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CHARGE TRANSPORT IN THE QUASI-ONE-DIMENSIONAL ORGANIC CHARGE DENSITY WAVE CONDUCTOR (FLUORANTHENE)$_2$X

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ABSTRACT

Due to its simple crystal structure the organic radical cation salt (fluoranthene)$_2$X can serve as a model system for quasi-one-dimensional conductors. The temperature dependence of the dc conductivity exhibits the typical behaviour of a quasi-one-dimensional metal with a Peierls transition at about 180 K to a charge density wave (CDW) ground state. Above the Peierls transition $\sigma_{\|}(T)$ can be described quantitavely within a model of CDW fluctuations leading to a pseudo gap in the electronic density of states. Below, the existence of a real energy gap $2\Delta(T)$ with a modified BCS-like temperature dependence determines the charge transport. On crystals from different charges intrinsic energy gaps $2\Delta(0) = 120 - 180$ meV have been found due to deviations from the ideal 2:1–stoichiometry in (FA)$_2$X.

For electrical fields exceeding a small sample dependent threshold ($E_T = 0.1 - 1$ V/cm) nonlinear conductivity and other collective CDW transport phenomena can be observed. On crystals with different energy gaps $2\Delta(0)$ we observe significant differences in dynamics of the nonlinearity as well as in the magnitude of the threshold field. Our observations indicate that defect and commensurability pinning of the CDW are of great importance for the nonlinear transport properties of (FA)$_2$X. On thermally quenched samples the existence of metastable states has been found, due to pinning of the CDW by randomly positioned impurities.

INTRODUCTION

Well before quasi-one-dimensional conductors were prepared experimentally, theoretical investigations of low dimensional systems have demonstrated that their electronic properties differ considerably from those materials, in which two or three dimensional motion of electrons is possible. Due to the special geometry of the Fermi surface, a one-dimensional electron gas is not stable at low temperatures. Depending on the dominating interaction different ground

states for example superconductivity, spin density waves (SDW) and charge density waves (CDW) have been predicted theoretically and observed experimentally in low dimensional systems.

The fluoranthene radical cation salts $(FA)_2X$ belong to the class of quasi-one-dimensional conductors with a Peierls transition to a CDW-ground state. In these crystals, the fluoranthene molecules (FA = $C_{16}H_{10}$) form segregated stacks of radical dimer cations $(FA)_2^{+\odot}$ along the crystallographic a-axis. The counterions, inorganic closed shell systems (for example PF_6^-, AsF_6^-, SbF_6^-), are located in channels between the FA-stacks. The strong π-electron wave function overlap together with the 2:1–stoichiometry lead to a half filled band and therefore to a high conductivity parallel to the stack axis. The large average FA-stack distance and the directed π-orbitals are responsible for the strong anisotropy of many of the physical properties for example the conductivities σ parallel and perpendicular to the stack axis. For $(FA)_2PF_6$ we have found $\sigma_{\|}/\sigma_{\perp} \approx 10^4$. Consequently theoretical concepts developed for quasi-one-dimensional conductors with a Peierls transition should be applicable to $(FA)_2X$. Here we present a short description of the dc conductivity and results about nonlinear conductivity and metastability.

DC CONDUCTIVITY OF $(FA)_2X$

Between room temperature and 4 K the dc conductivity of $(FA)_2X$ varies over more than 16 orders of magnitude with maximum values of $10^2 - 10^3$ $(\Omega cm)^{-1}$ — depending on the crystal — at room temperature.

Figure 1 shows an Arrhenius plot of $\sigma_{\|}(T)$ for $(FA)_2PF_6$ between 300 and 20 K. This plot can be clearly divided into four separate temperature regions:

- A. High temperature range (300 – 182 K):
  Despite of the relatively high conductivities at room temperature, no real metallic temperature dependence of the conductivity is observed. In this range the system can be characterized as a quasi-one-dimensional metal, in which fluctuations lead to a pseudo gap in the electronic density of states.

- Peierls transition (T_P = 182 K):
  At 182 K we observe a phase transition of second order, this is the Peierls transition leading to the CDW ground state of the system.

- B. Intermediate range (182 – 120 K):
  Below the Peierls transition a strong decrease of conductivity is observed due to the gradual opening of a real energy gap at the Fermi level with a modified BCS-like temperature dependence.

- C. Semiconducting range (120 – 50 K):
  Here the energy gap is almost completely open and one therefore measures thermally

activated conductivity with activation energies $\Delta(0) = 60 - 90$ meV for crystals from different batches.

- D. Low temperature range (T < 50 K):
  Below approximately 50 K deviations from the thermally activated behaviour indicate that impurity levels within the gap contribute to the conductivity.

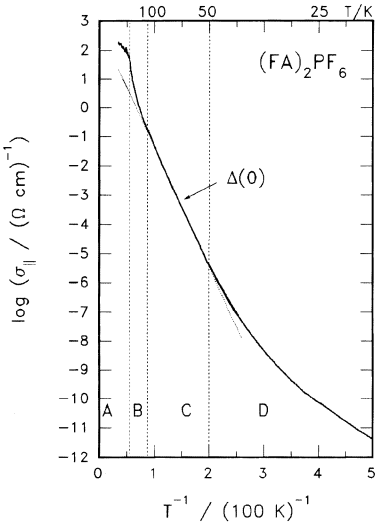

Fig. 1: Temperature dependence of the dc conductivity $\sigma_{\|}(T)$ of a $(FA)_2PF_6$ single crystal along the crystallographic a-axis; the dashed line represents thermally activated conductivity with an activation energy $\Delta(0) = 81$ meV

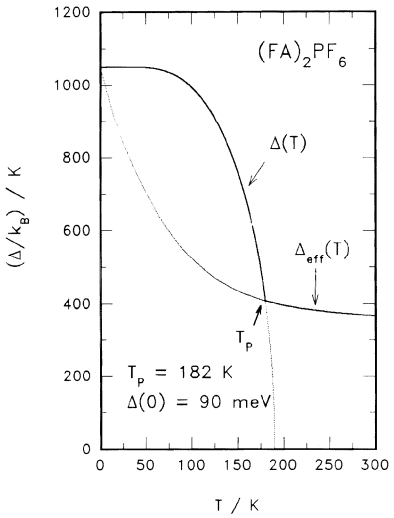

Fig. 2: Temperature dependence of the effective and Peierls gap for $(FA)_2PF_6$; the Peierls gap vanishes at a temperature $T_P^* = 190$ K, which is slightly higher than the observed phase transition temperature $T_P = 182$ K

In the following we will give a brief description of the observed temperature dependence of the dc conductivity in the ranges A, B and C (300 – 50 K), where the influence of defects is not dominant, with theoretical models developed for quasi-one-dimensional systems with a Peierls transition. (For a detailled discussion we refer to [1].)

Already from earlier experiments there has been strong evidence for a metallic character of $(FA)_2PF_6$ in the high temperature range. 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. As it is known from theoretical calculations [2], fluctuations in a one-dimensional electron-phonon system lead to a pseudo energy gap in the electronic density of states. Recently Johnston et al. 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 [3]:

$$R(T) = R_0 + A \cdot T^B \cdot [\, \exp\{\Delta_{eff}(T)/k_BT\} + 1 \,] \quad (1)$$

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.

Below the Peierls transition the charge transport is determined by the gradual opening of an energy gap. A mean-field calculation yields for the temperature dependence of this gap a modified BCS-like behaviour [4,5]. 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:

$$R(T) = A \cdot T^B \cdot \exp\{\Delta(T)/k_BT\} \quad (2)$$

We have found an 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 also the good agreement of the exponent $B = 0.7 - 1.0$ with the values obtained for the high temperature range.

Thus we conclude that the dc conductivity of $(FA)_2PF_6$ can be described quantitatively in a wide temperature range from room temperature down to 50 K, if one knows the functional form of only two physical quantities. These are the effective energy gap for the metallic range (caused by fluctuations) and the real energy gap in the ground state, which is the order parameter of the Peierls transition. The temperature dependence of $\Delta_{eff}(T)$ and $\Delta(T)$ is determined by the activation energy $\Delta(0)$ and the phase transition temperature T_P, both of which were measured. These two energy gaps are displayed in figure 2.

According to this figure the observed Peierls transition takes place at a temperature $T_P =$ 182 K, where the effective gap with only a weak temperature dependence passes into the strongly temperature dependent Peierls gap, which vanishes at a slightly higher temperature.

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

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 electronic 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.

Meanwhile the existence of a charge density ground state below the Peierls transition in $(FA)_2PF_6$ is confirmed by the observation of nonlinear conductivity and conduction noise in the nonlinear state [6] as well as a frequency dependence of the conductivity in the microwave range [7]. Detailed investigations of the nonlinear conductivity have revealed that the collective response in $(FA)_2PF_6$ depends strongly on the crystal quality and the stoichiometry.

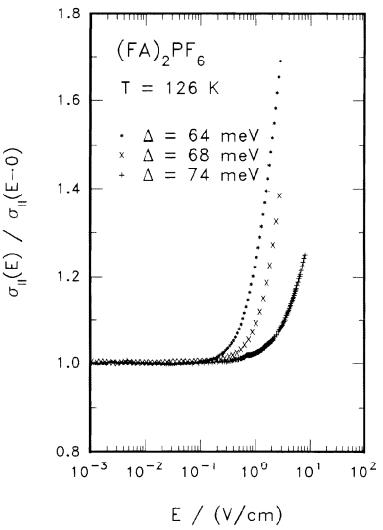

Fig. 3: Nonlinear conductivity of three $(FA)_2PF_6$ single crystals at the same temperature, but with different energy gaps $2\Delta(0)$

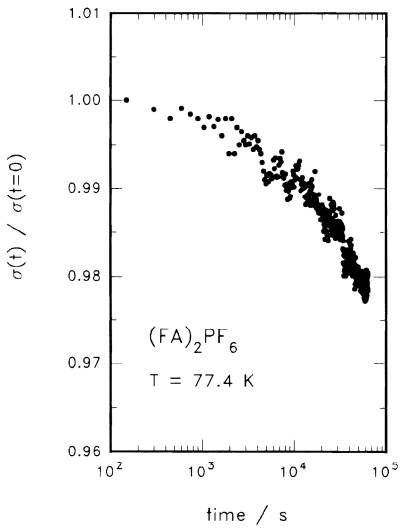

Fig. 4: Time dependence of the ohmic conductivity of a thermally quenched $(FA)_2PF_6$ single crystal (300 K to 77 K)

Figure 3 shows the nonlinear conductivity of three $(FA)_2PF_6$ single crystals from different batches at the same temperature. In all three crystals we measure a smooth onset of the nonlinearity, however significant differences in the magnitude of the threshold field and the dynamics of the nonlinearity are observed. These differences are clearly correlated with the energy gap determined from dc conductivity experiments: Crystals with a larger energy gap reveal a smaller dynamics of the nonlinearity and a higher threshold field. This behaviour can be explained by the relation between the energy gap and the wave length of the CDW. Both are determined by the Fermi momentum and therefore by the stoichiometry. In the mean field theory the energy gap $2\Delta(0)$ is proportional to $1/\omega_{2k_F}^2$ [8], where ω_{2k_F} represents the unperturbed phonon frequency of the high temperature range. In an ideal crystal $k_F = \pi/2a$ due to the 2:1-stoichiometry and therefore the wave length of the CDW ($\lambda_{CDW} = \pi/k_F$) is commensurable with the underlying lattice. However, because of slightly different crystal

growth conditions small deviations from the ideal stoichiometry occur, leading to different energy gaps and wave lengths of the CDW. Thus we conclude that crystals with a larger energy gap lie closer to the ideal 2:1–stoichiometry. The higher threshold field and the lower dynamics of the nonlinearity are in this picture a consequence of stronger commensurability pinning.

Beside commensurability pinning mainly defect pinning determines the nonlinear properties. The stochastic distribution of these impurities leads to the absence of long range order of the CDW and therefore to the existence of metastable states. Consequently the the ohmic conductivity depends on the thermal and electrical history of the sample. Figure 4 shows the time dependence of the ohmic conductivity of a thermally quenched $(FA)_2PF_6$ single crystal. The decay of metastable states leads to a decrease of conductivity, which follows a logarithmic or alternatively a strechted exponentional behaviour similar to other CDW-conductors.

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. Our results of the nonlinear conductivity and metastability indicate that $(FA)_2X$ is a CDW-conductor, in which deviations from the ideal 2:1–stoichiometry and defects determine the CDW transport properties.

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