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Low-frequency noise and memory effect in the charge-density-wave transport of $Rb_{0.30}MoO_3$

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Low-frequency noise (~ 1 Hz) is found in the nonlinear transport regime due to the depinning of the charge-density wave in the blue bronze $Rb_{0.30}MoO_3$ below the Peierls transition. These low frequencies are linear with the excess charge-density-wave current. The corresponding phenomena depend on the cooling process. Erratic voltage fluctuations follow a quenching without an applied dc current. Coherent pulses or oscillations depending on the cooling rate are found after a cooling with an applied dc current. We propose that these phenomena are related to the motion of charge-density-wave domains coupled to mobile defects.

INTRODUCTION

Considerable research effort has been concentrated these last years on the study of nonlinear transport properties associated with the depinning of charge-density waves (CDW's). Non-Ohmic behavior of the conductivity has been observed below a Peierls transition in the quasi-one-dimensional materials such as $NbSe_3$, TaS_3, $(TaSe_4)_2$ (Ref. 1) and has been attributed to the sliding of the CDW condensate when an applied electric field exceeds a well defined threshold value E_t. It has been established recently that the quasi-one-dimensional molybdenum blue bronzes $K_{0.30}MoO_3$ and $Rb_{0.30}MoO_3$ exhibit a Peierls transition at $T_p \sim 180$ K with an incommensurate CDW in the low-temperature phase.[2] Below T_p, a sudden onset of non-Ohmic behavior accompanied with large noise voltage is found above E_t.[3] Precursor voltge pulses occur just below E_t. The narrow-band noise voltage is superimposed on a broadband noise and includes "high"-frequency ($F \sim 10$ kHz) and very-low-frequency ($f \sim 1$ Hz) periodic voltage fluctuations. Both F and f depend linearly on the excess CDW current with slopes in the range of 10^5 and 1 $Hz/A\,cm^2$, respectively, for pure and V-doped $K_{0.30}MoO_3$.[4] We have shown that in $K_{0.30}MoO_3$ metastability associated with the CDW state is predominant: (i) at constant current $I > I_t$, the dc voltage depends logarithmically on time with relaxation time of several hours at 77 K;[5] (ii) hysteresis and switching in the V-I characteristics are found. These hysteretic properties are strongly affected by electron-irradiation-induced defects.[6] Metastable states involving short time scales, typically 1 ms, have recently been reported for $K_{0.30}MoO_3$.[7] Similar properties have also been found by several authors in TaS_3 (Ref. 8) and $NbSe_3$ (Ref. 9).

Some properties of the collective response of a CDW condensate have been explained phenomenologically either by considering the CDW as a rigid[10] or deformable[11] object with an overdamped motion in a periodic pinning potential or with a macroscopic Zener-type quantum tunneling of the CDW across potential barriers.[12] Metastable states have been incorporated in other recent models.[13] It has also been proposed that the noise voltage is induced at the contacts and due to a sheet of phase vortices in the CDW lattice.[14]

In this paper we report the observation of low-frequency voltage fluctuation in crystals of $Rb_{0.30}MoO_3$ rapidly quenched from above the Peierls transition. Several regimes of voltage fluctuations are found in the non-Ohmic state depending on the cooling rate and on the cooling process with or without an applied dc current. The frequency of these fluctuations varies linearly with the excess CDW current. The possible existence of CDW domains with mutual interactions and of domain walls coupled to mobile defects is proposed.

EXPERIMENTAL RESULTS

The samples investigated are single crystals grown by the electrolytic reduction of a Rb_2MoO_4-MoO_3 melt. Crystals used are platelets of typical size $5 \times 2 \times 1$ mm^3 parallel to the $(\bar{2}01)$ cleavage plane with the monoclinic $\vec{b}$ axis as the long direction. The measurements have been performed on freshly cleaved samples with parallel faces and thickness of the order of 150 μm, with the standard four-probe configuration and dc current along $\vec{b}$. Electrical contacts were made by evaporating indium stripes and soldering gold wires onto the evaporated areas. The current contacts covered the ends of the sample. The dc V-I characteristics were measured by slowly sweeping a dc current and the differential resistance was obtained as a function of the dc current by phase-locked detection. The low-frequency fluctuations were recorded under constant current on an x-t plotter. In all cases, the samples were immersed in liquid nitrogen to avoid self-heating. Different types of cooling were performed. For the "fast" cooling, the time scale involved for cooling from 300 to 77 K is a few seconds, while for the "slow" one the time scale is about 60 s.

Figure 1(a) shows the numerical derivative of the logarithm of the resistance as a function of the inverse temperature. The Peierls transition defined as the peak in this plot is found at 183 K. Figure 1(b) shows a typical differential resistance curve. A well defined threshold $E_t \sim 370$ mV/cm is found. Figure 2 shows the two types of voltage fluctuations appearing across the voltage leads depending on the cooling rate plotted as a function of time for different values of the current I_c applied during cooling. One should note that these results are obtained for large values of the dc measuring current $I \sim 10 I_t$. In these experiments, I_c and I have the same sign. For a fast cooling, periodic voltage

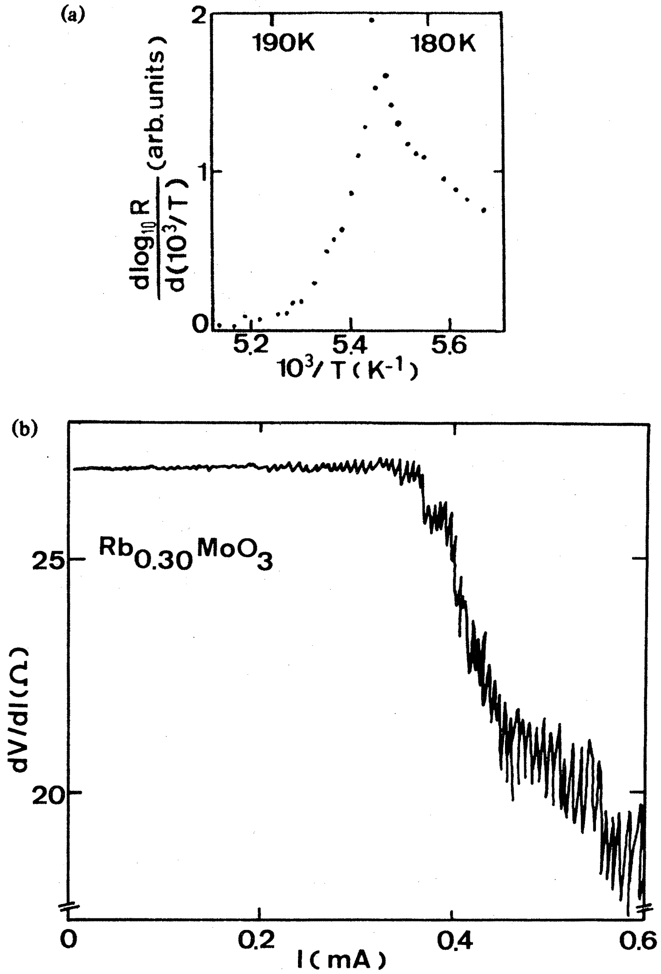

FIG. 1. (a) $Rb_{0.30}MoO_3$. Numerical derivative of the logarithm of the resistance as a function of the inverse temperature. (b) Differential resistances dV/dI as a function of the dc current I.

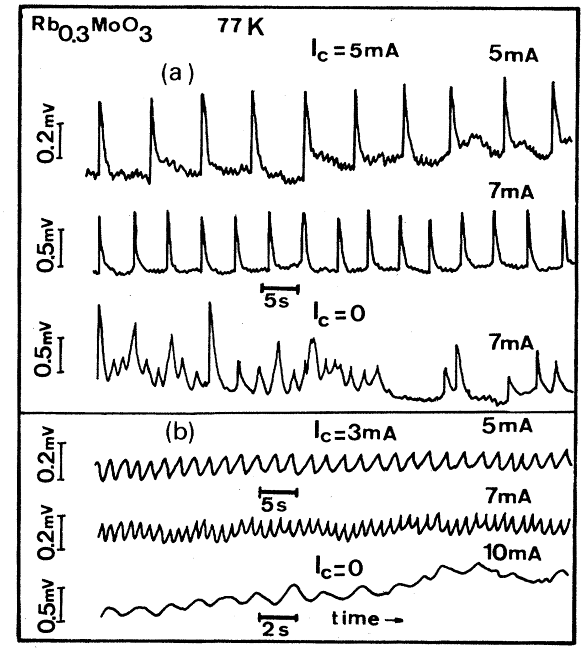

FIG. 2. Voltage fluctuations in quenched $Rb_{0.30}MoO_3$. (a) Regime of pulses found after a fast cooling (~5 s). For the two upper curves, the current applied during quenching was $I_c = 5$ mA. The measuring currents are 5 and 7 mA, respectively. Lower curve: chaotic oscillations for $I_c = 0$. (b) Regime of oscillations found after a slower cooling (~30 s).

pulses corresponding to a sudden increase in voltage at fixed current are found. The pulse height is nearly constant and the amplitude corresponds to ~1% of V_{dc}. From the pulse area, an electric charge Q ~30 μC is deduced. Voltage spikes obtained when $I_c = 0$ are also show. In this case, the spikes seem randomly distributed in time. The bottom curves show the results when the cooling rate is slower. Quasiperiodic voltage oscillations are found. One should note that the frequencies of these oscillations are different from those of the pulses. The voltage-oscillations amplitude is ~0.5% of V_{dc}. Those voltage fluctuations have been recorded during several hours and found to be very stable. After decreasing the measuring current to zero and keeping the sample a few hours in liquid nitrogen, the same voltage pulses were found again by increasing I to its former value. After a zero current cooling, the erratic voltage spikes vanish as a function of time after roughly one hour.

Figure 3 shows the frequency of the voltage fluctuations for the two cooling regimes and for different values of the current I_c applied during cooling, plotted as a function of the excess CDW current. This figure shows that the frequency is governed not only by I_c but also by the cooling rate. In both regimes, the frequency is linear with J_{CDW}.

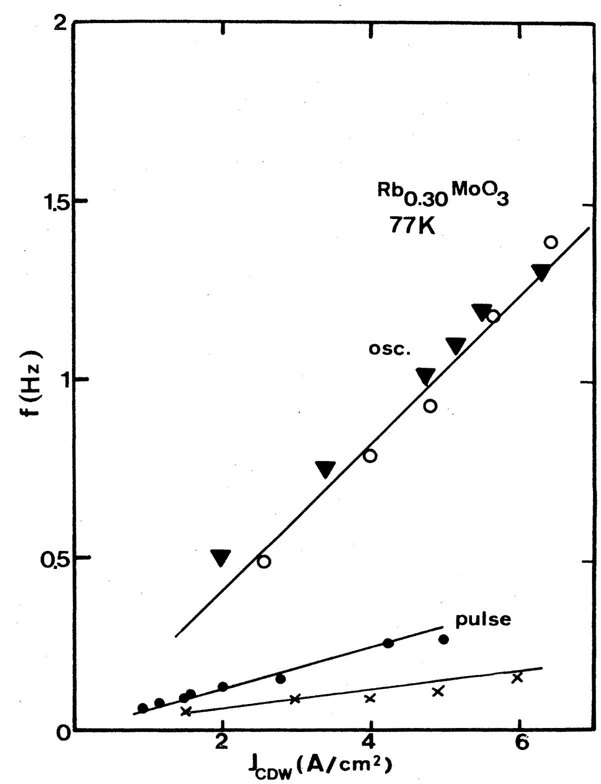

FIG. 3. Frequency of the voltage oscillations as a function of the measuring current, ○, ▼: oscillations for $I_c = 3$ and 8 mA, respectively. ●, ×: pulses for $I_c = 5$ and 3 mA, respectively.

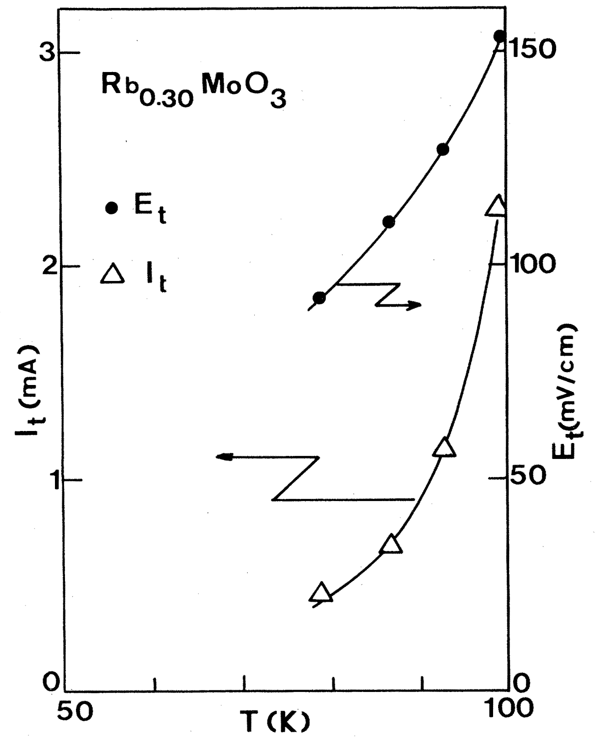

FIG. 4. Threshold current and threshold field as a function of temperature.

The slope is 0.06 $Hz/A\,cm^{-2}$ for voltage pulses and in the range of 0.2 $Hz/A\,cm^{-2}$ for oscillations. The high-frequency ($F \sim 10$ kHz) oscillations[3] have, up to now, not been found on the samples giving rise to low-frequency signals.

In Fig. 4, we have plotted the threshold current I_t and the threshold field E_t as a function of temperature. In the explored temperature range E_t and I_t are increasing with temperature. It should be mentioned that the smallest current I_c giving rise to voltage oscillations was ~ 2.5 mA, higher than the threshold current at all temperatures below 100 K.

DISCUSSION

It is now well established, either in the transition-metal trichalcogenides[8,9] or in the blue bronzes[5,7] that metastability is predominant in the CDW transport. It can be attributed to two mechanisms. The first and intrinsic one is the competition in these systems between the lattice periodicity and the $2K_F$ periodicity which is a consequence of the one-dimensional electron gas instability. When these two periodicities are incommensurate, one may expect frustration phenomena analogous for example to the spin-glass frustration.[15] The second extrinsic mechanism involves the existence of crystal defects such as nonstoichiometry or impurities which are believed to pin the CDW. In the case of the blue bronze, the $2K_F$ vector is clearly incommensurate above 100 K (Ref. 2) and locked below 100 K to a value close to 0.75.[16] It is not clear at the moment whether this value is exactly commensurate in some crystals and whether it depends on the crystal growth and crystal purity. On the other hand, the role of defects increasing the metastability has been established by electron irradiation experiments.[6] Very small irradiation doses can change the onset of nonlinearity of the V-I characteristic from a soft process (without switching) to an abrupt one (with switching). One can then conclude that both mechanisms are important.

Let us now discuss the origin of the slow voltage fluctuations corresponding to pseudofrequencies f in the Hz range. They can be due to fluctuations either in the CDW current or in the so-called Ohmic current, as has been suggested recently by Gill.[17] If we assume that the CDW are directly responsible for this, one can estimate a characteristic length scale L associated with these fluctuations, with $f = V_d/L$, where V_d is the drift velocity of the CDW. In the quasiclassical model of the CDW dynamics accounting for the high-frequency (F) noise,[18] it has been found that $F = V_d/\lambda$, where λ would be the superlattice period of the CDW. In the case of the blue bronze $\lambda \simeq 30$ Å, $F \sim 10$ kHz; therefore, $L = 30$ μm. One should note that this is a rather large length scale; it could be related either to an average distance between some special types of crystal defects or to some CDW domain size. The detailed mechanism of these low-frequency phenomena is, just as for the high-frequency ones, unclear at the moment. They may be induced in the bulk of the crystal or possibly under the contacts and would then involve some type of dislocations in the CDW lattice.[14]

One cannot, however, exclude that these slow voltage fluctuations are related to the Ohmic current. It is now well known that also the so-called Ohmic resistivity may show hysteresis effects and may depend on the history of the sample.[6,8] In the case of the semiconducting state of the blue bronze, the Ohmic resistivity is not intrinsic and has to be attributed to donor impurity levels in the Peierls gap. These levels possibly result from stoichiometry defects and may correspond to Mo^{5+} states. Such states are clearly seen by EPR spectroscopy.[19] One could consider that there are two (or several) types of Mo^{5+} states corresponding to two different neighboring Mo sites. If a $4d$ electron may jump between these two sites, the population of the two levels may depend on the history of the crystal. Similar phenomena have been found on other transition-metal oxides.[20] One may then speculate that these charge defects are coupled to the CDW and that the CDW motion could induce jumps with a well defined frequency proportional to the CDW velocity. It is, however, difficult to decide at present whether the low-frequency fluctuations must really be attributed to this mechanism.

One should note, at this point, that possible diffusion of mobile defects have been previously invoked to account for memory effects in some incommensurate insulating crystals.[21,22] In another context, it is well known in metallurgy that long scale diffusion of impurities and vacancies is responsible for serrated yielding curves obtained during a tensile deformation for example in Al alloys beyond the elastic regime.[23]

Whatever the detailed mechanism is in our case, the memory effects would be related to different possible arrangements of some mobile defects, such as the Mo^{5+} states just described. The incoherent spikes would correspond to a random arrangement of these defects while the coherent ones to some pseudoperiodic arrangement. The role of the cooling process is probably related to a temperature-dependent mobility of these defects, associated to a diffusion time increasing with decreasing temperature. When the crystal is cooled with a zero dc current, the CDW are pinned during the cooling and one freezes a random configuration of these defects. When the cooling current is nonzero and larger than the threshold current during at least part of the cooling, the defects coupled to the CDW (or possibly to CDW domain boundaries) may reach different configurations during the cooling, depending on the cooling rate. It is clear that a fast quenching induces states highly metastable and, therefore, irreversible phenomena, such as pulses, while a slower cooling gives rise to more stable configurations and to coherent oscillations.

One should note two additional points. The role of the temperature-dependent $\vec{q}$ vector in the blue bronze may also be important in relation with time-dependent and hysteresis phenomena. Different $\vec{q}$ vector values should correspond to different configurations for the CDW domains, possibly for discommensurations. The coupling of mobile defects with discommensurations should then be important.

The second point is related to the role of the alkaline metal. Although data reported in this article concern only $Rb_{0.30}MoO_3$, our results obtained for both $K_{0.30}MoO_3$ and $Rb_{0.30}MoO_3$, clearly show that the two compounds differ mainly through the time-dependent, high- and low-frequency phenomena, while the Peierls transition temperature and the order of magnitude of the threshold fields are the same. The origin of these results are presently not clear. One should, however, consider the role of nonstoichiometry related to the alkaline metal concentration and of possible motion for Rb^+ or K^+ ions.

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