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Zero-Bias Anomalies in Point-Contact Characteristics of α_t-(BEDT-TTF)$_2$ I$_3$.

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Abstract. – The zero-bias anomaly in point-contact characteristics of the organic superconductor α_t-(BEDT-TTF)$_2$ I$_3$ is investigated as a function of temperature and magnetic field. It is found that the zero-bias anomaly is insensitive to magnetic fields up to 5 T. In contrast, a structure at 5 meV, conventionally designated as the superconducting gap—but which is 4 times larger than the expected BCS gap—is strongly affected by magnetic fields above 1 T.

Introduction. – Tunnelling measurements, as pioneered by Giaever [1], provide a most direct evidence about the existence and the value of the superconducting gap Δ. For superconductors obeying BCS theory, the tunnelling conductance dI/dV vanishes for voltages V less than Δ/e (for normal-insulating-superconducting (n-i-s) structures) or $2\Delta/e$ (for s-i-s structures), and has a sharp maximum at $V = \Delta/e$ (or $2\Delta/e$). The vanishing of the conductance indicates that there are no states in the gap.

An alternative technique for obtaining similar information is point contact spectroscopy (PCS), as pioneered by Yanson [2]. In this technique one investigates n-s and s-n-s structures, utilizing the phenomenon of Andreev reflections, which increases the conductivity dI/dV for voltages less than Δ/e by as much as a factor of 2. The detailed theory for such junctions was worked out by Blonder, Tinkham and Klapwijk [3], who also studied the continuous transition from ideal Andreev reflection to Giaever tunnelling, as the impedance of the n-s interface increases. Thus, the information obtained by PCS is similar to that obtained by tunnelling, yet this technique does not necessitate to produce high-quality insulating layers, which is problematic in several «exotic» superconductors. Thus, good «break junctions» PCS data were obtained for high-T_c cuprate superconductors [4].

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In addition to the superconducting gap Δ, tunnelling and PCS measurements sometimes indicate structures at voltages much lower than Δ/e, and these are known as «zero-bias anomalies» (ZBA). In normal-state tunnelling (*i.e.* n-i-n structures), these have been known for quite some time; Shen and Rowell [5] observed maxima in the conductivity at zero bias, which they claimed could be explained by the Appelbaum-Anderson mechanism, and large resistance anomalies, which were not explained. More recently ZBAs were observed in tunnelling characteristics of YBCO [6], NdCeCuO [7] and KBaBiO [8]. These anomalies manifest themselves as a sharp maximum in the resistivity at zero bias in s-i-n structures, and as a sharp maximum in the conductivity at zero bias in s-n structures. The origin of the ZBA has not yet been established. One suggestion is that it is due to magnetic impurities in the boundary layer, giving rise to an Appelbaum-Anderson mechanism, which is a kind of a Kondo effect [9]. Another possibility is that it is a spectroscopic feature, due to the presence of states in the superconducting gap. When states are present at any energy eV, tunnelling is possible to these states, and as a result the tunnelling conductivity dI/dV at voltage V will not vanish. When there is a threshold for such states at an energy $\delta^{(0)}$, the tunnelling conductivity will vanish at lower voltages, accounting for the observed minimum. In BCS theory, such states do not exist. Therefore, the observation of such states is an indication of some deviation from BCS theory. In BCS theory, the gap function Δ is a constant (up to the high phonon energy), but in some generalizations of BCS theory, $\Delta(\varepsilon, \theta)$ is a function of the angle θ (of the k-vector of the electronic state) and/or of the energy ε. Specifically, in «d-wave pairing» $\Delta(\varepsilon, \theta)$ is proportional to $\cos\theta$ [10], and thus there are states present down to zero energy. When $\Delta(\varepsilon, \theta)$ has a sharp maximum at $\varepsilon = 0$ (the Fermi surface) and falls off sharply as going away from the Fermi surface, the excitation energy $E(\varepsilon) = \sqrt{\varepsilon^2 + \Delta(\varepsilon)^2}$ will have a minimum at a finite value of ε, and thus there are states present at energies between the minimum and $\Delta(0)$, the gap at the Fermi surface. A model based on this concept was proposed previously [11-13].

Thus, the ZBA serves as an indication of essential deviations from BCS theory, and is of vital importance for the elucidation of the superconducting mechanism in high-T_c cuprates as well as in other superconducting systems. In order to discriminate between the various possibilities for the origin of the ZBA, measurements of the magnetic-field dependence of the tunnelling characteristics are very useful. Such measurements have been carried out for YBCO by Lesueur and Greene [14].

The present work is concerned with ZBAs in organic superconductors of the $(BEDT\text{-}TTF)_2X$ ($X = I_3$, IAuI, $Cu(NCS)_2$, etc.) family. A «sign-changing» ZBA was observed on β-$(BEDT\text{-}TTF)_2I_3$ ($T_c = 1.2$ K) [15]. At temperatures of about 1 K this anomaly is a maximum in the conductivity (minimum in the resistance). At low temperatures, *i.e.* $T = 0.08$ K, the sign of the anomaly changes, and it becomes a minimum in the conductivity.

A ZBA was further investigated on α_t-$(BEDT\text{-}TTF)_2I_3$ ($T_c = 8$ K) [13]. The PCS data show very sharp structures in d^2V/dI^2 *vs.* V curves in three regions: $2\delta^{(0)} \approx 0.7$ meV, $2\delta^{(1)} \approx$ ≈ 8–10 meV and $2\delta^{(2)} \approx 20$–25 meV. It is the $\delta^{(0)}$ structure we here refer to as «ZBA». Describing the point-contact between two α_t-$(BEDT\text{-}TTF)_2I_3$ crystals as two s-n junctions in series, the width of the ZBA rescaled to a single s-n contact measured from the maximum to the half-intensity point is about 0.35 meV at 1.5 K.

A structure similr to the $\delta^{(1)}$ structure was also seen by Hawley *et al.* [16] by vacuum tunnelling into β-$(BEDT\text{-}TTF)_2$IAuI ($T_c \approx 4$ K), with $\delta^{(1)} \approx 2.5$–4 meV, and by Bando *et al.* [17] on κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ ($T_c = 10.4$ K) using a scanning tunnelling microscope (STM), with $\delta^{(1)} \approx 4.5$–6 meV. Bando *et al.* also observed structures at higher energies at about $3\delta^{(1)}$, which may correspond to the $\delta^{(2)}$ structure.

In the tunnelling data, the ZBA structures are resistivity maxima, while they appear as conductivity maxima in the PCS data. For normal superconductors, a similar change of sign may be accounted for by the BTK theory [3], in which a junction with a low tunnelling barrier, described by a parameter Z, has a drop in conductivity as the voltage exceeds the gap (Andreev reflection), while one with a high Z has an increase in conductivity at $eV = \Delta$ (Giaever tunnelling). This sign reversal may help to discriminate «genuine» spectroscopic features from «spurious» ones, such as Josephson tunnelling—that can give rise to a maximum in conductivity at zero bias—and critical-current effects. Effects where the electronic mean free path falls as eV exceeds the phonon frequency, due to spontaneous emission of phonons [18], giving rise to an increase in resistivity for point contact spectroscopy, but not affecting tunnelling data, are also excluded for the same reason.

In the present note, we present the magnetic-field dependence of the ZBA ($\delta^{(0)}$) and the $\delta^{(1)}$ structures in α_t-(BEDT-TTF)$_2$I$_3$. In addition we show a «tunnelling» curve for α_t-(BEDT-TTF)$_2$I$_3$ (dV/dI and dV^2/dI^2 curves) for a heterojunction between an α_t-crystal and a tungsten (W) wire.

Experimental and results. – Two α_t-(BEDT-TTF)$_2$I$_3$ crystals were pressed together in such a way that the current was flowing in the (a, b)-plane, and I-V curves were taken at various temperatures [13]. The second-derivative curves of the characteristics of such point-contacts at various temperatures are plotted in fig. 1. The three sharp structures referred to as $\delta^{(0)}$, $\delta^{(1)}$ and $\delta^{(2)}$ are clearly seen.

The magnetic-field dependence of the dV/dI and the d^2V/dI^2 curves for the homocontacts of the α_t-(BEDT-TTF)$_2$I$_3$ crystals, at a temperature of 1.6 K, and in magnetic fields up to 5 T, is shown in fig. 2. The magnetic field is approximately parallel to the current flow (*i.e.* in the (a, b)-plane). It is seen that the $\delta^{(1)}$ structure decreases strongly with magnetic fields of 1–2 T, the resistance dV/dI is significantly increased by the magnetic field in the low-voltage region ($V < 5$ mV), while the $\delta^{(0)}$ structure (as seen in the second-derivative curve) is almost unaffected even in a field of 5 T.

In fig. 3 we show the tunnelling characteristic of a n-i-s tunnelling contact; a W needle was

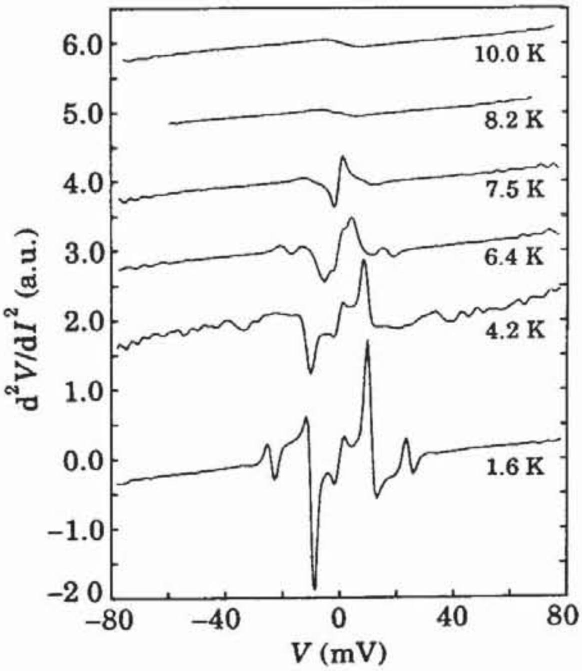

Fig. 1. – Second derivative (d^2V/dI^2) of the characteristics of an α_t-(BEDT-TTF)$_2$I$_3$ point contact (s-n-s homocontact) at various temperatures.

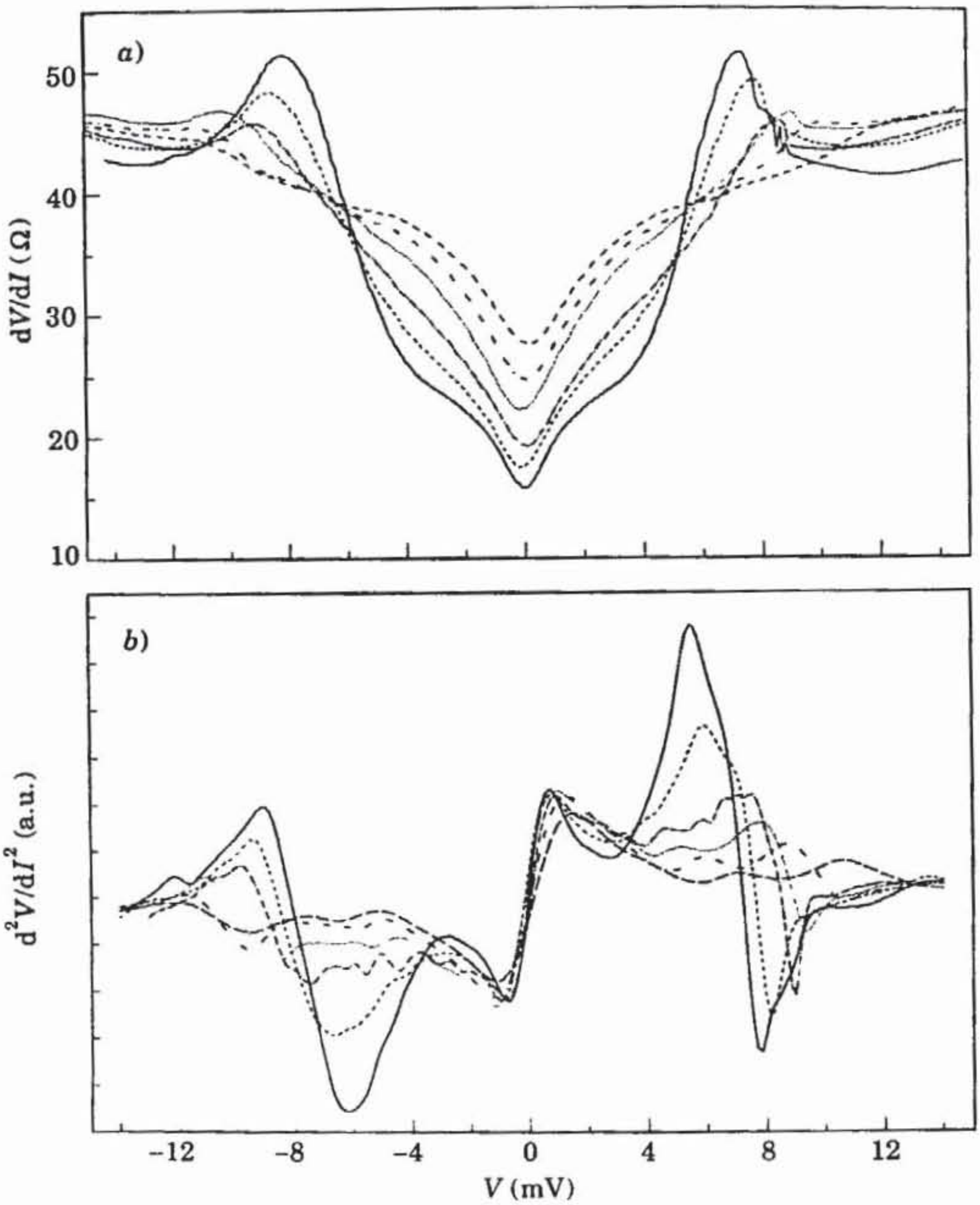

Fig. 2. – *a*) First derivative (dV/dI) and *b*) second derivative (d^2V/dI^2) of the characteristics of an α_t-(BEDT-TTF)$_2$I$_3$ s-n-s point contact in a magnetic field. --- 5 T, –·–·– 4 T, ···· 3 T, –·–·–·– 2 T, ---- 1 T, —— 0 T; $T = 1.6$ K.

moved against an α_t-(BEDT-TTF)$_2$I$_3$ crystal using an STM mechanism, until a finite (but very large) resistance was obtained. dI/dV and d^2I/dV^2 curves are shown ($T = 1.5$ K). A structure is clearly seen as a sharp conductivity maximum at 5.2 meV. The $\delta^{(0)}$ structure was not seen in this experiment (just like in the tunnelling measurements of Hawley [16] and Bando [17]). The nature of the insulating barrier (i) in this experiment is not known.

Discussion. – The features of the zero-magnetic-field *I-V* curves have been discussed previously [13]. Here we point out again that the $\delta^{(1)}$ structure at 5 meV is about four times higher than the expected BCS gap, this ratio being considerably larger than the corresponding ratio in high-T_c cuprates. In Raman spectra, phonons are observed at 3.5 meV and at 5 meV [19]. Thus, the $\delta^{(1)}$ structure coincides with one of the phonons. This may, or may not, be an accident, as discussed in [13].

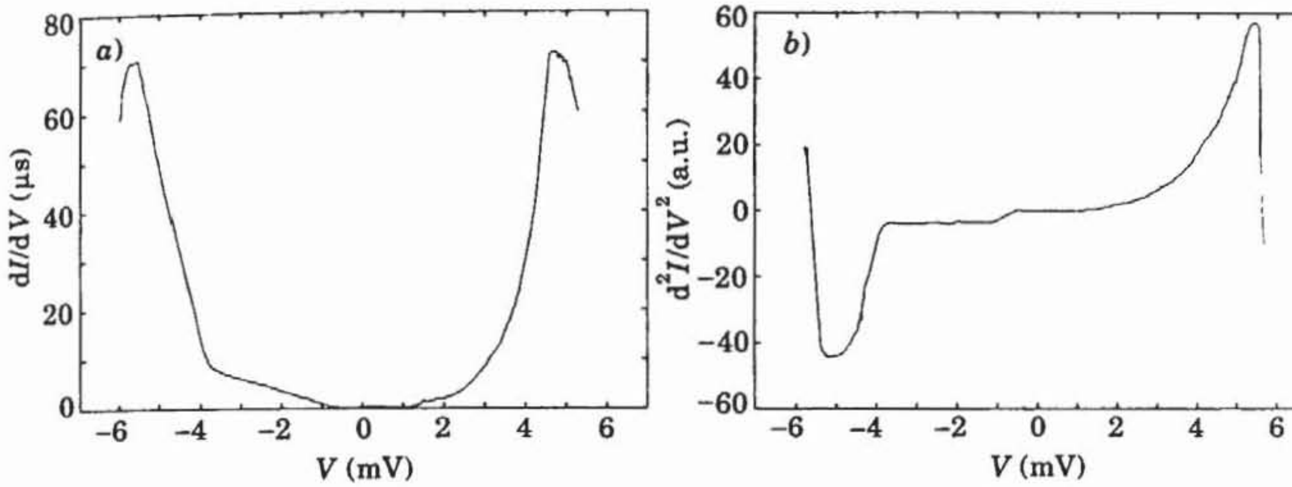

Fig. 3. – *a*) First derivative (dI/dV) and *b*) second derivative (d^2I/dV^2) of a tunnelling characteristic of a W-α_t-(BEDT-TTF)$_2$I$_3$ contact ($T = 4.2$ K).

The salient feature of the magnetic-field dependence is the strong field dependence of the $\delta^{(1)}$ structure, and the nearly field-independent behaviour of the $\delta^{(0)}$ structure. The critical field H_{c2} for α_t-(BEDT-TTF)$_2$I$_3$ (H in the (a, b)-plane) is about 11 T at 1.6 K [20], thus the field that drastically decreases the $\delta^{(1)}$ structure (1 to 2 T) is very low in comparison and thus is not expected to affect the superconductivity of this material. Even a field of 5 T has not a strong effect on the superconductivity, and thus the small effect on the $\delta^{(0)}$ structure is not altogether mysterious.

However, the ZBA is often attributed to an Appelbaum-Anderson effect [5, 14], which is a kind of Kondo effect involving scattering on spins in an insulating layer [9]. In a strong magnetic field, this effect gives rise to a structure at the Zeeman splitting energy $eV = g S \mu_B H$ [21]. Thus, this effect is modified by a magnetic field which polarises the spins. Since the energy involved here is about 0.35 meV, it should be affected by a Zeeman spin splitting of this order, *i.e.* a field of about 3 T for $g = 2$. The effect of the magnetic field on the $\delta^{(0)}$ structure thus seems to be too weak to account for the structure by this mechanism.

The effect of the magnetic field on the $\delta^{(1)}$ structure is strong; the $\delta^{(1)}$ structure is conventionally designated as the superconducting gap (however, see [13]). We are not aware of a «basic» physical mechanism by which Zeeman spin splitting should remove (or broaden) the superconducting gap structure.

Since we deal with Andreev reflections, orbital magnetic effects may affect the sharpness of the structures of the I-V curves. Thus, we may expect the magnetic field to broaden the structures when the cyclotron frequency ω_c is comparable with the widths of the structures. For an effective mass of $m_{eff} \approx m_0$, ω_c is about 0.35 meV in a field of 3.5 T, and about 0.7 meV (*i.e.* the width of the $\delta^{(1)}$ structure) in a field of about 7 T. De Haas-van Alphen oscillations in several BEDT-TTF salts indicate $m_{eff} \approx 3m_0$ [22]; this value can account (roughly) for the absence of an effect at 5 T in the $\delta^{(0)}$ structure; however, the large effect on the $\delta^{(1)}$ structure can be accounted for in this way only if m_{eff} is considerably less than m_0.

Recently it was suggested that, due to a very narrow Lindhard peak, the velocity has a maximum at the Fermi level [23]. If this is indeed the case, the inverse effective mass $1/m_{eff} = h^{-1} dv(k)/dk$ is zero right at the Fermi level, but becomes very large at some distance away from it. Such a very strong k-dependence of the effective mass can, in principle, account for these observations; however, such a mechanism is speculative at the present stage.

Orbital magnetic effects should increase the resistivity when ω_c is of the order of the scattering rate τ^{-1}. This rate is estimated to be about 100 meV at 300 K; the resistance ratio $\rho(300)/\rho(10)$ in good samples of BEDT-TTF radical salts is at least 1000 [24], and the resistivity continues to decrease below 10 K [25]. Thus, a scattering rate below 0.1 meV at 1.5 K is plausible, with $\omega_c \approx \tau^{-1}$ but: $\omega_c \ll \delta^{(0)}$, accounting for the increase in resistivity with magnetic field, without a significant effect on the zero bias anomaly.

Conclusion. – The PCS experiments on superconducting radical salts of BEDT-TTF indicate the presence of states in the gap, and thus of an essential deviation from BCS theory. States in the gap may be due to *d*-wave pairing, extended *s*-wave pairing or a very strong energy dependence of the gap function at very low energies [26]. The present experiments help us to discriminate between these possibilities. For *d*-wave pairing, states extend all the way to zero energy, thus there is no ZBA. Therefore we cannot account for our data by *d*-wave pairing in a «simplistic» way. Extended *s*-wave pairing can give rise to two gaplike structures—a minimum gap $\min[\Delta(0,\Theta)]$ and a maximum one $\max[\Delta(0,\Theta)]$. We may associate the minimum with $\delta^{(0)}$ and the maximum with $\delta^{(1)}$. Such a model was proposed for YBCO by Tachiki *et al.* [27]. However, the Fermi surface in BEDT-TTF salts is cylindrical [28] and therefore we doubt whether an anisotropy of more than 10:1 for the superconducting gap is plausible. Also, the lower gap suggests a low critical field, while the experiment shows that the $\delta^{(0)}$ structure is nearly field independent. The third possibility, namely a strong energy dependence of the gap [13], is in line with the normal-state properties of organic metals, which suggests a very strong *k*-dependence of the mean free path [23, 29]. A theory that predicts such a behaviour was proposed recently [30]. This theory is rather complicated, and we cannot describe it properly in the present short note, but an essential feature of it is an anomalous behaviour of the effective mass m^*, with a maximum at the Fermi surface and a rather small value a few meV away. This feature would be consistent with the present measurement of the field dependence of the $\delta^{(0)}$ and $\delta^{(1)}$ structures.

In conclusion, the observation of the ZBA in α_t-(BEDT-TTF)$_2$I$_3$ and its magnetic-field dependence may serve as an important experimental «fingerprint» that can help us to establish the mechanism of superconductivity in organic superconductors.

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