data suggest that the phonons that couple with the electrons are optical, with a frequency of 4 meV, and a rather low dispersion.

This frequency is surprisingly close to $\delta^{(1)}$. Therefore, it is possible that this coincidence is not accidental, and $\delta^{(1)}$ is the phonon frequency ω_{Ph}. This immediately explains the high value of $\delta^{(1)}/T_c$.

As for the temperature dependence, $\delta_{1/2}^{(1)}$ decreases with increasing temperature and may be roughly fitted with a BCS dependence, as Hawley et al [4] have shown. However, $\delta_M^{(1)}$ apparently does not vary with temperature. Unfortunately, the R vs. V curve broadens rapidly as temperature is increased, therefore it was not possible to determine the temperature dependence of $\delta_M^{(1)}$.

If we identify $\delta^{(1)}$ with ω_{Ph}, the problem arises why don't we see the Giaever structure at Δ_{BCS} (fig. 3). This is the strongest structure normally observed, and phonon structures are much weaker, as shown by the classical McMillan-Rowell theory [16].

A novel theory, that predicts a strong structure at ω_{Ph}, and none at Δ_{BCS}, has been proposed recently [17]. In this theory, the gap function $\Delta(\varepsilon)$ does not follow the conventional BCS behaviour, but has a sharp peak at $\varepsilon = 0$, and a very strong structure resembling a derivative of a δ-function at $\varepsilon = \omega_{Ph}$ (fig. 4a). There is also a structure at $\varepsilon = 2\omega_{Ph}$. This structure of the gap function gives rise to an excitation energy $E(\varepsilon) = \sqrt{\varepsilon^2 + |\Delta(\varepsilon)|^2}$ as shown in fig. 4b. This curve differs from the conventional $E(\varepsilon) = \sqrt{\varepsilon^2 + \Delta_{BCS}^2}$ curve by having the minimum away from $\varepsilon = 0$; actually, the lowest excitation energy Δ_{min} is much smaller than $\Delta(0)$. This minimum gap should play the role of Δ_{BCS} in both Giaever tunneling and Andreev reflection. At $\varepsilon = \omega_{Ph}$, there is a sharp peak in $E(\varepsilon)$, which implies a sharp minimum

in the density of states n(E) at this energy (a quasi-gap). This quasi-gap implies a minimum in the conductivity. $\sigma(E)$ at this energy, and consequently a maximum in the resistivity.

Both these features - namely a Δ_{min} much smaller than Δ_{BCS} (i.e. $\Delta(0)$), and a maximum of R(V) at ω_{Ph}, are indeed observed experimentally.

c. Relationship with other observations in superconducting BEDT-TTF radical salts.

Takahashi et al [18] reported measurements of the London penetration depth in crystals of $(BEDT-TTF)_2Cu(NCS)_2$ at low temperatures, that show a power-law behaviour: $\lambda_{London}(T) - \lambda_{London}(0) \sim T^2$ instead of the conventional BCS exponential behaviour. $\lambda_{London}(T) - \lambda_{London}(0) \sim \exp(-\Delta_{BCS}/T)$. These experimental results are still contested However, we wish to point out that the Δ that enters the BCS expression for the penetration depth is the minimum excitation energy Δ_{min}, which we identify with $\delta^{(0)}$, which is 3 to 6 times smaller than Δ_{BCS} for α_t-$(BEDT-TTF)_2I_3$. Such a low value of Δ_{min} implies a power-law behaviour in the temperature range investigated by Takahashi et al, just as it is the case for the heavy Fermions [19].

Saito et al [5] reported that H_{C2} can exceed the paramagnetic (Clogston) limit, that is obtained when the Zeeman energy $(1/2)\chi_S H^2$ exceeds the binding energy W, which in the conventional BCS theory is given by : $W = (1/2)n(E_F)\Delta_{BCS}^2$ This conventional expression for W is derived for a gap-funtion $\Delta(\varepsilon)$ which is constant up to $\varepsilon = \omega_{Ph}$, and zero above. Our $\Delta(\varepsilon)$ function is different (fig. 4a). Therefore we have to derive the binding energy by integrating over the energy ε using the expression:

$$W = \int_0^{E_F} \frac{\left(\sqrt{\varepsilon^2 + |\Delta(\varepsilon)|^2} - \varepsilon\right)}{\sqrt{\varepsilon^2 + |\Delta(\varepsilon)|^2}} n(\varepsilon)\, d\varepsilon$$

Since $\Delta(\varepsilon)$ is very large for $\varepsilon \approx \omega_{Ph}$, we obtain a contribution to the integral from this region which exceeds the contribution from the region $\varepsilon \approx 0$. Therefore, W is considerably larger than the conventional value [20]. As a result, the thermodynamic critical field, as well as the paramagnetic limit, are considerable larger than their conventional values, and therefore H_{C2} can be larger too.

Delhaes et al [21] found coexistence of antiferromagnetic spin fluctuations and superconductivity. Our theory predicts that these fluctuations not only coexist with superconductivity, but even enhance T_c. We cannot go into this here, but discuss this point elsewhere [20].

Last but not least we point out a striking analogy with the High-T_c cuprates In $YBa_2Cu_3O_7$, it was found by Wieck et al [22] (as well as by several other groups) that the IR reflectivity has a step-like behaviour at the phonon frequency (such as the phonon at 580 cm^{-1}). This step vanishes at and above T_c, but its frequency is temperature-independend; it is always the phonon frequency. This supports our claim that a gap-like behaviour can exist at the phonon frequency in α_t-$(BEDT-TTF)_2I_3$ as well.

CONCLUSIONS

α_t-$(BEDT-TTF)_2I_3$ crystals provide us with sharp, highly reproducible tunneling data, that we believe are definitive. Up to now, we are not able to obtain such good data with crystals of other BEDT-TTF radical salts. The α_t-$(BEDT-TTF)_2I_3$ crystals possess a mosaic type structure, which other single crystals of BEDT-TTF radical salts do not. With them, it is possible to produce compressed pellets that are good superconductors [23] and superconducting evaporated thin films [24]. Perhaps the ductility and malleability of these crystals, which may be due to their mosaic type structure, is responsible for the excellent electrical properties of the contacts, where the pressure is very large and probably anisotropic.

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