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# CHARGE DENSITY WAVE TRANSPORT IN THE PEIERLS DISTORTED STATE OF THE BLUE BRONZES $K_{0.30}MoO_3$ AND $Rb_{0.30}MoO_3$

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**Abstract** Charge density wave transport in  $A_{0.30}MoO_3$  ( $A=K, Rb$ ) is associated with sharp threshold electric fields and noise voltage including both high (10-100 kHz) and low ( $\sim 1$  Hz) frequencies as well as hysteresis and metastability.

## INTRODUCTION

The molybdenum blue bronzes  $A_{0.30}MoO_3$  ( $A=K, Rb$ ) are at 300 K metallic conductors. This is due to the charge transfer from the alkaline metal towards the conduction band which would otherwise be empty (as in  $MoO_3$ ).  $K_{0.30}MoO_3$  has been known for more than 10 years to show a metal to semiconductor transition in the vicinity of 180 K.<sup>1</sup> At 300 K, both the electrical conductivity<sup>2</sup> and the optical reflectivity<sup>3</sup> show anisotropies which establish that this compound is a quasi one dimensional metal. This is well accounted for by the existence in the crystal structure of infinite chains of  $MoO_6$  octahedra along the monoclinic b-axis.<sup>4,5</sup> Further x-ray studies have shown that the metal to semiconductor transition is a Peierls transition towards an incommensurate charge density wave (CDW) state, the b-component of the q-vector being found to be  $q_b = (0.74 \pm 0.01)b^*$  at 110 K.<sup>6</sup> In the semiconducting state, detailed studies of the dc voltage-current characteristics have shown that the conduction is non linear above a sharp threshold electric field  $E_t$ .<sup>7</sup> Other properties characteristic of CDW transport<sup>8</sup>, such as quasiperiodic noise voltage in the frequency range of 10 to 100 kHz have also been previously reported.<sup>9</sup>

## I - STRUCTURAL DATA

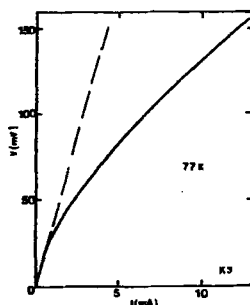
Sato et al. have previously reported that the  $q_b$  component of the wave vector increases with decreasing temperature, down to  $\sim 100$  K and keeps an incommensurate value (0.746) below.<sup>10</sup> Fleming et al. have reported that there is a lock-in transition at  $\sim 100$  K.<sup>11</sup>

Pouget et al.<sup>12</sup> have found by x-ray studies a constant value of  $0.7495 \pm 0.0005$  below 100 K. The low temperature  $q_b$  value very likely depends on the stoichiometry and (or) the purity of the crystals and may be commensurate in the best samples. It should also be noted that the  $q_c$  component may depend on the applied electric field above  $E_t$ , which may indicate some deformation of the CDW.<sup>13</sup>

## II - THRESHOLD BEHAVIOR

Fig. 1 shows typical data for the dc V vs I characteristics. Depending on the sample and for a given sample on the temperature, three types of behaviour for the threshold are found. Most samples show a smooth threshold as shown on Fig. 1a. Some show a switching from the Ohmic regime to the non linear one, with voltage pulses in the Ohmic regime precursor to the switching. Fig 1b is characteristic of a two state system, the crystal "hesitating" for  $E < E_t$  between the two regimes. On Fig. 1c is shown a mixed behaviour with a lower smooth threshold field  $E_{t1}$  and a higher sharp one  $E_{t2}$ . These results

FIGURE 1a dc voltage vs current characteristic of  $K_{0.30}MoO_3$  at 77 K showing a smooth threshold.



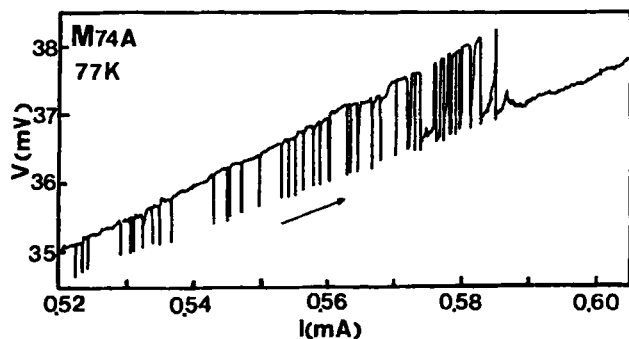


FIGURE 1b V-I curve of  $K_{0.30}MoO_3$  showing precursor pulses and switching.

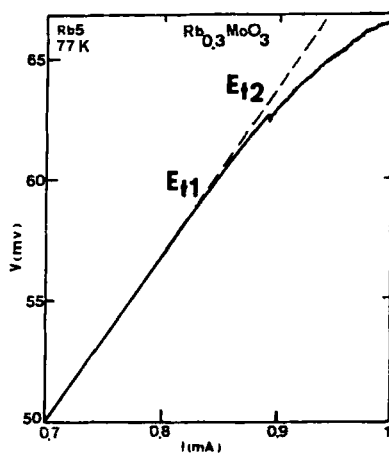


FIGURE 1c V-I curve of  $Rb_{0.30}MoO_3$  showing a smooth threshold  $E_{t1}$  followed by a switching at  $E_{t2}$ .

suggest that the onset of the non linear regime is related to two processes : the nucleation of conducting CDW filaments parallel to the high conductivity axis and the transverse propagation of these filaments. The effect of electron irradiation induced defects on the threshold behavior may corroborate this picture.<sup>14</sup> The existence of conducting CDW "canals" has also been proposed recently by Joos and Murray.<sup>15</sup> In this context, one can define two intrinsic

threshold fields, a nucleation field  $E_t^n$  and a propagation field  $E_t^p$ . Depending on the relative value of  $E_t^n$  and  $E_t^p$ , different behaviours may be expected as found experimentally. The data obtained by Hall and Zettl indicate that in the case of  $\text{NbSe}_3$  both threshold fields have different temperature dependences.<sup>16</sup>

### III - 'HIGH FREQUENCY' CURRENT OSCILLATIONS

Fig. 2a shows the spectral analysis of the noise voltage. Several peaks corresponding to a fundamental and several harmonics are found in the range of 10 to 150 kHz for dc currents larger than the threshold value. As in  $\text{NbSe}_3$  and  $\text{TaS}_3$ , the frequency  $F$  is proportional to the excess CDW current  $J_{\text{CDW}}$  (Fig. 2b), a.c. conductivity

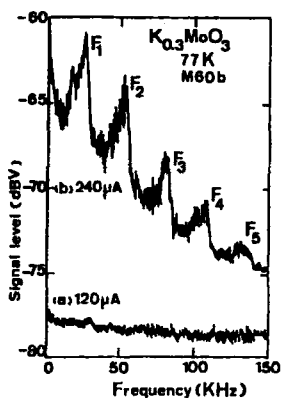


FIGURE 2a Fourier analysis of the narrow band noise of  $\text{K}_{0.3}\text{MoO}_3$  at 77 K. Threshold current : 130  $\mu\text{A}$ .

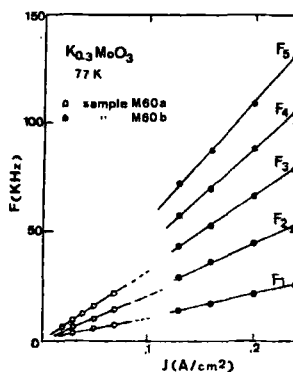


FIGURE 2b Frequencies of the narrow band noise as a function of the excess CDW current at 77 K for two samples of  $\text{K}_{0.3}\text{MoO}_3$ .

measurements are also consistent with this periodic noise.<sup>17</sup>  $F$  is the so-called washboard frequency ;  $F = v_d/\lambda$ , where  $v_d$  is the drift velocity of the CDW and  $\lambda$  the superlattice period.<sup>8</sup> The slope  $F/J_{\text{CDW}} = 1/ne\lambda$  where  $n$  is the concentration of electrons con-

densed in the CDW is therefore expected to be the same for  $\text{K}_{0.30}\text{MoO}_3$  and  $\text{Rb}_{0.30}\text{MoO}_3$ . Our results are inconsistent with this prediction (Fig. 3). The order of magnitude of this slope is also

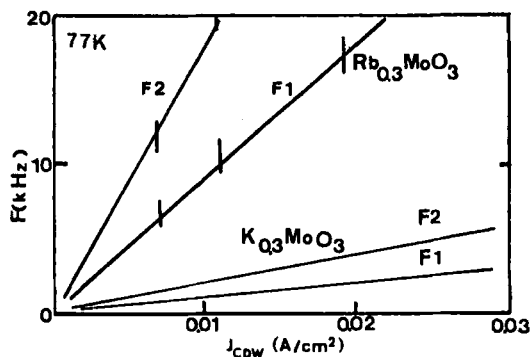


FIGURE 3 Frequencies of the narrow band noise as a function of the excess CDW current at 77 K for  $\text{Rb}_{0.30}\text{MoO}_3$  and  $\text{K}_{0.30}\text{MoO}_3$ .

found to be 20 to 200 times larger than the value obtained by assuming that all the conduction electrons are condensed in the CDW and with  $\lambda \approx 4b$ . These discrepancies might be related to the complicated band structure of the blue bronze, with a doubly orbital degenerate conduction band.<sup>6</sup> Fig. 4 also shows that in  $\text{K}_{0.30}\text{MoO}_3$  this slope is temperature dependent even at temperatures lower than 80 K, where the Peierls gap should be constant.

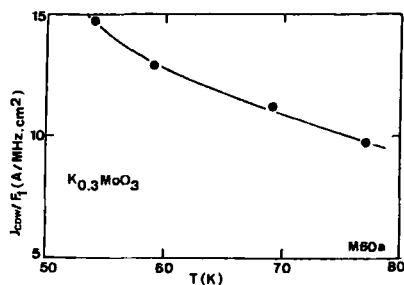
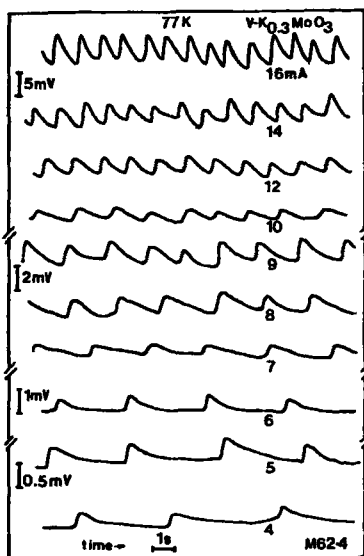


FIGURE 4 Slope  $J_{\text{CDW}}/F_1$  as a function of temperature.

## IV - 'LOW FREQUENCY' PHENOMENA

Very low frequency ( $\sim 1$  Hz) as well as time dependent, hysteresis and memory phenomena are commonly found in the blue bronzes<sup>7,9,18</sup>. They indicate that metastability, very likely related to CDW domains coupled with crystal defects, is predominant in these compounds. Fig. 5 shows typical data for low frequency oscillations found in a V doped  $K_{0.30}MoO_3$  crystal above the threshold. These

FIGURE 5 Voltage oscillations as a function of time for a V-doped  $K_{0.30}MoO_3$  sample quenched from 300 to 77 K with an applied dc current  $I = 5$  mA. The molar concentration of  $V_2O_5$  in the melt was 2 %. The threshold current was 3mA. The measuring current is indicated.



low frequencies  $f$ , are also found to be proportional to the excess CDW current (Fig. 6). The sensitivity of these low frequencies to the presence of impurities clearly indicate that they are the consequence of some interaction of the CDW domains (boundaries) with defects.



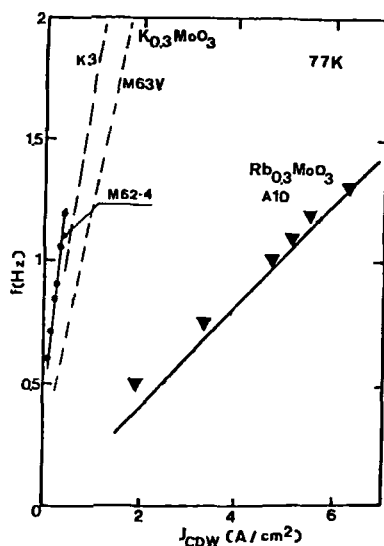


FIGURE 6 Voltage oscillations frequency as a function of excess CDW current in pure and V-doped  $\text{K}_{0.30}\text{MoO}_3$  and in  $\text{Rb}_{0.30}\text{MoO}_3$  quenched from 300 to 77 K with a dc current.

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