

MICROWAVE CONDUCTIVITY OF β -(ET)₂IAuI

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The 34 GHz microwave conductivity of the 2:1, β -phase compound of bis(ethylenedithio) tetrathiafulvalene (BEDT-TTF or "ET") with the diiodoaurate anion (IAuI)⁻ has been measured from 20 to 300 K. This material is an ambient-pressure organic superconductor with $T_c \approx 5$ K. A cavity perturbation technique in the skin-depth-limited regime was used. The conductivity varies as the inverse square of the temperature over the entire temperature range. The room-temperature conductivity is $6 \Omega^{-1} \text{ cm}^{-1}$, rather low for the conductivity of an organic "metal".

This paper describes a measurement of the microwave conductivity of β -(ET)₂IAuI, where ET is the bis(ethylenedithio) tetrathiafulvalene or BEDT-TTF molecule and (IAuI)⁻ is a linear, symmetric pseudotrihalide. This compound is extremely interesting because it exhibits the highest ambient pressure superconducting transition temperature (nearly 5 K) of any organic superconductor [1,2]. Our measurements were made at 34 GHz at temperatures between 20 and 300 K; over this range the conductivity varies as the inverse square of the temperature. The magnitude of the conductivity is in good agreement with far infrared measurements on sister samples [3]. However, the room-temperature conductivity is only $6 \Omega^{-1} \text{ cm}^{-1}$. This value is sufficiently small that the usual Drude metallic picture of free carriers diffusing along the electric field cannot be applied.

The conductivity was measured using the cavity perturbation technique. The apparatus used has been described previously [4]. The sample is placed at the electric field maximum of a rectangular TE₀₁₂ resonant cavity. The transmission and phase shift upon transmission through the cavity, measured at five to

seven frequencies around the resonant frequency by use of a microwave interferometer, are used to calculate the quality factor, Q , and resonant frequency, ω_0 , of the cavity [4]. The cavity is attached to the cold tip of a continuous-flow cryostat; the heat load imposed through the waveguide limits the minimum temperature to 20 K.

The sample was a single crystal, prepared as previously described [1,2]. The dimensions were $0.4 \times 0.4 \times 1.5$ mm, with the long axis being the stacking axis. With these dimensions, the skin depth will be smaller than the sample size so long as the conductivity is larger than $0.02 \Omega^{-1} \text{ cm}^{-1}$.

In the skin-depth limit, the fields do not penetrate the entire volume of the sample and the cavity loss, $1/Q$, varies as the inverse square root of the sample conductivity [4,5]. Furthermore, the resonant frequency shift (from that of the empty cavity) is determined by geometric factors: the depolarization factor and volume of the sample; it is independent of the sample dielectric constant.

The conductivity, σ , is calculated from the following equations:

$$\Delta(1/2Q) = \frac{9\epsilon_0\sqrt{\mu_0}}{64\sqrt{2}} \frac{W+H}{\alpha} \left(\frac{\alpha}{N_z}\right)^2 \sqrt{\frac{\omega^3}{\sigma}}, \quad (1)$$

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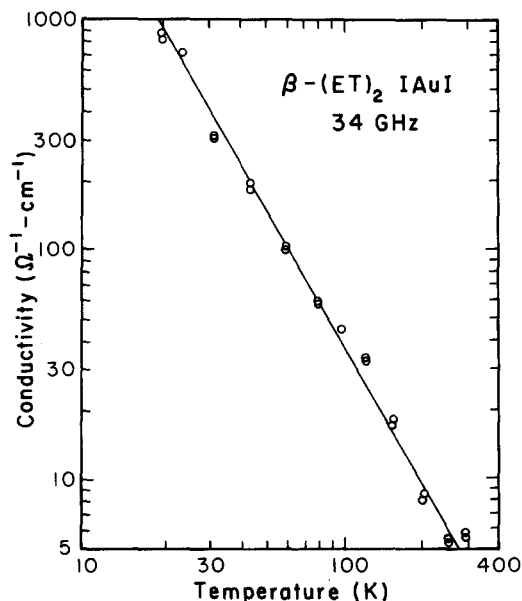


Fig. 1. Microwave conductivity versus temperature for β -(ET)₂(IAuI). Note the logarithmic scales. The line shows a T^{-2} behavior.

$$|\Delta\omega|/\omega_0 - \Delta(1/2Q) = \alpha/N_z, \quad (2)$$

where

$$\Delta(1/2Q) \equiv \frac{1}{2} |1/Q_{\text{sample}} - 1/Q_{\text{empty}}|,$$

$$|\Delta\omega|/\omega_0 \equiv |\omega_{0 \text{ empty}} - \omega_{0 \text{ sample}}|/\omega_{0 \text{ empty}}.$$

The other quantities in eqs. (1), (2) are the volume filling fraction, $\alpha = 2V_{\text{sample}}/V_{\text{cavity}}$; the (long-axis) depolarization factor, N_z ; the sample width, W ; length, L ; the dielectric constant (permeability) of free space, ϵ_0 (μ_0); and the angular frequency, ω . In transcribing eq. (1) from refs. [4,5], we have assumed that it is the volume of the skin region which determines the loss and thus have replaced the factor $2\pi a$, the perimeter of the ellipsoid or cylinder, by $2(W+L)$.

Fig. 1 shows the microwave conductivity of (ET)₂IAuI between 20 and 300 K. On cooling, the conductivity increases from $6 \Omega^{-1} \text{ cm}^{-1}$ at 300 K to nearly $900 \Omega^{-1} \text{ cm}^{-1}$ at 20 K. We measured the 300 K conductivity in the direction perpendicular to the molecular stacking axis, obtaining $\sigma_{\perp} \approx 1.8 \Omega^{-1} \text{ cm}^{-1}$. This value corresponds to an anisotropy ratio of approximately 3:1.

In the stacking direction, $\sigma_{\parallel} \sim T^{-2}$ over the entire temperature range, as shown by the solid line in fig. 1. This quadratic power-law behavior is typically seen above the conductor-insulator transition temperature in many organic conductors, such as TTF-TCNQ or the Bechgaard salts [6–8]. Mechanisms which have been proposed to govern the dc conductivity include conduction by charge or spin density waves [9], scattering involving two-phonon (“two libron”) processes [10], scattering by one-phonon processes including optical branches [11], and electron-electron scattering [12].

As compared to other organic conductors, such as TTF-TCNQ or the Bechgaard salts, the room temperature conductivity that we have measured is extremely small. It is, however, of the same order of magnitude as the microwave and dc conductivity of other 2:1, β -phase ET salts. Values between 10 and $33 \Omega^{-1} \text{ cm}^{-1}$ have been reported for the I_3^- , PF_6^- , and ClO_4^- salts [13–18]. Only the ReO_4^- has been found to have a higher value: $200 \Omega^{-1} \text{ cm}^{-1}$ at room temperature [19].

Furthermore, these microwave measurements are in good agreement with an extrapolation to zero frequency of the far infrared conductivity as determined by Kramers-Kronig analysis of the 30 and 300 K polarized reflectance [3]. In this respect the ET compound also differs significantly from other highly conducting organic crystals (TTF-TCNQ and the Bechgaard salts) where the low-temperature microwave and dc conductivity is typically a factor of ten or more larger than the far infrared conductivity [20–22].

Finally, we note that the notion of metallic conductivity (in the sense of the Drude model, where carrier motion is limited by a mean free path) cannot be applied to the ET compounds over much of the temperature range. According to the Drude formula, the dc or microwave conductivity is given by

$$\sigma = ne^2 l / m^* v_F, \quad (3)$$

where n is the carrier concentration, e is the electronic charge, m^* is the effective mass of the carriers, v_F is the Fermi velocity and l is the mean free path. The room-temperature conductivity ($6 \Omega^{-1} \text{ cm}^{-1}$) is, however, so low that the mean free path is much smaller than the intramolecular spacing for any reasonable choice of the other quantities in eq. (3),

implying that the concept of a mean free path does not apply.

We estimate the Drude-model mean free path in the following way. We obtain the ratio of carrier concentration to effective mass and the Fermi velocity from the plasma frequency, $\omega_p = (ne^2/\epsilon_0 m^*)^{1/2}$. We begin by assuming that the measured plasma frequency gives the one-electron parameters of a three-quarter-filled tight binding band, with (on average) half a hole per molecule. Thus we initially neglect the dimerization gap caused by the inequivalence of the two ET molecules per unit cell [23,24] as well as correlation effects [25]. Because the plasma frequency is larger than the interband splitting caused by the dimerization and is also larger than typical low-lying charge-transfer bands, it should be relatively insensitive to these effects [26]. For a three-quarter-filled tight binding band,

$$\omega_p = (2\sqrt{2}e^2 a^2 t / \pi \epsilon_0 \hbar^2 V_m)^{1/2},$$

$$v_F = \sqrt{2}ta/\hbar.$$

Here, t is the transfer or hopping integral, $a = 4.5 \text{ \AA}$ is the intramolecular spacing, and V_m is the volume per ET molecule.

Polarized reflectance measurements [3] for the chain-axis direction give $\omega_p = 1.94 \times 10^{15} \text{ s}^{-1}$ ($10.280 \text{ cm}^{-1}/1.27 \text{ eV}$) from which we infer $t = 0.22 \text{ eV}$ and $v = 2.2 \times 10^7 \text{ cm/s}$. The Drude-model mean free path, from

$$l = (v_F / \epsilon_0 \omega_p^2) \sigma, \quad (4)$$

would then be $l = 0.04 \text{ \AA}$ at 300 K and $l = 6 \text{ \AA}$ at 20 K.

Even the 20 K value is only slightly more than the 4.5 \AA spacing between ET molecules or the $3.5\text{--}3.7 \text{ \AA}$ sulfur-sulfur contact distances.

These crude comparisons between the Drude-model mean free path and the lattice constant would be modified only by factors of order 2 if more realistic electronic structures were used. For example, band structure calculations [23] suggest a half-filled conduction band, with one electron per ET dimer. If this were assumed then the carrier concentration would be a factor of 3 smaller, making $l = 0.12 \text{ \AA}$ at 300 K and $l = 20 \text{ \AA}$ at 20 K. These distances should be compared with the 9.1 \AA repeat distance along the stacking direction.

In summary, we find that the microwave conductivity is strongly temperature dependent, is in agreement with the far infrared conductivity, and suggests an unrealistically short mean free path. One possible explanation for the latter result would be to assume that not all of the valence electrons contribute to the conductivity; some must be rendered ineffective in transport, either through the creation of many gaps in the band structure by structural distortions or on account of strong electron-electron interactions. We note however that specific heat measurements [26] show that the superconducting transition in $\beta\text{-(ET)}_2\text{IAuI}$ involves a large change in the Fermi-surface density of states, suggesting that all of the valence electrons do participate in the superconducting behavior. A second possibility is that the effective transport velocity and mass are not the Fermi velocity and band mass but are instead some much smaller speed and larger mass. This would be the case if the electrons were very strongly coupled to the lattice.

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