MICROWAVE CONDUCTIVITY OF THE ORGANIC CHARGE DENSITY WAVE CONDUCTOR (FLUORANTHENE)₂X

CONDUCTOR (FLUORANTHENE)$_2$X

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ABSTRACT

We have investigated the temperature dependence of the microwave conductivity of the organic CDW-conductor (FA)$_2$X at frequencies of 4.2, 10.2 and 23.5 GHz and compared our data with the d.c. conductivity of these crystals [1].

Down to temperatures of about 80 to 60 K an excellent agreement has been found. In the quasi-metallic high temperature range no frequency dependence of the conductivity is observed. Upon cooling a sharp phase transition already known from d.c. measurements occurs at temperatures T_P of 182 to 175 K depending on the counterion X$^-$ = PF$_6^-$, SbF$_6^-$. At temperatures far below this Peierls transition, however, deviations from d.c. results are observed; while the d.c. conductivity displays thermally activated behaviour the microwave conductivity leads into a plateau and remains almost constant down to 4 K. The onset of this plateau lies at temperatures from 80 to 60 K. At 20 K the microwave conductivity at 10.2 GHz is about 10 orders of magnitude higher than the d.c. values. We interpret these results as a clear signature of the Fröhlich mode resulting from the CDW ground state in (FA)$_2$X. The agreement of microwave and d.c. data even at temperatures below the Peierls transition can be ascribed to screening of the CDW by thermally excited charge carriers.

INTRODUCTION

Fluoranthene radical cation salts, e.g. (FA)$_2$X (X = PF$_6$, AsF$_6$, SbF$_6$), are highly conducting crystals, whose simple crystal and molecular structure make them a model system for quasi-one-dimensional organic conductors [2].

The fluoranthene molecules, planar aromatic hydrocarbons without heteroatoms form segregated stacks along the crystallographic a-axis. At room temperature they are slightly dimerized and in an ideal crystal one dimer carries one elementary electrical charge. The anions, inorganic closed shell ions, are located in channels between the FA-stacks. The 2:1-stoichiometry together with the π–electron wave function overlap within the FA-stacks leads to a half filled conduction band and therefore to a high conductivity parallel to the stack axis. The large average distance between the FA-stacks and the directed π–orbitals are responsible for the strong anisotropy of

many of the physical properties, for example the conductivity parallel and perpendicular to the a-axis.

Meanwhile it is well established that the electronic ground state of the system below the Peierls transition temperature, which depends on the size of the counterion, corresponds to a charge density wave. In the CDW state $(FA)_2X$ displays transport properties similar to other organic or inorganic CDW-conductors. Among them are nonlinear conductivity above a small sample dependent threshold field, conduction noise in the nonlinear state and metastability phenomena [3,4,5].

Here we present experimental results of the microwave conductivity $\sigma(\omega)$ of $(FA)_2X$ single crystals at frequencies of 4.2, 10.2 and 23.5 GHz as a function of temperature.

EXPERIMENTAL

The $(FA)_2X$ crystals used for the frequency dependent conductivity and d.c. conductivity measurements were taken from the same batches. Typical crystal dimensions for the microwave measurements were 2.5 mm × 100 μm × 50 μm, where the needle axis corresponds to the a-axis.

The microwave conductivity at all frequencies was measured with a resonant cavity technique. The complex conductivity of the sample was determined from the normalized frequency shift Δf and the change of the quality factor ΔQ of a resonant cavity, obtained by inserting the sample (Q_p, f_p) and removing it from the cavity (Q_0, f_0).

$$\Delta Q = \frac{1}{2}\left(\frac{1}{Q_p} - \frac{1}{Q_0}\right) \qquad \Delta f = \frac{f_p - f_0}{f_p} \tag{1}$$

The resonance frequencies and the quality factors were determined by detecting the reflected or transmitted power for several frequencies and fitting a Lorentzian line shape to the readings.

The microwave conductivity $\sigma(\omega)$ can be determined from ΔQ and Δf with the aid of a perturbation technique [6]. In all of the measurements the electric field penetrates the whole sample and consequently no corrections for the skin effect were necessary.

For samples with a microwave conductivity higher than a critical value $\sigma(\omega) > \sigma(\omega)^{crit.}$ the deelectrization leads to a degradation of the electric field in the sample [7]. In this case the imaginary part of the permittivity $\epsilon''(\omega) = \sigma(\omega)/(\epsilon_0 2\pi f)$ is proportional to the reciprocal of ΔQ. In contrast to that, at low microwave conductivity $(\sigma(\omega) < \sigma(\omega)^{crit.})$ we get ϵ'' directly proportional to ΔQ. In this region ϵ' can be determined from the frequency shift Δf.

Our measurements at 4.2 and 23.5 GHz were performed in transmission. In this case sample and cavity can be cooled down to liquid nitrogen temperature only. The equipment at 10.2 GHz is built up for reflection measurements. There only the sample is cooled in a standard vaporizer cryostat for ESR measurements down to liquid helium temperature. The cylindrical cavity, driven in the TM_{010} mode, is separated from the sample by a quartz glass tube. The a.c. losses of the tube predominate the increase of conductivity of the copper cavity, which is only cooled down by radiation. This leads to the decrease of Q_0 for 300 K > T > 100 K.

EXPERIMENTAL RESULTS

Figure 1 shows a comparison of the temperature dependence of the microwave conductivity measured at 10.2 GHz and the d.c. conductivity [1] of two $(FA)_2PF_6$ single crystals between 300 and 20 K.
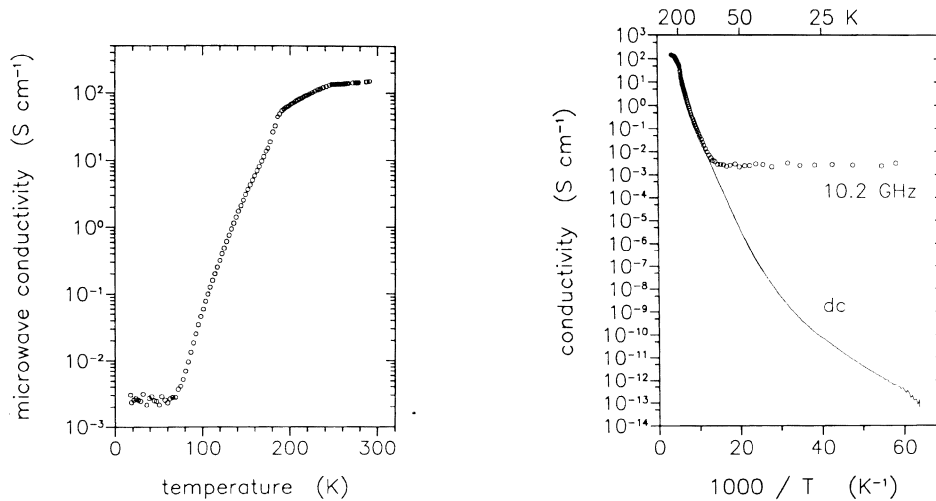
Figure 1: Conductivity of FA_2PF_6 at (o) 10.2 GHz and (—) d.c.

The qualitative features of the data are as follows:

- Between room temperature and the Peierls transition temperature T_P no frequency dependence is observed, in consistence with the metallic properties of the system in the high temperature range, though however, no real metallic temperature dependence of the conductivity is observed.

- At T_P (182 K) both methods observe a sharp phase transition of second order [1], this is the Peierls transition leading to the CDW ground state.

- Below the Peierls transition both d.c. and microwave conductivity strongly decrease with almost the same temperature dependence down to about 80 K.

- At temperatures far below the Peierls transition, however, deviations from d.c. results are observed: while the d.c. conductivity displays thermally activated behaviour the microwave conductivity leads into a plateau and remains almost constant down to 4 K. On this crystal the onset of the plateau lies at 80 K. At 20 K the microwave conductivity at 10.2 GHz is about 10 orders of magnitude higher than the d.c. values.

Figure 2 shows the measured Q values used for the data analysis. For temperatures below 80 K ΔQ is approximately constant and by a factor of three higher than the experimental limits. To ensure the validity of our data, especially the existence of the plateau, we investigated a much larger crystal (figure 3). At low temperatures we found a significant difference between Q_0 and Q_p, confirming our results displayed in figure 1. There are no data for temperatures above 125 K available, because the cavity was detuned by the large sample volume and the higher conductivity.
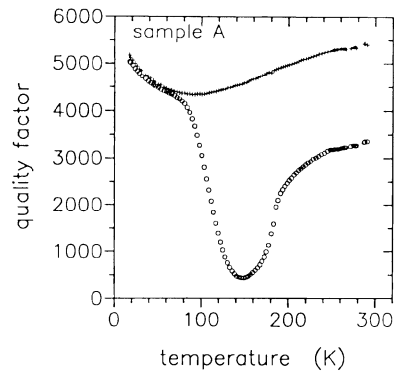
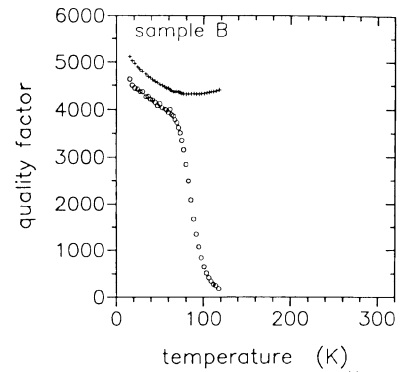Figure 2: Quality factor Q_P (o) with and Q_0 (+) without sample in the cavity
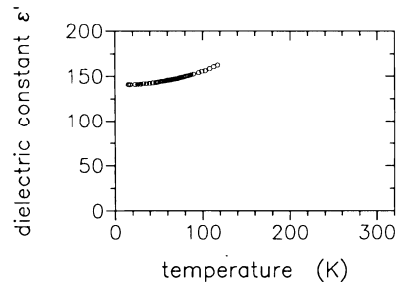
Figure 3: Quality factor of a larger crystal

Figure 4: Dielectric constant $\epsilon'(T)$ of FA_2PF_6 at 10.2 GHz

The dielectric constant ϵ' of $(FA)_2PF_6$ is shown in figure 4. It could only be determined at low temperatures and low microwave conductivity respectively. A slow decrease is observed with decreasing temperature and typical values of about 150 are measured.

Within the experimental error there is no difference between the data for our three microwave frequencies down to about 80 K. For frequencies other than 10.2 GHz we were not able to measure below liquid nitrogen temperature due to experimental limitations. Therefore a shift of the plateau with the frequency could not be detected.

DISCUSSION

The Peierls transition turns the electronic properties of a quasi-one-dimensional system like $(FA)_2X$ from metallic to semiconducting by opening a single-particle gap 2Δ at the whole Fermi surface. Therefore, as far as single particle processes are involved, the electrical conductivity is independent of frequency for $\omega < 2\Delta/\hbar$. In $(FA)_2X$ one yields from d.c. conductivity measurements and polarized optical reflectance spectra values for the semiconducting gap of $2\Delta = 120 \ldots 180$ meV, corresponding to infrared frequencies of $30 \ldots 45$ THz. Consequently the observed plateau of the microwave conductivity at 10.2 GHz for $T < 70$ K can not be explained by single particle excitations.

Similar to other CDW conductors this additional conductivity in the microwave frequency range can be attributed to the collective response of the electrons condensed in the CDW. This response originates from interactions of the CDW with the underlying lattice and impurities, which lead to a finite pinning frequency usually in the microwave range. Due to inhomogeneous pinning and damping effects typically a moderately broadened frequency dependent response is observed.

The magnitude of the pinning frequency can be estimated from the simple model of a rigid CDW in a harmonic pinning potential [8]. For this purpose one has to introduce an effective mass of the CDW condensate, the so-called Fröhlich mass, which is given by:

$$M^* = m^* \left(1 + \frac{4\Delta^2}{\lambda \hbar^2 \omega_{2k_F}^2} \right) \tag{2}$$

For $(FA)_2X$ follows with $m^* \approx m_0$, $\Delta/k_B \approx 700 \ldots 1050$ K, $\lambda \approx 0.3$ and $\hbar\omega_{2k_F}/k_B \approx 50$ K [1]:

$$M^* = (2.6 \ldots 5.8) \cdot 10^3 \, m_0$$

This value is comparable to other CDW conductors.

The pinning frequency ω_0 can be calculated [8] from:

$$\omega_0^2 = \frac{2e E_T k_F}{M^*} \tag{3}$$

For an electrical threshold field of $E_T \approx 0.1$ V/cm [3] and $k_F = \pi/2a$, where $a = 6.61$ Å is the lattice constant, this equation yields:

$$\omega_0/2\pi \approx 0.2 \ldots 0.3 \text{ GHz} ,$$

which represents a relatively small value as compared to other CDW conductors.

In $(FA)_2X$ nonlinear conductivity experiments gave clear evidence for a broad distribution of microscopic thresholds (weak onset of nonlinearity). Consequently one has to expect a fairly broad frequency dependent response. Furthermore screening and damping of the CDW by normal carriers have to be taken into account. Thus at low temperatures, when normal electrons are frozen out, these effects become unimportant and the collective response can be detected.

Further temperature dependent experiments in a wider frequency range are necessary in order to get more information about the Fröhlich mode in $(FA)_2X$ and the pinning mechanism in this material.

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