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CHARGE DENSITY WAVE TRANSPORT IN THE BLUE BRONZES $K_{0.30}MoO_3$ AND $Rb_{0.30}MoO_3$

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ABSTRACT

We report data on non linear conductivity and both slow and fast voltage oscillations in the blue bronzes $K_{0.30}MoO_3$ and $Rb_{0.30}MoO_3$. These properties are attributed to the depinning of the CDW. The data obtained on $Rb_{0.30}MoO_3$ are very similar to those obtained previously on $K_{0.30}MoO_3$. We have studied in details the slow phenomena, time dependent effects, voltage pulses or coherent oscillations both in "pure" and doped $K_{0.30}MoO_3$. While pulses are found in the "pure" samples, the doped ones rather show oscillations, more or less coherent depending on the cooling process with or without a dc current. We propose that the slow phenomena are related to the CDW domain boundaries, discommensurations or dislocations in the CDW lattice. We suggest that possible diffusion of defects, possibly impurities, coupled either with the CDW modulation or with the domain boundaries, may account for the time dependent and memory effects.

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I INTRODUCTION

While the transition metal trichalcogenides such as $NbSe_3$ and TaS_3 have been known now for several years to exhibit non linear conductivity attributed to charge density wave (CDW) transport (1), similar properties have now been found also in the molybdenum blue bronze $K_{0.30}MoO_3$ (2) and in the transition metal tetrachalcogenides, such as $(TaSe_4)_2$ I (1). In the family of the molybdenum bronzes, the conduction band, built on hybridized p_π-4d orbitals, is partially filled due to charge transfer from the outer s electrons of the alcaline metal, leading to a metallic behaviour. $K_{0.30}MoO_3$ is at room temperature a quasi-one dimensional metal and these properties are well accounted for by the presence in the crystal structure of infinite chains of MoO_6 octahedra parallel to the direction of highest conductivity (monoclinic b-axis) (3). It has been shown that the metal to semiconductor transition which takes place at 180 K, is a Peierls transition and x-ray studies have established that the semiconducting phase is incommensurate with a wave vector component along b, $q_b = (0.74 \pm 0.01)b^*$ at 110 K (4). Recent neutron scattering data have corroborated this result and established that q_b is incommensurate down to 6 K (5).

In the incommensurate phase, detailed studies of the dc voltage-current characteristics have shown that the conduction is non linear above a sharp threshold electric field E_t, with a switching from the ohmic regime to the non ohmic one ; E_t is typically of the order of 100 mV/cm at 77 K. For dc current close to or larger than the threshold value, an anomalously large noise voltage is found with both fast oscillations with frequencies F in the range of 10 kHz and slow pulses with a time scale of typically 1s (2). The non linear properties have been attributed, as in $NbSe_3$ and related compounds, to the depinning of the incommensurate CDW by the electric field. It has also been shown that the noise frequency F is proportional to the excess current density j_{CDW} carried by the CDW (6). This is also consistent with results found in $NbSe_3$ and accounted for by a classical model describing the CDW as a particle sliding in a periodic potential. In the case of $K_{0.30}MoO_3$, the existence of hysteresis and time dependent effects associated with long relaxation times (1 hour or longer) has also been established (6). These results point out the importance of metastability in the CDW transport. We had also suggested that they could be due to the motion of domain walls, possibly discommensurations.

The experimental data on charge density wave transport have lead to an intense theoretical work. While the classical model (1) (7) was consistent with the linear relationship between F and j_{CDW} and predicted that $F/j_{CDW} = 1/ne\lambda$ where n is the condensed electrons density and λ a characteristic length found to be the superlattice period, it did not account for the exponential dependence of σ on the electrical field. Bardeen proposed therefore a model in which the depinning of the CDW is described by a Zener type tunneling through a gap at the Fermi surface determined by the pinning frequency (8). More recently, Barnes and Zawadowski (9) proposed a Josephson type theory in which the two macroscopic quantum states are the two components q and -q of the incommensurate CDW. Impurity scattering would induce in such a system an energy density periodic in space with a period $\lambda/2$ and therefore quantum oscillations with frequencies $F = v/(\lambda/2)$ where v is the drift velocity of the CDW ; this would correspond to a ratio $F/j_{CDW} = 2/ne\lambda$. This value may be consistent with most recent experimental data (10). In a different approach, Klemm and Schrieffer (11) have proposed a microscopic theory supporting the classical model and accounting for the existence of a threshold field and of characteristic noise frequencies.

All previous models are based on the fact that the voltage oscillations and noise are related to bulk properties of the sample. Some experimental data are however possibly not inconsistent with a local mechanism : the noise voltage would then be induced at the contacts (12). Ong et al have proposed that the oscillations could be created by a sheet of phase vortices located under the contacts (13). At the present time, the local or non local origin of the CDW conduction noise is not clear.

Another important aspect of the experimental data on CDW transport is the existence of hysteresis, time-dependent effects and metastability, as previously reported by Gill (14). However, most of the experimental and theoretical studies are rather poor in this respect. Only the time dependent mean field theory developed by

D.S. Fisher accounts for an hysteretic behavior close to the threshold (15) ; in this theory, the CDW is considered as a deformable medium and not as a rigid macroscopic object.

In section II of this article we first describe the experimental techniques. In section III, we report data obtained on the Rubidium blue bronze $Rb_{0.30}MoO_3$ and show that this compound has properties very similar to those of $K_{0.30}MoO_3$. We also describe new results on what we call the fast phenomena, the high frequency (F ~ 10 kHz) voltage oscillations, for both $K_{0.30}MoO_3$ and $Rb_{0.30}MoO_3$. Then, we emphasize for both compounds the importance of metastability and of slow phenomena with a time scale of ~ 1s ; we report for doped $K_{0.30}MoO_3$ samples, the existence of very low frequency (f ~ 1 Hz) coherent voltage oscillations and show that these low frequencies also depend linearly on the CDW current.

In the last section we discuss mostly the origin of the slow phenomena, in relation with the behaviour and the nature of the boundaries separating the CDW domains, discommensurations or CDW dislocations. We also discuss the role of impurities and suggest that they may not always be inert and that possible diffusion processes could be partly responsible for time-dependent effects.

II EXPERIMENTAL TECHNIQUES

The single crystals used in this study were grown by the electrolytic reduction of a K_2MoO_4 or Rb_2MoO_4 : MoO_3 melt in the stoichiometric proportions. The Fe or Mn doped crystals were obtained by adding the appropriate proportions of Fe_2O_3 or MnO_2 respectively in the melt. The crystals are platelets parallel to the ($\bar{2}01$) cleavage plane and elongated along the crystallographic b-axis, with typical dimensions 5 x 2 x 1 mm^3. Transport measurements have been carried out on samples of typical size 3 x 1 x 0.1 mm^3 using the standard four probe arrangement with the dc current parallel to b. Two probe configuration was also used occasionnally. For most measurements, the samples were immersed in liquid nitrogen in order to avoid self-heating. Electrical contacts were made by evaporating indium on freshly cleaved crystals and soldering gold wires 50 μm in diameter onto the evaporated areas. The voltage contacts were ~ 60 μm wide and the current contacts covered the ends of the samples. The contact resistances were found one order of magnitude smaller than the sample resistance. The V-I curves were recorded by slowly sweeping a dc current. Currents and voltages were measured by conventional digital voltmeters. The high frequency voltage oscillations were detected by means of an amplifier and analyzed with a Tektronix 7L5 spectrum analyzer. The low frequencies phenomena were recorded on a x-t plotter.

III RESULTS

III-1 Voltage-current characteristics

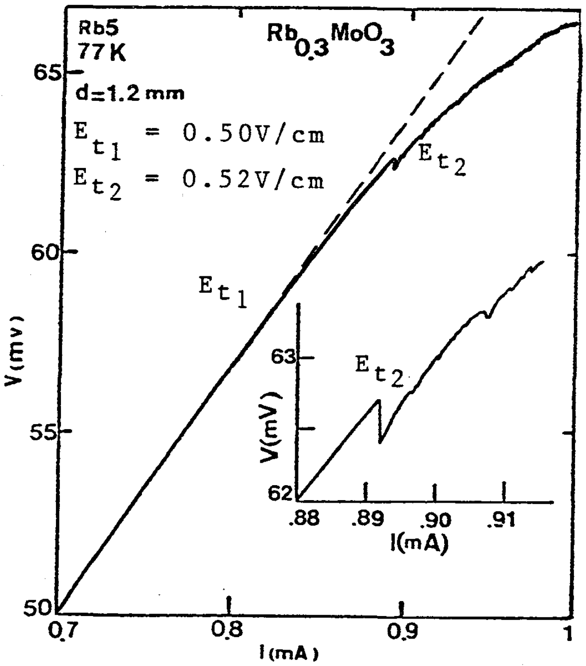

Fig.1 : Voltage vs current curve. Two threshold fields E_{t1} and E_{t2} are shown. The inset shows the switching at E_{t2} and voltage pulses in the non-Ohmic regime. The distance between the voltage contacts is d = 1.2 mm. The sweeping time is ~ 3 mn for the interval given in the inset.

The V-I curve obtained on a $Rb_{0.30}MoO_3$ sample at 77 K is given in Figure 1. The V-I curve is slightly non linear above a first threshold field E_{t1} and shows a jump at a higher sharp threshold field E_{t2}. The inset shows more clearly the switching at E_{t2} and the low frequencies pulses. These results are very similar to those reported for pure $K_{0.30}MoO_3$.

III-2 Fast phenomena

Above E_t, the noise voltage contains broad band and quasi-periodic noise. Fourier analysis of the noise on a $Rb_{0.30}MoO_3$ sample reveals two discrete frequencies F_1 and F_2 which increase proportionally to the CDW current density J_{CDW} as shown in Figure 2. The value of the F_1/J_{CDW} ratio is ~ 1 $MHz.A^{-1}.cm^2$.

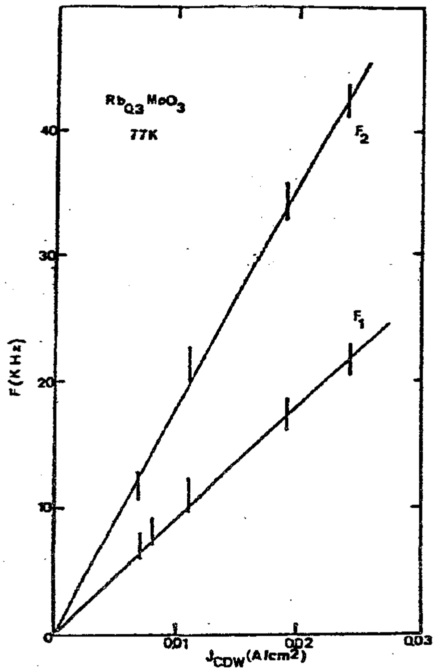

Fig.2 : Noise frequency as a function of excess CDW current density measured at 77 K.

We have also studied the temperature dependence of F_1/J_{CDW} on a pure $K_{0.30}MoO_3$ sample over a limited temperature range because the CDW current was found to decrease slowly vs time above 80 K. F_1/J_{CDW} increases slowly with the temperature, as shown in fig. 3.

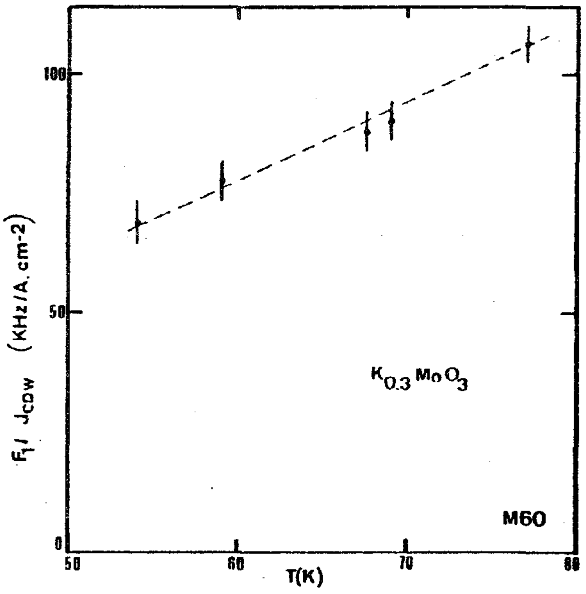

Fig.3 : F_1/J_{CDW} as a function of temperature for pure $K_{0.30}MoO_3$.

III-3 Slow phenomena

a) Regime of pulses in pure $K_{0.30}MoO_3$.

At constant current, we have previously reported (2) that pulses of transient voltage corresponding to a sudden decrease in V_{dc} were produced just below and above E_t (Fig.4). Below E_t the pulses have a short rise time, typically $\tau \sim 3$ ms with a length ~ 100 ms while above E_t, the rise time is much longer with $\tau \sim 60$ ms and a length ~ 200 ms. The magnitude of the pulses was ~ 2% of V_{dc} below E_t and ~ 1 % above.

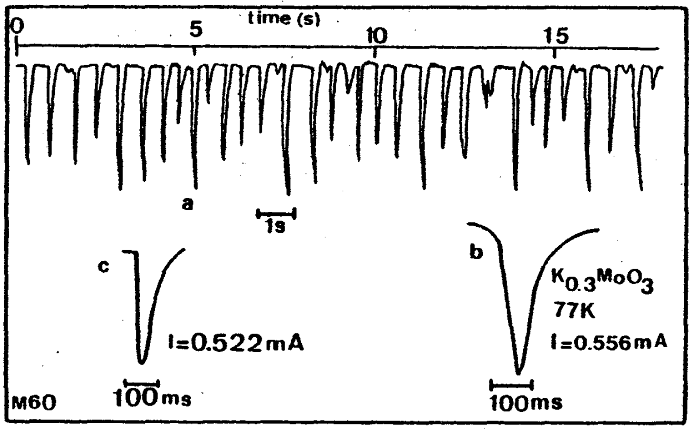

Fig.4 :

a) Pulses as a function of time for $I = 0.556$ mA. The current at the threshold field is $I_t = 0.525$ mA.

b) Oscillogram trace of a pulse for $I > I_t$.

c) Oscillogram trace of a pulse for $I < I_t$.

b) Time dependent effects.

In pure $K_{0.30}MoO_3$ the V-I curve is not always stable as a function of time. We have recorded the evolution of V_{dc} as a function of time at constant current on a sample showing large hysteresis in the V-I curve as seen in fig. 5. The inset shows that the drift of V_{dc} from A to A' is not a monotonous function of time and that V_{dc} exhibits positive and negative steps.

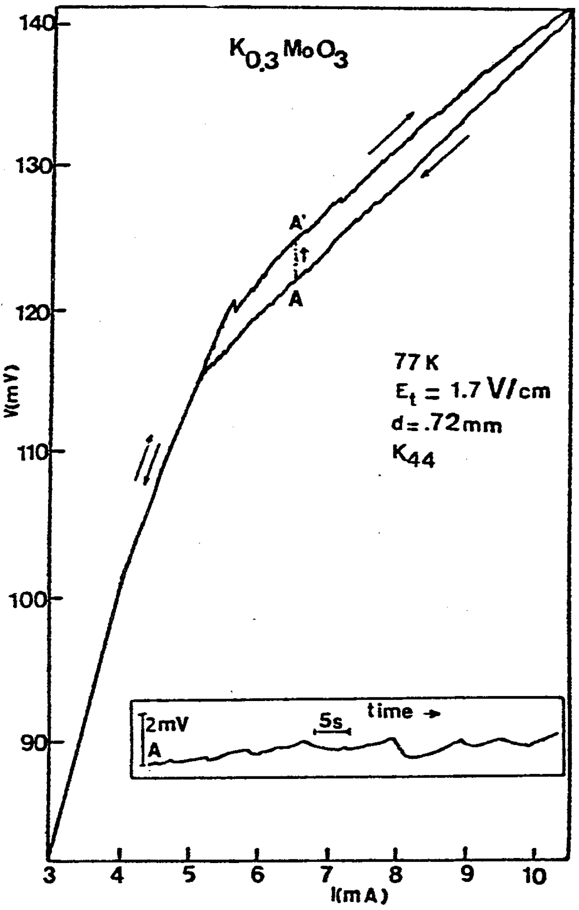

Fig.5 : Voltage vs current curve showing large hysteresis. The inset shows the drift of the voltage from A to A' at constant current. The distance between the voltage contacts is d =.72mm.

c) Low frequency voltage oscillations

We have observed unusually low frequency voltage oscillations in the Hz range mainly on doped $K_{0.30}MoO_3$. In Figure 6, is shown the V-I curve for a Fe doped sample. The onset of the non-Ohmic conductivity is not so well defined as in pure $K_{0.30}MoO_3$. In Figure 7 are shown low frequency voltage oscillations as a function of time recorded for various values of the dc current. The oscillations (a) and (h) are periodic but not stable as a function of time. They were coherent for only $\sim$ 15 cycles. The curves (b) to (g) were found aperiodic.

We have found that these oscillations could be made coherent on very long time scales (at least several hours) by applying a dc current during the cooling down to 77 K. In pure $K_{0.30}MoO_3$, only pulses were found and the corresponding pseudo-frequencies did not seem to depend on the electrical history of the samples.

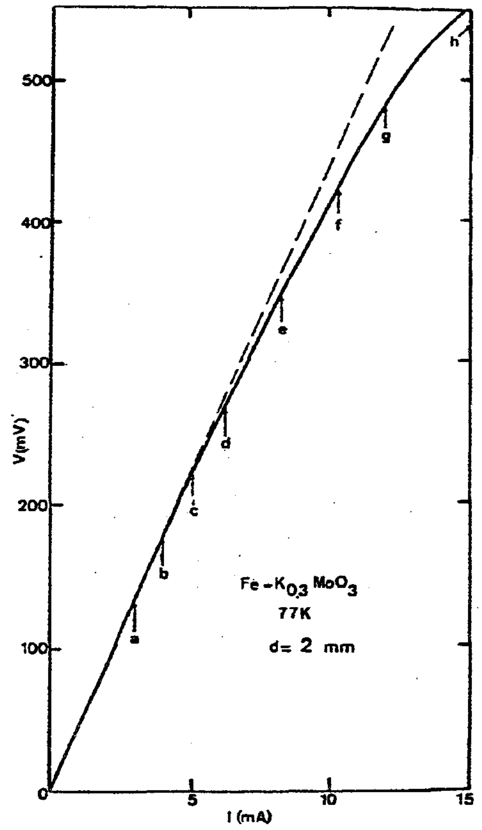

Fig.6 : V-I curve for a Fe-doped $K_{0.3}MoO_3$ sample. The molar concentration of Fe_2O_3 in the melt was 3 %. Distance between voltage contacts d = 2 mm.

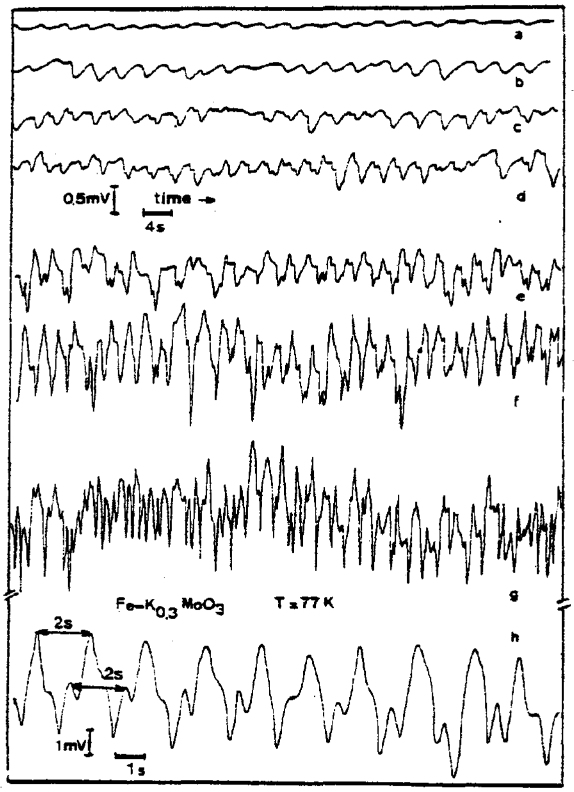

Fig.7 : Voltage oscillations as a function of time for different values of the dc current. The sample was cooled down to 77 K with a zero current.

Typical results are given in Figure 8 for a Mn doped sample cooled with a dc current smaller than the critical current at the threshold. Large amplitude and incoherent oscillations were found if the sample was cooled in a zero current while small amplitude and coherent oscillations were found when cooling with a dc current I_c smaller than the threshold value at 77 K ($I_c \sim 0.7 I_t$ at 77 K). The frequency of these oscillations increases almost linearly with the CDW current density as shown in Figure 9.

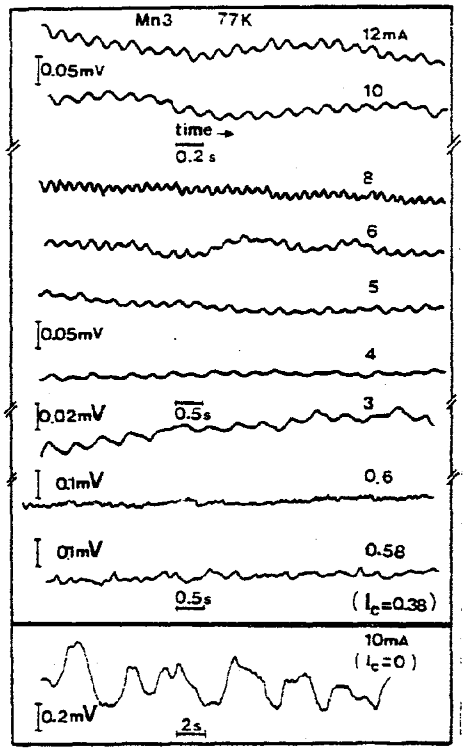

Fig.8 : Voltage oscillations as a function of time for a Mn-doped $K_{0.3}MoO_3$ sample cooled down to 77 K with a dc current. I_c = 0.38 mA ; I_t = 0.58 mA at 77 K. The bottom curve shows incoherent oscillations obtained when I_c = 0. The molar concentrations of MnO_2 in the melt was 2 %. Distance between voltage contacts d = 1 mm.

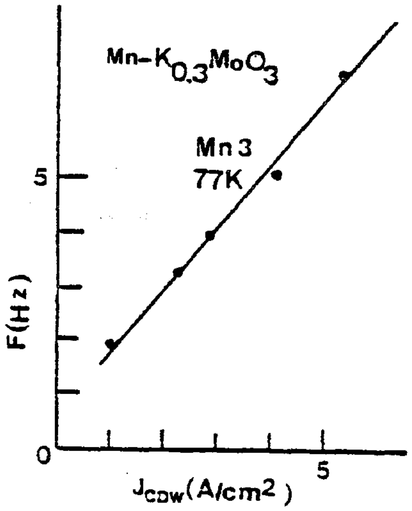

Fig.9 : Voltage oscillations frequency as a function of excess CDW current density in a Mn-doped sample at 77 K.

IV DISCUSSION

Let us first discuss the properties of $Rb_{0.30}MoO_3$. It has been already reported that the transport properties, the Peierls transition temperature and the incommensurate state are very similar in $K_{0.30}MoO_3$ and $Rb_{0.30}MoO_3$(4). The same is true for the non linear transport properties ; the threshold fields are of the same order of magnitude in both compounds and slow pulses are also found in $Rb_{0.30}MoO_3$. Taking into account all the data we have collected up to now, it is difficult to decide what are the differences between both compounds. This corroborates that the main role of the alcaline metal in this class of compounds is to provide the charge transfer which fills partially the conduction band ; it should also be noted that, in spite of the difference of size of K^+ and Rb^+, the lattice parameters of both compounds do not differ from more than 2 % (24).

The frequencies F of the fast voltage oscillations are in $Rb_{0.30}MoO_3$ also proportional to the CDW current. The value of 1 $MHzA^{-1}cm^2$ found for F/J_{CDW} is, as for $K_{0.30}MoO_3$, much larger than the value of $1/ne\lambda \simeq 4 \times 10^{-3}$ MHz $A^{-1}cm^2$ estimated in the classical model, with $\lambda \simeq 4b$ and assuming a complete charge transfer from the alcaline metal. This could be due to the fact that only filaments of the crystal take part in the CDW transport ; the existence of a sharp threshold in the V-I characteristic makes this explanation very unlikely. Our data therefore do not seem to be consistent neither with the simple classical model nor with the Josephson type model.

In the absence of a simple picture accounting for the high frequency oscillations it is difficult to understand the increase of the ratio F/J_{CDW} with increasing temperature between 50 K and 80 K in $K_{0.30}MoO_3$. It should be noted that in the same temperature range the q vector seems to be constant (5). This variation could however be related to a decrease of the density of the electrons condensed in the CDW with increasing temperature.

Among the slow phenomena, the regime of pulses found in the pure samples of $K_{0.30}MoO_3$ (Fig.4) is puzzling. In order to measure unambiguously the amount of electrical charge Q corresponding to a single pulse we have performed two contacts measurements with a constant applied dc voltage and have recorded the current vs time ; Q is then found to be in all cases in the range of 0.5 to 1 µC ; this indicates that the pulses involve a comparatively macroscopic object. They could be attributed to local (contact) phenomena ; however, the motion in the bulk of the crystal of any charged object could give rise to such a pulse ; the short rise time would correspond to the sudden displacement of this object and the long decay time (~100 ms) to the slow relaxation of the rest of the sample.

In the regime of pulses found for $E < E_t$, the CDW are static and pinned and each pulse could be due to the depinning of a small region of the crystal. Such a local depinning involves the displacement of some domain boundaries. One can invoke the motion of domain walls such as discommensurations as proposed in other models (16). We also suggest that the motion of dislocations in the CDW lattice may be important for these results. The existence of such dislocations had already been proposed several years ago by Lee and Rice (17).

Above the threshold field, the pulses are superimposed on the CDW transport ; the CDW current should then correspond to an average stationary velocity and the pulses to fluctuations of the velocity of some domain boundaries. In this context, the time dependent effects and especially the drift towards the ohmic regime indicates that some domain boundaries become pinned as a function of time, very likely because they reach sometimes potential barriers that they cannot overcome.

One should note at this point the similarities of our results with those concerning the displacement of a single Bloch wall in a ferromagnetic crystal (18) ; the Barkhausen noise recorded when the wall is constrained to move with a constant velocity is very similar to the regime of pulses in the case of CDW transport in $K_{0.30}MoO_3$.

There is also some analogy between our data and the time-dependent and hysteretic properties related to vortices motion in type II superconductors (19). The motion of flux bundles (bunch of vortices), pinned by irregularities also gives rise to pulses, in some cases with pseudofrequencies decreasing logarithmically with time. However, the time scale of the pulses is much shorter in the case of vortices motion and our results are more reminiscent of the properties related to the motion of a Bloch wall.

In the CDW systems, the pinning of the CDW and the existence of metastability seem to have been attributed mostly to impurities and to crystal defects. However, it has been shown recently by le D'Haeron and Aubry (20) that in an incommensurate system, the CDW Fröhlich type conductivity should vanish if the electron-phonon coupling is larger than a critical value ; in this situation, the motion of the CDW requires the overcoming of a Peierls-Nabarro type barrier, even in the absence of any extrinsic disorder in the system. The existence of metastability is thus a consequence of the competition between the two periodicities determined by the lattice and the Fermi wave vector.

The importance of this mechanism compared to impurity pinning could be elucidated by the study of doped samples. Our data obtained on samples doped with non isoelectronic transition metal impurities in rather large concentrations (~1% at) seem to indicate two tendencies :

1) The threshold fields are comparable in the doped samples and in the "pure" ones.

2) A regime of coherent low frequency (~1 Hz) voltage oscillations is found in most doped samples.

These results are puzzling ; one could suggest that the impurities enter the crystals on sites non active for the CDW such that interlayers sites ; this does not seem to be the case in Fe doped $K_{0.30}MoO_3$, as Mossbauer studies on Fe^{57} indicate that Fe enters in substitution on all Mo sites (21). One could invoke a weak pinning by the impurities and the presence of other defects, such as vacancies due to non stoechiometry in the "pure" samples. But one has then to understand why the presence of large concentrations of impurities favour the existence of low frequency coherent oscillations rather than pulses as in the pure samples. The situation at present is not clear.

We would like however to suggest another possible role of the impurities. It is well known in the case of a Bloch wall in an FeSi single crystal that Carbon impurities are involved in the potential wells in which the wall is eventually trapped. These impurities diffuse in the crystal and, when the Bloch wall moves, cause the potential wells to be dragged along ; this leads to instability phenomena and in some regimes to quasiperiodic behaviour (18). A similar but more sophisticated mechanism has been proposed recently to account for memory effects in an incommensurate insulating system, deuterated thiourea (22). In this case, the defects, possibly impurities, are assumed to interact with the modulated potential ; the diffusion of the defects would then lead at thermal equilibrium to a modulated impurity concentration.

We suggest that a diffusion mechanism could account in the case of the blue bronze for the role of the cooling process. When the sample is cooled in the absence of a dc current, the defects would reach during cooling a repartition determined either by the superlattice q vector and (or) by the configuration of the CDW domains at some intermediate temperature, depending on the cooling speed, as q is temperature dependent. When cooling is performed with a dc current, the CDW motion during the cooling would lead to a different distribution of the defects at low temperature. In the first case, the inhomogeneous distribution would be responsible for the large and chaotic oscillations and in the second one the possibly more homogeneous configuration for small and coherent oscillations.

The proportionality of both the low frequencies f and the high frequencies found for the voltage oscillations show that both are determined by the CDW drift velocity ; one may then suggest that f is related to the average size of the CDW domains. As F is expected to be related to the superlattice wavelength (~30 Å in our case) the order of magnitude of the low frequency f may indicate an average domain size of roughly 30 μ. These speculations should now be corroborated by more detailed studies of memory effects for the low frequency oscillations and obviously by direct observation of CDW domains.

The coherence of both the low and high frequencies oscillations for typical sample volumes of $10^8 \mu^3$ is surprising ; this should be compared with recent results obtained by Gruner et al (23) which seem to indicate the vanishing of the high frequency oscillations in the thermodynamic limit. It is not clear whether our results support such a model. But they certainly indicate the existence of very strong interdomain couplings.

V CONCLUSION

We have shown in this article that both $Rb_{0.30}MoO_3$ and $K_{0.30}MoO_3$ show non linear conductivity characterized by a threshold electric field and fast voltage oscillations which have to be attributed to CDW transport. These properties are accompanied by time dependent effects, low frequency pulses or coherent oscillations which depend on the cooling process, with or whithout a dc current. This shows the importance of metastable states in these samples. Metastability must be associated with the existence of CDW domain boundaries, discommensurations or dislocations in the CDW lattice. We suggest that impurities, vacancies or other crystal defects, responsible for the pinning of the CDW, may be coupled to the CDW modulation or to the domain boundaries and if they are able to diffuse, may account for the memory and time dependent properties.

Our results, as well as those obtained on the transition metal tri and tetrachalcogenides, show clearly that any further progress in the understanding of CDW transport will first require direct observation of CDW domains, in spite of the intense theoretical work already performed on this subject.

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