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Charge Density Waves in Organic Conductors: $(Fluoranthene)_2X$ as a Model System

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Abstract

Due to its simple molecular and crystalline structure, the organic conductor $(FA)_2X$ ($X = PF_6$, AsF_6, SbF_6) can be regarded as a model system to study the Peierls instability and charge density wave transport phenomena. In this contribution we give a short introduction to the field of low-dimensional conductors and compare our experimental data with theoretical predictions for quasi-one-dimensional conductors with a Peierls transition to a charge density wave ground state.

1. Introduction

Well before quasi-one-dimensional conductors could be 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 [1, 2]. This unconventional behaviour is related to the presence of a Fermi surface with large parallel areas separated by a single wave vector $q = 2k_F$ (k_F is the Fermi wave vector), leading to instabilities of the low-dimensional electron gas. Depending on the dominating interaction (electron–electron or electron–phonon interaction) different ground states, for example, superconductivity, spin density waves (SDW) and charge density waves (CDW), can be observed in these systems.

For systems with dominating electron–phonon interaction the ground state is characterized by a gap in the single particle excitation spectrum associated with a periodic lattice distortion and a spatial modulation of the electronic charge density ρ, a CDW. In the one-dimensional case, the resulting charge density is given by

$$\rho(x) = \rho_0 + \rho_{CDW}(qx + \phi) \tag{1}$$

where ρ_0 is the average electron density in absence of the lattice distortion, ρ_{CDW} the amplitude of the electronic density wave, $q = 2k_F$ the CDW wave vector and ϕ the phase with respect to the underlying lattice. Since the wavelength of the CDW, $\lambda_{CDW} = 2\pi/2k_F$, is controlled by the Fermi momentum, it is generally uncorrelated with the undistorted lattice periodicities. Depending on the band filling, the periodicity of the CDW can be either commensurate (λ_{CDW} equal to a rational multiple of the lattice constant) or incommensurate with the underlying lattice.

When the wavelength λ_{CDW} is incommensurate with the lattice, the phase ϕ is arbitrary and – as has been shown already by Fröhlich [2] – a current could be carried not by the motion of individual electrons, but by the frictionless sliding of the CDW as a whole. Fröhlich's theory of superconductivity, however, neglects the real structure of the crystal: Commensurability of the CDW with the underlying lattice (commensurability pinning), interaction with defects and lattice irregularities (defect pinning) and Coulomb interaction between adjacent chains (Coulomb pinning) in two chain systems destroy the translational invariance of the CDW and pin the phase to the lattice [3]. Before the CDW can slide, it has to overcome potential barriers. Therefore, an electrical field larger than a critical value, the so-called threshold field E_T, is necessary. Above E_T the CDW is driven into a current carrying state by executing a translational motion, leading to nonlinear current voltage characteristics [4]. Meanwhile experiments have revealed that CDW transport is much richer than originally envisioned by Fröhlich and the most prominent features of this collective charge transport are: nonlinear electrical conductivity above a small sample dependent threshold field, conduction noise in the nonlinear state in form of periodic voltage oscillations and broad band noise, a frequency dependent conductivity well below the characteristic single particle energies, ac-dc-interference phenomena, metastability, hysteresis and memory effects [5].

Originally, the observation of these collective transport phenomena was limited to inorganic systems such as the transition metal compounds $NbSe_3$, TaS_3, $(TaSe_4)_2I$ and $(NbSe_4)_{3.33}I$ [5] and the blue molybdenum bronzes like $K_{0.30}MoO_3$ [6]. But meanwhile it has been found in materials such as TTF-TCNQ [7, 8], where the charge transport is determined by organic molecules, too. A further group of organic compounds with a CDW ground state are the arene radical cation salts and as prototypes the fluoranthene radical cation salts $(FA)_2X$ [9–11]. In the following, we give a brief introduction to our model system $(FA)_2X$ and an overview of the experimental state of affairs about the Peierls transition and CDW transport in our system.

2. Crystal structure of $(FA)_2X$

Due to their simple crystalline and molecular structure, the fluoranthene radical cation salts can be regarded as model systems for quasi-one-dimensional conductors. Fluoranthene (FA) is a purely aromatic hydrocarbon $C_{16}H_{10}$ and X stands for centrosymmetric inorganic closed shell counterions, for example PF_6^-, AsF_6^-, SbF_6^-. Without going into details the basic features of the crystal structure can be

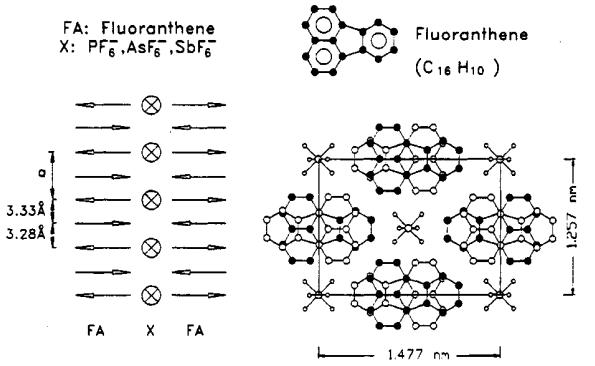

Fig. 1. Schematic crystal structure of $(FA)_2X$ at room temperature: projection on the a-c- and b-c*-plane; top: the aromatic hydrocarbon fluoranthene $C_{16}H_{10}$ (H-atoms are omitted).

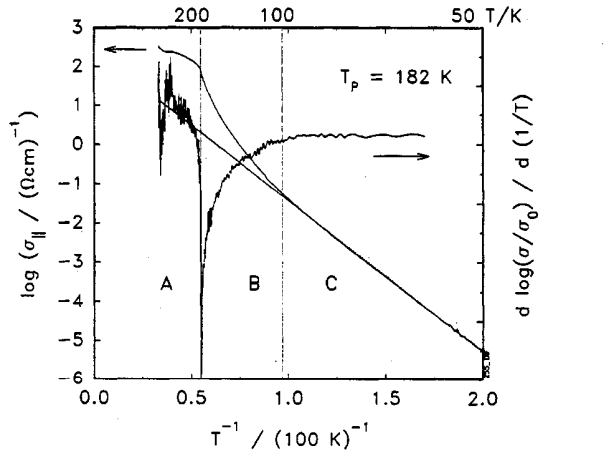

Fig. 2. Temperature dependence of the dc-conductivity $\sigma_\parallel(T)$ together with the logarithmic derivative $d(\log \sigma_\parallel)/d(1/T)$ of a $(FA)_2PF_6$ single crystal; the Peierls transition at T_P can be clearly identified from the singularity in the derivative.

seen in Fig. 1 [12]. The fluoranthene molecules form segregated stacks of radical dimer cations $(FA)_2^{+\odot}$, with strongly overlapping π-electron wave functions along the stack and weak overlap perpendicular to it. This leads to a quasi-one-dimensional electronic band structure along the chain direction. The metallic properties result from the charge transfer of the donor to the acceptor stack. In $(FA)_2X$ each fluoranthene dimer transfers one electron to each acceptor molecule X. In an ideal crystal we thus achieve a half filled conduction band and consequently $(FA)_2X$ is a good conductor along the chain direction with a room temperature conductivity in the order of 1000 S/cm, whereas the conductivity perpendicular to the chains is between 10^3 and 10^4 times smaller. The corresponding Fermi surface in $(FA)_2X$ shows therefore so-called nesting properties, which favour the onset of the Peierls transition.

Direct evidence for a Peierls transition in $(FA)_2X$ came from X-ray investigations by V. Ilakovac and J. P. Pouget [13]. Their experiments have revealed that in $(FA)_2PF_6$ a Peierls transition takes place at about 180 K. Due to large pre-transitional fluctuations, diffuse $2k_F$ lines are observed well above the phase transition temperature. At the phase transition these diffuse lines condense into sharp superlattice spots with the reduced wave vector $q_S = (\frac{1}{2}, 0, 0)$, leading to a commensurate CDW with λ_{CDW} equal to twice the lattice constant a.

3. Results and discussion

3.1. *DC-conductivity of* $(FA)_2X$

Figure 2 shows the temperature dependence of the dc-conductivity $\sigma_\parallel$ of a $(FA)_2PF_6$-crystal parallel to the stack axis. The basic features of the data are as follows.

Despite of high dc-conductivity values of up to 1000 S/cm no metallic temperature dependence is measured in the high temperature range A (300 K – phase transition). At about 182 K we detect a second order phase transition, the already mentioned Peierls transition. The transition temperature T_P can be precisely determined from the logarithmic derivative (see Fig. 2), which shows a sharp discontinuity due to an abrupt change in curvature. The Peierls transition in $(FA)_2X$ depends on three-dimensional coupling effects and therefore on the size of the counterion. For $(FA)_2AsF_6$ we measure a phase transition temperature of about 181 K, and for $(FA)_2SbF_6$ $T_P \approx 175$ K, respectively. Below the Peierls transition (in range B) the conductivity strongly decreases, due to the gradual opening of a temperature dependent BCS-like energy gap. Below about 120 K the energy gap is almost completely open, therefore thermally activated conductivity with activation energies between 60 and 90 meV is measured on crystals from different batches.

In the following we give a brief description of the measured temperature dependence by means of a theoretical model developed for quasi-one-dimensional conductors that undergo a Peierls transition. For a detailed discussion we refer to [9, 14].

Theoretical investigations within the mean field theory have shown that below the Peierls transition a gradual opening of a BCS-like energy gap occurs [15]. The mean field theory, however, neglects the important influence of fluctuations, which preclude the occurrence of a phase transition in a strictly one-dimensional system with short-range interactions at finite temperatures. A weak three-dimensional coupling – always present in a real quasi-one-dimensional conductor – reduces the influence of fluctuations and leads to a phase transition at finite temperatures, however significantly lower than predicted by mean field theory. In $(FA)_2PF_6$ we measure a phase transition temperature of about 182 K, whereas from mean field theory depending on the energy gap (120–180 meV) a transition temperature between 400 and 600 K would be expected. Consequently, one has to distinguish two temperature ranges. Below the phase transition, where the gradual opening of a modified BCS-like energy gap determines the charge transport, and above, where the influence of fluctuations is important [16]. As has been shown by Lee, Rice and Anderson [17], these fluctuations lead to a pseudo-gap in the electronic density of states.

Recently, it has been shown that the temperature dependence of $\sigma_\parallel$ can be described quantitatively with simple models developed for quasi-one-dimensional conductors [9]. It has been found that due to its high one-dimensionality $(FA)_2X$ behaves in the whole temperature range investigated like a one-dimensional semiconductor with an effective gap Δ_{eff} in the high temperature range due to fluctuations and a BCS-like energy gap below the Peierls transition.

Detailed theoretical investigations [14] have led to further improvements, yielding an expression for the electrical conductivity valid in the whole temperature range.

$$\sigma(T) = e^2 N \frac{aMc^2E_F^2}{2\pi E_1^2 \hbar\, \Delta(T)} \ln\left\{1 + \exp\left(-\frac{\Delta(T)}{k_B T}\right)\right\} \qquad (2)$$

Equation (2) has been derived by solving the one-dimensional Boltzmann equation, making realistic assumptions about relaxation processes (scattering by longitudinal acoustic phonons, charged counter ions ineffective) and the band structure in this highly one-dimensional system. In this equation N represents the number of conducting chains per unit area, M the mass of the fluoranthene molecule, a the lattice constant in chain direction, E_1 the deformation potential, c the sound velocity and $\Delta(T)$ the effective gap $\Delta_{eff}(T)$ or the real gap $\Delta_{real}(T)$ depending on the temperature range. With this equation – it contains only one fit parameter (the sound velocity) – the temperature dependence of $\sigma_{\|}$ can be described quantitatively in the whole temperature range displayed in Fig. 2 over more than eight orders of magnitude in the electrical conductivity. For further details of the theory we refer to a forthcoming paper [14].

3.2. *Nonlinear conductivity*

Below the Peierls transition in the CDW ground state $(FA)_2X$ displays transport phenomena similar to other CDW conductors. Figure 3 shows the normalized conductivity of a $(FA)_2PF_6$ single crystal *vs.* the logarithm of the electrical field for various temperatures below the Peierls transition. For this crystal we find ohmic behaviour up to electrical fields of about 0.5 V/cm. For higher fields the conductivity increases. In the whole temperature range investigated the onset of this nonlinearity is smooth and as a consequence the threshold field E_T is not precisely defined. During cooling no significant shift in the threshold field is measured. The low value of E_T excludes single particle processes such as warm or hot carriers and Zener tunneling as the origin of the nonlinearity. Rather the low threshold gives strong evidence for a CDW contribution. On crystals from different batches we measure pronounced differences in the dynamics of the nonlinearity and the threshold field (values between 0.1 V/cm and a few V/cm have been measured on crystals from different batches), pointing to a significant influence of defect and commensurability pinning.

Detailed investigations have revealed that the collective response in $(FA)_2X$ is clearly correlated with the measured energy gaps in the CDW ground state: crystals with a larger energy gap show higher threshold fields and reduced dynamics of the nonlinearity. This indicates that the CDW in $(FA)_2X$ is very close to commensurability. The crystal differences can be explained by deviations from the ideal 2 : 1 stoichiometry [11].

In CDW conductors the nonlinear conductivity can be described by a two fluid model. These two fluids consist of the electrons thermally excited above the energy gap and electrons condensed in the CDW. In the nonlinear state the current is then composed of an ohmic part and a CDW contribution.

$$I_{tot} = I_{Ohm} + I_{CDW} \qquad (3)$$

Figure 4 shows the temperature dependence of the ohmic part and the CDW-current measured at a fixed value of the electrical field. Both parts display thermally activated behaviour with approximately the same activation energy. This scaling behaviour of the CDW current and the ohmic current was first observed on inorganic CDW conductors by Fleming [18], and is in accordance with classical theories [19, 20], in which the CDW is treated as an extended elastic medium. 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.

3.3. *Nonlinearity and noise*

Perhaps the most spectacular observation in the field of CDW transport is that the response to dc-fields contains periodic components, known as narrow band noise, accompanied by a substantial increase of broad band noise [21]. The narrow band noise spectrum consists of one fundamental frequency and many harmonics, whereas the broad band noise shows a $1/f$-behaviour.

In $(FA)_2X$ the nonlinear conductivity is also accompanied by a significant increase of noise. Figure 5 shows the differential resistance together with the voltage noise created in the crystal and in a reference resistor. This diagram clearly

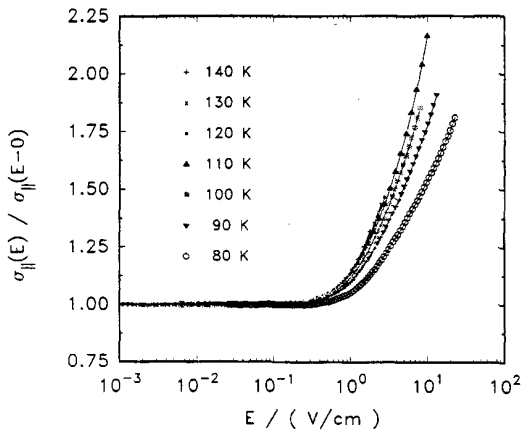

Fig. 3. Nonlinear conductivity of one $(FA)_2PF_6$ crystal at different temperatures from 140 to 80 K.

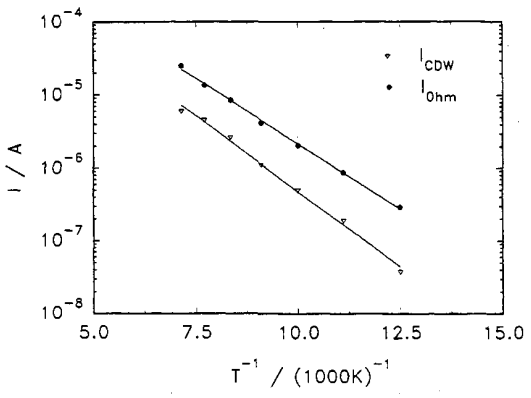

Fig. 4. Temperature dependence of the ohmic current and the CDW current.

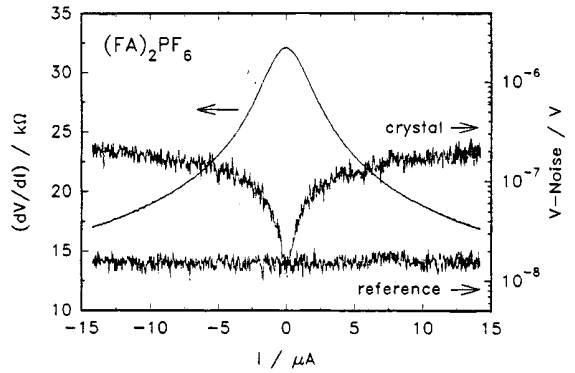

Fig. 5. Correlation between the nonlinear conductivity and the voltage noise created in the crystal and in a reference resistor.

demonstrates that the increase of noise is correlated with the beginning of the nonlinearity. The voltage noise mainly increases in the vicinity of the smooth threshold and seems to saturate at higher electrical fields, which is typical for CDW conductors. As our spectral investigations point out, we observe a broad band noise which shows a $1/f$-behaviour. However, we do not observe narrow band noise.

In CDW conductors the existence of a sharp threshold field and the existence of narrow band noise have been interpreted as the consequence of long range phase coherence in the current carrying state. This phase coherence is very sensitive to defects and three-dimensional coupling effects. In $(FA)_2X$ this long range order may be absent for various reasons. First of all, the high one-dimensionality reduces three-dimensional coupling and a long range order. Furthermore, in comparison to inorganic CDW conductors it is likely that our crystals possess a higher defect concentration. The consequences of these effects are a broader distribution of microscopic threshold fields and no long range order of the CDW, leading to a smooth onset of the nonlinearity and a lack of narrow band noise.

On the other hand, for systems near commensurability, the ground state is not necessarily an incommensurate CDW. The theory of McMillan [22] predicts for a band filling close to commensurability an "intermediate" state called nearly commensurate, where, the commensurate regions are interrupted by discommensurations in which the CDW changes the phase. These discommensurations can be charged and can carry a current. In an ideal commensurate crystal the concentration of these discommensurations is zero. In real systems it depends on the deviation from the ideal stoichiometry.

The nonlinear conductivity would in this picture arise from CDW defects. Consequently, no coherent motion of the CDW as a whole is observed in our crystals, which seems to be the prerequisite for narrow band noise.

3.4. *Frequency dependent conductivity*

A further characteristic feature of CDW conductors is a frequency dependence of the conductivity well below the characteristic single particle energies. Similar to the nonlinear conductivity above a sample dependent threshold field, this frequency dependence is a consequence of the interaction of the CDW with the lattice (pinning). This pinning shifts the oscillator strength of the ideal Fröhlich mode to finite frequencies, into the gap.

Frequency dependent investigations in inorganic CDW conductors have been performed in a very broad spectral range and several responses for excitation energies smaller than the Peierls gap have been identified [23]. The strong variation of $\sigma(\omega)$ at microwave frequencies is attributed to the response of the oscillating pinned mode, whereas the increase of $\sigma(\omega)$ in the radio frequency range comes from the dynamics of internal deformations.

Figure 6 shows a comparison of the temperature dependence of the microwave conductivity measured at 10.2 GHz and the dc-conductivity of two $(FA)_2PF_6$ single crystals between 300 and 20 K [24]. The qualitative features of the data are as follows: Between room temperature and the Peierls transition temperature T_P no frequency dependence of the conductivity is observed. At T_P (182 K) both methods observe the sharp phase transition. Below the Peierls transition both dc and microwave conductivity strongly decrease with almost the same temperature dependence down to about 80 K. At even lower temperatures, however, deviations from dc results are observed: while the dc-conductivity displays thermally activated behaviour, the microwave conductivity leads into a plateau and remains almost constant down to 4 K. At 20 K the microwave conductivity at 10.2 GHz is about 10 orders of magnitude higher than the dc values.

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. Further temperature dependent experiments in a wider frequency range are in progress in order to get more information about the Fröhlich mode in $(FA)_2X$ and the pinning mechanism in this material [25].

3.5. *Metastability*

Experiments on inorganic CDW conductors have shown that their transport properties depend on the thermal and electrical history of the sample. By applying a large electrical field or quenching a sample metastable states can be generated [26]. In general a slow logarithmic decay or alternatively a stretched exponential behaviour of these metastable states is observed. Figure 7 shows the time dependence of the conductivity of a $(FA)_2PF_6$ crystal which was quenched from room temperature down to liquid nitrogen temperature. The relaxation back to equilibrium can be

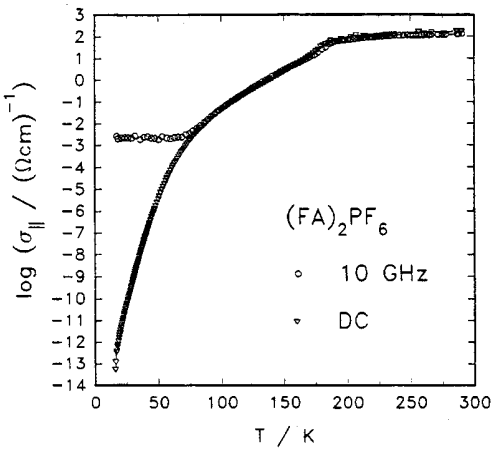

Fig. 6. Temperature dependence of $\sigma_{\parallel}$ of FA_2PF_6 at 10.2 GHz and dc.

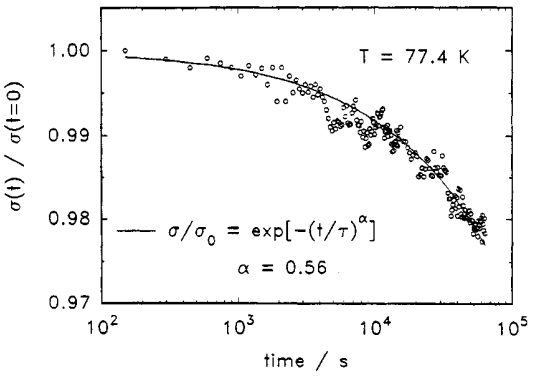

Fig. 7. Time dependence of the ohmic conductivity $\sigma(t)$ of a thermally quenched $(FA)_2PF_6$ single crystal (300 K to 77 K).

monitored through measuring the ohmic resistance. Here the data can be well described by a stretched exponential behaviour with

$$\frac{\sigma}{\sigma_0} = \exp\left[-(t/\tau)^{\alpha}\right] \tag{4}$$

yielding an exponent α of approximately 0.5, typical for a hierarchically coupled system [27, 28]. This glassy behaviour indicates a lack of long range order. Microscopic theories regard a deformable CDW, which is pinned by randomly positioned impurities. In such a system many metastable states exist from which the system can relax to the ground state.

4. Conclusion

In conclusion, we have shown that $(FA)_2X$ is an excellent model system to study the Peierls transition in quasi-one-dimensional conductors. We were able to show that fluctuations and the gradual opening of a BCS-like energy gap determine the electronic properties in the normal state. In the CDW ground state of this highly one-dimensional conductor typical CDW transport phenomena can be observed. Our investigations indicate that the CDW transport in $(FA)_2X$ is dominated by slight deviations from the commensurate situation, by defects and the high degree of one-dimensionality.

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