## PRESENT RESULTS AND FUTURE PROSPECTS IN CHARGE DENSITY WAVE SYSTEMS

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## ABSTRACT

The general properties of charge density wave motion are briefly reviewed. Then the emphasis is essentially made on new developments such as the use of scanning tunneling microscopy for the observation of the charge density wave structure, the boundary conditions in the depinning, the damping and screening effects related with the properties of the charge density wave at helium temperature and finally the description of the charge density wave ground state as a disordered medium as revealed by specific heat measurements below 1 K.

## 1. INTRODUCTION

It is now very well known that systems of restricted dimensionality undergo instabilities at low temperature. According to the relative strength of several electron-electron coupling, the modulated ground state can be a charge density wave (CDW) or if the spin orientation is concerned, a spin modulated wave (SDW).

The CDW is characterized by a charge modulation with a periodicity  $q = 2k_F$  as  $\rho_{cl} = \rho_0 + 2\rho_q \cos(qr+\phi)$  where  $\rho_0$  is the uniform electron density. The phase,  $\phi$ , specifies the position of the CDW relative to the lattice ions. The local electron charge density is partly neutralized by a concomitant displacement of each ion to a new equilibrium position. The superlattice periodicity leads to the opening of a gap  $\Delta$  in the electronic distribution. The amplitude of this gap is derived from the thermally activated electrical conductivity, or in the case of NbSe<sub>3</sub> by a tunneling experiment [1]. The experimental values are much larger than those derived from the mean field low coupling theory, i.e.  $2\Delta(0) = 3.5 \text{ kT}_c$ , reflecting large fluctuations or/and strong coupling effects.

The opening of a gap below  $T_p$  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,  $\phi$ , 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 energe-

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tically 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 with the sound velocity (in which case the interaction would be strongly modified). CDW condensation may thus arise in any set of galilean frames with uniform velocity, v, giving in the laboratory frame an electronic current density,

$$J = -n_0 ev \tag{1}$$

where  $n_0$  is of the order of the electron number density condensed in the band below the CDW gap. This Fröhlich 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,  $\phi$ , can in fact be pinned to the lattice, for example by impurities or by a long-period commensurability between the CDW wavelength and the lattice or by Coulomb interaction between adjacent chains. Oscillations of the pinned CDW are expected to produce a large low-frequency ac conductivity and a large dielectric constant. 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 Fröhlich 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 mode.

A complete survey including an exhaustive list of references will be found in recent review articles [4] and conference proceedings [5]. In this paper after a short description of the general properties of the sliding CDW the emphasis will be essentially made on the recent developments in the field and the likely trends for the future.

## 2. GENERAL PROPERTIES OF THE SLIDING CDW STATE

A general consensus exists at the present time concerning the qualitative properties of the current-carrying CDW state which can be summarized as follows :

- The existence of a threshold electric field,  $E_T$ , above which the d.c. electrical conductivity increases.
- The strongly frequency dependence of the conductivity in the range of a few MHz a few GHz.
- A noise generation above the threshold which can be analysed as a combination of a periodic time dependent voltage and a broad band noise following a 1/f variation.
- Interference effects between the a.c. voltage generated in the crystal in the non-linear state and the external rf field.
- Hysteresis and memory effects and metastability.

But the qualitative explanation of all these properties is far to be elucitated. In general, the phase of the CDW is dependent on time and coordinates :  $\phi(\mathbf{r}, t)$ . In the classical rigid model [6,7], the

CDW is described with a unique dynamical variable  $\phi(t)$  and the equation of motion is that of an overdamped oscillator. For E slightly higher than E<sub>T</sub>, the extra d.c. current carried by the CDW varies as  $J_{CDW} \sim (E-E_T)^{1/2}$  while experimental results show a nearly 3/2 power law. Some attempts have been made to explain the regime near  $E_T$  [8] establishing some analogy between the vicinity of  $E_T$  and the critical behaviour of a second order phase transition, leading to the 3/2 exponant. The deformability of the CDW from interaction with impurities has also been taken into account. When the local distortions of the CDW are small, i.e. when the velocity of the CDW is large, the impurity potential can be considered as a perturbation. In this approximation the asymptotic behaviour of the conductivity has been calculated [9] and the deviation from the limit  $E \rightarrow \infty$  found to follow the law ;

$$j = \sigma_{F \to \infty} E - C\sqrt{E}$$

Thus in classical models analytic variations of the non-linear conductivity are derived only in the two limits  $E \rightarrow E_T$  and  $E \rightarrow \infty$ . In the other hand, the expression of  $\sigma(E)$  calculated by Bardeen [10] in his quantum approach :

$$\sigma(E,T) = \sigma_{a}(T) + \sigma_{b}(T) \left(1 - \frac{E_{T}}{E}\right) \exp - \frac{E_{0}}{E}$$

is experimentally followed from E<sub>T</sub> to 50-100 E<sub>T</sub> in all the CDW compounds.

The nature of the pinning is still not solved. A very popular model by Fukuyama-Lee-Rice shows that in the case of weak pinning -accumulation of small phase disturbances over a great number of disturbing centers in a domain size in which the average CDW phase does not change more than  $\sim \pi$ - E<sub>T</sub> varies as the square of the impurity concentration e. On the other hand, in the case of strong pinning caused by large amplitude pinning potential, the CDW phase is fixed at the impurity site and E<sub>T</sub> is proportional to c. While the weak pinning approach is commonly used, a strong pinning model has been recently developed by Tucker *et al.* [11] showing that the local CDW pinning at the impurity site will be always strong and the dc CDW motion is only possible by phase slip processes whereas far away from the impurity the average CDW phase is correlated as in the weak pinning regime. This question is still controversial since experimentally the variation of E<sub>T</sub> is between c and c<sup>2</sup> although recently it has been shown that the CDW in Ta doped NbSe<sub>3</sub> is weakly pinned [12].

In all the sliding CDW compounds except  $K_{0,3}MoO_3 E_T$  increases rapidly when T is reduced following an activated law

$$E_{T}(T) = E_{o} \exp\left(-\frac{T}{T_{o}}\right)$$

with  $T_o \sim 10-100$  K. This dependence has been explained by Maki [13] from resulting of important thermal fluctuations with  $T_o$  proportional to  $\xi \simeq v_F/T_c$ .

Finally the collective motion in CDW transport is evidenced by the experimental verification of the simple equation J = nev. If v is assumed to be the product of the CDW periodicity by the frequency v as measured from the narrow band noise, then  $J/v = ne\lambda$ . Experimentally J/v is linear and the slope yields the number of carriers ne condensed below the CDW gap in good agreement with the determination from chemical bonds [7]. A direct observation of the CDW motion as a bulk property has been brought by NMR measurements. In the static situation, the NMR spectrum is inhomogeneously broadened by the spatial variation of the hyperfine field which occurs below the Peierls transition [14]. The effect of the CDW motion is the NMR-lineshape motional narrowing [15] and the appearance of sidebands in the spectra at the same frequency as that detected in noise analysis [16].

## 3. NOVEL COMPOUNDS

The number of materials exhibiting collective transport properties has largely increased in the last years. After NbSe<sub>3</sub> and other transition metal trichalcogenides as ortho TaS<sub>3</sub> and mono TaS<sub>3</sub>, NbS<sub>3</sub>, inorganic compounds in the molybdenum oxyde family as K<sub>0.3</sub>MoO<sub>3</sub> and halogened transition metal tetrachalcogenides as (TaSe<sub>4</sub>)<sub>2</sub>I, (NbSe<sub>4</sub>)<sub>2</sub>I, (NbSe<sub>4</sub>)<sub>10</sub>I<sub>3</sub> have been discovered. Non linearity has also been detected in the organic material TTF-TCNQ in a limited range of temperature between 54 K and 49 K where a unique CDW develops on the TCNQ stacks [17].

More recently a new field has been opened with the collective properties in SDW materials in particular (TMTSF)<sub>2</sub>NO<sub>3</sub> [18], (TMTSF)<sub>2</sub>PF<sub>6</sub> [19] and (TMTSF)<sub>2</sub>ClO<sub>4</sub> [20]. For this latter compound, the SDW phase is stabilized in zero magnetic field by a rapid temperature quenching which suppresses the ClO<sub>4</sub> ion ordering or under magnetic field in a series of SDW subphases. Below  $T_{SDW}/2$  the threshold field is temperature independent. Narrow band noise has also been observed in (TMTSF)<sub>2</sub>ClO<sub>4</sub> with the linear relationship between the fundamental frequency and the excess current [20].

But the non-linear properties observed in CDW systems are now used as keys for the demonstration of electron crystallization. Thus in graphite, the magnetoresistance anomalies at very high H and very low T are described as the consequence either of an electron crystal or a CDW induced by the magnetic field [21]. The existence of a 3D Wigner crystal in low carrier concentration samples of Hg<sub>0.76</sub>Cd<sub>0.24</sub>Te induced by a magnetic field at low temperatures is supported by the non-linear current voltage characteristics with a threshold electric field of  $\sim 1$  mV/cm. The Wigner crystal is pinned by disorder and a finite electric field is necessary for sliding [22]. Similarly the metalinsulating transition of a two-dimensional array of electrons through Coulomb interactions on a helium film deposited on a dielectric substrate results from the pinning of the lattice phase by the substrate imperfections [23]. Noise properties of such a system are similar to those of CDWs. Wigner crystals induced in various configurations as for instance, besides those already quoted above, two-dimensional electron gas in a GaAs/GaAlAs heterojunction [24] under a magnetic field will be of a special interest in the future.

# 4. CDW STRUCTURE BY SCANNING-TUNNELING MICROSCOPY

The modulation of the ion positions can be detected by X-ray, neutron or electron diffraction measurements. Superlattice spots appear near the main Bragg spots that correspond to the unmodulated structure. Measurements of the inverse separation of these superlattice spots give the CDW wavelength. In real space, images of the CDWs have been obtained using high resolution electronic diffraction. This method is very well suited to study defects in the CDW lattice induced, for instance, by electron irradiation.

However the more promising technique is by scanning-tunneling microscopy [25] (STM). According to the simple tunneling theory, when a small amplitude voltage bias V is applied, the tunneling current between two surfaces separated of d is :

$$I = \alpha V \exp[-\sqrt{\phi} d]$$

where  $\phi$  is the extraction potential. For  $\phi \sim 4 \text{ eV}$ , a change in d of 1 Å yields a change in I of one order of magnitude. Thus the STM microscope consists of a small tip sweeped along the surface to be analysed. Keeping the tunneling current I constant, the z deflection is recorded as a function of x and y which generates a three-dimensional image of the surface : z(x,y). The electronic structure of the electrodes has been taken into account by Tersoff and Hamman [26]. Modelizing the tip as a spherical potential well, they found the tunneling current to be :

$$I = \alpha V D(E_F) \rho(r_0, E_F)$$

where  $D(E_F)$  is the density of states (DOS) of the tip at the Fermi level, and  $\rho(r_0, E_F)$  the DOS of the surface at the Fermi level and at the position  $r_0$  of the tip. Then the STM yields an image of the electronic surface structure by following the spatial modulation of the DOS at the tip position. On the other hand, the atomic force microscope [27] (AFM) studies the atomic surface structure and it is of current interest to relate images from both techniques [30].

As far as CDWs are concerned, the modulation of the conduction electron density at the CDW wavelength is easily detected by the STM and the z deflection is related to the fraction of electrons transferred into the CDW condensate. The layered transition metal dichalcogenides have been intensively studied by the STM technique at nitrogen [28] and helium [29] temperatures. The STM images reflect the amplitude of the CDW charge modulation -weak in the case of 2H-NbSe<sub>2</sub>, and very strong in the case of 1T-TaSe<sub>2</sub>. However AFM images obtained on 1T-TaSe<sub>2</sub> and 1T-TaS<sub>2</sub> at room temperature have only shown the atomic surface structure but no sign of the CDW superstructure [30]. This puzzling result is tentatively explained by the pressure effect on the CDW induced by the probe in the AFM technique. The two independent CDWs in NbSe<sub>3</sub> have very recently been revealed [31] by STM. The CDW modulations are localized on different types of chains as predicted by band-structure calculations. The sliding CDW has also been studied with the STM method [32]. By keep-

ing fixed the tunneling tip position, sharp peaks in the Fourier-transformed spectra of the tunneling current have been found when the current bias exceeds the threshold value for CDW depinning. When sliding the hill and valley of the CDW modulates the distance d between the tip position and the surface. Then the tunneling current is modulated with a time period  $\tau = \lambda_{CDW}/v$  with v the CDW velocity as in the case of the narrow band noise. This technique also shows that the depinning is inhomogeneous through the cross-section and that the CDW starts to slide at the surface.

Finally STM images reveal the importance of the crystal defects on the CDW charge modulation. The range of perturbation induced by a given defect and the redistribution of CDW contours around impurities located at the surface are now accessible by this technique [33] which can be very useful for studying the pinning effects in CDW dynamics.

## 5. BOUNDARY EFFECTS

The threshold electric field,  $E_T$ , for CDW depinning results from the competition between the elastic energy of the CDW and the pinning energy provided by impurities randomly distributed in volume. However boundary conditions have to be taken into account. At the electrodes where the CDW velocity vanishes, the condensate CDW current should be converted in quasi particules and this process can only occur at places where the Peierls gap  $\Delta$  is zero.

By analogy with type II superconductors Maki [34] has described vortices around which the phase rotates of  $2\pi$ . If one draw the planes corresponding to  $\phi = 2n\pi$  (n algebraic integer), these vortices look like edge dislocations. Around the dislocation core the phase gradient is gigantic : the core is a normal area with  $\Delta = 0$ . A continuous flow of vortices moving perpendicular to the chain axis may assure a transition between a moving part and a static one. The electrons injected at the electrode travel as excitations to the vortex core where they can condense easily ( $\Delta = 0$ ), and when two electrons per chain have been condensed the core is translated to the next chain ...

If Maki has given an equivalent description of the Abrikosov-Gor'kov vortices in superconductors, Gor'kov [35] and Batistic *et al.* [36] have treated the equivalent of the superconducting weak links. Neglecting the transverse variations for a very thin film of CDW sample it was shown that phase slippage centers are necessary to accomodate the electrons arriving (or leaving) from an electrode.

The strong deformations of the CDW at the electrodes are revealed in size effects measurements by measuring the threshold field as a function of the distance between electrodes. The threshold voltage sharply increases when & is reduced [37]. V<sub>T</sub> then can be written as

$$V_{\rm T} = E_{\rm P}L + V_{\rm O} \tag{8}$$

where the first term results from the bulk pinning and  $V_0$  has been interpreted as the potential necessary for the nucleation of a vortex or a phase slip center, typically 0.2 mV to 0.5 mV for NbSe<sub>3</sub> at T = 40 K and 1 mV for TaS<sub>3</sub> at T = 120 K. However such a small value for  $V_0$  discre-

dits a nucleation process in which  $V_0$  should be larger than  $2\xi_{ll}/E_c/\lambda$  with  $\xi_{ll}$  the amplitude coherencelength along the chains; with the well accepted values for NbSe<sub>3</sub>,  $V_0$  is found to be ~ 20 mV, two orders of magnitude larger than the experimental value. As in elastic theories for metals, a smoother mechanism is the growth of bubbles from preexisting dislocations acting for instance as Frank-Read sources. In this case, the reduction in energy delivered by the external source for enlarging the loops is  $2\pi\xi_{\perp}/D$  where D is the diameter of the loop. With the measured  $V_0$ , D is typically 500 Å to 1000 Å much less than the transverse dimensions of the sample (~ 10<sup>4</sup> Å).

Then  $V_0$  can be differently interpreted. A recent critical state model has been developed [38] in which, in addition to the bulk pinning, the growth of dislocation loops acting as Frank-Read sources are hindered by pinning from impurities.  $V_0$  is the consequence of this irreversible pinning suffered by dislocation loops. The growth of dislocation loops should appear at any velocity discontinuity to release the charge accumulation. Depinning under inhomogeneous conditions can be achieved by applying a thermal gradient along the sample length [39] or when several independent sources deliver current in different segments of the same crystal [40].

Besides pinning by the contacts, careful experiments have also shown that  $E_T$  increases with decreasing the cross-sectional area A of the sample [41,42] with a correlation with C/A the ratio of the crystal circumference C to the cross section A.

The growth and the motion of dislocations in the CDW superlattice is now inescapable for explaining the experimental results. But the way how the CDW moves however remains uncertain : as a whole as the sidebands in NMR spectra suggest [16] or through phase-slip at the strong pinning impurity sites in the bulk [11] or at the surface. Recently the measurement of the drift velocity of current carriers has been found to be much larger than the mean CDW velocity ; it was then proposed [43] that the translation of the CDW is effected by the glide of dislocation rings formed at the interface between the bulk sample and a surface layer with a slightly different q vector.

# 6. DEPINNING OF THE CDW AT HELIUM TEMPERATURE : DAMPING AND SCREENING EFFECTS

The equation of motion of the CDW with a single degree of freedom has been phenomenologically derived as that of a particle moving in a periodic pinning potential. The dielectric constant arising from the oscillations of the CDW is then

$$\epsilon(\omega) \sim \frac{\Omega_p^2}{\omega_p^2 - \omega^2 + \mathrm{i}\Gamma\omega}$$

with  $\Omega_p^2 = 4\pi ne^2/m^*$ , m<sup>\*</sup> the Fröhlich mass,  $\Gamma$  the damping,  $\omega_p$  the pinning frequency. In the low frequency limit the dielectric constant follows a relaxational response  $\varepsilon(\omega) = \varepsilon(0)/1 + i\omega\tau$  with  $\tau = \Gamma/\omega_p^2$ . However in order to fit the experimental dielectric response, internal degrees of freedom should be included through a distribution of relaxation times [44] and  $\varepsilon(\omega) \sim \varepsilon(0)/[1+(i\omega\tau)^{1-\alpha}]^{\beta}$ 

where  $\alpha$  and  $\beta$  characterize the width of the distribution of relaxation times and the skewness respectively.

Experimentally it was found that the dielectric relaxation time  $\tau$  and the static dielectric constant  $\varepsilon(0)$  exhibit an Arrhenius temperature dependence [44,45]. Also in conductivity measurements the amplitude of extra conductivity  $\sigma_{CDW}$  at a given  $E/E_T > 1$  decreases exponentially when the temperature is reduced with the same activation energy as the normal free carrier conductivity [46]. Thus the viscous forces or the friction of the CDW seems to diverge when T is reduced and the dissipation mechanism must imply normal carrier dissipation. These results have been explained by taking into account screening effects of the CDW deformations and long range Coulomb interactions [47,48]. The charged CDW deformations are electrostatically coupled to normal electrons and then the total current should be written as :

$$j = \varepsilon \dot{E} + \sigma E + j_{CDW}$$

where the first term is the displacement current with  $\varepsilon$  the dielectric constant, the second one the linear ohmic current where  $\sigma$  is thermally activated as exp(- $\Delta/kT$ ) and the last term the extra CDW current. The relevant parameter is now  $\omega\varepsilon/\sigma$  or  $\omega/\omega_1$  ( $\omega_1 = \sigma/\varepsilon$ ).

- At low frequencies, or at relatively high temperature, the conduction electrons are able to screen the CDW deformations. This back flow current induces a ohmic dissipation which accounts for the enhanced damping.
- When  $\omega \epsilon/\sigma \gg 1$  at low temperature, the few normal electrons are no more able to screen the CDW deformations and there are Coulomb interactions of the CDW with itself. These Coulomb-Coulomb interactions introduce a high frequency plasmon mode in the CDW excitations. Thus the ac response show two modes : an overdamped low frequency mode dominant at high temperature which strongly interact with normal carriers and a high frequency (microwave range) underdamped mode dominant at low temperatures [49].

The explanation of the splitting in two modes of the pinned phason excitations has been recently brought [48,50] : that comes from a breaking of a selection rule by the non-uniform pinning due to the disordered nature of the CDW. However the interpretation of the high frequency pinning peak (and especially its polarization) is still controversial [11,48,50].

Following this analysis, the CDW current is expected to vanish at very low temperature due to the huge enhancement of the damping. However in K<sub>0.3</sub>MoO<sub>3</sub> at helium temperature an abrupt increase of the current by several orders of magnitude occurs above a threshold voltage in the range of 10 V/cm - 100 V/cm [51-53]. At 4.2 K for a threshold V<sup>\*</sup> = E<sup>\*</sup>/L, a switching appears between the insulating state at low voltage to a highly conducting state in which the current increases apparently with a zero differential resistivity as :  $\sigma_{CDW} \propto j/E_T^*$ . Two threshold fields have then to be considered :  $E_T$  corresponds to the depinning of the CDW at high temperature, and  $E_T^*$  which abruptly appears below 40 K such as  $E_T^* \sim 10^3 E_T$ . Both depinning processes are overlapping in a

small temperature range. The sharp (I-V) characteristics at low temperature is now commonly associated with CDW depinning although earlier measurements on the same kind of compounds were explained by impact ionization [54]. This low temperature non-linear state is characterized by large broad noise, periodic current oscillations the frequency of which is increasing with the current [51,55-57], intermittency, negative differential resistance region [57]. However the linear relation between J<sub>CDW</sub> and the fundamental frequency shows, if CDW motion is involved, that only a small part (~ 1 %) of the cross-section is in the non-linear state [51,57]. Below E<sub>T</sub>\*, the polarization (defined as P = 2ed where e is the electric charge and d the displacement of the CDW) resulting from bipolarity voltage pulses shows a divergent behaviour [58] when E<sub>T</sub>\* is approached and for a given  $E < E_T^*$ , a time dependence following a stretched-exponential form [52]. On the contrary, when unipolar pulses are applied, the polarization is reversible [54] and linear with E up to E\*. This reversible polarization has been attributed [59] to the rigid displacement of the CDW while the remanent polarization would reflect configurational change between weakly CDW domains induced by the reversal of the voltage step. Thus at low temperatures in this scheme, the internal CDW excitations are frozen and the CDW moves rigidly with a single degree of freedom.

Thus the image which emerges from the above analysis is the following [49,60] : at high temperature when screening of CDW deformations occurs, the CDW depinning is associated with the low frequency mode in the ac response. When T is reduced and when the long range Coulomb forces become effective, the low frequency mode is shifted at very low frequencies ; the CDW is more rigid and the unique mode associated with the sliding CDW is the pinned mode in the 100 GHz range. The only damping effect now is the coupling of phasons with the phonon bath, which should vanish at T = 0. However finite damping still occurs for instance at the electrodes in the CDW-normal electron conversion process which excludes any superconductivity state by CDW sliding.

Although very appealing, the discussion above however shows several important drawbacks. The first one is the very particular temperature dependence of  $E_T$  and  $E_T^*$  with an apparent discontinuity around 30-40 K in a temperature range where strong anomalies are revealed in proton channeling anomalies [61]. In other CDW systems, insulating at low temperature as TaS<sub>3</sub>, it seems that there is an unique threshold field the value of which is increasing continuously when T is reduced [62]. Since negative differential resistance has been observed [57], breakdown avalanche and non uniform current paths are also probably favoured and filamentary conduction may take place. That might also be connected with the so small cross-section of the sample participating to the non-linear state. When a voltage is applied at low temperature, other excitations can also be created as solitons or kinks on single chains. Such local excitations have been invoked for the explanation of non-linear behaviour at helium temperature of other one-dimensional systems as TTF-TCNQ [63], or TaS<sub>3</sub> [64]. Finally the CDW ground state is far from equilibrium and many metastable states are present which relaxe over a very long time as it will be now presented in the last part.

## 7. LOW ENERGY EXCITATIONS OF CDW METASTABLE STATES

The CDW ground state results from the interaction between the CDW elasticity with the randomly distributed impurities. Due to this randomness, the E = 0 ground state comprises many metastable states which are defined as local deformations of the pinned CDW phase. These metastable states have been essentially characterized through the polarization induced when an electric field is applied. However, as in other disordered materials as glasses, spin glasses or polymers, the metastable states are expected to contribute to the thermodynamical properties at very low temperature.

Then the specific heat shows an excess contribution at low temperature : beyond the regular phonon term in T<sup>3</sup>, a T<sup>v</sup> contribution appears below 1 K with v = 0.32 in TaS<sub>3</sub> [65], 0.22 in (TaSe<sub>4</sub>)<sub>2</sub>I [66], ~ 1 in NbSe<sub>3</sub> [67] and 0.6 in K<sub>0.3</sub>MoO<sub>3</sub> [67]. Moreover in the temperature range where these excitations are detectable, the thermal relaxation does not follow an exponential decay. For heat pulse duration de ~ 1 s,  $\Delta T(t)$  was shown to decrease with a stretched exponential variation with a time constant showing an Arrhenius variation with an activation energy of 0.3-0.4 K. But the recovering towards the equilibrium depends of the duration during which the small thermal increment has been applied. These aging effects bind even more the CDW systems with the other disordered compounds [68].

Thus at low temperature, the relaxation processes occur over a very broad distribution. The CDW metastable states can be described as a frozen landscape of potential wells and hills with some height and depth for inhibiting the evolution of the system in phase space. The time necessary for the system to jump from one metastable state to another is thermally activated as :  $\tau = \tau_0 \exp(W/kT)$ . The small activation energy (0.3-0.4 K) measured in the energy relaxation reflects the very small barrier height between metastable states. A very small perturbation in energy (as small as  $10^{-6} \text{ eV}$ ) allows the system to explore many neighbouring states. The CDW degrees of freedom are not frozen at low temperatures and excitations between many metastable states on a very long time scale are detectable.

Finally other experiments have shown these metastable states : at low temperature magnetoresistance at liquid helium temperature in NbSe<sub>3</sub> exhibits large amplitude Shubnikov-de Haas oscillations which reveals a rather simple Fermi surface. As approximated to an ellipsoïd, the volume occupied by this pocket is about 0.1 % of the Brillouin zone leading to a carrier concentration of ~  $10^{18}$  cm<sup>-3</sup> very close to the number obtained by the Hall constant. The period of quantum oscillations is slightly sample dependent varying for instance between 0.36 MG to 0.3 MG when H is applied // to the (b,c) plane. But when the CDW is depinned and repinned at low temperatures [69], the period of the oscillations decrease and in the case H // (b,c) is always 0.29 MG. This shift in the extrema of the Shubnikov-de Haas oscillations means that the Fermi surface has been modified during the depinning-repinning process. The volume of the Fermi surface pocket has been reduced by ~ 10 % which would increase the CDW wave vector of  $10^{-4}$  (there are ~  $10^{21}$  e/cm<sup>3</sup> in the band affected by the CDW). One can think that when cooled through the Peierls transition, the CDW is away from its equilibrium state and that the depinning-repinning operation has released local distortion towards a better equilibrium state.

## 8. CONCLUSIONS

This new collective conducting state induced by a CDW sliding is now well established and it has been found in different families of quasi one-dimensional materials. The general properties of this state are more or less well analysed although in the recent years, new unexpected properties have been discovered. However in spite of all these efforts most of the fundamental questions remain unsolved. Progress in crystal growth quality and a better characterization of defects either in the crystal structure or in the CDW structure will be crucial for further developments in the field. The central point for understanding the non-linear properties remains to know how the CDW phase slides and especially the role of phase dislocations. These dislocations are necessary at the electrodes for the CDW condensate -normal current conversion and these processes are probably at the origin of at least a part of the observed periodic noise. But the nature of the pinning -strong pinning or weak pinning interaction- in the volume still remains unsettled. However as recently shown, impurity pinning can be mixed with other pinning origins as surface pinning or pinning at the electrodes. Consequently any reliable study of pinning effect should separate these different contributions. The switching in the I(V) characteristic of K<sub>0.3</sub>MoO<sub>3</sub> at helium temperature shows a new conducting state with a transition from an overdamped disordered motion to a underdamped motion. Experiments on other CDWs insulating at helium temperatures have to be performed in order to establish definitively the generality of this behaviour. Then very interesting would be the scaling between the threshold  $E_{T}^{*}$  and the pinning energy proportional to  $\omega_D^2$ . Role of contacts which seems to strongly affect the value of  $E_T^*$ needs also to be investigated. However aging effects in energy relaxation measurements below 1 K have revealed the strong disordered nature of the CDW state which allows analogy with other disordered materials as spin glasses. Metastable states are separated by energy barriers which extend to arbitrary low values. Thus these results have to be consistently analysed with those which indicate the non-deformability of the CDW for  $E < E_T^*$ . New techniques have been recently used as NMR and tunneling in the sliding state. STM microscopy might be very useful for studying locally pinning effects but inherent in the technique only at the surface. The similar collective mode has been shown to exist in a few SDW systems. Other SDW conductors have to be studied and the interaction of impurities on the threshold field better established.

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