Electronic Properties of Quasi-One-Dimensional Compounds with a Charge / Spin Density Wave Ground State

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First, a review of the general properties of the collective transport induced by the charge (CDW)/spin (SDW) density wave motion in quasi-one-dimensional conductors is presented. Then the emphasis is specifically made on three recent developments in this field, namely:
– high spatial resolution X-ray study of the field-induced CDW deformations;
– quantum interference effects in magnetotransport of a sliding CDW through columnar defects;
– manifestation of disorder in the CDW/SDW ground state in thermodynamic properties at very low temperatures.

1. Collective Transport in Quasi-One-Dimensional Systems

Collective transport phenomena are among the most fascinating properties in solid state phisics. The best known example is superconductivity where the energy gap in the excitations at the Fermi level, as found by BCS, does not prevent conductivity. This is so because the interaction involved does not require a specified reference frame and because Coopers pairs can be built either in states "k and $-k$" or "$k+\kappa$ or $-k+\kappa$". The latter state leads to a uniform velocity such as $mv_s = \hbar\kappa$.

However in 1954, before BCS, Frölich [1] proposed a model in a jellium approximation in which a sliding charge density wave (CDW) could lead to a superconducting state. It is now well recognized that in systems of restricted dimensionality the interaction between ions and electrons, the so-called electron–phonon interaction, leads to structural (Peierls) instabilities at low temperature. According to the relative strength of several electron–electron coupling, the modulated ground state can be a CDW or, if the spin orientation is concerned, a spin–density wave (SDW).

Below the Peierls transition temperature T_p, the system is driven in a modulated state of the conduction electron density: $\rho(x) = \rho_0[1 + \cos(Q_0x + \phi)]$, accompanied by a periodic lattice distortion of the same wavelengh, $2\pi/Q_0$, where $Q_0 = 2k_F$ is the modulation wave vector (generally incommensurate; k_F is the electronic Fermi momentum). The new periodicity opens a Fermi surface gap in the electron density of states and leads to the appearance of new satellite Bragg reflections.

The opening of a gap below the Peierls transition temperature is reminiscent of semiconductors, but the essential feature of a CDW is that its wavelength, $\lambda_{CDW} = 2\pi/2k_F$, is controlled by the Fermi surface dimensions and is generally unrelated to the undistorted lattice periodicities, i. e., the CDW is incommensurate with the lattice. Consequently the crystal no longer has a translation group and in contrast to semiconductors, the phase ϕ of the lattice distortion is not fixed relative to the lattice but is able to slide along q. This phenomenon is easy to understand if we recognize that if the lattice is regular, no position is energetically favoured and no locking results. In more theoretical terms: if we think of the CDW as resulting from an electronic interaction via the lattice phonons, this interaction is the same in every galilean frame, provided that the frame velocity is small compared to the sound velocity. CDW condensation may thus arise in any set of galilean frames with uniform velocity, v, giving in the laboratory frame an electronic current density,

$$J = -n_0ev, \tag{1}$$

where n_0 is of the order of the electron number density condensed in the band below the CDW gap. This Frölich mode is a direct consequence of translation invariance. In practice, as shown by Lee, Rice and Anderson [2] this translation invariance is broken because the phase, ϕ, can in fact be pinned to the lattice, for example by impurities or by a long–period commensurability between the CDW wave–length and the lattice or by Coulomb interaction between adjacent chains. An applied dc electric field, however, can supply the CDW with an energy sufficient to overcome the pinning, so that above a threshold field, the CDW can slide and carry a current. Unfortunately, damping prevents superconductivity. This extra conductivity associated with the collective CDW motion, called Frölich conductivity, has been observed [3] for the first time in 1976 and since this time, an intense experimental and theoretical activity has been devoted to the understanding of the properties of this collective transport model [4,5].

Non–linear transport properties have been observed in transition metal trichalcogenides as $NbSe_3$, TaS_3, halogened transition metal tetrachalcogenides as $(TaSe_4)_2I$, $(NbSe_4)_{10}I_3$, in molybdenum oxide $K_{0.3}MoO_3$, etc. A similar behaviour has also been found in SDW organic Bechgaard salts $(TMTST)_2X$.

The properties of the new current–carrying state can be summarized as follows.

The dc electrical conductivity increases above a threshold field E_T.

The conductivity is strongly frequency-dependent in the range of 100 MHz–a few GHz.

Above the threshold field, noise is generated in the crystal which can be analysed as the combination of a periodic time dependent voltage and a broad noise following a $1/f$ variation.

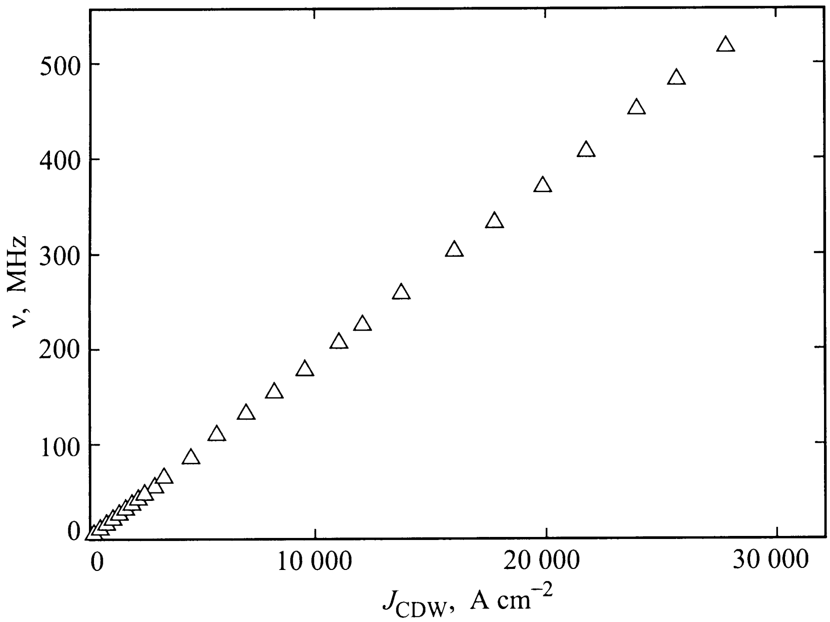

Figure 1. Variation of the current J_{CDW} carried by the CDW as a function of the fundamental frequency measured in the Fourier–transformed voltage for an orthorhombic TaS_3 sample at $T = 127$ K. The slope $J_{CDW}/\nu = ne\lambda_{CDW}$ leads to the number of electrons condensed below the CDW gap.

Interference effects occur between the ac voltage generated in the crystal in the non–linear state and an external rf field (Shapiro steps).

Hysteresis and memory effects are observed, principally at low temperature.

Inside a domain, where the phase ϕ is only time dependent, a simple equation of motion has been derived [4]:

$$\phi'' + \Gamma\phi'' + \omega_p^2 \sin\phi = Q_0 \frac{eE}{M^*}, \tag{2}$$

where E is the applied field, $Q_0 = 2\pi/\lambda_{CDW}$, ω_p the pinning frequency and M^* the Frölich mass.

For a dc field E higher than E_T, the "$\sin\phi$" force term gives rise to a velocity modulation at a fundamental frequency, ν, and its harmonics which can be considered as the origin of the ac voltage generated in these systems. It has to be noted that the λ_{CDW} assumed periodicity for the force means that the fundamental frequency is linked to the mean CDW velocity by $v_{CDW} = \lambda_{CDW}\nu$. Therefore, according to Eq. 1, the extra-current carried by the CDW is given by

$$J_{CDW} = n_0 e v_{CDW} = n_0 e \lambda_{CDW} \nu. \tag{3}$$

According to Eq. 3, the slope of J_{CDW}/ν is a measurement of the number of electrons condensed below the CDW gap. The extra-current J_{CDW} is measured from the non-linear $V(I)$ characteristics. Fig. 1 shows the linear relationship between J_{CDW} and ν for an orthorhombic TaS_3 sample. The number of electrons deduced from the ν/J_{CDW} slope is of the order of the electron concentration in the bands affected by the CDW condensation, as it can be calculated from band structures or from chemical bonds. This result can be considered as the proof of the Frölich conductivity [4]. When the field overcomes the threshold one, the electrons, which were trapped below the CDW gap, coherently participate in the electrical conductivity.

The general properties of the sliding CDW state are now relatively well established. New lines of research are at the present time developed. Some of them are described in the following.

2. Current Conversion in the Sliding CDW State of $NbSe_3$

Phase slippage is a general phenomenon in condensed matter systems with complex order parameters. When external forces impose different order parameter phase velocities ϕ_1 and ϕ_2 in two regions 1 and 2 of the same system, the phase conflict at the boundary between the two regions is released by the formation of vortices at a rate given by $\dot\phi = \dot\phi_1 + \dot\phi_2$. Phase slippage has been intensively studied in narrow superconducting channels, in superfluids and more recently, in quasi-one-dimensional conductors with a CDW ground state.

Phase slippage is required at the current electrodes for the conversion from free to condensed carriers [6]. CDW wave fronts must be created near one electrode and destroyed near the other. This process is mediated by CDW-phase dislocation loops which climb to the sample surface, each dislocation loop allowing the CDW to progress by one wavelength.

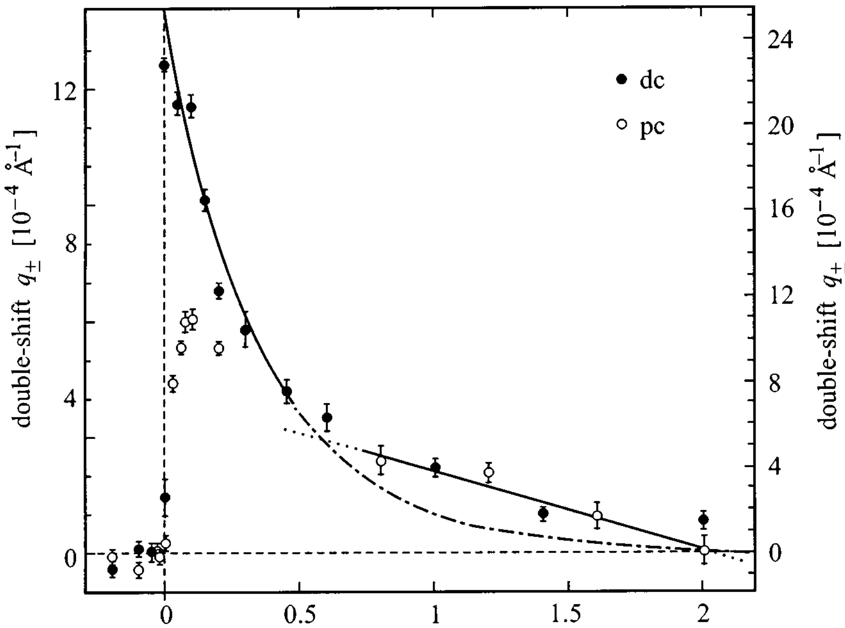

Figure 2. (Double-)Shift $q_{\pm} = Q(+I) - Q(-I)$ of the satellite position Q as a function of the position x between the injection electrode $x = 0$ and the midpoint between electrodes ($x = 2$ mm) in $NbSe_3$ at $T = 90$ K ($I/I_T = 2.13$). The vertical and horizontal dashed lines indicate the contact boundary and the line of zero shift, respectively (from [7]).

We have performed [7] at the ESRF high resolution X-ray scattering measurements of the variation $q(x)$ of the CDW wave vector $Q(x) = Q_0 + q(x)$ along a thin $NbSe_3$ whisker of cross-section 10μm $\times$ 2μm and length 4.1 mm (between electrodes).

For a fixed *direct current* of $I/I_T = 2.1$ (I_T: threshold current), the shift $q_{\pm} = Q(+I) - Q(-I)$ between satellite positions Q measured with positive and negative current polarities vanishes below the electrodes and rises abruptly to a maximum value at the electrode boundary (fig. 2). With increasing distance x from the contact, $q_{\pm}(x)$ decays exponentially. For $x > 0.5$ mm, a cross-over to a linear decrease of the satellite shift is observed with $q_{\pm}(x)$ crossing the line of zero shift at the midpoint between the electrodes ($x = 2$ mm; beyond ($x > 2$ mm) the sign of $q_{\pm}(x)$ is inverted).

The corresponding data for the applied *pulsed current* (100 Hz, 100 μs pulses) of the same amplitude I reveal a different spatial profile: vanishing below the electrode, $q_{\pm}$ rises smoothly with increasing x to reach its maximum at a distance of about 100 μm from the contact boundary, the maximum shift taking half the maximum value observed for the direct current. After a smooth decrease with increasing distance x, $q_{\pm}\{\mathrm{pc}\}$ joins the linear dependence of $q_{\pm}\{\mathrm{dc}\}$ with the same slope ($x > 0.5$ mm). This important difference between the satellite shift profiles $q_{\pm}(x)$ for applied direct and pulsed current indicates a strongly spatially dependent relaxational behaviour of the CDW deformations.

A semi-microscopic model [8] relates the CDW deformation q to the mismatch η between the longitudinal CDW stress U and the electrochemical potential μ_n of the charge carriers remaining metallic or being excited above the Peierls-gap at the given temperature:

$$q \propto \eta \equiv \mu_n - U. \tag{4}$$

From this model one can interpret the exponential regime as phase-slip dominated and the linear regime as a consequence of transverse pinning of the CDW dislocation loops blocking the normal-to-condensed carreir conversion.

3. Magneto-Oscillations of the CDW Conduction in Presence of Columnar Defects

Akin to superconductivity, the aim of the experiment was the search of a flux quantification effect produced by the collective response of the CDW condensate. Quantum interference phenomenon is realized around "holes" of a diameter $D = 100$ Å produced by heavy ion irradiation on thin $NbSe_3$ samples. One expects the CDW into motion to pass over a hole without conversion if the diameter of the hole is smaller than the transverse amplitude coherence length $\xi_{\perp}$. In a magnetic field, each defect hole serves as a "solenoid" which contributes to the flux dependent scattering of the depinned CDW. It was shown in [9] that the presence of columnar defects induces oscillations in the non-linear CDW conductivity as a function of H, when H is oriented parallel to the axes of the defects.

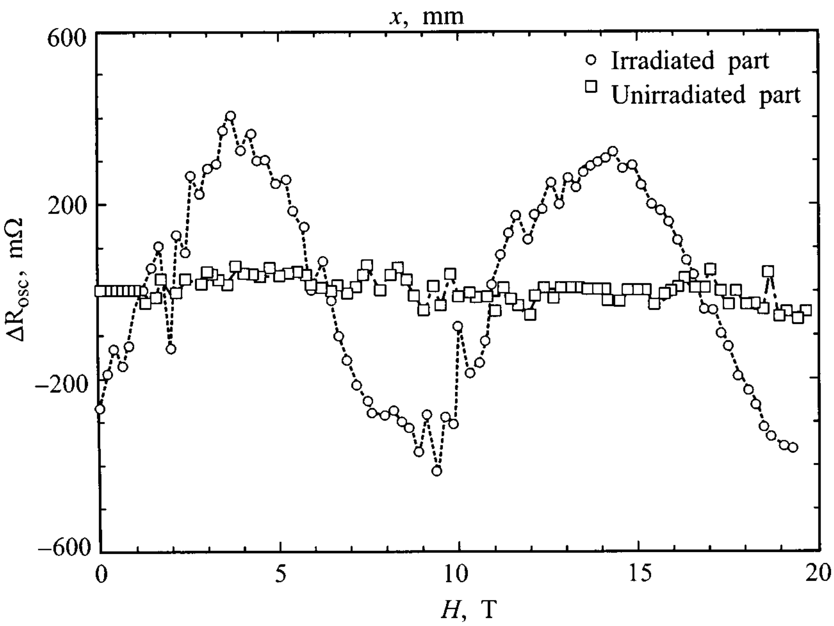

Figure 3. Variation of the oscillatory part of the magnetoresistance irradiated $NbSe_3$, ΔR_{OSC}, as a function of the magnetic field at $T = 52\,K$ for an applied current 2.5 the threshold value (from [9]).

Irradiation was carried out with Xe, Pb or U ions with energy ranging from 0.25 to 6 GeV. Structural analysis performed by transmission electron microscopy on thin (thickness: $0.1\,\mu$m) $NbSe_3$ samples irradiated simultaneously with the samples used for electrical measurements reveal latent traces with amorphous cores (columnar defects) in the crystalline matrix with diameter $15 \pm 2\,$nm.

Fig. 3 shows the variation of the oscillatory part of the magnetoresistance as a function of H [9]. If the columnar defect size is taken for the scattering of the sliding CDW, the expected period of the magnetoresistance oscillation can be evaluated as $\Delta H = \alpha\phi_0(\pi D^2/4)$, with $D = 15\,$nm and $\alpha = 1/2$, $\Delta H = 11.3\,$T consistent with the experimental value of 9.8 T (as shown in Fig. 3). The $\phi_0/2$ periodicity is in agreement with the instanton model [10]. An alternative model has been developed [11], in which the Aharonov–Bohm flux is shown to modulate the CDW threshold; then the periodicity $\phi_0/2$ results from ensemble averaging over random scattering phases, similarly to the case of a collection of mesoscopic metallic rings.

The magnetoresistance of the irradiated part of a $NbSe_3$ sample has been measured with H parallel and perpendicular to the axes of columnar defects. Clearly, oscillations in the magnetoresistance are only observed when H is parallel to the defects and disappear for the perpendicular orientation.

An important feature for the observation of the oscillatory behaviour of $R(H)$ is the phase coherence of the sliding CDW between potential probes: this phase coherence is lost for samples thicker than the phase correlation length perpendicular to the chains (typically less than $1\,\mu$m) and also for dc current above $2 \sim 3I_T$ (as seen from the lost of complete mode locking above these currents on irradiated samples).

4. Slow Dynamics of Energy Relaxation at Very Low Temperature in CDW/SDW Compounds

DW systems in their grond state exhibit typical "glassy behaviour" for numerous electrical properties, the deep origin of the disorder being the pining of the DW phase by randomly distributed impurities, lattice defects, or approach of the commensurability. This random ground state is characterized by many metastable states with very broad relaxation times spectrum.

These metastable states are the best revealed from low temperature thermodynamical measurements. Along a systematic study of numerous CDW compounds ($(TaSe_4)_2I$, TaS_3, $NbSe_3$, [12]) and SDW (in organic $(TMTSF)_2PF_6$ [13], $(TMTTF_2)Br$, [14]) by means of specific heat (fig. 4) and energy relaxation techniques in the T-range between $\sim 70\,$mK an $\sim 10\,$K, we have established several characteristic "glassy" properties:

i) Additional excitations to regular phonons contribute to the specific heat for $T \leqslant 1\,$K according to a T^{ν} law, with $\nu < 1$ [12].

ii) In the same T-range, the specific heat becomes strongly time-dependent: the heat relaxation after a short heat perturbation of order of 1 s, becomes nonexponential. We have also shown that the relaxation kinetics depends strongly on the duration of the heat perturbation ("aging effect" similar to the case of spin-glasses). The time necessary to achieve thermodynamic equilibrium at $T < 1\,$K exceeds hours. The heat relaxation is thermally activated with an activation energy depending on the duration of the perturbation. It is of the order of $\sim 1{-}2\,$K if the system has reached its thermodynamic equilibrium [15, 16]. Properties

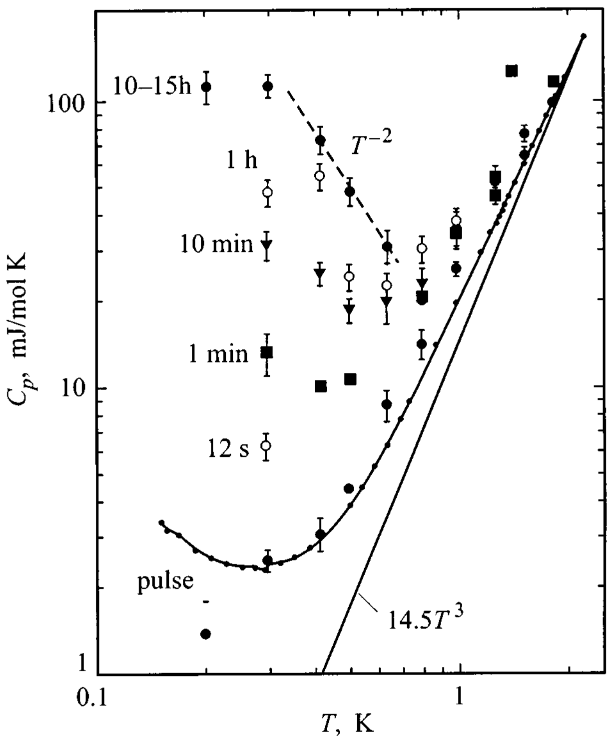

Figure 4. Dependence of the specific heat of $(TMTSF)_2PF_6$ on the duration of energy delivery: from a pulse of less than 1 s up to 10–15 h. The continuous curve represents data calculated from the initial T increment in response to heat pulses. Other data are obtained by total integration of the energy release. The straight line (T^3) is the estimated lattice contribution. The contribution of metastable states below 0.5 K evolves from a T^{-2} tail for short time relaxation to a well-defined Schottky anomaly at the thermal equilibrium (splitting energy $\epsilon_s = 0.9$ K and ratio of degeneracy $g_1/g_0 \simeq 12$ (from [14])).

i) and ii) are common to structural glasses or orientationally disordered crystals. However, energy relaxation effects are here of much larger intensity than in usual glasses. A theoretical model [17] which ascribes the origin of the long-lived metastable states to strong pinning centers located close to commensurability regions could interpret the experimental features.

iii) Finally, in the case of the SDW system $(TMTSF)_2PF_6$, an anomaly in the specific heat at $T \approx 3$ K has been identified as a glassy transition, since it exhibits all properties such as hysteretic behaviour, sensitivity to the previous thermal history, characteristic of the usual freezing of supercooled liquids [18]. This interpretation is supported by low-frequency dielectric measurements [19].

5. Conclusions

Our recent experiments in CDW/SDW systems have allowed the study of CDW phase dislocation loops for the current conversion at electrodes, of the role of long-lived metastable states in the thermodynamic properties at very low temperature, of quantum interference phenomena in presence of columnar defects. Thanks to a recent development in lithography techniques on single crystals [19], multiply connected submicron structures were patterned on CDW samples, opening the possibility of studies at the mesoscopic scale.

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