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# Some electronic properties of the organic superconductor $\beta$-(BEDT-TTF)$_2$I$_3$

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**Résumé.** — Nous avons mesuré de 300 K à 4,2 K la magnétorésistance, la susceptibilité et l'anisotropie magnétique de monocristaux du supraconducteur organique bi-dimensionnel $\beta_L$-(BEDT-TTF)$_2$I$_3$. A partir de la magnétorésistance suivant $c^*$, nous avons calculé une valeur de 0,5 meV pour l'intégrale de transfert $t_c$ dans un modèle de liaisons fortes. De plus, ces mesures indiquent que l'anisotropie de conductivité dans le plan *a-b* à basse température est d'un facteur cinq. La faible valeur du temps de relaxation (0,5 ps à 9 K) indique que le transport électronique entre plans devient incohérent, ce qui peut affecter la température de transition supraconductrice. La densité d'états dérivée de la susceptibilité de spin est en bon accord avec celle obtenue par chaleur spécifique. Lorsque le champ magnétique est dirigé perpendiculairement aux plans conducteurs, l'anisotropie magnétique provient en partie d'un diamagnétisme des électrons de conduction qui varie avec la température.

**Abstract.** — We report some results of magnetoresistance, magnetic susceptibility and magnetic anisotropy measurements on single crystals of the two dimensional organic superconductor $\beta_L$-(BEDT-TTF)$_2$I$_3$ from 4.2 to 300 K. From the $c^*$ magnetoresistivity we deduce a value of 0.5 meV for the tight binding transfer integral $t_c$, and show that there is significant conductivity anisotropy (a factor 5) in the *a-b* plane at low temperatures. A short value of the relaxation time, 0.5 ps at 9 K, indicates that electron transport between planes is becoming incoherent, which may affect the superconducting transition temperature. The static spin susceptibility shows little enhancement relative to the specific heat. The magnetic anisotropy data give evidence for a temperature dependent conduction electron diamagnetism when the magnetic field is perpendicular to the conducting planes.

## Introduction.

The organic conductor bis(ethylenedithio)tetrathiafulvalene tri-iodide, $\beta$-(BEDT-TTF)$_2$I$_3$ or $\beta$-ET$_2$I$_3$ becomes superconducting at 1.5 K under ambient pressure. But under a relatively small pressure of 500 bars or if a certain pressure-temperature cycle is used to avoid phase transition lines near 150 K, the bulk superconducting transition temperature ($T_c$) can be raised to above 8 K [1]. Although the pressure-temperature diagram is complex, the main difference between the high and low $T_c$ phases is thought to be the extra disorder in the low

$T_c$ phase arising from disordered arrangements of the terminal $-C_2H_4$ groups of the ET molecules [2].

The crystal structure of $\beta$-$ET_2I_3$ was determined by Shibaeva *et al.* [3] and discussed in the context of electron band theory by Mori *et al.* [4]. The latter authors showed that the ET molecules stack face to face to form a column along the crystallographic (011) axis. In the more commonly used crystallographic notation of Shibaeva *et al.* [3] this stacking axis is actually the $(1\bar{1}0)$ axis ; the *a-b* plane is highly conducting and the least conducting direction is parallel to the $c^*$ axis. The crystals are usually in the form of platelets whose large face is the *ab* plane.

Recent observations of Shubnikov de Haas magnetoresistance oscillations in the low [5] and high [6] $T_c$ phases of $\beta$-$ET_2I_3$ as well as in the related superconductor $ET_2IBr_2$ [5, 7] show that the Fermi surface is closed in the *a-b* plane. There is only very weak electron overlap along the lowest conductivity $c^*$ axis and thus $ET_2I_3$ crystals are examples of macroscopic 2D crystals with a cylindrical Fermi surface.

For the more one-dimensional Bechgaard salts whose Fermi surface is open in the *a-b* plane, we have previously shown how $c^*$ magnetoresistance [8] and magnetic anisotropy measurements [9, 10] can give useful information about the band structure.

In this short paper dedicated to Professor Friedel we report similar measurements and analysis for the low $T_c$ phase of $\beta$-$ET_2I_3$.

**Experimental.**

For measurements of the $c^*$ resistivity and magnetoresistance, single crystal samples were cut to the required length with a new razor blade. Their orientation was determined from the initial crystal morphology and confirmed by measurement of the ESR *g*-factor. More recently some more magnetoresistance measurements were made with current parallel to the *a* axis on a long crystal prepared by Batail and Lenoir, as part of a Hall effect study [11]. For the latter crystal the two pairs of voltage contacts on opposite sides of the crystal gave different values for the resistance ratio ($R(300)/R(4.2) = 300$ and 1 000). Therefore subsequent magnetoresistance measurements were made with voltage contacts encircling the crystal. These last results, which gave a resistance ratio of 190, are shown in figure 3. The unusual behaviour obtained for the two pairs of Hall contacts may possibly have been caused by the anisotropy in the *a-b* plane discussed below, which if present, implies that the needle axis ($a$) is not a principal axis of the conductivity tensor.

In all cases electrical contacts were made with silver paint on to evaporated gold contact areas. No significant irreversible jumps due to microcracks occurred during the measurements. The field orientation could be varied by rotating the sample at low temperatures.

Measurements of the magnetic susceptibility and magnetic anisotropy were made with the same equipment as in previous studies of the Bechgaard salts [9, 10].

**Results and discussion.**

i) *Magnetoresistance* : the overall behaviour of the $c^*$ resistivity is shown in figure 1. Below 8 K there is a partial superconducting anomaly associated with a small quantity of the high $T_c$ phase. The resistance ratio ($R(300)/R(9)$) is 310 and the average room temperature conductivity along $c^*$ for several samples is 0.1 $(\Omega\text{cm})^{-1}$. A $T^2$ power law in the $c^*$ resistivity can be identified from 8 to 80 K, with a coefficient of $5.5 \times 10^{-5}$ $\Omega\text{cm/K}^2$. This is 220 times larger than the $T^2$ term in the *a-b* plane (1, 12). Such behaviour is consistent with the proposal (1, 12) that the $T^2$ law in the *a-b* plane arises from electron-electron scattering,

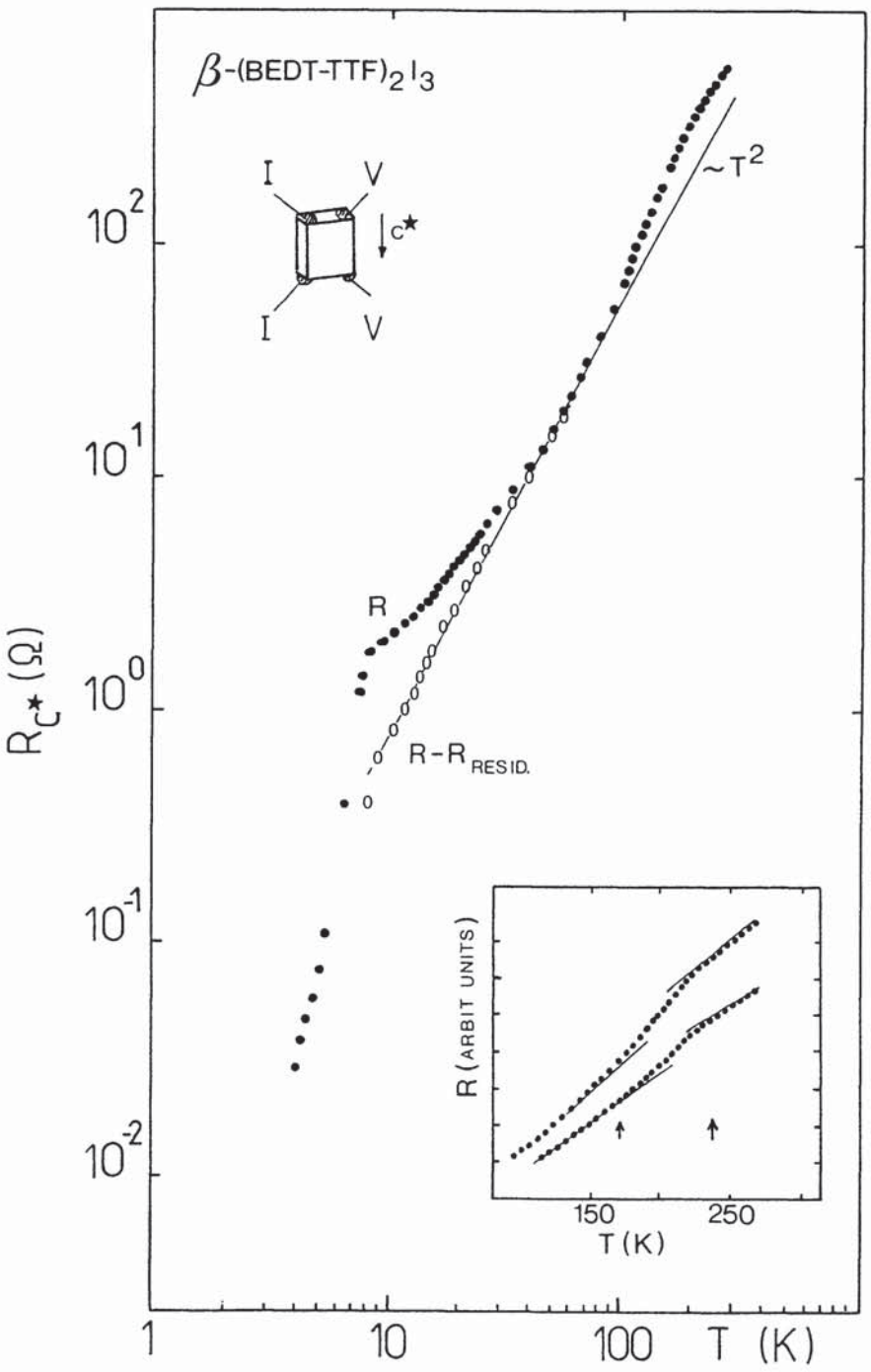


Fig. 1. — Overall temperature dependence of the $c^*$ resistance of the low $T_c$ phase of $\beta\,(ET)_2\,I_3$ on a log-log scale. The room temperature conductivity is 0.1 $(\Omega\text{cm})^{-1}$. On subtraction of the residual resistance a $T^2$ law is obeyed up to 80 K. The inset shows the S-shaped anomaly at 200 K associated with the phase transition there, for two crystals.

since in this picture the relaxation time ($\tau$) is proportional to $T^{-2}$. Thus one would also expect to observe the same law in the $c^*$ direction, but with a greatly increased coefficient associated with the lower Fermi velocity in that direction.

Figure 2 shows the angular dependence of the $c^*$ resistivity when $H$ was rotated in the $a$-$b$ plane. Similar behaviour was observed at higher temperatures and for another crystal. Although two of the calculated Fermi surfaces are of almost circular cross-section [1], we believe that the strong angular dependence (a factor of five in $\Delta\rho/\rho$ $(H = 0)$) is an indication

of substantial anisotropy of the Fermi velocity in the *a-b* plane. In a one-electron picture the magnetoresistance can be calculated from the following standard equation for the conductivity tensor $\sigma_{ij}$ :

$$\sigma_{ij} = \frac{-e^2}{4\pi^3} \int \frac{\mathrm{d}S}{\hbar |v_k|} \int v_i(0)\, v_j(t)\, \mathrm{e}^{-t/\tau}\, \mathrm{d}t \tag{1}$$

where $\mathrm{d}S$ is an integral over the Fermi surface, $v_i$ and $v_j$ are components of the Fermi velocity $v_k$, in the $i$ and $j$ directions and $\tau$ is the relaxation time. The time dependence of $v$ is determined by the Lorentz force equation. From equation (1) it follows that for $\underline{H} = (0, H, 0)$ in the *a-b* plane $(\Delta\rho/\rho)_{c^*}$ is proportional to the average value of $v_x^2$. Thus the anisotropy in magnetoresistance goes as $\overline{v}_x^2/\overline{v}_y^2$. The same ratio also determines the anisotropy in the square of the plasma frequency $\omega_p^2$ and in the conductivity in zero field. The experimental optical data [13] do show anisotropy of 2.8 in values of $\omega_p^2$ obtained from Drude fits at 40 K. Actually if one disregards the Drude fits and just looks at the measured reflectance data the anisotropy appears to be even larger. Namely the measured reflectance edges for light polarised parallel and perpendicular to the stacks are at frequencies which differ by a factor 2.4, i.e. a factor 6 in (frequency)$^2$, in even better agreement with our estimate. The related superconductor $ET_2IBr_2$ shows a factor of 10-15 anisotropy in $\rho_{c^*}$ in a field of 15 T at 1.5 K [7]. From our data the maximum magnetoresistance occurs for $H$ perpendicular to the ET stacks. Within the model discussed below where the magnetoresistance arises from the Lorentz force, this implies that the direction of maximum Fermi velocity, and hence that of maximum conductivity, is along the stacking axis. This is in agreement with optical data in reference [14].

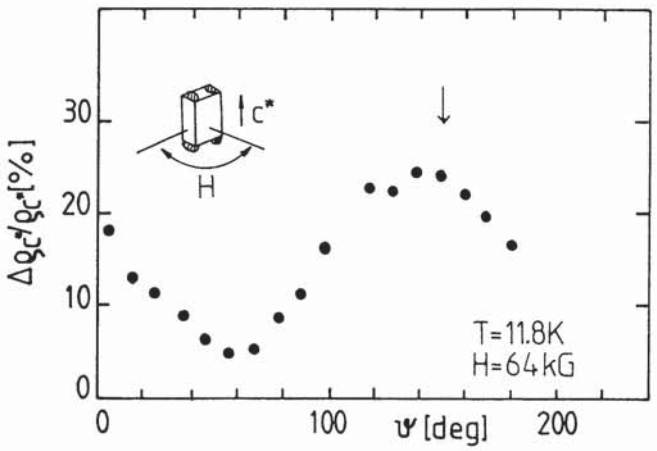


Fig. 2. — Angular dependence of the magnetoresistance in the completely normal state at 11.8 K, for current $\underline{J} /\!/ \underline{c}^*$ and $\underline{H}$ rotated in tha *a-b* plane. The arrow corresponds to $H$ perpendicular to the ET stacking axis which is the (110) direction in the standard structure [3].

Thus, according to the results in figure 2 although the calculated Fermi surface is nearly cylindrical [1] (and is almost forced to be so by geometrical constraints arising from the presence of Brillouin zone boundaries) there is an anisotropy in Fermi velocity of a factor 2.2, and in conductivity and magnetoresistance of a factor 5. However if this result is correct there are then problems in understanding the observed absence of anisotropy [1] in the slope of the upper critical field $H_{c2}$ near $T_c$ for $H$ in the *a-b* plane.

Kohler plots of the $\rho_{c^*}$ and needle or $a$-axis conductivity data are shown in figure 3. The $c^*$ results correspond to the maximum magnetoresistance with $H$ in the $a$-$b$ plane and perpendicular to the stack axis. The needle axis data also correspond to the maximum magnetoresistance, namely $H$ along $c^*$ in this case. They have a tendency to saturate at a lower value than the $\rho_{c^*}$ data which follows an $H^2$ law over most of the field range. In both cases Kohler's law is obeyed within experimental accuracy, testifying to the validity of the relaxation time approximation. The $c^*$ magnetoresistance data can be analysed to obtain various transport parameters. From equation (1) it follows that $(\Delta\rho/\rho)_{c^*} = (\Omega\tau)^2$ where the cyclotron frequency $\Omega$ is given by :

$$\Omega = \frac{eH}{\hbar c^0} v_x \cdot c \,. \tag{2}$$

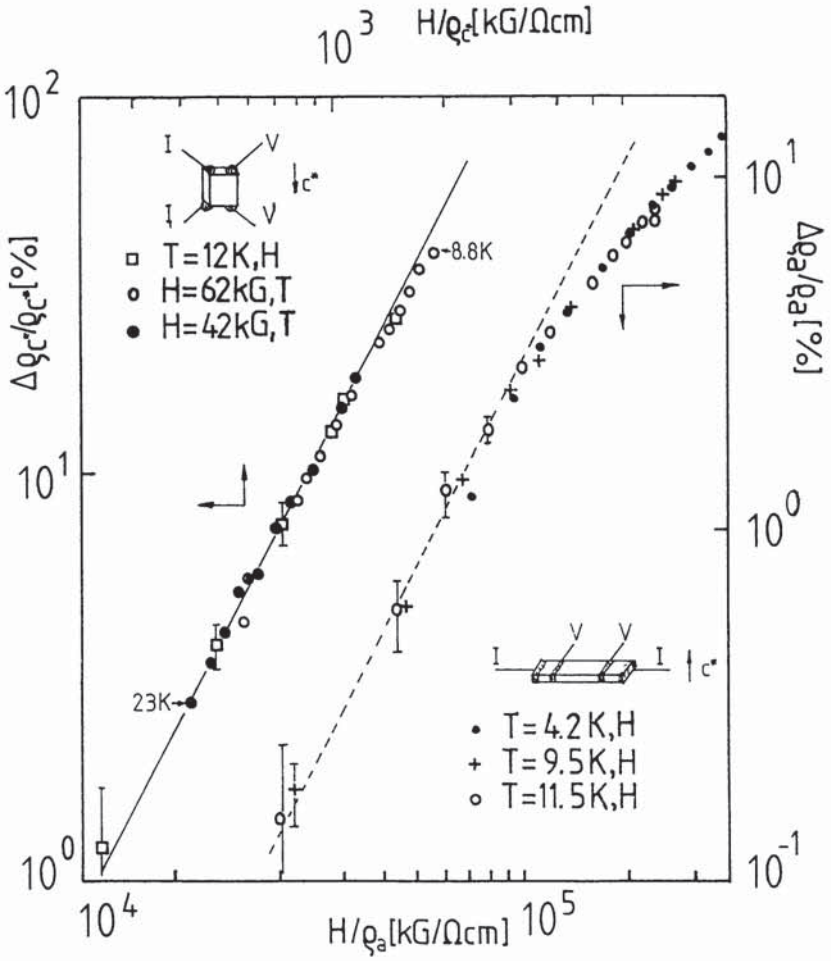


Fig. 3. — Kohler plots ($\Delta\rho/\rho_{H=0}$ *vs.* $H/\rho_{H=0}$) for the magnetoresistance of the low $T_c$ phase of $\beta$-(ET)$_2$I$_3$, left hand and top scales $\underline{J} /\!/ \underline{c}^*$, $\underline{H}$ perpendicular to the stack axis, maximum field 62 kilogauss. Right hand and bottom scales $\underline{J} /\!/ \underline{a}$, $\underline{H} /\!/ \underline{c}^*$, maximum field 67 kilogauss. The data were obtained either by sweeping the field (letter $H$) at fixed temperature, or by sweeping the temperature (letter $T$) at fixed field. Room temperature conductivities were 33 and 0.1 $(\Omega\text{cm})^{-1}$ for $a$ and $c^*$ directions respectively.

In equation (2) $v_x$ is the RMS average Fermi velocity along the stacks, $c^0$ is the velocity of light and $c$ is the transverse lattice parameter ($15.26 \times 10^{-8}$ cm). The derivation of the above formula has been discussed in detail for the Bechgaard salts where the Fermi surface is open

in two directions. In the present case, where the Fermi surface is closed in the *ab* plane, it is only strictly true in the low field limit, for the high field limit, equation (1) would have to be evaluated numerically. In the low field case which applies to the data in figure 3, $v_c(t) = \ddot{v}_c(0) \cdot t^2/2$ and $\ddot{v}_c(0)$ is simply obtained by twice differentiating the tight binding dispersion formula for $v_c$ and using the Lorentz law :

$$\frac{dk_c}{dt} = \frac{ev_x}{\hbar c^0} \cdot H \,. \tag{3}$$

From the data in figure 3 we estimate that for $\rho_{c*}$, $\Omega\tau = 1$ at $H = 10$ T, hence the mean free path along the stacks ($v_x \tau$) is 420 Å at 9 K. If $v_x$ is given by a tight binding formula with effective values of $t_x = 0.1$ eV and an intermolecular spacing of 3.5 Å then we find that $\tau = 0.53$ ps. Using the same value of $\tau$, the Fermi radius determined in reference [4] and the measured value of $\rho_{c*}$ we find that the transfer integral along $c$ is $t_c = 0.42 \pm 0.05$ meV. The estimated error arises from uncertainties in $\rho_{c*}$ due to a change in residual resistance ratio from 300 to 200 on thermal cycling. If we use the density of states from low temperature specific heat measurements [15] instead of that from $v_x$, i.e. $7.5 \times 10^{33}$ instead of $8.9 \times 10^{33}$ states/erg/cm$^3$, then $t_c$ is 0.46 meV. The values obtained for the $(TMTSF)_2X$ salts at ambient pressure using the same method were 1 meV for X = $ClO_4$ [8, 16] and 0.1 meV for X = $PF_6$ [17].

The above value for $t_c$ for the low $T_c$ phase of $\beta$-$(ET)_2I_3$ is in excellent agreement with the value determined from beats in Shubnikov de Haas oscillations for the high $T_c$ phase [6]. Such a low value of $t_c$ leads to mean free path along $c$ of only 0.3 lattice parameters at 9 K in the low $T_c$ phase and this is very close to the residual value at $T = 0$. While we do not believe that it affects our analysis of the magneto-resistance [17], it may be important in suppressing the superconductivity of the low $T_c$ phase. Namely it has recently been suggested that because of the disordered arrangements of the -$C_2H_4$ groups, $\tau$ may be up to 20 times smaller in the low $T_c$ phase and that such a strong effect on $T_c$ may be an indication of unusual triplet pairing superconductivity [2]. The present analysis shows that the electron propagation between the planes is incoherent ($t_c < \hbar/\tau$) in the low $T_c$ phase but that it is coherent in the high $T_c$ phase and this provides a possible alternative explanation for the depression of $T_c$.

ii) *Magnetic measurements* : the static susceptibility of a collection of small single crystals of $\beta$-$(ET)_2I_3$ has been measured using the Faraday method. The spin susceptibility obtained after subtracting the calculated core diamagnetism of $-5.41 \times 10^{-4}$ emu/mole is shown in figure 4. The results agree well with those in reference [18]. Such data are a useful complement to NMR and ESR studies. The estimated spin susceptibility at low $T$ is $3.6 \times 10^{-4}$ emu/mole. It is very close to the value derived from the low temperature specific heat data [15], which is $3.3 \pm 0.4 \times 10^{-4}$ emu/mole, so both the specific heat and spin susceptibility have similar enhancement factors. There is still a little (30 %) temperature dependence in the spin susceptibility, much less than in other more one-dimensional organic conductors where changes by a factor of two often occur. This may be related to the fact that in most organic conductors, much of the temperature dependence of the spin susceptibility arises from thermal expansion. In the present case the effect is smaller because the volume, i.e. pressure dependence, of the susceptibility of $\beta$-$(ET)_2I_3$ is smaller [19].

Some preliminary measurements of the susceptibility anisotropy have been made and are shown in figures 5a and 5b. As shown in the upper part of figure 5a the anisotropy of susceptibility in the *ab* plane is temperature independent, this fact and the magnitude [10] suggest that it is entirely due to the anisotropy in the molecular core diamagnetism. However

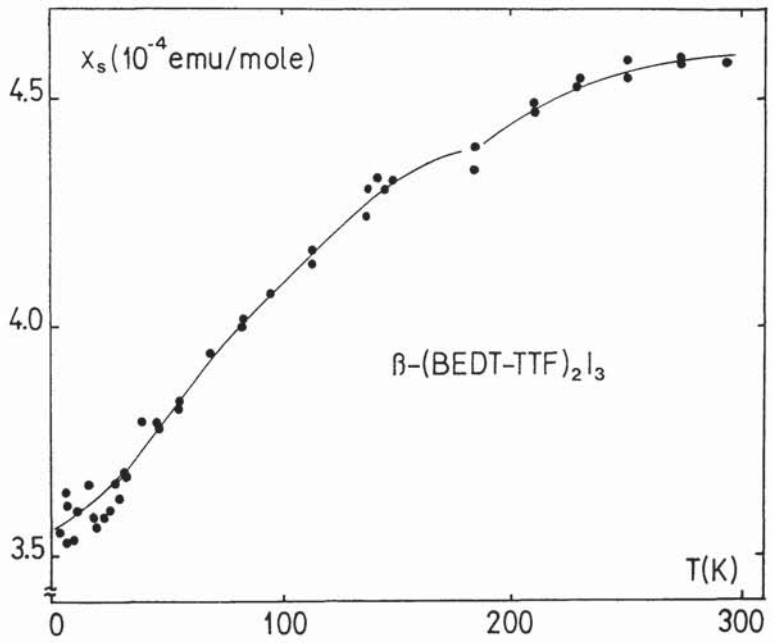


Fig. 4. — Spin susceptibility of the low $T_c$ phase of $\beta$-$(ET)_2I_3$ *versus* temperature, (1 mole = 1149 gms). The core diamagnetism of $-5.41 \times 10^{-4}$ emu/mole has been subtracted.

the results in the lower part of figure 5a show that there is some temperature dependent anisotropy in the other two crystallographic planes which both contain the $c^*$ axis. It is most probably a consequence of closed orbits in the *a-b* plane. The presence of such orbits will lead to a conduction electron diamagnetism whose principal axes correspond to the crystallographic axes (or the reciprocal lattice vectors) rather than the molecular axes. As shown in figure 5b the principal axis of the susceptibility is not a molecular axis, since otherwise the sine curve would cross zero at approximately 25° to $c^*$ corresponding to the 25° angle between the long axis of the ET molecule and the $c^*$ axis [3]. Indeed, the position of the zero crossing is temperature dependent (Fig. 5b) and continues to change down to 4.2 K. Cylindrical orbits of the appropriate area [6] and with the free electron mass lead *via* the Landau-Peierls formula [20] to an extra diamagnetism of $-0.27 \times 10^{-4}$ emu/mole along the $c^*$ axis. This is of the order of the effects observed but a more detailed analysis is required to confirm this and to determine the temperature dependence. The observed anisotropy is much smaller than in the organic conductor HMTSF-TCNQ [9] where it was ascribed to small pockets of holes and electrons, and it should not have a significant effect on the determination of the spin susceptibility.

In summary we have reported our unpublished data for the electronic properties of the low $T_c$ phase of $\beta$-$(ET)_2I_3$. They are generally in agreement with the established picture [1] especially with regard to the the $T^2$ law and electron-electron scattering. However some new points such as the anisotropy in the *a-b* plane, the possibility of incoherent electron propagation in the $c^*$ direction and the susceptibility anisotropy have been raised.

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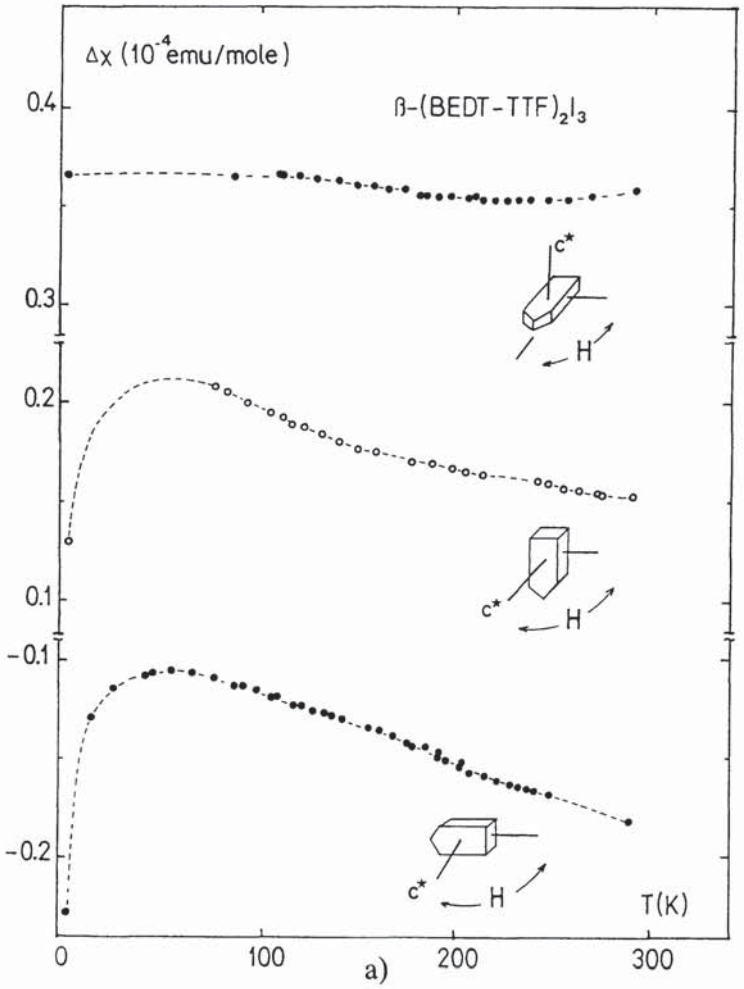


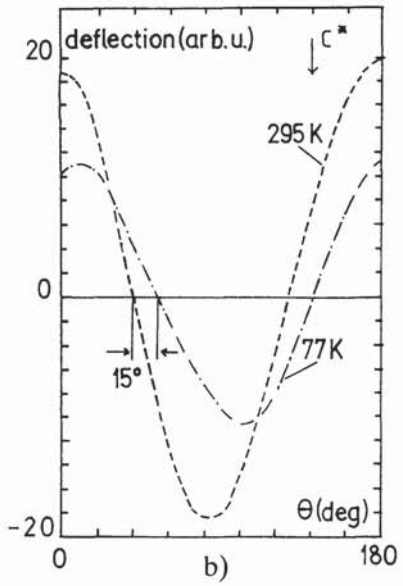


Fig. 5. — (a) Susceptibility anisotropy *versus* temperature for a single crystal of $(ET)_2I_3$. Upper curve $H$ in the *ab* plane. Lower curves : two orientations showing the anisotropy between the *ab* plane and the $c^*$ axis. The data was derived from the measured torque on a single crystal at a fixed angle to the magnetic field. This angle corresponded to the maximum of the sine curve at room temperature. (b) Sine curves corresponding to the lowest curve in figure 5a, which was taken at an angle $\theta = 90°$. They show that the principal axis of the susceptibility tensor is not along the long molecular axis (25° to $c^*$), and that its position is temperature dependent. This dependence continues down to 4.2 K (not shown).

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