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Charge density wave transport in inorganic linear chain compounds

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Article de mise au point

Résumé. — Un nouveau type de transport collectif par glissement d'une onde de densité de charge sur le réseau cristallin a été mis en évidence ces dernières années dans des conducteurs inorganiques quasi unidimensionnels tels que les trichalcogénures NbSe_3 , TaS_3 , les tétrachalcogénures $(\text{TaSe}_4)_2\text{I}$, $(\text{NbSe}_4)_{10/3}\text{I}$ et les bronzes bleus de molybdène $\text{A}_{0.3}\text{MoO}_3$ ($\text{A} = \text{K}, \text{Rb}, \text{Tl}$). Nous décrivons les propriétés structurales et électroniques de ces matériaux et leurs étonnantes propriétés de transport non linéaire attachées au mouvement de l'onde : champ électrique seuil, bruit, réponse à une excitation alternative, hystérésis, effets mémoires. Nous rappelons quelques modèles théoriques décrivant la dynamique de l'onde de densité de charge.

Abstract. — In quasi-one dimensional inorganic conductors such as the transition metal trichalcogenides NbSe_3 , TaS_3 , the tetrachalcogenides $(\text{TaSe}_4)_2\text{I}$, $(\text{NbSe}_4)_{10/3}\text{I}$ and the molybdenum blue bronzes $\text{A}_{0.3}\text{MoO}_3$ ($\text{A} = \text{K}, \text{Rb}, \text{Tl}$) a new collective transport by the macroscopic sliding of a so-called charge density wave through the lattice has been reported. We review the structural and electronic properties of these different classes of materials and describe their intriguing non linear transport properties associated with the charge density wave motion : threshold electric field, noise phenomena, response to ac fields, hysteresis and memory effects. We survey some relevant theoretical models for the dynamics of the charge density wave.

Introduction.

As a consequence of their anisotropic crystal structure, some materials behave as if they had less than three dimensions. Among the quasi-two dimensional conductors examples are the dichalcogenides TaS_2 , TaSe_2 [1], the purple molybdenum bronzes $\text{A}_{0.9}\text{Mo}_6\text{O}_{17}$ [2] ($\text{A} = \text{Li}, \text{Na}, \text{K}$), $\text{TiMo}_6\text{O}_{17}$ [3] and the molybdenum oxides Mo_4O_{11} [2]. Among the quasi-one-dimensional compounds, one finds the organic conductors [4] such as TTF-TCNQ or $(\text{TMTSF})_2\text{X}$ ($\text{X} = \text{PF}_6, \text{ClO}_4$) and inorganic conductors such as the transition metal trichalcogenides NbSe_3 , TaS_3 , the tetrachalcogenides $(\text{TaSe}_4)_2\text{I}$, $(\text{NbSe}_4)_{10/3}\text{I}$ [5] and a completely different family, the molybdenum blue bronzes $\text{A}_{0.3}\text{MoO}_3$ ($\text{A} = \text{K}, \text{Rb}, \text{Tl}$) [6, 7]. These different classes of materials offer exciting opportunities to condensed matter physicists and chemists to study the concept of « charge density wave ».

These compounds are unstable towards lattice distortions of wave vector $2 K_F$ where K_F is the wave

vector at the Fermi energy ; they undergo a phase transition called Peierls transition [8] associated with the onset of a « charge density wave ». The ground state is characterized by a periodic lattice distortion $u(x)$ coupled to a spatial periodic modulation $\rho(x)$ of the concentration of conduction electrons called charge density wave (CDW).

In a one dimensional case the resulting configuration can be written : $\rho(x) = A \cos(2 K_F x + \phi)$ where A is the amplitude and ϕ the phase of the CDW. The associated atomic lattice displacement is : $u(x) = U_0 \sin(2 K_F x + \phi)$ where U_0 is much smaller than a lattice distance ($U_0 < 0.1 \text{ \AA}$). Since the wavelength $\lambda = 2 \pi / 2 K_F$ is determined by the Fermi surface, it will usually be incommensurate with the underlying lattice, that is λ will not equal a rational multiple of a lattice translation. When the concentration of electron per atom in the filled band is a rational number, the CDW is commensurate. The CDW is a one-dimensional modulation of both the electron density and of the structure along the direction of highest conductivity.

Fröhlich [9] has shown that, when $2K_F$ is incommensurate with the lattice, the phase ϕ of the CDW with respect to the lattice is arbitrary and a current could be carried, not by the motion of individual electrons, but by the sliding of the CDW at no cost in energy. This *collective* transport of electrical current by a moving CDW would lead to superconductivity. However, in real crystals impurities or defects destroy the translational invariance of the CDW and pin it to the lattice. It is by now well established that pinning forces play a crucial role in electrical properties. The CDW has to overcome potential barriers before the motion begins. The CDW can be depinned by a very weak electric field larger than a critical value E_t , the so-called threshold field. Above E_t , a rich variety of non linear transport phenomena are found : they include broad band noise, periodic voltage oscillations, metastability phenomena. This new transport mechanism leads also to anomalous frequency dependent conductivity and anomalous response to combined ac and dc fields.

Since the discovery in 1976 by Monceau *et al.* [10] of CDW transport in the linear chain compound NbSe_3 an enormous interest in this field has emerged. Motivated by the possibility that other systems with a high conductivity axis may also provide a realization of the Fröhlich conductivity, it has been shown later, that this new effect appeared also in TaS_3 [11], $(\text{TaSe}_4)_2\text{I}$ [12], $(\text{NbSe}_4)_{103}\text{I}$ [13] and in the blue bronzes $\text{A}_{0.30}\text{MoO}_3$ ($\text{A} = \text{K}, \text{Rb}, \text{TI}$) [6, 7]. CDW is now an exciting problem in many body physics both theoretically and experimentally. Several international conferences have been devoted to this field and the dramatic increase of the number of papers on CDW's shows the vitality of this subject [14].

In this review, we give in section 1 a description of the Peierls instability ; in section 2 we describe the crystal structures and the Peierls transitions of the materials where non linear CDW transport occurs ; in section 3 we report some unusual phenomena which give evidence for CDW conductivity ; in section 4 we survey some theoretical models which have been advanced to account for this new type of conductivity.

1. Peierls instability.

Peierls has shown more than thirty years ago [8] that a one dimensional conducting chain of uniformly spaced atoms is unstable at 0 K against a periodic distortion with wavevector $\pm 2K_F$. The gain in electronic energy is always larger than the elastic energy required to distort the lattice. The lowering of energy results from the decrease in energy of the occupied states just below the Peierls gap ; the states which are raised in energy just above the gap are unoccupied. Figure 1 shows the band structure

Fig. 1. — Density of states $\varepsilon(K)$ of a one-dimensional system : a) undistorted state $T > T_P$; b) distorted state $T < T_P$; c) Temperature dependence of the Peierls gap 2Δ .

$\varepsilon(K)$ of a quasi-one dimensional conductor above and below the Peierls transition temperature T_P .

The gap which opens at the Fermi energy is proportional to the amplitude of the distortion. The temperature dependence of the gap 2Δ is illustrated in figure 1c. Within mean field theory, the excitation of electrons across the gap reduces the size of 2Δ to zero at T_P [15].

In a one dimensional conductor the Peierls transition is a metal-to-semiconductor transition ; in a quasi two-dimensional conductor the transition is associated with partial opening of gaps at the Fermi surface and is a metal-to-metal transition. The Peierls transition has been investigated in several organic and inorganic low dimensional conductors : polyacetylene, organic charge transfert salts, transition metal di, tri and tetrachalcogenides, blue and purple bronzes and molybdenum oxides Mo_4O_{11} . In the organic salt TTF-TCNQ non linear conductivity has been reported recently [16].

An instability occurs if the response $\Delta\rho(q)$ of the electron gas to a small perturbing potential $V(q)$ becomes macroscopic. If $\Delta\rho(q) = X(q)V(q)$ where $X(q)$ is the response function, a static distortion occurs if $X(q) \rightarrow \infty$. $X(q)$ is given by :

$$X(q) \propto \sum_K \frac{f_K(1 - f_{K+q})}{\varepsilon_{K+q} - \varepsilon_K}$$

where ε_K is the energy of states with wavevector K and f_K the Fermi occupation factor. $X(q)$ is large for a given q which connects many filled states to empty states of the same energy. This property is called nesting of the Fermi surface. A Fermi surface with plane sections will produce a $X(q)$ which diverges

when q spans the Fermi surface. In a quasi-one dimensional case, the Fermi surface consists of two parallel planes separated by a distance $2 K_F$ and allows a strong divergence of $X(q)$.

2. Crystal structures and Peierls transitions.

Direct evidence for the onset of a CDW state comes from electron diffraction microscopy or from X-ray scattering. Each main Bragg peak has a series of satellite peaks around it ; the satellite peaks have a very weak intensity, $\approx 10^{-3}$ or less of the intensity of the strongest Bragg peak. Up to now it is only in the two dimensional compound TaS₂ that the CDW state has been observed recently in the real space by scanning tunnelling microscopy [17]. In the tri- and tetrachalcogenides the expected satellite spots in the CDW state have been observed by electron microscopy [18-22]. However, in the case of the blue bronzes, the satellite peaks have been observed only by X-ray scattering experiments [23], since these bronzes are extremely sensitive to electron irradiation which creates permanent damage [24].

2.1 TRICHALCOGENIDES. — The trichalcogenide NbSe₃ was first synthetized by chemical vapor transport at $T \approx 700^\circ\text{C}$ by Meerschaut and Rouxel in 1975 [25]. NbSe₃ appears as needle shaped single crystals, several mm long, somewhat flexible along the needle axis, and with a typical cross section of $50\text{ }\mu^2$.

The structure consists of chains along the b-axis of trigonal prisms qf Se with transition metal approximately at the centre of each chalcogen prism. The chains are linked in the c-direction by interchain Nb-Se bonds (Fig. 2). The conductivity along the chains is large $\sigma \approx 10^4\text{ }\Omega^{-1}\text{cm}^{-1}$. NbSe₃ is not highly anisotropic, the ratio between $\sigma_{\parallel b}$ and $\sigma_{\perp b}$ is

≈ 10 and the CDW onset suppresses only part of the Fermi Surface. Two CDW transitions occur, one at $T_1 = 145\text{ K}$, the other one at $T_2 = 59\text{ K}$ leaving the system metallic. These two independent transitions are marked in the resistivity as a function of temperature by two anomalies [26] as shown in figure 3. These anomalies can be suppressed by high electric fields or high frequencies [27]. The components of

Fig. 2. — Crystal structure of NbSe₃ (from Ref. [10]).

Fig. 3. — Resistivity as a function of temperature of NbSe₃; current along the fiber axis (from Ref. [26]).

Table I. — Parameters of the Peierls transitions, crystal symmetry and components of wavevector of the Peierls distortion.

	T_p (K)	Anisotropy factor $\frac{\sigma_{\parallel}}{\sigma_{\perp}}$	Resistivity at 300 K	Threshold E_t (V/cm)	Symmetry	q_a (a^* unit)	q_b (b^* unit)	q_c (c^* unit)	References
NbSe ₃	144 59	~ 10	6×10^{-4}	0.1 0.01	Monoclinic	0 0.5	0.2412 0.2604	0 0.5	[18]
O-TaS ₃	215	~ 100	5×10^{-4}	2	Orthorombic	1/2	1/8	1/4 at $T < 130\text{ K}$	[19]
m-TaS ₃	240		5×10^{-4}		Monoclinic	0	0.254	0	[20]
(TaSe ₄) ₂ I	263		1.5×10^{-3}	2	Tetragonal	1	0	0.943	[21]
(NbSe ₄) _{10/3} I	285		10^{-2}	1	Tetragonal	0	0	0.487	[22]
A _{0.3} MoO ₃ (A = K, Rb)	180	~ 100	10^{-3}	0.05	Monoclinic	0	0.250 $T < 100\text{ K}$	0.5	[23]

the wavevector of the distortion are temperature independent and are listed in table I which gives also data for other CDW materials.

While NbSe_3 is not very anisotropic and remains metallic below T_2 , TaS_3 has been found to be more anisotropic, $\sigma_{\parallel}/\sigma_{\perp} \approx 100$. The phase transition is a metal-to-semiconductor transition and the Fermi Surface is completely destroyed. In TaS_3 , weaker interchain bonding allows the occurrence of two polytypes, orthorhombic and monoclinic. Orthorhombic TaS_3 has a Peierls transition at 215 K [11]. The resistivity of 0- TaS_3 as a function of temperature is shown in figure 4. The wavevector of the distortion is temperature dependent and locks to $0.25 c^*$ at ≈ 130 K [28]. Monoclinic TaS_3 is isotype with NbSe_3 and shows two transitions at $T_1 = 240$ K and $T_2 = 160$ K respectively [25].

Fig. 4. — Resistivity and its logarithmic derivative as a function of reciprocal temperature of orthorhombic TaS_3 . T_p is the Peierls transition temperature and T_0 is the commensurate-incommensurate transition temperature (from Ref. [5]).

2.2 TETRACHALCOGENIDES. — The large class of tetrachalcogenides have the general formula $(\text{MX}_4)_n\text{Y}$ where $\text{M} = \text{Nb}, \text{Ta}$, $\text{X} = \text{S}, \text{Se}$, $\text{Y} = \text{Cl}, \text{Br}, \text{I}$ and $n = 2, 3, 4, 10/3$. They were synthesized for the first time by Meerschaut *et al.* [21] by chemical vapour transport by heating the elements in sealed quartz tubes at 500–600 °C. $(\text{MX}_4)_n\text{Y}$ crystals are platelets a few mm long and with a cross section of a few tenths of mm^2 .

The structure of $(\text{TaSe}_4)_2\text{I}$ consists of chains of MSe_4 along the c axis, the iodine atoms are located in the channels between the chains. The interchain distance M-M is much larger than the intrachain distance. In each TaSe_4 chain, the Ta atom is located

Fig. 5. — Crystal structure of $(\text{TaSe}_4)_2\text{I}$ (from Ref. [21]).

at the centre of a rectangular antiprism of 8 Se atoms (Fig. 5).

$(\text{TaSe}_4)_2\text{I}$ shows a Peierls transition at 263 K from a metallic to a semiconducting state. The electrical anisotropy is enhanced by the presence of I atoms; $(\text{TaSe}_4)_2\text{I}$ is more anisotropic than the trichalcogenides. $(\text{NbSe}_4)_{10/3}\text{I}$ has a slightly different crystal structure and shows a Peierls transition at 285 K.

2.3 MOLYBDENUM BLUE BRONZES. — The molybdenum bronzes have the general formula $\text{A}_x\text{M}_y\text{O}_z$ where A is an alkali metal. The alkali atom donates its outer electron to the conduction band of the transition metal. They belong to the large class of transition metal oxides which often exhibit metal-semiconductor transitions or CDW instabilities.

While the quasi-one dimensional blue bronze $\text{A}_{0.30}\text{MoO}_3$ ($\text{A} = \text{K}, \text{Rb}, \text{Tl}$) shows a metal insulator transition at 180 K [2] the quasi-two dimensional purple bronze $\text{K}_{0.9}\text{Mo}_6\text{O}_{17}$ shows a metal-to-metal transition at 120 K (2) due to a CDW instability and $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ becomes superconductor below 1.9 K [30].

Single crystals of blue bronze $\text{K}_{0.30}\text{MoO}_3$ were synthesized more than twenty years ago by Wold *et al.* [31] by electrocrystallization of a molten mixture $\text{K}_2\text{MoO}_4\text{-MoO}_3$ at 550 °C. They appear as platelets of typical size 5 mm $\times$ 2 mm $\times$ 1 mm. Samples as large as 6 cm^3 have been grown recently by this method [14e]. The metal-insulator transition at 180 K was discovered in 1965 by Bouchard *et al.* [32]. It was only in 1983 that the transition was shown to be a Peierls transition by Pouget *et al.* [23] and that CDW transport was reported by Dumas *et al.* [33].

The crystal structure is monoclinic [34]. It can be viewed as a quasi-two dimensional one but the electronic properties are quasi one-dimensional. The structure is built upon sheets of MoO_6 octahedra

Fig. 6. — Crystal structure of the blue bronze $K_{0.30}MoO_3$ showing infinite slabs of MoO_6 separated by the alkali ions ($\bullet$) and the infinite chains of MoO_6 parallel to the b axis (from Ref. [34]).

sharing edges. The MoO_6 octahedra are separated by the alkali ions. The structure bears some analogy with that of $(TaSe_4)_2I$. The structure can also be viewed as made of infinite chains of MoO_6 along the monoclinic b -axis sharing corners (Fig. 6). There are three independent Mo sites and two of them are involved in the infinite chains. All the alkali sites are occupied. The CDW is incommensurate along the high conductivity monoclinic b -axis; the wavevector q_b is temperature dependent down to ≈ 100 K; below 100 K, q_b is temperature independent and extremely close to the commensurate value 0.25 [23].

Figure 7 shows the resistivity as a function of temperature for $Rb_{0.30}MoO_3$ which is isotype of $K_{0.30}MoO_3$. The resistivity is one order of magnitude

Fig. 7. — Resistivity as a function of reciprocal temperature of $Rb_{0.30}MoO_3$ for different crystallographic orientations (from Ref. [6]).

larger in the plane of the layers than along the high conductivity b -axis. Across the layers, ρ is more than three orders of magnitude larger. The blue bronzes are therefore extremely anisotropic materials. The low dimensional electronic properties can be understood easily with the crystal structure.

3. Charge density wave transport.

3.1 NON LINEAR CONDUCTIVITY. — The competition between pinning forces and the external applied field is responsible for non linear phenomena. The collective motion of the CDW provides an additional contribution to the conductivity resulting in a non linear current.

Voltage characteristic can be observed by measuring voltage-current characteristics $V(I)$ or $\sigma(E)$ or the derivative dV/dI vs. I by lock-in detection. The threshold field E_t for the onset of non linearity is defined when dV/dI starts to decrease. Two or four probes configuration for the leads are used. Considerable care in the preparation of the electrical contacts has to be taken to obtain a current density in the sample as homogeneous as possible.

Non linear conductivity above a well defined electric threshold field E_t was first reported by Fleming and Grimes [35] in $NbSe_3$. Below E_t , the conductivity is Ohmic. E_t is as low as 5 mV/cm. Examples of $V(I)$ and dV/dI vs. I curves are given in figure 8 for TaS_3 [28]. The onset of non linearity can be smooth or marked by an abrupt switching from the linear to the non linear state depending on the samples or the temperature. In the case of $K_{0.30}MoO_3$ [6], precursor voltage spikes of very low frequency (≈ 1 Hz) occur just below threshold in samples exhibiting a switching at E_t as shown in

Fig. 8. — a) Voltage vs. current characteristic; b) differential resistance; c) broad band noise voltage versus applied current I in ortho- TaS_3 at $T = 142.4$ K (from Ref. [28]). $E_t = RI_t/l$, l is the distance between voltage contacts.

Fig. 9. — Voltage vs. current characteristic of $K_{0.30}MoO_3$ showing precursor pulses (from Ref. [6]).

figure 9. $V(I)$ curves usually show an hysteretic behaviour. The temperature dependence of the threshold is controversial at the moment in the case of the blue bronze, especially above 100 K temperature above which the wavevector is temperature dependent. Doping with impurities leads to an increase of E_t . According to the theory of Lee and Rice discussed in section 4 pinning centres can be classified as strong and weak. In the weak pinning case, the phase of the CDW is adjusted over a distance larger than the mean impurity separation while in the strong pinning case the phase is adjusted at each impurity site.

The non-linear conductivity is due to the motion of the CDW since no structural change in the CDW appears with the applied field [36]. Moreover, this effect is collective since the energy provided by the electric field over a distance l has to be larger than kT ; writing $eE_t l > kT$ one finds $l \approx 10^4$ lattice constants.

3.2 BROAD BAND NOISE AND PERIODIC VOLTAGE OSCILLATIONS. — Just above threshold a broad band noise voltage, orders of magnitude larger than that observed in ordinary semiconductors is observed as illustrated in figure 9. An astonishing and one of the most discussed phenomenon associated with CDW transport is the observation of coherent voltage oscillations, also called « narrow band noise » superimposed on the broad band noise. These oscillations generated above E_t were first discovered by Fleming and Grimes [35] in $NbSe_3$ by Fourier analysis of the noise voltage at a given fixed current. The noise spectrum consists of sharp peaks in the Fourier spectrum with one fundamental frequency and its harmonics as shown in figure 10. Voltage oscillations can also be observed directly by measuring the response to a current pulse. The oscillations are superimposed on the dc voltage response. The frequency increases linearly with the excess CDW current I_{CDW} defined as $I_{CDW} = I_{mes} - I_{ohmic}$ where I_{mes} is the measured current and $I_{ohmic} = V/R$ is the current extrapolated from the Ohmic portion of the $V-I$ curve.

If the voltage oscillation is associated with the

Fig. 10. — Fourier spectrum of the noise voltage in $NbSe_3$; $E_t = 80.4$ mV/cm (from Ref. [37]).

time required for the CDW to travel of one wavelength λ then $f = V_{CDW}/\lambda$ where V_{CDW} is an average velocity and since $j_{CDW} = nev_{CDW}$ one finds [37] $f/j_{CDW} = 1/ne\lambda$. Taking values of λ deduced from X-ray data, the value of n which is found is in good agreement with that obtained from other transport measurements.

Convincing evidence for the motion of the CDW above E_t has been found in $NbSe_3$ [38] and in the blue bronzes [39] by NMR experiments on the Nb and Rb nuclei respectively with an applied current in the sample larger than the threshold current. The observed motional narrowing of the NMR lineshape is due to the modulation of the electric field gradient on the Nb or Rb sites when the CDW slides, figure 11.

The exact origin of the periodic voltage oscillations is still controversial : is it generated in the bulk of the sample or near the end contacts where the carriers condensed in the CDW are converted into normal carriers ? Verma *et al.* [40] have found that the

Fig. 11. — Motional narrowing of the ^{87}Rb NMR line shape as a function of the current in $Rb_{0.3}MoO_3$. $I_T \approx 8$ mA. (Segransan *et al.* Ref. [39]).

frequency observed in the Fourier spectrum was split into two frequencies by application of a thermal gradient ΔT along a sample of NbSe_3 . For $\Delta T \neq 0$ each frequency has been attributed to one end contact. These authors have therefore concluded that the noise was generated at the end contacts. However, additional splittings of the frequency have been found by Brown *et al.* [41] when one increases ΔT . In the case of the blue bronze, the application of a thermal gradient did not lead to a splitting of the frequency [42]. Other experiments using non perturbing contact potentials show that most of the narrow band noise is generated in the bulk [43].

3.3 FREQUENCY DEPENDENT CONDUCTIVITY. — The ac dynamics also shows that the CDW motion is collective. If one assumes single particle excitations at ≈ 10 MHz, frequency range where σ is strongly frequency dependent, the energy is $\approx 10^{-7}$ eV. Near the Peierls transition temperature the energy per degree of freedom is $kT \approx 10^{-2}$ eV several orders of magnitude larger than the energy given above. Therefore, the number of thermal degrees of freedom in CDW materials is much smaller than the number of particles. In the CDW state, σ_{ac} is frequency dependent at microwave frequencies and much larger than σ_{dc} . This is in contrast with a classical metal where one expects a frequency dependent conductivity only in the optical region.

The temperature dependence of σ_{ac} as a function of temperature is illustrated in figure 12 for TaS_3 [14a]. $\text{Re } \sigma$ increases with ω and $\text{Im } \sigma$ has a maximum in the region where $\text{Re } \sigma$ depends strongly on ω . From the experimental data a giant dielectric constant $\epsilon = \text{Im } \sigma / \omega$ is found : $\epsilon \approx 10^7$.

In the non linear regime where the CDW is depinned a change in σ_{dc} is found as a result of an applied ac field of arbitrary frequency and amplitude.

Monceau *et al.* [37] have observed peaks in the differential conductivity when an external rf field is

applied. They correspond to steps in V - I curves, and are due to interference effects between the applied ac field and the dc induced voltage oscillations. Typical results are shown in figure 13. They are analogous to those found in Josephson junctions.

Fig. 13. — Differential conductivity dV/dI as a function of a bias current with an applied ac field (from Ref. [37]).

3.4 HYSTERESIS AND MEMORY EFFECTS. — Several experiments [14e] indicate that a CDW is a deformable system and that the non linear transport depends on the past electrical and thermal history of the sample. For example, in $\text{Rb}_{0.30}\text{MoO}_3$, very low frequency voltage oscillations (≈ 1 Hz) are generated well above threshold when the sample is cooled rapidly from 300 K to 77 K with an applied current as it can be seen in figure 14. It appears that the transition between pinned and current carrying state is not instantaneous. The switching and hysteresis at threshold is associated with long times required to establish the non linear state. The random distribution of pinning centres is expected to lead to metastable states [44] associated with domains of the CDW which are less pinned than others. The randomness in these CDW materials suggest some

Fig. 12. — Microwave conductivity σ_{mw} and dc conductivity σ_{dc} of ortho- TaS_3 as a function of reciprocal temperature (from Ref. [14a]).

Fig. 14. — Voltage vs. current characteristic of $\text{Rb}_{0.30}\text{MoO}_3$ after quenching with an applied current $I_c = 5$ mA (from Ref. [6]).

similarities with spin glasses where a broad distribution of relaxation times is involved. As in glassy materials, σ_{ac} can also be described at low frequency (< 500 MHz) by the empirical formula $\sigma(\omega) = A(i\omega/\omega_0)^\alpha$ $\alpha < 1$.

Among the remarkable effects due to the existence of metastable states is the pulse sign memory effect [45] illustrated in figure 15. When voltage pulses have opposite polarities a transient enhancement of the non linear conduction (« overshoot ») is observed.

Fig. 15. — Pulse sign memory effect (from Ref. [45]).

Structural evidence for the metastability of the CDW has been given by Tamegai *et al.* [45] and by Fleming *et al.* [47] in the case of the blue bronze. Fleming *et al.* have found that the width of a superlattice peak was broader after an electric field has been applied during a short time. By cooling with an applied field $E > E_c$, the transverse width of the peak was increased. These results indicate a loss of long range order in the direction transverse to the incommensurate component of the wavevector. Another illustration of the relaxation of the CDW is the generation of a thermally stimulated depolarization current, as found by Cava *et al.* [48] in the blue bronze, obtained after cooling the sample with an applied electric field. By heating, a weak thermally stimulated current is generated, the sample acting in this situation as a current source. On the other hand, Kriza *et al.* [49] have found that the dielectric relaxation in the blue bronze obeys a stretched exponential behaviour $P(t) = P_0 \exp - (t/\tau)^\alpha$ where $P(t)$ is the time dependent polarization. The stretched exponential law is a common feature in disordered materials [50], spin glasses, polymers. In a CDW system, the disorder would be due to random distribution of impurities.

One should note that relaxation effects are found in the Ohmic resistance. The Ohmic resistance depends on the past thermal and electrical history of the sample (see in Ref. [14e]).

3.5 COMPLEMENTARY TECHNIQUES. — A detailed understanding of the CDW transport requires also local methods of investigation. Nuclear magnetic resonance has been proved to be an extremely useful microscopic tool to probe CDW motion *via* the induced motional narrowing effect [38, 39]. While

NMR experiments involve intrinsic probes (Nb in NbSe_3 , Rb in $\text{Rb}_{0.3}\text{MoO}_3$), electron paramagnetic resonance and Mössbauer spectroscopy involve extrinsic probes, Mo^{5+} defects in $\text{K}_{0.3}\text{MoO}_3$ and ^{57}Fe respectively. These experiments have shed recently some light on the nature of the defects involved in the pinning of the CDW [51].

The consequences of the CDW motion on the mechanical properties of the host crystal have been reported in the case of NbSe_3 and TaS_3 . In particular, a small decrease of the Young modulus is found when the CDW is sliding [52]. Ion-channelling technique has also shed some light on the metastability of the CDW in $\text{K}_{0.3}\text{MoO}_3$ [53].

The elementary excitations of the CDW condensate, namely the phase excitation (phason) and amplitude excitation (amplitudon) have been investigated by optical and inelastic neutron scattering [55] experiments. Since the blue bronze can be grown as large single crystals it is well adapted for neutron experiments.

Direct visualization of CDW domains with and without a current in the sample would be extremely helpful in elucidating the CDW transport mechanism. In this context, dark field electron microscopy experiments in NbSe_3 and TaS_3 have been reported [56], but no clear conclusions can be drawn from these experiments.

4. Theoretical models.

While it is well accepted that the observed non linear transport properties are due to the collective motion of a charge density wave the detailed explanation is still controversial ; in particular, the origin of the periodic voltage oscillations (bulk effect or local under the contacts) is not yet fully elucidated. It is not yet clear whether the CDW moves as a whole as proposed by Fröhlich or by generation of « discommensurations » or phase slips. We discuss below some recent theoretical approaches.

4.1 CLASSICAL RIGID MODEL. — In this model [5, 14], the response of the CDW to an external fields is that of an harmonic oscillator. A good fit of the high frequency conductivity is obtained in assuming that the oscillator is overdamped. The CDW is analogous to a particle moving in a sinusoidal potential of period λ which represents the effective potential due to the impurities (λ being the period of the CDW). To this potential a linear ramp with a slope proportional to E is superimposed. The particle accelerates and slows down in this potential. This leads to a time dependent current with frequency proportional to the dc current. This model explains the field and frequency dependence of the conductivity and the narrow band noise but does not describe satisfactorily the detailed form of the V - I curves nor the broad band noise and hysteresis.

4.2 DEFORMABLE MODELS. — To remove the divergence of the differential conductivity found in the classical model, it is necessary to incorporate the internal degrees of freedom of the CDW. The deformable model of Fukuyama, Lee and Rice [57] takes into account the impurity induced deformation of an incommensurate CDW. The phase of the CDW adjusts locally to minimize the sum of the elastic energy of the CDW and the impurity pinning energy. These authors define a domain size inside which the phase is coherent. From experimental data, the size of a domain is macroscopic (a few microns). A great number of experimental results indicate that the internal deformation of the CDW is essential in understanding the glassy behaviour of the CDW.

In recent deformable models metastable states have been studied in details [44] by numerical simulations. More recently, a quasi-commensurate CDW has been considered in close analogy with the mechanical deformation of crystals [58]. The CDW is not rigid ; it is elastically displaced at low fields and CDW defects (« discommensurations » or dislocations of the phase) are pinned by impurities. At threshold, CDW defects are nucleated and begin to move leading to a permanent plastic flow which is ascribed to the CDW current. Similarities with the crystal plasticity and « Portevin-Le Chatelier » effect, where a coupling between lattice dislocations and impurities is involved, have been discussed.

4.3 VORTEX MODEL. — In this picture [40] the periodic voltage oscillations at constant current is due to the creation of phase vortices at the interfaces where the CDW has a discontinuity (near the electrical contacts). At the contacts, the velocity of the CDW drops abruptly to zero and carriers condensed in the CDW become normal carriers. This carrier conversion process occurs by periodic nucleation of phase vortices which move transverse to the motion of the CDW.

4.4 QUANTUM MODEL. — In a very different approach, Bardeen [59] has suggested that quantum effects are essential in the dynamics of a CDW. He has proposed that the CDW can tunnel across

potential barriers before depinning occurs. The small periodic potential leads to a small gap across which the CDW is excited by the electric field. This model is analogous to the Zener tunnelling in semiconductors. Introducing a finite coherence length l , this model gives a threshold E_t and the conductivity obeys the law $\sigma \propto (1 - E_t/E) \exp - (E_0/E)$ which reproduces satisfactorily experimental results in some cases. This model provides a good fit to various ac-dc coupling experiments (see Ref. [14e]).

5. Conclusion.

Since the discovery in NbSe₃ of an entirely new form of conduction in solids due to the motion of a charge density wave considerable progress has been made in the understanding of the associated non linear transport. Detailed studies of this unusual conduction process have revealed a wealth of phenomena of great complexity. The fascinating CDW transport properties are now observed in three different classes of materials. NbSe₃ is the unique system which remains metallic at low temperature. Up to now, no widespread agreement exists on the origin of the coherent voltage oscillations which appear spontaneously above threshold. Among the variety of phenomena observed in these CDW materials, they are considered as one of the clearest signature of CDW motion. The role of interactions between lattice defects and CDW defects (discommensurations or phase dislocations) which seems preponderant in the case of the blue bronze as well as metastability phenomena, have to be explored further. Sophisticated methods of investigation have emerged ; local methods seem promising. On the other hand, it would be interesting to find other classes of materials showing charge density wave transport.

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