$\alpha$- and $\beta$-(BEDT-TTF)$_2$I$_3$: Two Dimensional Organic Metals

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Abstract Electronic properties of $\alpha$- and $\beta$-(BEDT-TTF)$_2$I$_3$ crystals are reported.

BEDT-TTF [bis(ethylendithio)tetrathiofulvalene] salts have caused considerable interest, since Saito et al.\(^1\) have proved strong intermolecular contacts and exchanges in more than one direction. Additionally, Parking et al.\(^2\) reported a superconducting transition in a ReO$_4$-derivative under pressure. Electrochemical methods using I$_3^-$ as counterions yield several crystallographic phases\(^3\)-\(^7\), with different physical properties, e.g. $\alpha$-(BEDT-TTF)$_2$I$_3$ ($\alpha$-\(\perp\)) and $\beta$-(BEDT-TTF)$_2$I$_3$ ($\beta$-\(\perp\)). The former has a metal to insulator transition at 135 K\(^3\)-\(^4\) which can be suppressed above 15 Kbar\(^8\).

$\beta$-\(\perp\) stays metallic down to 1.4 K. There the crystals become superconducting at ambient pressure\(^5\),\(^8\). Other triiodide phases seem to show superconducting transitions even at 2.5 K\(^6\),\(^7\). Figure 1 shows the projection of the unit cells of $\alpha$-\(\perp\) onto the bc-plane (left) and of $\beta$-\(\perp\) onto the ac-plane. Both phases crystallize in the triclinic space group P\(\overline{1}\) ($\alpha$-\(\perp\): a = 9.211 Å, b = 10.850 Å, c = 17.488 Å, $\alpha$ = 96.95°, $\beta$ = 97.97°, $\gamma$ = 90.75°; $\beta$-\(\perp\): a = 6.615 Å, b = 9.097 Å, c = 15.291 Å, $\alpha$ = 94.35°, $\beta$ = 95.55°, $\gamma$ = 109.75°).
and are two dimensional organic metals.

The first order phase transition in \( \alpha-1 \) at 135 K can be utilized to demonstrate the validity of the Wiedemann-Franz-law

\[
\frac{K_e}{\sigma} = \frac{\pi^2}{2}\frac{k_B^2}{e^2} \frac{T}{L_0 \cdot T},
\]

Here \( K_e \) is the thermal conductivity of the charge carrier, \( \sigma \) the electrical conductivity, \( T \) the temperature and \( L_0 = 2.44 \cdot 10^{-8} \frac{V^2}{K^2} \) the Lorentz-number. Fig. 2 shows the temperature dependence of the total thermal conductivity \( K \) shows the tals of \( \alpha-1 \). Assuming that the difference of 1.5 mW/(cm\(^2\)K) in \( K \) at 135 K is due to the contribution \( K_e \) of the charge carriers in the metallic range and taking the typical value of the electrical conductivity at 135 K \( \sigma_{135} = 450(\Omega \cdot \text{cm})^{-1} \) we obtain a value

![Fig. 1) Structure of \( \alpha-1 \) (left) and \( \beta-1 \) (right).](image)

![Fig. 2) Thermal conductivity of \( \alpha-1 \).](image)
\[ K_e/(a_{135} \cdot T) = 2.5 \cdot 10^{-8} \cdot v^2/K^2. \] Even if we assume that \( a_{135} \) is only correct within an error of 20% this value agrees quite well with the Lorentz-number. In addition the results of Fig. 2 demonstrate that in an organic metal the contribution to \( K \) due to the lattice phonons predominates the contribution of the charge carriers in contrast to the usual metals.

In our preparation of \( \alpha-\) using THF\(^3,4\) we always observed canted rhombohedrons of \( \beta-\). Fig. 3 shows the microwave conductivity as measured at 10 GHz by the cavity perturbation method between 3 and 300 K. A very similar temperature dependent conductivity behaviour was observed with dc-methods. Typical room temperature conductivities range around \( 35(\, \Omega \, \text{cm})^{-1} \). Nevertheless, the peak in the microwave conductivity at about 125 K is sensitive to the microwave power. For somewhat higher microwave field strength (\( x \)) the conductivity increases stronger and already at higher temperatures (\( T \approx 200 \, \text{K} \)). Further experiments are in progress in order to explain this behaviour.

**Fig. 3)** Microwave conductivity at 10 GHz of \( \beta-\).
ESR-experiments indicate a temperature independent susceptibility between 300 and 4.2 K. The ESR-linewidth at room temperature can be used to discriminate between $\alpha$-1 and $\beta$-1 (70 to 110 Gauss for $\alpha$-1 and 20 to 25 Gauss for $\beta$-1 depending on the orientation of the crystals with respect to the magnetic field).

Temperature dependent thermopower measurements prove a metallic state down to low temperatures (Fig. 4) but around 120 K a phase transition might occur. From the slope of the thermopower above 150 K it can be estimated that the width of the conducting band in a-direction is about 2/3 of the bandwidth in b-direction in good agreement with optical reflectance measurements. Volume superconductivity in $\beta$-1 at ambient pressure and a diamagnetic transition temperature of 1 K is reported separately.

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REFERENCES