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PEIERLS INSTABILITY AND CHARGE DENSITY WAVE TRANSPORT IN THE QUASI ONE-DIMENSIONAL ORGANIC CONDUCTOR $(FLUORANTHENE)_2X$

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Abstract: Crystals of $(FA)_2X$ are highly one-dimensional organic conductors with a Peierls transition to a charge density wave ground state.
The temperature dependence of the d.c. conductivity and nonlinear conductivity results will be discussed.

INTRODUCTION

Already in the year 1955 Peierls[1] theoretically proposed a metall to semiconductor transition for a coupled one-dimensional electron-phonon system. But only after the synthesis of such materials in the early 1970s this proposal could be verified in experimental studies. Meanwhile several inorganic and organic compounds are known to have electrical properties characteristic of one-dimensional conductors with a Peierls transition to a charge density wave ground state.

The fluoranthene radical cation salts belong to the class of organic CDW-conductors. In $(FA)_2X$ the aromatic hydrocarbon fluoranthene ($C_{16}H_{10}$) forms stacks of dimer radical cations $(FA)_2^{\odot+}$ along the crystallographic a-axis (with a lattice constant a = 6.6 Å) segregated by counterions $X^- = PF_6^-, AsF_6^-, SbF_6^-$.[2] The overlap of the π-electron wave functions together with the 2:1-stoichiometry lead to a half filled conduction band, which can be well described by a tight-binding model.

Due to the crystal structure one can expect a high anisotropy of electrical transport properties. As a measure therefor can serve the ratio of the conductivities parallel and perpendicular to the highly conducting a-axis. For $(FA)_2PF_6$ we have found $\sigma_{||}/\sigma_{\perp} \approx 10^4$, which characterizes this system as highly one-dimensional. As a consequence, theoretical concepts developed for one-dimensional conductors should be applicable to the system $(FA)_2X$.

D.C. CONDUCTIVITY AND PEIERLS INSTABILITY

Figure 1 shows the temperature dependence of the d.c. conductivity $\sigma_{\|}(T)$ of a $(FA)_2PF_6$ single crystal along the crystallographic a-axis from room temperature down to 20 K.

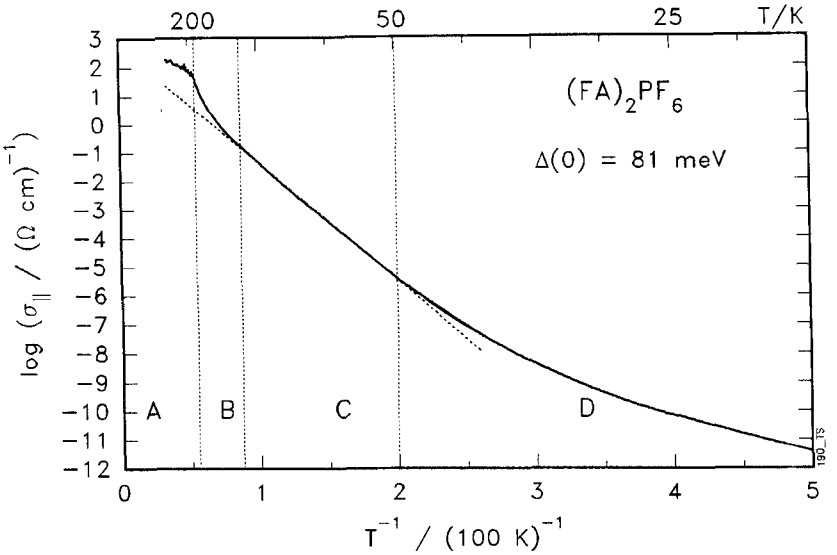

Figure 1: Temperature dependence of the d.c. conductivity $\sigma_{\|}(T)$ of a $(FA)_2PF_6$ single crystal along the crystallographic a-axis

This Arrhenius plot can be clearly divided into four temperature regions. In the high temperature region A (300 – 182 K) one measures relatively high conductivities of $10^2 - 10^3$ $(\Omega cm)^{-1}$ at room temperature but no real metallic temperature dependence. At 182 K a sharp phase transition of second order takes place, which leads to an abrupt change of the curvature of $\sigma_{\|}(T)$. This Peierls transition turns the electronic properties of the system from metallic to semiconducting. Below, in the intermediate range B (182 – 120 K) the gradual opening of an energy gap at the Fermi level determines the charge transport. In the semiconducting region C (120 – 50 K) one finds thermally activated behaviour of the d.c. conductivity with activation energies $\Delta(0)$ of 60 – 90 meV depending on the crystal. At lower temperatures (range D) deviations from this behaviour indicate that impurity levels within the gap contribute to the conductivity. In the following the measured temperature dependence between 300 and 50 K will be described quantitatively with theoretical models developed for one-dimensional conductors.

From the crystal structure as well as optical[3] and magnetic resonance[4] experiments it is expected that in the high temperature range $(FA)_2X$ possesses a metallic character. The observed non-metallic temperature dependence of $\sigma_{\|}(T)$ $(d\sigma_{\|}/dT > 0)$ in this range is a consequence of the high one-dimensionality of the system. For it is known from theoretical calculations[5] that in a one-dimensional

electron-phonon system fluctuations lead to a pseudo energy gap in the electronic density of states. Recently Johnston et al.[6] introduced a model to describe the temperature dependence of the electrical resistance of a quasi one-dimensional conductor by means of a temperature dependent pseudo energy gap:

$$R(T) = R_0 + A \cdot T^B \cdot [\, \exp\{\Delta_{pseudo}(T)/k_B T\} + 1\,] \qquad (1)$$

In this equation a mean free path of electrons $l(T) \propto T^{-B}$ has been assumed and R_0 represents a phenomenological offset. Figure 2 shows a fit of equation (1) to the experimental data with good agreement between 200 and 290 K. The mobility exponent B takes values from 0.8 – 1.1 for different crystals, which is typical for metals at high temperatures. This indicates that in $(FA)_2PF_6$ metallic behaviour in the high temperature range is suppressed by fluctuations.

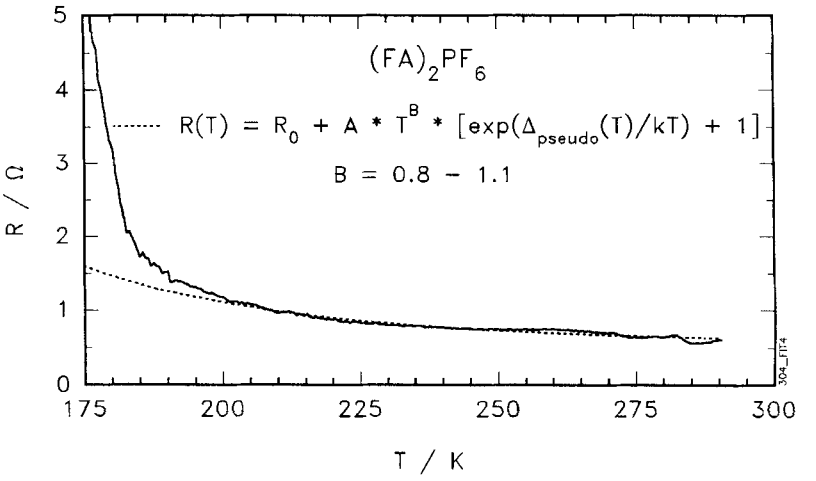

Figure 2: Fit of the Johnston model to the experimental data in the high temperature range

Below the Peierls transition the charge transport is determined by the gradual opening of an energy gap. A mean-field calculation[7] yields for the temperature dependence of this gap a BCS-like behaviour. Based on these theoretical results we were able to describe the temperature dependence of the electrical resistance with the analogon of equation (1), in which the offset R_0 has been neglected and the Fermi-Dirac distribution replaced by Maxwell-Boltzmann statistics:

$$R(T) = A \cdot T^B \cdot \exp\{\Delta_{BCS}(T)/k_B T\} \qquad (2)$$

Figure 3 shows the excellent fit of this equation to the experimental data below the Peierls transition over more than eight orders of magnitude in the electrical resistance. Remarkable is the good agreement of the exponent B with the values obtained for the high temperature range.

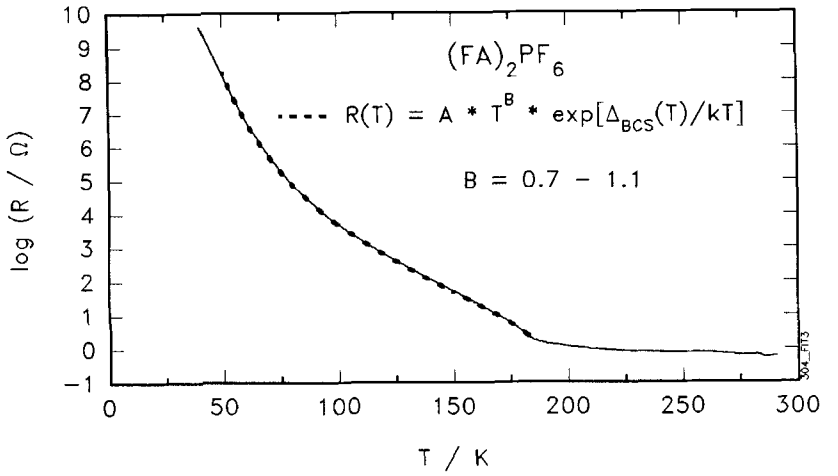

Figure 3: Fit of equation (2) to the experimental data below the Peierls transition

For counterions other than PF_6^- we observe a similar behaviour of $\sigma_{\|}(T)$, however, as expected for a highly one-dimensional conductor the Peierls transition temperature depends on three-dimensional coupling effects and therefore on the size of the counterion.

NONLINEAR CONDUCTIVITY AND CDW-TRANSPORT

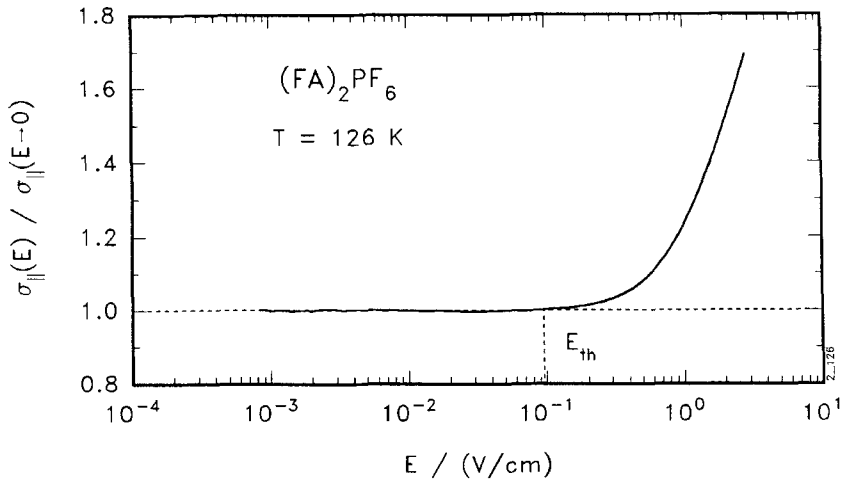

Figure 4: Nonlinear conductivity of a $(FA)_2PF_6$ single crystal at 126 K

The Peierls transition not only causes a gap in the electronic density of states at the Fermi level but also a periodic distortion of the lattice connected with a

modulation of the charge density, a so-called charge density wave (CDW). Under ideal conditions the electrons condensed in the CDW can move through the lattice even for arbitrarily small electrical fields. In a real crystal, however, the CDW is pinned by impurities and defects (impurity pinning) and/or the electrostatic potential of the lattice ions (commensurability pinning). Therefore a finite electrical field exceeding a sample dependent threshold is necessary for a collective motion of the CDW.[8,9]

Figure 4 shows the nonlinear conductivity of a $(FA)_2PF_6$ single crystal at a temperature well below the Peierls transition. Ohmic behaviour is observed up to electrical fields of about 0.1 V/cm, above, the conductivity increases. The onset of this nonlinearity is smooth, as a consequence the threshold field is not precisely defined. The low value of the threshold excludes single particle processes as the origin of nonlinearity, rather this gives clear evidence for a collective charge transport due to sliding CDWs.

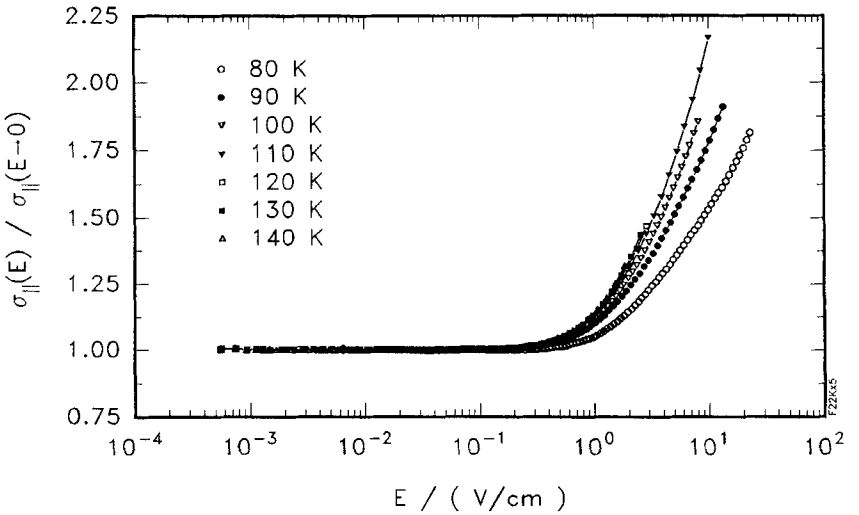

Figure 5: Nonlinear conductivity of one $(FA)_2PF_6$ crystal at different temperatures from 140 to 80 K

The temperature dependence of the nonlinearity between 140 and 80 K is shown in figure 5. For all temperatures investigated the onset of nonlinearity is smooth and no significant shift of the threshold is observed. Upon cooling the dynamics of nonlinearity is reduced by considerably less than a factor of 2, whereas the ohmic conductivity decreases for about two orders of magnitude over the same temperature range. This means that the nonlinear conductivity has also to be strongly temperature dependent.

A decomposition of the total current measured at fixed electrical field according to:

$$I_{tot} = I_{Ohm} + I_{CDW} \tag{3}$$

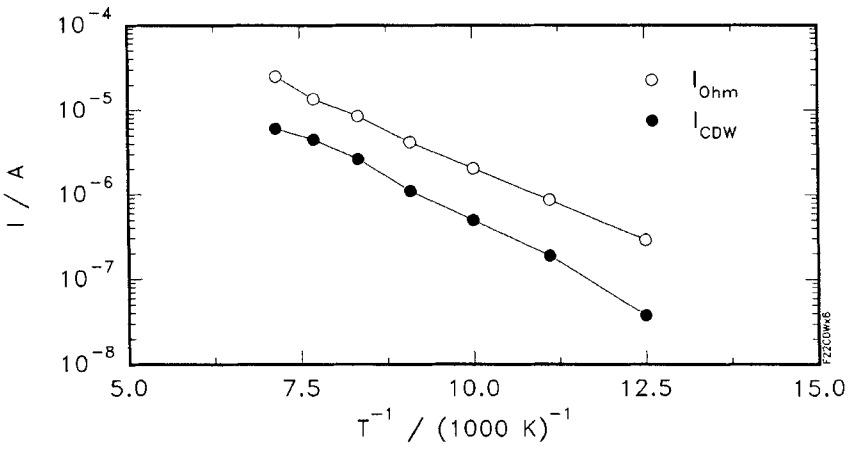

Figure 6: Temperature dependence of the ohmic and the CDW-current

shows (cf. fig. 6) that both parts exhibit thermally activated behaviour with almost the same activation energy. This scaling behaviour of the CDW-current and the ohmic current is in accordance with classical theories, in which the CDW is treated as an extended elastic medium.[10,11] In these models the CDW interacts with its environment via electrostatic screening and Coulomb interactions. The freeze out of normal electrons leads to an enhanced damping of the CDW and therefore causes a decrease of CDW-conductivity with approximately the same activation energy as the ohmic part.

In conclusion we have shown that $(FA)_2X$ can be regarded as a model system for studying the Peierls instability itself and the charge density wave transport phenomena occuring in the ground state of the Peierls semiconductor.

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