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in the CR absorption of inversion electrons in InSb via discontinuities in the CR masses and linewidths near the bulk LO-phonon energy. The resonant self-energy correction of the two-dimensionally confined electrons is enhanced as compared to that of the bulk electrons, indicating an enhanced electron-optical-phonon interaction near the surface of a polar semiconductor.

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## Nonlinear Conductivity and Noise in the Quasi One-Dimensional Blue Bronze K<sub>0.30</sub>MoO<sub>3</sub>

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Nonlinear electrical conductivity associated with a large noise voltage has been observed in the semiconducting charge-density-wave state of the blue bronze  $K_{0.30}MOO_3$ . A well defined and strongly temperature-dependent threshold field for the onset of the nonlinear conductivity is found. Both broadband noise and quasiperiodic noise are detected above the threshold field. These results, including the observation of long relaxation times, are discussed in relation with the current models for charge-density-wave transport.

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Much effort has been devoted these last years to the study of the nonlinear transport properties of two transition-metal trichalcogenides, NbSe<sub>3</sub> (Ref. 1) and TaS<sub>3</sub>.<sup>2</sup> These compounds are quasi one-dimensional metals at room temperature and show Peierls transitions related to chargedensity-wave (CDW) instabilities below. In the CDW state, the conductivity is non-Ohmic above a sharp threshold electric field  $E_t$ . In the nonlinear regime, both broadband and so-called narrow-band noise involving well defined frequencies and their harmonics have been found.<sup>3</sup> These results support a model of a new type of collective transport due to the sliding of the CDW, related to either a depinning<sup>4</sup> or a tunnel $ing^5$  of the CDW. Up to now, the search for similar effects in other classes of compounds had been unsuccessful.

We report now the observation of nonlinear conductivity occurring above sharp threshold fields as well as of broadband and quasiperiodic noise in a transition-metal oxide, the so-called blue bronze  $K_{0.30}MoO_3$ . In addition to properties similar to those of NbSe<sub>3</sub> and TaS<sub>3</sub>, we have observed, close to the threshold field, an intermittent regime of voltage pulses, with a time scale of the order of 1 s, and in all cases time-dependent effects suggesting the importance of metastable states. We propose that these properties are due to the sliding of the CDW under the effect of the

## electric field.

 $K_{0.30}MoO_3$  presents a semiconductor-to-metal transition at  $T_c = 180$  K.<sup>6</sup> It has been shown recently that at room temperature, it is a quasi one-dimensional (1D) metal.<sup>7,8</sup> The 1D properties of  $K_{0.30}MoO_3$  are well accounted for by the presence in the crystal structure<sup>9</sup> of infinite chains of  $MoO_6$  octahedra parallel to the direction of highest conductivity (monoclinic *b* axis). More recently, it has been shown, on the basis of x-ray diffuse scattering, that the transition at 180 K is related to a Peierls distortion.<sup>10</sup> In the semiconducting state, weak satellite peaks are found at  $0a^*$ ,  $0.74b^*$ , and  $0.5c^*$ , corresponding to an incommensurate period along *b*.

Single crystals of the blue bronze have been obtained by the electrolytic reduction of a K<sub>2</sub>MoO<sub>4</sub>-MoO<sub>3</sub> melt. Crystals are platelets of typical size  $5 \times 2 \times 1$  mm<sup>3</sup>, parallel to the (201) cleavage plane, with b as the long direction. The measurements have been performed on cleaved samples with parallel faces and thickness of the order of 100  $\mu$ m, with the standard four-probe configuration, with the dc current parallel to b. The contacts have been made either with silver or gold paste or by evaporating Cr or In; in all cases, the current contacts covered the ends of the crystals; in the case of evaporated contacts, the voltage contacts were 60  $\mu$ m wide. The smallest contact resistances were obtained with evaporated In; in the semiconducting phase and in the explored temperature range, they were at least 1 order of magnitude smaller than the sample resistance. The measurements have been performed either in a conventional-type liquid-helium cryostat using He as an exchange gas or by immersing the sample in liquid nitrogen; the identity of the results obtained at 77 K by both methods showed that there was no self-heating of the samples. The V-I curves were obtained by slowly sweeping a dc current, and recording the voltage measured with a dc digital voltmeter. The noise or pulses generated in the sample were measured across the voltage contacts by means of a 0-35kHz band-pass amplifier and visualized on an oscilloscope screen or recorded on an x-t plotter. The output noise voltage was also detected with a Tektronix 7L5 spectrum analyzer. All the data given in this article have been obtained on the same crystal, but similar results have been found on several samples with contacts of different nature.

Figure 1 shows a typical V-I curve, obtained at 77 K after cooling the sample from above  $T_c$ .



FIG. 1. dc voltage-current curve showing a sharp threshold field  $E_t$  and switching from the Ohmic regime to the non-Ohmic one (distance between voltage contacts, 2 mm;  $E_t = 0.136$  V/cm). Inset: the onset of pulses for field slightly smaller than  $E_t$  and the noise for  $E > E_t$ ; the sweeping time was 5 min for the interval shown in the inset.

The threshold field  $E_t$  is defined by the jump in the measured voltage; the inset shows that noise (intermittent pulses as shown below) appears just below the threshold field; above  $E_{i}$ , noise of higher frequency is detected. One should note that a slow drift of  $E_t$  towards higher values has been observed as a function of time at a given temperature. In all cases the crystals are found at 77 K in the same virgin state after reheating above  $T_{c}$ . We have also observed that some samples show large hysteresis effects although they were not detected on the crystal used for the data reported here. One should mention that hysteresis effects and a sharp jump of the voltage at the threshold value had also been observed recently on NbSe. by Zettl and Gruner.<sup>11</sup>

The threshold field  $E_t$  deduced at increasing temperatures T from either a jump or a kink in the V-I curve is shown in Fig. 2 as a function of T. A maximum is found in the vicinity of 100 K. At a fixed temperature (77 K), when the dc current I, obtained by increasing values, is maintained just below the critical current  $I_t$  corresponding to  $E_t$ , a recording of V versus time tshows, in addition to the dc time-independent voltage, pulses, typically 100 ms long, with a height of the order of 2% of  $V_{dc}$  [Fig. 3(a)]. These pulses occur at well separated intervals (~1 s) and therefore correspond to an intermittent regime; the average time between two pulses increases versus t and this regime vanishes after



FIG. 2. Threshold field  $E_t$  as a function of temperature. Data taken in a He cryostat with He as exchange gas except for the point  $\Delta$  taken with the sample immersed in liquid N<sub>2</sub>.

a time of the order of 10 min, as shown in Fig. 3(b). By a slight increase of  $I(I < I_t)$ , a similar intermittent regime is found again. The typical shape of these pulses is shown in Fig. 3(c). When the dc current reaches  $I_t$ , a steep increase in the noise voltage is found. An analysis of this noise shows that it includes simultaneously broadband noise, intermittent pulses faster than below  $E_t$ , and quasi-periodic noise. Figure 4 shows the results of a spectral analysis of this noise performed at 77 K above 20 Hz, for higher values of I. Discrete frequencies including a fundamental and several harmonics are found in the range of a few kilohertz; the height of the different components decreases with increasing frequency. All frequency components are shifted towards higher values with increasing currents. We have also observed that, under the measurement conditions (T = 77 K), these frequencies are not stable as a function of time; they slowly drift towards smaller values in times of the order of one hour: simultaneously the peaks get broader but the ratios between one frequency and the others are kept constant.

In order to discuss these results, one should first wonder whether they could be accounted for by well-known sources of nonlinearity, switching, and noise in semiconductors. Phenomena such as impact ionization, avalanche breakdown, or Zener breakdown usually involve comparatively large electric fields and no sharp threshold. The Gunn effect could give rise to slightly similar properties, as already pointed out by Fleming<sup>3</sup>; however, the threshold values would be much larger (~1000 V/cm) than in our case. The similarity of our results with those already reported for NbSe<sub>3</sub> and TaS<sub>3</sub> suggests that they cannot be at-



FIG. 3. Intermittent regime found for E slightly smaller than  $E_t$  (I=0.522 mA). (a) The voltage pulses as a function of time. (b) Number of events  $\Delta N$  during a given time interval (10 s) as a function of time, showing the extinction of this regime after a few minutes. (c) Typical shape of a pulse (oscillogram trace).

tributed to a single-particle process but rather to the collective sliding of CDW under electric fields larger than  $E_t$ . Two models have been previously proposed to account for these properties. In the classical model, the CDW is treated as a particle moving in a periodic potential well with an overdamped response.<sup>4,12</sup> In the quantum one, the tunneling of CDW through potential barriers is considered as a Zener-type tunneling



FIG. 4. Output voltage (detected through a spectrum analyzer, 20 Hz-5 MHz) as a function of frequency for different dc currents. (a) Ohmic regime, I = 0.512 mA,  $E < E_t$ . (b) I = 0.571 mA,  $E > E_t$ .

through a CDW gap.<sup>5</sup> It has already been noticed by Zettl and Gruner<sup>11</sup> that both models cannot, without further developments, describe hysteresis, switching, and time-dependent properties. Those phenomena suggest description in terms of coupled domains separated by relatively rigid walls. These domains could possibly be related to discommensurations<sup>13</sup> and the walls considered as charged solitons, pinned by impurities or by the lattice, as proposed by Bak.<sup>14</sup>

One should note that the temperature dependence of the threshold field  $E_t$  (Fig. 2) with a sharp maximum at  $T \simeq 100$  K is different from what has been found in NbSe<sub>3</sub> (Ref. 3) and TaS<sub>3</sub>.<sup>2</sup> It probably involves two competing mechanisms. At high temperatures (100 K < T < 180 K), the decrease of  $E_t$  may follow the decrease of the order parameter (Peierls gap) which vanishes at  $T_c$ . The origin of the steep rise below 100 K is not clear at the present time.

Now, at a fixed temperature in the intermittent regime found for fields just below  $E_t$ , each pulse could correspond to a soliton (or a small number of solitons) passing under a contact. The extinction of this regime as a function of time could be explained by a distribution of potential wells of various depths and by the quenching of the system in the deepest ones after some time. For electric fields larger than  $E_t$ , the periodic response may imply a rather regular lattice of solitons, which would become somewhat more disordered as a function of time. The frequencies found in  $K_{0,30}MoO_3$  are 1 to 2 orders of magnitude smaller than in the trichalcogenides; this could mean that in our case the involved "objects" are comparatively "heavier" and/or the damping coefficient larger. Obviously, further detailed studies, such as the temperature and current dependence of those phenomena, should now be performed. However, at this point, one may notice that, while analogies with the onset of turbulence in hydrodynamics<sup>3</sup> and with the properties of Josephson junctions<sup>11</sup> have already been pointed

out, some other aspects, such as metastability, hysteresis, and long relaxation times, could be compared with the well-known properties of magnetic materials.

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