Point-contact spectroscopy of α_t-(BEDT-TTF)$_2$I$_3$: an alternative interpretation

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We report on point-contact measurements on the organic superconductor α_t-(BEDT-TTF)$_2$I$_3$ ($T_c \approx 8$ K). The dV/dI vs V characteristics of homocontacts of this material show strong nonlinearities which, interpreted as a gap-structure, lead to extremely high values of Δ/kT_c. Among other possibilities, we discuss the anomaly in terms of a strongly enhanced McMillan–Rowell structure $\Delta(\varepsilon)$ at $\varepsilon = \Delta_{BCS} + \omega_{ph}$. The enhancement is caused by deviations from the Eliashberg equations due to strong coupling ($\lambda = 1$–2) together with an Einstein phonon spectrum.

Introduction

Since the discovery of superconductivity in the organic metal (BEDT-TTF)$_2$X [1] a continuous rise of the superconducting transition temperature was achieved by varying the anion group X. Starting from $T_c \approx 1.3$ K in β-(BEDT-TTF)$_2$I$_3$ [2] it is today possible to reach transition temperatures of more than 10 K in e.g., (BEDT-TTF)$_2$CuNCS [3]). In contrast to the earlier discovered TMTSF$_2$X family of organic superconductors [4], the properties of the BEDT-TTF materials are rather two- than one-dimensional (e.g., [5]), a property shared with many high-T_c superconductors.

Tunneling and point-contact experiments on the lower-T_c compounds β-(BEDT-TTF)$_2$I$_3$ and (BEDT-TTF)$_2$I$_2$Au gave evidence for an anomalously high value of the ratio Δ/kT_c up to 2–3 times the BCS value [6,7]. This is again a similarity to results obtained on high-T_c superconductors (e.g., [8]).

In this work, we report on point-contact experiments on α_t-(BEDT-TTF)$_2$I$_3$. This material has a transition temperature of 8 K and is obtained from the α-phase of (BEDT-TTF)$_2$I$_3$ by annealing [9]. The unmodified α-phase is semiconducting below a metal–insulator transition temperature of 135 K. We discuss several possibilities of an interpretation of the strong nonlinearities found in the dV/dI vs. V characteristics of α_t-(BEDT-TTF)$_2$I$_3$ point contacts. Interpreting them in the conventional way as a gap structure, we obtain even larger values of Δ/kT_c.

Experimental

Single crystals of α_t-(BEDT-TTF)$_2$I$_3$ were prepared by the method described in [9]. The samples had the form of thin plates with typical dimensions $0.1\times2\times2$ mm. Two samples were mechanically made to touch in order to form a point contact. Due to the shape of the single crystals, the contacts were always aligned in the *ab*-direction (the direction of the lower resistivity).

Electrical contacts on the samples were made by silver-paint on evaporated gold spots. The dV/dI vs. V characteristics were recorded by a standard four-terminal lock-in technique. The measurements were done in the temperature range 1.5–15 K and in magnetic fields up to 5 T.

On first touch, the contacts usually were high-ohmic (~1 kΩ), their characteristics were noisy and irreproducible. Lower-ohmic contacts with resistances in the range 1–50 Ω were obtained by applying voltages of a few hundred mV to the high-ohmic contacts. Now, qualitatively reproducible characteristics with strong nonlinearities could be measured. From a theoretical point of view, additional measurements on heterocontacts between α_t-(BEDT-TTF)$_2$I$_3$ and a normal metal would be interesting. However, we did not manage to make high-quality heterocontacts so far.

Results

We show two examples of temperature-dependent characteristics α_t-(BEDT-TTF)$_2$I$_3$ point contacts in Figs 1 and 2. In the normal state, the characteristics show more or less pronounced zero-bias maxima in the dV/dI vs V characteristics. The width and height of the zero-bias maxima were not reproducible and

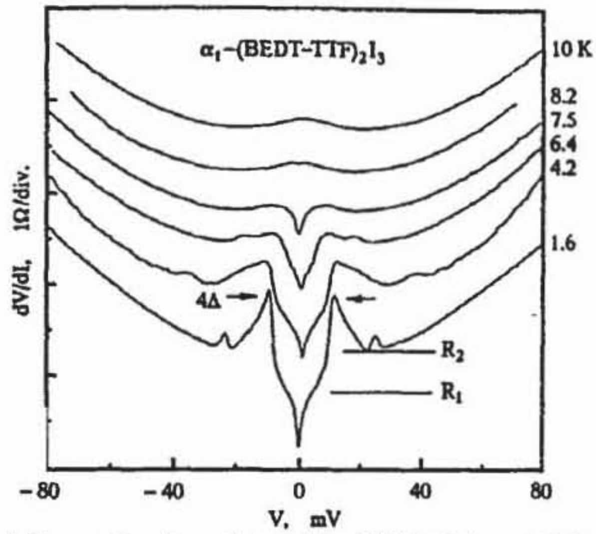

Fig. 1. Temperature dependence of the dV/dI vs V characteristics of an α_t-(BEDT-TTF)$_2$I$_3$ point contact. The differential resistance is approximately 5.5 Ω at $V = 80$ mV for all curves. The ratio of resistances R_2/R_1 is approximately 2 (see text).

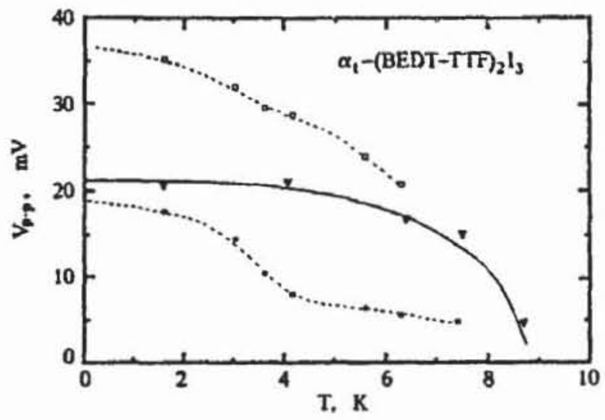

Fig. 3. Temperature dependence of the position of some structures in the characteristics of Figs 1 and 2. Triangles: from Fig. 1 (4Δ). Squares: structure (1) from Fig. 2. Open squares: structure (2) from Fig. 2. The solid line is a BCS-like dependence Δ(T), the dashed lines are «guides to the eye».

seems to depend strongly on local properties of the contact region, determined e.g., by mechanical stresses or an insulating surface barrier. An increase of the temperature to more than 15 K usually caused an irreversible broadening of the maximum.

Below T_c strong nonlinearities due to the superconductivity arise. At the lowest temperature, we can distinguish between several parts of the superconducting anomaly:

1) a narrow zero-bias minimum with an almost diverging differential resistance close to zero bias,

2) a broader zero-bias minimum, clearly separated from the first one, with maxima at its edges at voltages in the range 8–11 mV (we call this the «main structure»),

3) additional maxima at higher voltages (harmonics).

In Fig. 3, we show the temperature-dependent position of some of the maxima in these characteristics.

For our «best» curves, the temperature dependence of the position of the main-structure maxima seems to be like the BCS dependence of the energy gap Δ. Note that the normal-state zero-bias maximum was small in this case indicating a not strongly disturbed contact region.

The critical field H_{c2} of the type II superconductor α_t-(BEDT-TTF)$_2$I$_3$ is above 10 T at $T = 1.6$ K for fields parallel to the c-axis. Therefore, we could not suppress the superconductivity completely in our maximum field, but we observed a quite unusual magnetic field dependence of the superconducting anomaly in the characteristics (Fig. 4). While structure (1) seems to be not strongly affected by the field,

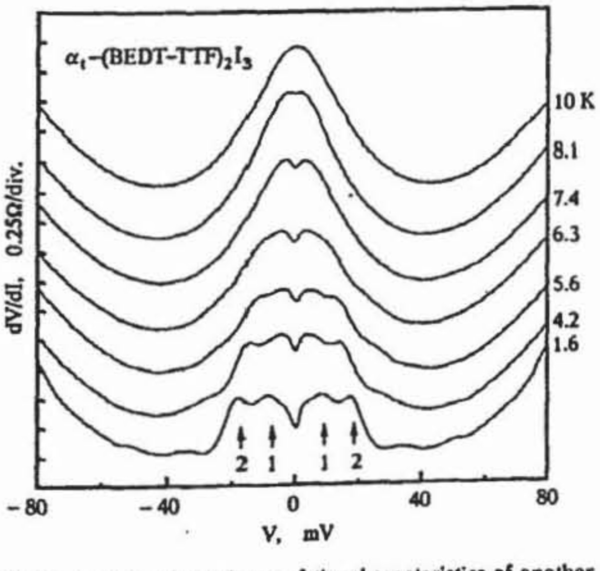

Fig. 2. Temperature dependence of the characteristics of another α_t-(BEDT-TTF)$_2$I$_3$ contact showing strong nonlinearities in the normal state. The resistance at $V = 80$ mV is 5 Ω for all curves.

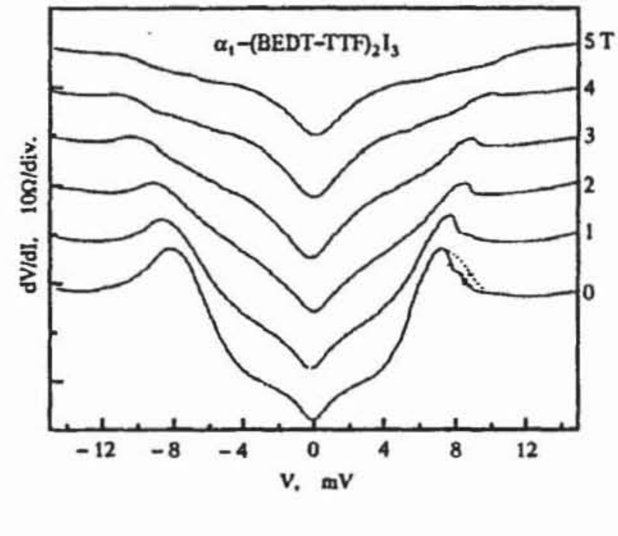

Fig. 4. Magnetic field dependence of the characteristics of an α_t-(BEDT-TTF)$_2$I$_3$ point contact. The resistance dV/dI is approximately 40 Ω at $V = 12$ mV for all curves. Around the maxima a hysteresis was observed (as indicated for positive voltages).

there is a strong broadening and flattening of the main structure. The position of the maxima moves to higher voltages linear in the magnetic field, with a slope of approximately 0.25 mV/T.

Discussion

We call structure (1) «Zero Bias Anomaly» (ZBA) following Gurvitch et al. [10], who observed a similar structure in YBCO. Such a structure was also observed in $K_xBa_{1-x}BiO_3$ by Hinks et al. [11], and reported at this conference by Smith on NdCeCuO. Thus, the appearance of this structure is quite general.

We make attempt to regard this structure as a spurious effect: Josephson tunneling, a critical current effect or some non-equilibrium phase (or quasiparticle distribution) in line with the theory of Yanson, Khlus, and their associates [12,13] presented at this conference. However, for high-T_c material a similar structure is present also in the tunneling regime, where it appears as a maximum in the resistivity. For this reason, it is possible that this structure is of spectroscopic origin, showing e.g. a strongly smeared energy gap. We shall discuss this point later in more details.

The most «obvious» way to interpret the main structure (2) is to associate it with the superconducting gap. Since our contacts are in a metallic regime (we always observed minima in the differential resistivity), we must assume that Andreev reflections are responsible for the observation of the gap, although not in a straightforward way like in N/S heterocontacts between a normal metal and a superconductor [14]. First of all, we note that our contacts do not have zero resistance at $V = 0$, so that the contact region must be normal-conducting, e.g. due to mechanical distortions. Therefore, there are two N/S boundaries between the distorted region and the superconducting material at both sides of the contact. At these boundaries Andreev reflections are possible. For a current flow from one side of the contact to the other two Andreev reflections must happen, giving rise to an observation of structures connected with 4Δ instead of 2Δ as in a N/S contact. For a more detailed discussion of this mechanism, we refer to [15].

Interpreting the structure in this way, we obtain values of Δ in the range 4–5.5 meV. Since the BCS gap should be $\Delta_{BCS} = 1.3$ meV for $T_c = 8$ K, we obtain abnormally large ratios $\Delta/kT_c \approx 3$-4 times the BCS value from our measurements. Note that the variation of the differential resistance (as indicated in the figure) due to this structure is approximately 2 for the «best» characteristics, as expected in case of Andreev reflections in a clean metallic contact [14]. However, we are not able to explain such high gap values theoretically even for very strong coupling.

Another possible interpretation is in terms of nonequilibrium phases, or distributions, arising because the mean free path $l(\varepsilon)$ drops sharply when $\varepsilon \approx \omega_{ph}$, as discussed by Khlus, Yanson, Kulik, Omelyanchouk and others at this conference. A strong nonlinearity is expected at voltages around, but not necessarily exactly at a phonon frequency ω_{ph}. For a detailed discussion, we refer to [12].

The broadening of the structure in a magnetic field seems to fit better such a model than a spectroscopic one, because it seems unlikely that a gap broadens in a magnetic field. In experiments on normal superconductors, a similar structure ascribed to a nonequilibrium distribution was found to broaden with the temperature [12].

However, tunneling experiments on β-$(BEDT\text{-}TTF)_2I_3$ and $(BEDT\text{-}TTF)_2I_3Au$ show quite broad gap structures as well [6,7]. Our results on α_t-$(BEDT\text{-}TTF)_2I_3$ thus might show a tendency to an increasing of the ratio Δ/kT_c with increasing of transition temperatures in the BEDT-TTF family.

In this work we want to discuss an alternative interpretation in terms of a giant McMillan–Rowell structure. The «normal» phonon structure is enhanced by orders of magnitude when $\Delta(\varepsilon) \approx \omega_{ph}$. For an Einstein spectrum, the gap function $\Delta(\varepsilon)$ at $\varepsilon = \Delta_{BCS} + \omega_{ph}$ is about 3–4 times larger than $\Delta_{BCS} = \Delta(0)$ (see Fig. 5). The theory predicts that the real part of $\Delta(\omega_{ph})$ is comparable with ω_{ph} for a value of λ close to 1. This was pointed out Omelyanchouk [16], and we discussed it earlier in more details [17].

The problem here is that even when $\mathrm{Re}\Delta(\varepsilon) = \varepsilon$, $\mathrm{Im}\Delta(\varepsilon)$ is large and the term $\mathrm{Re}\,[\Delta(\varepsilon)(\varepsilon^2 - \Delta^2(\varepsilon))^{-1/2}]$ in the Eliashberg equation does not diverge. We carried out numerical calculations [18] showing that even when $\mathrm{Im}\Delta(\varepsilon)$ is included, there is a singularity for a value of λ somewhat larger than the value that just gives $\mathrm{Re}\Delta(\varepsilon) = \varepsilon$.

For a comparison with our results, we must assume that the width of the main structure now gives $4\Delta(\varepsilon) \approx 4(\Delta_{BCS} + \omega_{ph})$, i.e $\Delta(\varepsilon) \approx 4$–5.5 meV. From Raman measurements, we know that there is an Einstein phonon at an energy of $\omega_{ph} \approx 4$ meV in α_t-$(BEDT\text{-}TTF)_2I_3$ [9]. Therefore, $\Delta_{BCS} + \omega_{ph}$ is indeed not far away from the experimental values.

The higher-order structures (3) are interpreted as the harmonics of the main structure. Harmonics were seen before, e.g. by Akimenko et al. [19]. We [17] attributed the second harmonic here to an inherent effect, following from an extension of Eliashberg theory.

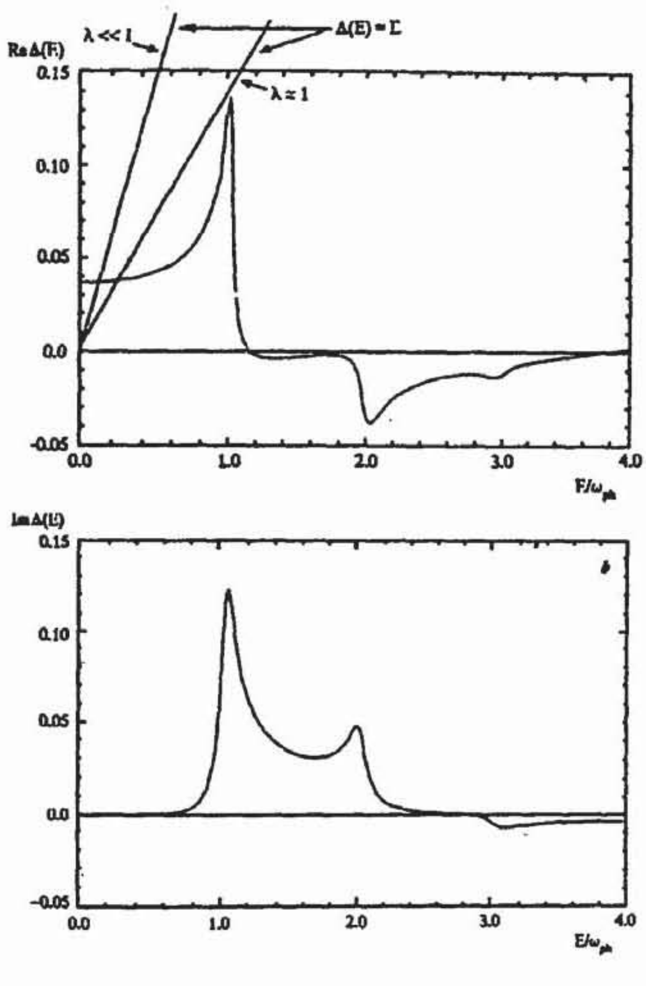

Fig. 5. Real and imaginary parts of $\Delta(\varepsilon)$ for an Einstein phonon spectrum. For $\lambda = 1$, Re $\Delta(\varepsilon) = \varepsilon$ at $\varepsilon = \Delta(0) + \omega_{\text{ph}}$.

When we interpret the main structure as a phonon structure, we are faced with the dilemma, where did the Giaever structure at Δ_{BCS} go ? We suggest that we see the minimum excitation energy in structure (1), the ZBA. In Fig. 5 we show our proposed form of $\Delta(\varepsilon)$. Right on the Fermi surface (FS), $\Delta(0) = \Delta_{\text{BCS}} = 1.76 - 2kT_c$. At energies ε smaller than Δ_{BCS} (say, 0.2 to 0.3 Δ_{BCS}) $\Delta(\varepsilon)$ falls sharply, so that the minimum excitation energy is obtained slightly away from the FS. As ε increases further towards ω_{ph}, $\Delta(\varepsilon)$ rises sharply and has a huge maximum at $\varepsilon = \omega_{\text{ph}} + \Delta_{\text{BCS}}$, giving rise to the main structure.

We obtained the sharp fall in $\Delta(\varepsilon)$ at very low energies theoretically, when we solved the gap equation in the presence of a strong Coulomb interaction [20]. Because of this sharp fall, the Coulomb interaction does not suppress T_c but may actually enhance it [21]. The Coulomb interaction in the cuprates, as well as in the organics, is undoubtedly extremely strong, and «conventional» theory (i.e. the McMillan equation for T_c or some similar theory [22]) cannot account for the high value of T_c with the Coulomb interactions properly included.

Relationship with normal-state properties

Superconductiong properties are intimately related with normal state properties; this is the case for the organics as well as for the cuprates. A salient normal state property, presented at this conference by Kirtley, is the linear voltage dependence of the tunneling conductivity in the normal state. The question arises, whether this is an inherent property (as suggested, for example, dy Varma et al. [23]) or a spurious property, as suggested by Kirtley et al. [24].

Our position is that this linear voltage dependence is an inherent property, following from a linear energy dependence of the density of states near the Fermi level, i.e. $N(\varepsilon) \sim \varepsilon$, where ε is measured from the Fermi energy. This feature is present in the Altshuler–Aronov theory for highly disordered systems [25]. We suggest that this feature is present also in ordered systems, when the screening (for states near the Fermi level) is reduced, for example because of low-dimensionality. This gives rise to a strongly k-dependent effective Coulomb interaction. We present a theory for the superconductivity based on this concept elsewhere [21]. The anomalous normal state properties of the cuprates as well as of the organic metals (i.e. $\rho \sim T$ for elastic scattering in YBCO, and $\rho \sim T^2$ for electron-phonon scattering in the organics, the anomalous Hall constant in both families and the anomalous TEP in the cuprates, etc.) follow «automatically» from the relationship $N(\varepsilon) \sim \varepsilon$ [26].

Summary

The point-contact characteristics of α_t-(BEDT-TTF)$_2$I$_3$ show strong nonlinearities due to the superconductivity, which do not easily fit into the existing theories. In case of a spectroscopic origin of these structures, interpreted in the conventional way, we find extremely high values for the energy gap Δ. As a possible explanation we discussed a strongly enhanced McMillan-Rowell structure, i.e. an observation of an energy-dependent $\Delta(\varepsilon)$. Such an approach appears to be promising for high-T_c cuprate superconductors as well. There is a theoretical description of these effects up to first order for N/S heterocontacts [16], but a complete description, in particular for homocontacts, is missing so far.

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