

BAND STRUCTURE CALCULATION AND TUNNELING MEASUREMENTS

IN $(\text{BEDT-TTF})_2\text{X}$ ($\text{X} = \text{I}_3, \text{IAuI}$)

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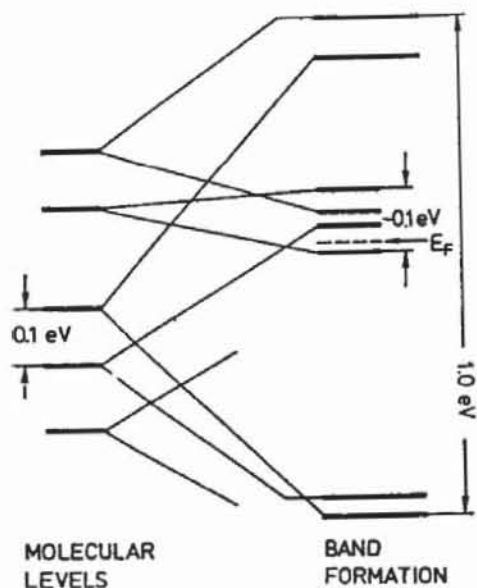
INTRODUCTION

At about the same time when Little proposed room-temperature superconductivity in organic polymers, it was suggested that the high- T_c of the more conventional A-15's is associated with their one-dimensional electronic band structure¹. When TTF-TCNQ was discovered in 1973, it was suggested that the electron-phonon coupling in this 1-D organic molecular crystal is responsible for the metal-to-insulator (Peierls) transition at 52 K^2 , and reducing λ will cause a crossover to a superconducting state³. Since then, the electronic structure, the conduction mechanism, and the superconducting mechanism were subject to controversy. Therefore, it is of some importance to establish whether the electronic band structure, and conduction mechanism, are similar to those in more conventional metals, and whether the superconductivity mechanism is the normal BCS phonon-mediated interaction

AN AB-INITIO BAND CALCULATION FOR $\beta\text{-(BEDT-TTF)}_2\text{I}_3$

The extended-Huckel method has been used extensively for the description of the electronic band structure of organic metals for more than a decade⁴. In this method, only one molecular orbital is considered - the highest occupied (HOMO) or lowest unoccupied (LUMO) one, and banding of this orbital is treated by the tight-binding approximation. Calculations of this type have been performed for ET salts since the work of Mori⁵. These calculations account for the 2-D band structure, the recent dHvA and Shubnikov data described by Tokumoto in this conference, as well as other phenomena described in the talks of Saito, Uemura, Ishiguro, Eldridge, Whangbo, and Kasowski.

As the organic molecule gets larger, the molecular levels get denser, and eventually their separation becomes less than the bandwidth (Fig. 1). As a result, different molecular levels overlap. This effect can be treated by the tight-binding approximation, as in the work of Whangbo et al (this conference), but also by other "standard" methods employed for calculating band structures of normal metals. We employed the ASA method of Williams⁶ for the calculation of the band structure of $\beta\text{-(BEDT-TTF)}_2\text{I}_3$. Such a calculation is very difficult because of the large number of atoms per unit cell (55); the low symmetry (PI) and particularly because the atomic spheres occupy only about 1/3 of the total volume.



Schematic energy level diagram indicates how molecular levels broaden to form bands.

Figure 1

The separation between molecular levels is smaller than bandwidth.

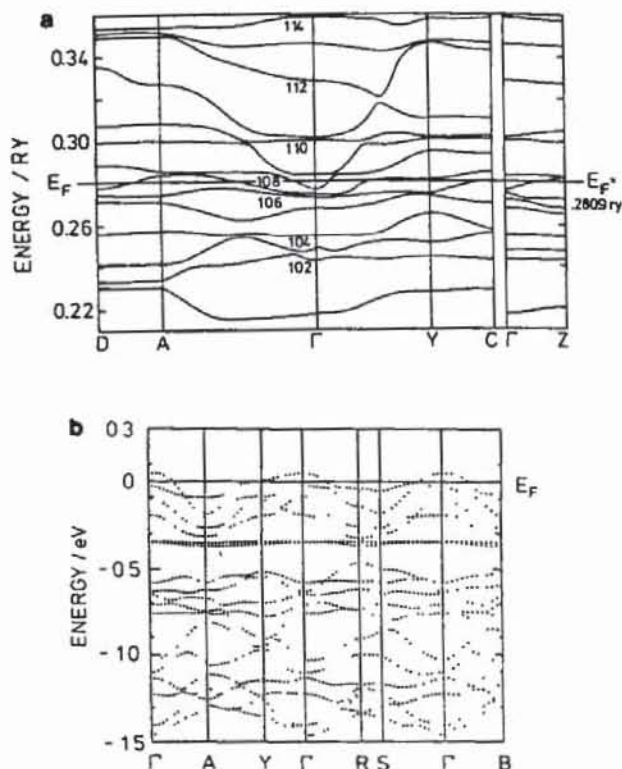


Figure 2

E vs. k curves for β -(ET)₂I₃. Top: IBM 3090. Bottom: Cray II.

We carried out some preliminary calculations; the volume between the atomic spheres is filled with "empty" spheres, so that the total volume of the atomic and empty spheres equals the volume of the unit cell. Thus, there is some overlap between the spheres. It turns out that when the positions, and radii, of the empty spheres are not precise, the calculation does not converge at all. We were able to obtain convergence after a meticulous placing and adjustment of the radii of the spheres⁷. Still, the calculation on an IBM 3090 takes a very long time, and could be carried out only on weekends and holidays. A significant improvement can be achieved by using a Cray II⁸. In Fig. 2 we show the band structure as calculated by the IBM (a) and Cray (b). In (a), the charges on all carbons and sulphurs are set to be equal, to reduce the size of the required CPU space and computing time. In (b), the charges on crystallographically (and chemically) inequivalent carbons are allowed to adjust themselves self-consistently. (b) gives the correct density of states, but not correct spin densities (as determined by NMR). Nor is the Fermi surface accurate, as determined by the dHvA method. Calculation (b) suggests a large energy gap about 50 meV above the Fermi level. To test for this gap, we performed a vacuum tunneling experiment in Nijmegen (Fig. 3). If there is a gap close to E_F , there should be rectification, as in ordinary semiconductors. The I-V curves are found to be precisely symmetric, (for positive and negative voltages) up to 2 V, thus we feel that there cannot be a gap close to E_F ; note that Fig. 2a does not show such a gap. Our conclusion is that the accuracy of our energy levels is not yet adequate; since the bands are so densely spaced, errors of ~ 0.1 eV can distort the band structure very much. We are not yet in a position to say whether the ASA method is suitable to achieve the high accuracy required. We may note the similarity to "normal" metals like V₃Si, Nb₃Sn for which initial band calculations were rather inaccurate, and it took more than a decade to achieve adequate accuracy⁹.

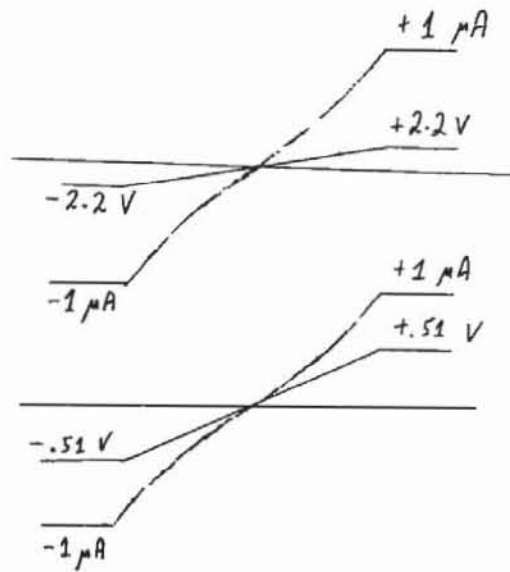


Figure 3
 Vacuum Tunneling on β -ET. No gap is seen close to E_F .

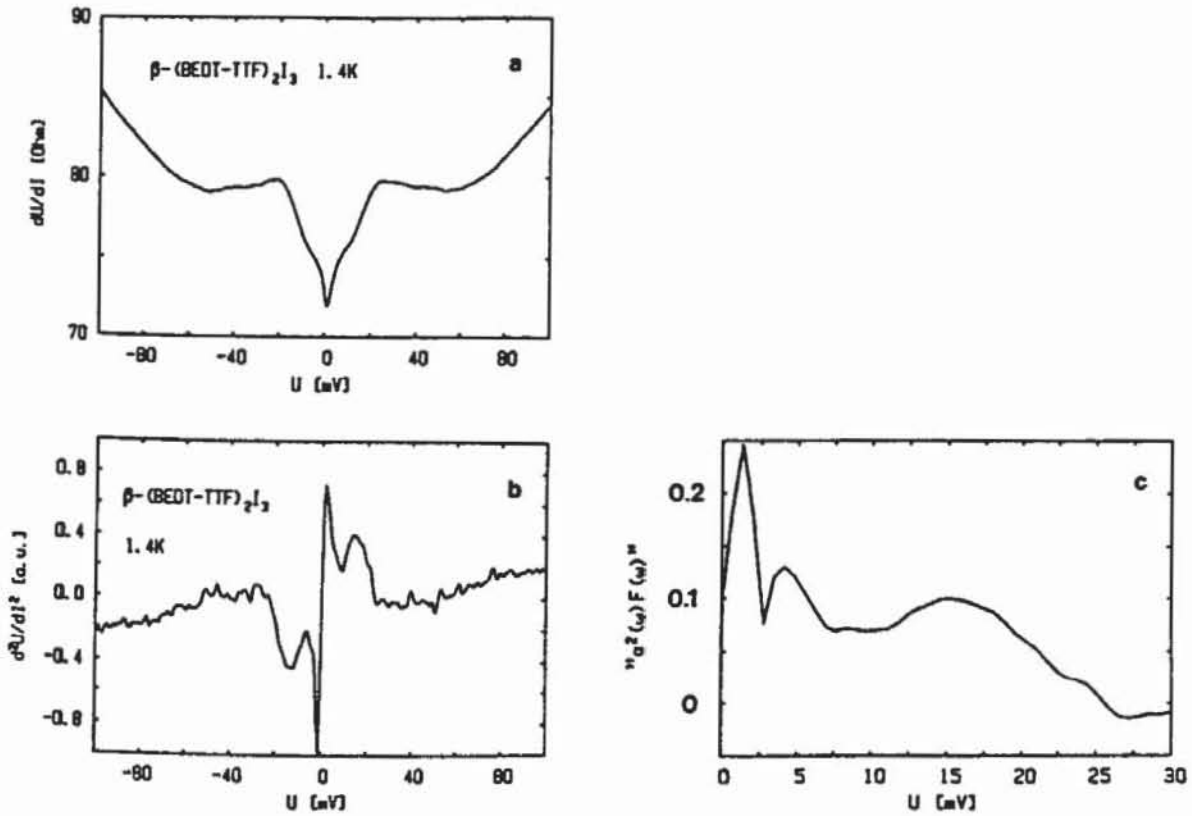


Figure 4
 R & dR/dI vs. V curves for β -ET

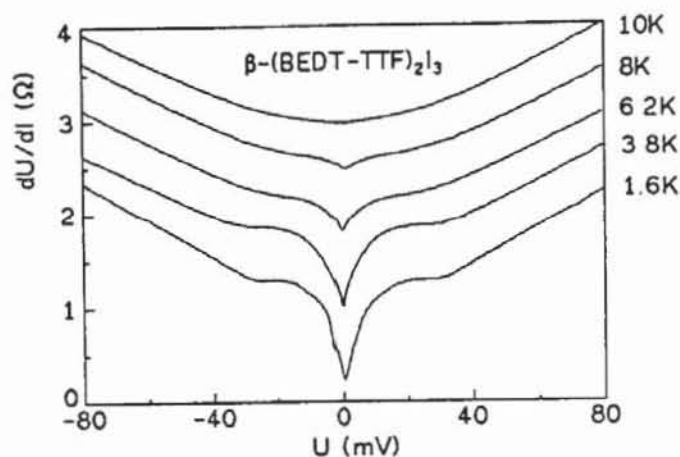


Figure 5
Rvs. V curves for β -ET at various
Temperatures.

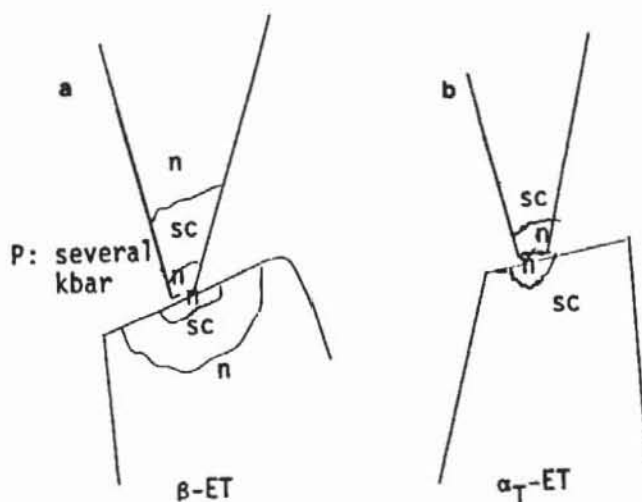


Figure 6
Configuration for point-contact
spectroscopy. Contact pressure
has a drastic effect.

In any case, we demonstrated that a band calculation by conventional methods is at all possible; moreover, the two-dimensional nature is apparent already at the present stage, and the shape of the Fermi surface is at least approximately correct.

POINT CONTACT SPECTROSCOPY AND TUNNELING - REVIEW

Point contact spectroscopy and tunneling measurements have been carried out on ET salts with I_3 and $IAuI$ since 1986^{10,11}. In Fig. 4 we show R vs. V and dR/dI vs. V curves for β - $(BEDT-TTF)_2I_3$. These curves were taken at a temperature above T_c of this material ($T_c = 1.35$ K) and therefore attributed to the normal state¹¹. In Fig. 5 we show R vs. V curves up to 10 K¹². It is seen that the structure disappears at 8 - 8.5 K, which is the maximum value of T_c under pressure. This behavior was verified on a large number of samples. Thus, we attribute the structure to the superconducting state under pressure. Since the crystals are pressed against each other, and the contact radius is about a few hundred Angstrom, even a force of a milligram gives rise to a pressure of a few kbar, as can be verified by the breaking of the surface area throughout the experiment. Thus, we have a structure as illustrated in Fig. 6. The pressure at the contact area is estimated

to be a few kbar, therefore T_c is small and at about $T \approx 1.5$ K the material is normal. At some distance from the contact area, the pressure falls to about 1-2 kbar, and T_c is about 8 K. At a larger distance, the pressure is small and T_c has the bulk value of about 1.35 K, thus for $T = 1.5$ K the material is normal. Thus we have four n-s interfaces, and the voltage per interface is the overall voltage divided by 4. Thus, the sharp structure occurs at about 0.25 meV and a broad structure occurs at about 3.75-4 meV (Fig. 4). The presence of 4 interfaces causes considerable smearing, therefore it is difficult to draw definitive conclusions from these data.

It is possible to avoid the pressure at the interface by vacuum tunneling (or tunneling in helium gas). Measurements on ET IAUl by this method were performed by Hawley et al.¹⁰ and by us¹¹. In Fig. 7a we show a dI/dV vs. V curve reconstructed from the I-V curves of Hawley et al, for a crystal-to-gold needle interface. In Fig. 7b we show a dI/dV vs. V curve reported by us for a crystal-to-crystal interface. Fig. 7a suggests a gap of about 2.5 meV (as suggested by Hawley et al from an I^2 vs. V^2 curve). Fig. 7b suggests a gap of about 0.7 meV. At an early stage it was suggested that perhaps in the needle-to-crystal tunneling the needle touches a grain of the crystal, and the tunneling is between this grain and the bulk of the crystal, thus it is s-to-s tunneling and Δ has to be halved to 1.25 meV; or that in the crystal-to-crystal tunneling one surface is not superconducting, but normal, therefore Δ should be doubled (to about 1.4 meV). However, it seems that both data are good and such excuses are fortuitous. Moreover, the structure of Fig. 7a is measured between half-maximum points, while between the maxima the width corresponds to about $\Delta \approx 4$ meV; while in the data of Fig. 7b, if we measure the distance between half-maximum points, the width corresponds to $\Delta \approx 0.35$ meV. Thus, the difference between 7a and 7b is about a factor of 7 (for half-intensity points) or 6 (for the maxima of dI/dV), and such a large discrepancy cannot be accounted for by attributing it to faulty measurements.

We note that the shape of Fig. 7b agrees very well with the BTK theory¹³, and the value of $\Delta = 0.7$ meV corresponds very well to the BCS value for $T_c \approx 4.1$ K ($2\Delta/k_B T_c \approx 4$, which agrees with the BCS value to within the accuracy of the experiment). In contrast, Fig. 7a gives a value 4 to 6 times the BCS value, as pointed out already by Hawley et al. Values of $2\Delta/k_B T_c$ between 2 and 10 were reported in ref. 11 (Table I). There it was suggested that the vacuum tunneling data for ET-IAUl are the most trustworthy; however, on the basis of more experiments we feel that all the values reported in Table I are credible, and it is not possible to establish a unique value of $2\Delta/k_B T_c$.

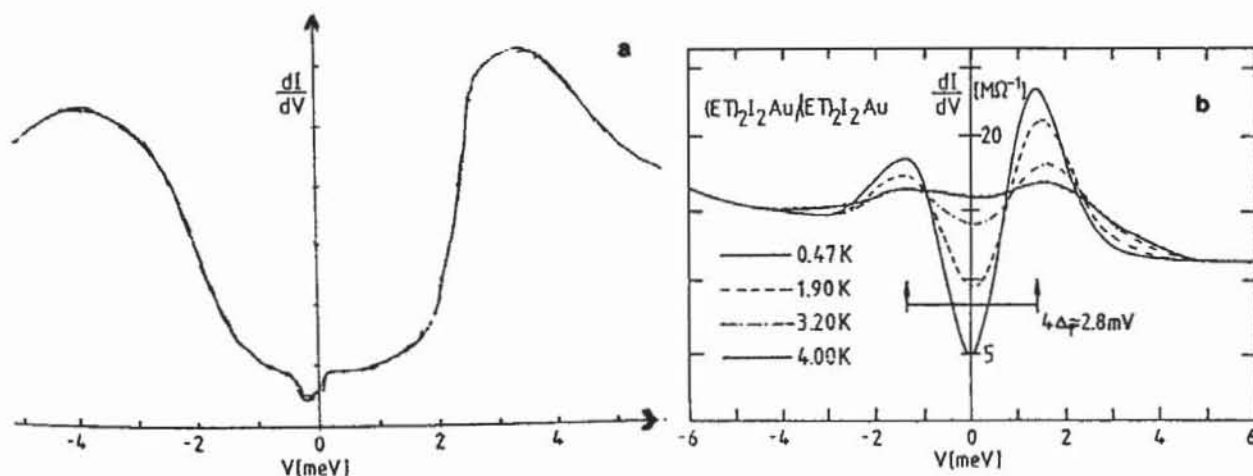


Figure 7
 dI/dV vs. V tunneling curves for ET-IAUl.
 Left: Hawley et al. (reconstructed). Right: Nowack, Poppe, et al.

POINT CONTACT SPECTROSCOPY - NEW DATA

To avoid the ambiguity of 4 n-s interfaces (Fig. 6a) we performed experiments on α_T -(BEDT-TTF) $_2$ I $_3$, for which $T_c = 8-8.5$ K at ambient pressure; thus there are only 2 n-s interfaces (Fig. 6b). R vs. V and dR/dI vs. V data are shown in Fig. 8. The α_T crystals have a slight mosaic structure, but the angle between the individual crystalites is only a few degrees¹⁴. The crystals are pressed against each other with an orientation in which the current flows along the a-b planes.

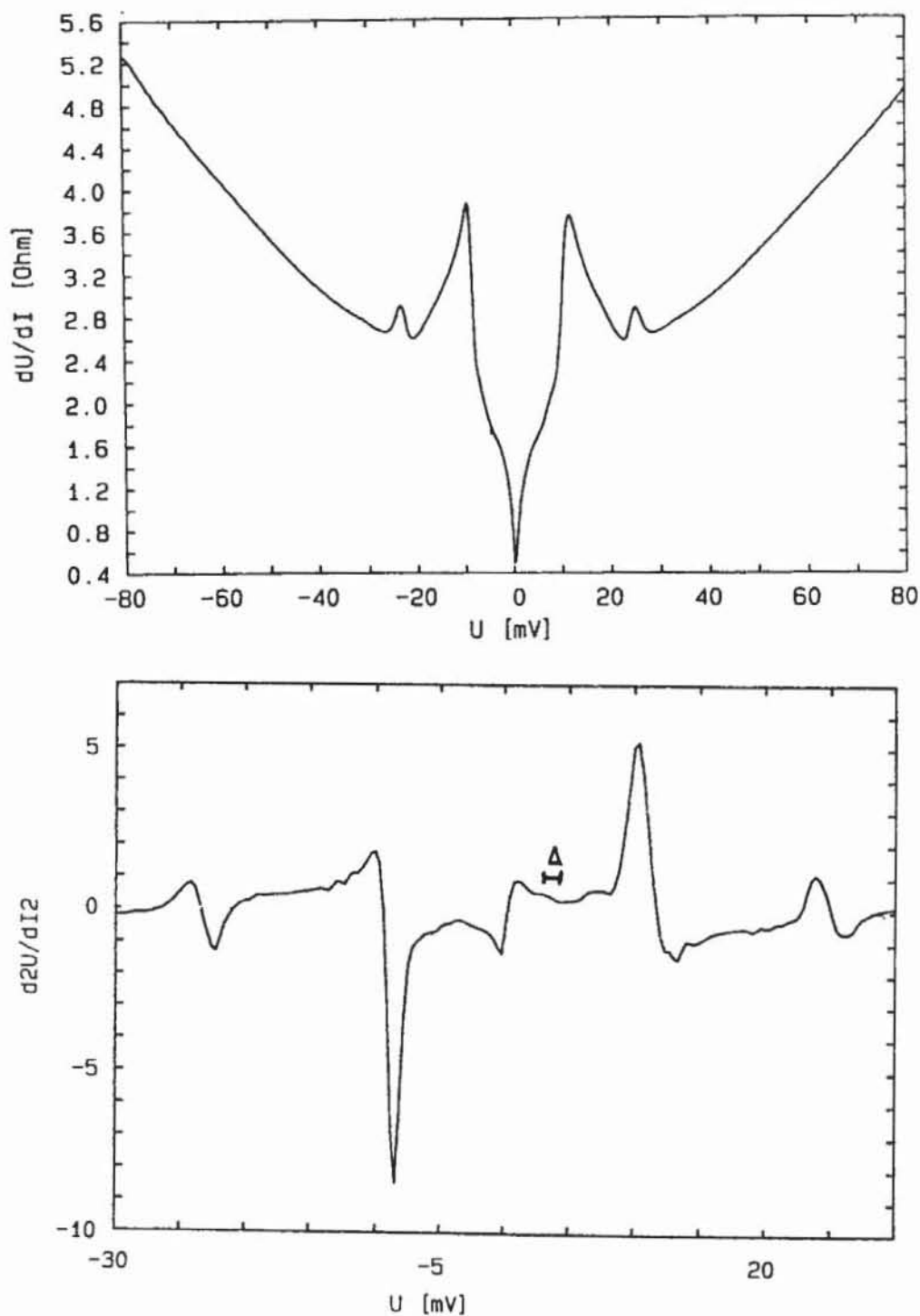


Figure 8
R vs. V and dR/dI vs. V curves for α_T -(ET) $_2$ I $_3$ at $T = 1.5$ K.

Note that the R vs. V curve indicates a very sharp minimum at V=0; the width of this minimum is less than 0.5 mV. Near V = ±10 mV, there is a sharp rise in R to a maximum, followed by a slight fall. Near ±20 mV, there is another sharp structure. Between these three structures, the curve of dR/dI vs. V is quite flat, without discernible structure.

We wish to point out that the data of Fig. 8 are DEFINITIVE. We performed measurements over a period of several years with more than a dozen crystals, with several measurements being taken for each pair of crystals. The data are reproducible, and did not change as the quality of the crystals improved over the last years. The very sharp rise of R with V near ±10 mV is by itself an indication of the high quality of the data. (Note in contrast Fig. 4, which shows how this structure is smeared out when the crystals are not so "good").

Since we have an s-n-s structure, the measured voltage is twice the voltage of each n-s interface; therefore the "giant" structure occurs at a voltage of about 5 mV across an n-s interface. We denote the structure near V=0 by $\delta^{(0)}$; the structure near 5 mV by $\delta^{(1)}$, and the structure near 10 mV by $\delta^{(2)}$. We denote the voltage at which R is maximum (for point contact spectroscopy) or minimum (for vacuum tunneling) by M; i.e. $\delta^{(0)}_M$, $\delta^{(1)}_M$, $\delta^{(2)}_M$. We denote the voltage at the half-maximum point by $\frac{1}{2}$, i.e. $\delta^{(0)}_{\frac{1}{2}}$, $\delta^{(1)}_{\frac{1}{2}}$, $\delta^{(2)}_{\frac{1}{2}}$. This is nearly the same voltage as that when dR/dI is maximum, i.e. the second derivative vanishes, or the extrapolation of the I^2 vs. V^2 curves (Hawley et al¹⁰). The data for all samples, old and new, are summarised in Table I.

Table I

	T K	$\delta_M^{(0)}$ $\delta_{\frac{1}{2}}^{(0)}$	$\delta_M^{(1)}$ $\delta_{\frac{1}{2}}^{(1)}$ (mV)	$\delta_M^{(2)}$ $\delta_{\frac{1}{2}}^{(2)}$	T _c K
β -(BEDT-TTF) ₂ I ₃ (point contact)	0.08 1.4	0.5 0.21 0.5 0.3			1.35 ?
(BEDT-TTF) ₂ IAuI (Poppe) (Hawley et al) (vacuum tunneling)	0.47 2.4	0.7 0.35	4 2.5		4.1 4.1
α_T -(BEDT-TTF) ₂ I ₃ (point contact)	1.4	0.25	5.2 4.5	11.5 12.5	8.5

Note that all ET crystals (β -ET I₃, ET IAU I, α_T ET) possess nearly the same value of δ . Also, the discrepancy between the Argonne and Julich vacuum tunneling data is accounted for - the Argonne group measured $\delta^{(1)}$, while the Julich group measured $\delta^{(0)}$.

Note that δ is independent of T_c; thus the quantity $2\delta/k_B T_c$ doesn't seem to be meaningful, in accord with the data of Table I of ref. 11.

It is instructive to compare this with the Raman data on ET crystals¹⁵ (Fig. 9). The Raman data indicate a sharp line at about 4 meV. This line is extremely sharp for the α -phase, and slightly split for the α_T phase. Since Raman data are due to a q=0 mode, this is an optical phonon. Because of its low frequency, it is probably a libron. We suggested^{11,7} that due to the 2-D band structure, a libron around the c-axis possesses a linear coupling with the electrons. The line at 15 meV is a stretching vibration

of I_3 , which probably does not interact too strongly with the BEDT-TTF molecule. The lines at higher energies are harmonics of this stretching mode. Thus, the phonon seen by the Raman experiments is amazingly close to the giant structure seen in the I-V curves at 5 mV.

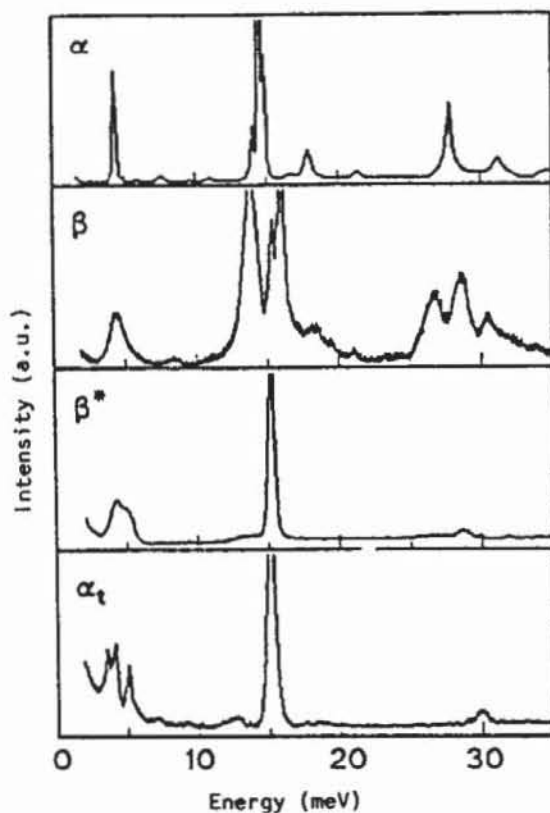


Figure 9
Raman data for various
(BEDT-TTF) $_2$ I $_3$ salts.

POSSIBLE INTERPRETATION OF THE I/V CURVES

(a) Attempt at a Conventional Interpretation

A conventional interpretation of the R vs. V data is based on the BTK theory¹³. This theory accounts for the maximum in R at $eV = \Delta$ (Δ being the superconducting gap parameter) for a good n-s interface, due to Andreev reflection, while for a "bad" interface (i.e. with an oxide, or other insulating layer) normal tunneling gives rise to a minimum in R at this voltage (following the McMillan-Rowell theory¹⁶). Harmonics of the gap are frequently seen in High- T_c superconductors as well¹⁷.

The minimum in R at zero voltage can be attributed to a Josephson effect, or more likely to a proximity effect induced in the normal region by the superconductor across the interface. Thus, for this interpretation, $\delta^{(1)} \equiv \Delta$.

This interpretation poses the following dilemmas:

- (1) Δ is independent of T_c . For all superconductors, with T_c ranging from 1.35 K (possibly) to 8.5 K, Δ is about 4-5 meV.
- (2) $2\Delta/k_B T_c$ is unreasonably large. This was already pointed out by Hawley et al.⁽¹⁰⁾ We tried to account for this large value (about 4 to 6 times the BCS value) by means of soft phonons, with the aid of D. Rainer, using the Bergmann-Rainer algorithm¹⁸, without success. We tried a soft phonon with an energy of 1 meV, with a huge coupling to the electrons¹¹, and were not able to get even close to these values of $2\Delta/k_B T_c$.
- (3) We have to assume that the very close coincidence between $\delta^{(1)}$ and ω_{ph} is a pure accident. In superconductivity theory there is no tendency whatsoever of Δ to "stick" to ω_{ph} ¹⁹.

We may try a two band model, like that of Kresin (this conference), where $\delta^{(0)}$ represents the gap of one band, and $\delta^{(1)}$ of the other. However, the differences (a factor of 16) seem to be too large for such a model.

(b) Unconventional Interpretation

We may assume that the close agreement between $\delta^{(1)}$ and ω_{ph} is not an accident, i.e.

$$\delta^{(1)} \equiv \omega_{ph}.$$

Since $\delta^{(1)}_M$ is nearly temperature independent, while $\delta^{(1)}_{\frac{1}{2}}$ falls with increasing temperature (and can be roughly fitted to the temperature dependence of a BCS gap, as pointed out by Hawley et al), it makes more sense to identify $\delta^{(1)}_M$ with ω_{ph} .

Thus, there is no structure in the I/V curves at the BCS gap Δ (about 1.4 - 1.6 meV); the region of possible values of Δ for weak and strong coupling is indicated in Fig. 8b, and it is seen that there is no structure there. (A similar absence of IR absorption at the gap energy was reported by Eldridge et al at this conference).

This interpretation poses the following dilemmas:

(1) It is not consistent with the conventional McMillan-Rowell theory. According to it, the "Big" structure is at $eV/2 = \Delta$, as discovered by Giaever.

(2) T_c is unexpectedly large for $\omega_{ph} \approx 4$ meV. Even if μ^* is very small, a value of $T_c = 8.5$ K or up to $T_c = 12.5$ K (for some ET salts, as discussed by Williams at this conference), requires a very large value of λ . According to Kresin et al²⁰, $T_c = 0.18 \langle \omega^2 \rangle^{\frac{1}{2}} \sqrt{\lambda / (1 + 2.6\mu^*)}$.

For $\mu^* = 0.2$, $\omega = 4$ meV, $T_c = 12.5$ K, we need: $\lambda = 3.5$.

At first sight, these dilemmas appear overwhelming. However, a novel theory, suggested originally for the high T_c superconductors, gives $\Delta(\epsilon)$ vs. ϵ curves strikingly similar to the observed dR/dI vs. V curve²¹. We sketch such a theoretical curve in Fig. 10. This theory is based on a novel solution of the Migdal-Eliashberg ladder diagram equation for the case of an Einstein spectrum²².

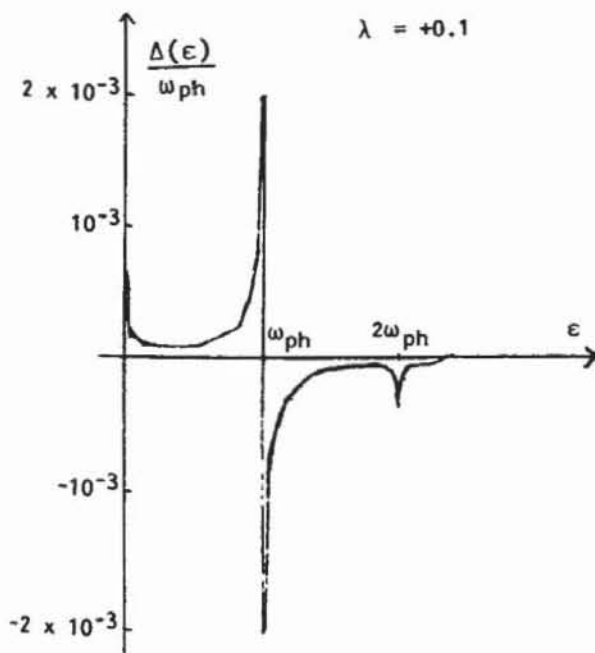


Figure 10

A novel calculation of the gap function $\Delta(\epsilon)$ vs. ϵ for an Einstein spectrum.

There is structure at $\epsilon = 0$, ω_{ph} , $2\omega_{ph}$ but not at $\epsilon = \Delta(0)$.

In any case, the fact that $\delta^{(1)}$ and ω_{ph} coincide (at least approximately), and there is virtually no structure in the I/V curves at other energies, is a strong indication that the superconductivity is due to phonons, and specifically the 4 meV phonon. This is in accord with the prediction made in 1973 when TTF-TCNQ was discovered³, and subsequent work²³. This is also in line with the work of Whangbo et al, and Ishiguro, presented at this conference, about the role of the inter-molecular phonons, their softness, and T_c .

REFERENCES

- 1) M. Weger, Rev. Mod. Phys. 36(1964)175 ; Solid State Physics 28(1973)1.
- 2) J.P. Ferraris, D.O. Cowan, V.V. Walatka, J.E. Perlstein, JACS 95(1973) 948; L.B. Coleman, M.J. Cohen, D.J. Sandeman, F.G. Yamagishi, A.F. Garito, A.J. Heeger, Solid State Com. 12(1973)1125.
- 3) H. Gutfreund, B. Horovitz, M. Weger, J. Phys. C. 7(1974)383; Phys. Rev. B12(1975)3174.
- 4) A.J. Berlinsky, J.F. Carolan, L. Weiler Solid State Com. 15(1974)795; M. Weger, Solid State Comm. 19(1976)1149.
- 5) T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito, H. Inokuchi, Chem. Lett. 1984,957.
- 6) A.R. Williams, J. Kubler, C.D. Gelatt Phys. Rev. B19(1979)6094.
- 7) J. Kubler, M. Weger, C.B. Sommers, Solid State Comm. 62(1987)801.
- 8) J. Kubler & C.B. Sommers, Proc. ICSM Tokyo 1989.
- 9) T. Jarlborg, A.A. Manuel, M. Peter, Phys. Rev. B27(1983)4210.
- 10) M.E. Hawley, K.E. Gray, B.D. Terris, H.H. Wang, K.D. Carlson, J.M. Williams, Phys. Rev. Lett. 57(1986)629.
- 11) A. Nowack, M. Weger, D. Schweitzer, H.J. Keller, Solid State Comm. 60 (1986)199; A. Nowack, U. Poppe, M. Weger, D. Schweitzer, H. Schwenck, Z. Phys. B 68(1987)41.
- 12) A. Nowack, Thesis, Koln University, 1990.
- 13) G.E. Blonder, M. Tinkham, T.M. Klopwijk, Phys. Rev. B 25(1982)4515.
- 14) D. Schweitzer, Proc. ICSM Tokyo 1989.
- 15) R. Swietlik, D. Schweitzer, H.J. Keller, Phys. Rev. B36(1987)6881.
- 16) W.L. McMillan, J.M. Rowell, in "Superconductivity", R.D. Parks Ed. Marcel Dekker 1969.
- 17) A.I. Akimenko, N.M. Ponomarenko, V.A. Gudimenko, I.K. Yanson, P. Samuelli, P. Kus, Sov. J. Low Temp. Phys. 12(1989)
- 18) G. Bergmann & D. Rainer, Z. Phys. 263(1973)59.
- 19) P. Allen & R. Dynes, Phys. Rev. B12(1975)905.
- 20) V. Kresin, H. Gutfreund, W.A. Little, Solid State Comm. 51(1984)339.
- 21) M. Weger, R. Englman, B. Halperin, NATO ASI on HTSC, Bad Windsheim, Aug. 1989, R. Kossowsky & S. Methfessel Edts; in "Recent Prog. in Many Body Theory", Y. Avishai Ed. Plenum Press 1990.
- 22) R. Englman, M. Weger, B. Halperin, Physica C162-164(1989)1339; Solid State Comm. 71(1989)17.
- 23) B. Horovitz, H. Gutfreund, M. Weger, Mol. Cryst. Liq. Cryst. 79(1982) 235.