PHYSICAL REVIEW B VOLUME 37, NUMBER 2 15 JANUARY 1988-I

Coupling between single-particle and collective excitations in a charge-density-wave system: Field dependence of nonlinear conduction in the blue bronze $K_{0.3}MoO_3$

G. Mihály,*† P. Beauchêne, J. Marcus, J. Dumas, and C. Schlenker
Laboratoire d'Etudes des Propriétés Electroniques des Solides, Centre National de la Recherche Scientifique, B. P. 166, 38042 Grenoble Cédex, France
(Received 3 August 1987)

We have investigated nonlinear characteristics of high-quality $K_{0.3}MoO_3$ single crystals in the temperature range of 30–100 K covering eight orders of magnitude in current and more than three decades in voltage. At some temperatures, high-field measurements were extended up to 1000 times the threshold electric field E_T for nonlinear conduction. In the wide field and temperature range of the experiments, the charge-density-wave conductivity follows the empirical form $\sigma_{CDW} \propto \sigma_n (E_T/E)(E/E_T - 1)^a$, where σ_n is the conductivity of normal carriers. Our results suggest that damping of the collective mode arises from dissipative normal currents induced by dynamic deformation of the charge-density wave.

Collective charge transport by means of sliding charge-density wave (CDW) results in nonlinear conduction in several linear chain compounds below the Peierls transition temperature.[1–5] At low electric fields the CDW is prevented from moving by pinning to impurities and normal conductivity characterizes the single-particle excitations of the system. Above the depinning threshold conductivity is strongly enhanced by the field-dependent CDW transport. Despite considerable experimental[6–8] and theoretical[9–12] activity a coherent picture of the CDW damping mechanism is still lacking. Experiments aimed to determine the field dependence of CDW conductivity in $NbSe_3$ (the most investigated material in this respect) were fitted by different analytic forms with different physical meanings.[6,7] A low-temperature divergence of CDW "viscosity" in semiconducting systems, as reported recently by Fleming *et al.*,[8] may well arise from enhanced damping due to normal carrier screening.[10] A thermally activated depinning process[11] has also been suggested, however.

In this Rapid Communication we present results of detailed measurements on the field dependence of sliding charge-density-wave conduction in the potassium blue bronze[13] $K_{0.3}MoO_3$. Our experiments demonstrate the strong coupling between single-particle and collective excitations of the Peierls-Fröhlich system and indicate that damping of CDW motion arises from dissipative normal current induction in the sliding state. These observations favor the screening prediction of Sneddon.[10] Recent low-temperature experiments[14–16] revealing that freezing out of normal carriers results in a different type of sliding conduction with anomanously low damping also call attention to the role of single-particle excitations in the damping mechanism at higher temperatures.

$K_{0.3}MoO_3$ single crystals were grown by standard electrocrystallization. Copper contacts were deposited by electroplating on cleaved surfaces previously cleaned by dilute aqueous solution of NH_3. Gold wires were attached to copper areas by silver paste. We obtained the best copper contacts with a pulsed current electrolysis: approximately 20-mA current pulses of length 10 ms and separation $\geqq 100$ ms were applied 10–20 times for a crystal of usual size. In case of such preparation the contact resistance was negligible even in the metallic phase as it was measured by comparing four- and two-probe configurations.

Most experiments reported in the present paper were performed on crystal A with dimensions of $3.85 \times 0.37 \times 0.066$ mm^3. The homogeneous current injection for this crystal is reflected in the high value of the Ohmic conductivity observed both in the metallic and the semiconducting phase: $\sigma(300\ \text{K}) = 2.5 \times 10^3\ \Omega^{-1}\ \text{cm}^{-1}$ and $\sigma(78\ \text{K}) = 12.5\ \Omega^{-1}\ \text{cm}^{-1}$. Above the threshold electric field the whole crystal cross section participates in sliding CDW conduction as indicated by sharp peaks in the narrow-band noise spectra[14] with temperature-independent frequency per current-density ratio of 11.4 kHz cm^2/A.[17] The high sample quality is reflected in the nonlinear characteristics as well.

At low voltage levels I-V curves were recorded by a continuous method with a constant current configuration. Effects of metastable CDW states were reduced by several field cycles preceeding the first experiment at a given temperature. At higher fields we carried out pulsed experiments with pulse length in the range of 1 μs–100 ms. Large resistances were applied in series with the pulse generator to be close to a current driven arrangement. Curves measured in two- and four-probe configurations coincided when scaled with the contact distance. For technical reasons we preferred two-probe experiments at low temperatures and a four-probe configuration at high temperatures.

Determination of the current-voltage relation corresponding to steady-state values requires a careful analysis of the pulse shape. While at short times the influence of nonexponential polarization current distorts the pulses, for long times it is the resistance decrease due to Joule heating, which may lead to systematic error. Fortunately the characteristic time of polarization effects strongly decreases with increasing field, thus the pulse length could

always be shortened below the heating limit. (Both polarization and heating time scales vary with the temperature as well.) Voltage and current values averaged over several pulses (4–64) were recorded at fixed time delay, t_d, measured from the leading edge of the pulses. With increasing voltage t_d was decreased by decades. Overlapping ranges of I-V curves recorded with different time delays gave an additional check of the measurements. The computer-controlled experimental setup consisted of a TK 2230 digital storage oscilloscope, a HP 214B pulse generator, and TK AM 502 differential amplifiers.

Figure 1 shows the field dependence of the conductivity normalized to the low-field Ohmic value at $T=78$ K. The onset of charge-density-wave conduction results in sharp nonlinearity as shown in the inset. Then the conductivity increases orders of magnitudes and at electric fields of a few V/cm it reaches a metallic value of about 1000 Ω^{-1} cm^{-1}. In this "high field" range $\sigma(E)$ is still not saturated.

In Fig. 2 we plotted the total current as a function of voltage on logorithmic scales at different temperatures. At low voltages straight parts with slope 1 correspond to singe-particle conductivity, σ_n. It shows an activated behavior; $\sigma_n \propto \exp(-\Delta/kT)$, with an activation energy $\Delta=480$ K in the $T=50$–100 K temperature range. The lowest temperature where Ohmic conduction could be clearly observed was $T=48$ K for this crystal. Below this no Ohmic segment can be detected in the I-V curve: The threshold voltage decreases below the sensitivity of the experiment. (The temperature dependence of the threshold field is shown by full circles for sample A in Fig. 3.)

Well above the threshold, where charge-density-wave conduction dominates over single-particle contribution, the current follows a power law as a function of the voltage. The exponent is given by the high-field slope of the curves plotted on logarithmic scales. We observed this high-field power-law dependence over several orders of magnitude in current, especially at low temperatures where the voltage could be increased up to about 1000 times the threshold. The exponent, α, is temperature dependent as shown on Fig. 3.

We emphasize that the strongly damped CDW conduc-

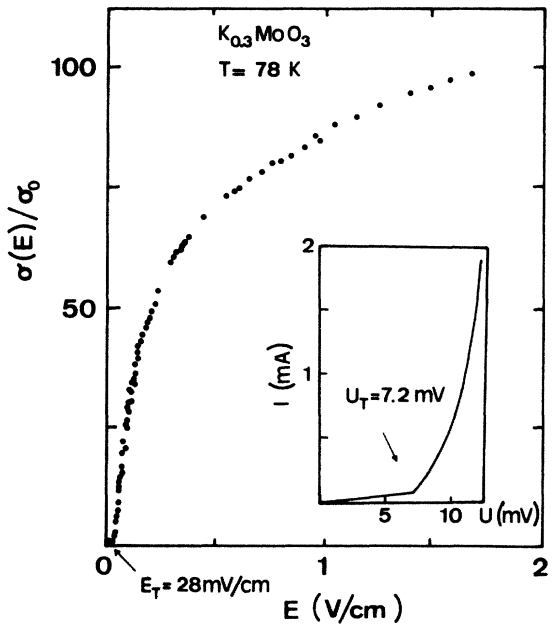

FIG. 1. Nonlinear conductivity measured at $T=78$ K on sample A by four-probe pulsed technique. Data are normalized to the normal conductivity, $\sigma_n=12.5$ Ω^{-1} cm^{-1}. Segment of I-V curve close to the threshold recorded by continous method is enlarged in the inset.

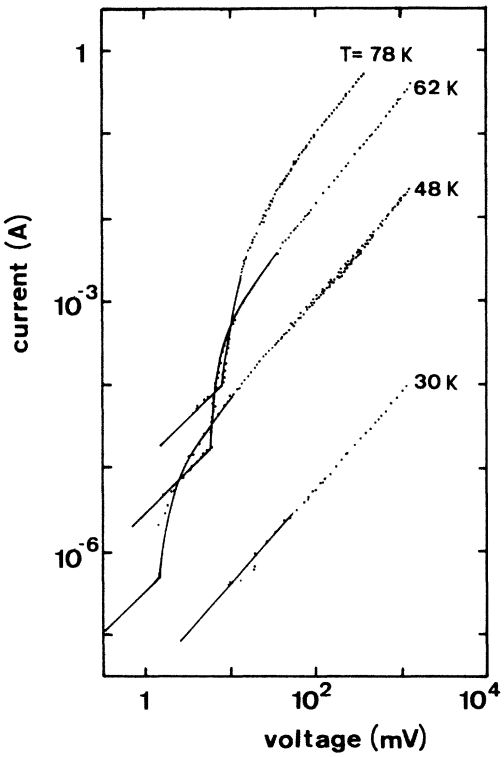

FIG. 2. I-V curves of sample A plotted on logarithmic scales. Continous lines: dc method; dots: pulsed technique.

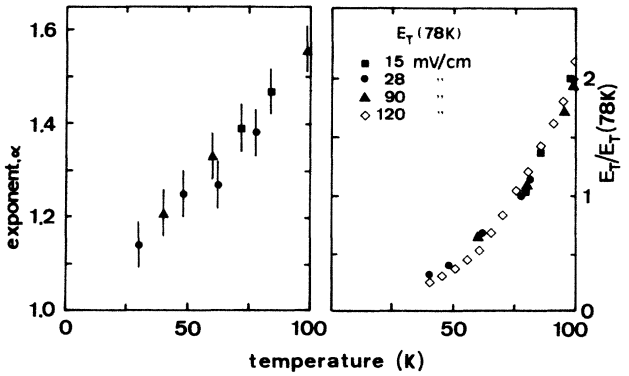

FIG. 3. Temperature dependence of the exponent α and the threshold field E_T. Crystal dimensions: sample A (●), 3.85 ×0.37×0.066 mm^3, B (■), 5×5×0.9 mm^3, C (▲), 3×0.85×0.15, and D (◇), 3.6×0.36×0.06 mm^3. The same samples were investigated in Refs. 14 and 15.

tion is still present at low temperatures (even below 30 K), but it is hard to distinguish from an Ohmic conduction because the exponent tends towards one and simultaneously the threshold goes to zero as the temperature is lowered. Figure 3 shows that this behavior does not depend on the crystal quality; we have found similar temperature dependence of α and E_T for all samples investigated.

The power-law dependence is not only a high-field limit for the charge-density-wave current. If data shown on Fig. 2 are plotted on the same scales by substracting the normal-current component ($I_n = V/R_n$) and the voltage is measured from the threshold, then the I-I_n vs V-V_T plots give straight lines in a much wider range. Figure 4 shows the current density as a function of electric field at $T = 78$ K both on logarithmic and linear scales. The dotted line is the power-law variation with exponent determined from the logarithmic plot. We found that the

$$j_{\mathrm{CDW}} \propto \left(\frac{E}{E_T} - 1\right)^{\alpha} \tag{1}$$

curve gives a satisfactory description for the field dependence from *about 10% above the threshold up to the highest fields of the experiments.* We note that both the normal resistance (which determines the normal current subtraction) and the threshold field are measured values and were not used as free parameters to fit the data to the dotted line.

The same analysis performed at different temperatures gives a simple empirical form for the CDW conductivity:

$$\sigma_{\mathrm{CDW}} = \sigma_n k \frac{E_T}{E}\left(\frac{E}{E_T} - 1\right)^{\alpha}, \tag{2}$$

where k is a temperature-independent constant ($k = 20$ for sample A). Although nonlinear curves of $K_{0.3}MoO_3$ crystals prepared and measured in different laboratories show large scattering, we believe that Eq. (2) is a general expression for σ_{CDW} in this compound. In high-field measurements performed on several samples of different qualities we found that sample dependence appears in the above empirical form only through the proportionality factor k and the absolute value of E_T.

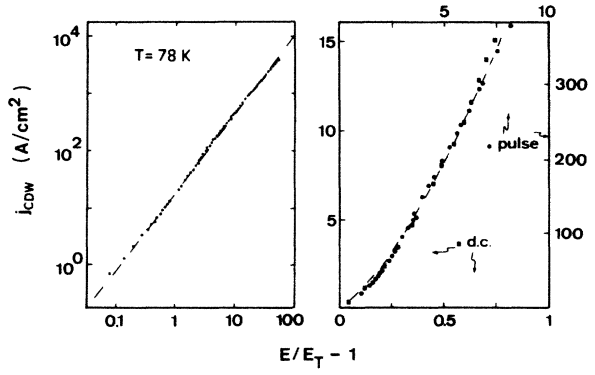

FIG. 4. CDW current density vs electric field at $T = 78$ K (sample A). Dotted line is the power-law dependence with exponent $\alpha = 1.4$.

It is well established that the magnitude of E_T is correlated with the impurity content.[18] We have found, in addition, that the sharpness of nonlinear conduction in most cases is limited by the quality of the contacts.[19] The temperature-independent parameter k in Eq. (2) reflects the homogeneity of CDW current injection; the lower v/j_{CDW} is observed in narrow-band noise study the higher k value is found in Eq. (2). Such a correlation suggests that in case of smooth I-V curves CDW current flows only in a small fraction of the crystal.

CDW current injection is much more sensitive to contact quality than the normal current component. In a two-probe experiment, where contacts on a high-quality sample were destroyed by a chemical reaction, we observed only a factor of 3.5 decrease in the apparent normal conductivity while k dropped nearly two orders of magnitude. Since the threshold voltage did not change, we conclude that variation both in normal and CDW conduction arise from the decrease of active cross section of the contacts.

Due to the single-particle gap in the normal conductivity, σ_{CDW} also seems to be activated when measured at fixed field [see Eq. (2) and Fig. 2]. In the exact temperature dependence however variation of $\alpha(T)$ and $E_T(T)$ cannot be neglected. Differences in activation energies of σ_{CDW} reported in recent papers[8,20,21] may arise from these terms since experiments were performed at different field levels.

One of the most important conclusions of Eq. (2) is that in a wide field and temperature range the collective response of CDW is determined by the single-particle conductivity. It is valid even in the high-field limit where σ_{CDW} exceeds the normal conductivity by orders of magnitudes. Our results strongly suggest that dissipative normal currents induced by dynamic deformations cause the damped nature of the collective mode.

The possibility of increased damping due to coupling of CDW deformation to normal electrons was theoretically predicted by Sneddon.[10] In his model normal currents develop to screen fluctuating charges associated with the CDW deformations and these dissipative currents lead to CDW damping. Such a mechanism is consistent with the fact that the temperature dependence of σ_{CDW} is mainly determined by the normal conductivity. Deviation between the predicted and the experimentally observed field dependence might arise from corrections due to high-frequency terms in σ_n.

The characteristic frequency of single-particle currents induced by dynamic deformation of CDW depends on the drift velocity, v_D. (It is of the order of $\omega \sim v_D/L_c$, where L_c is the length scale of CDW distortions.) We raise the possibility that the observed power law field dependence reflects the frequency dependence of normal conduction in a semiconductor "disordered" by dynamic CDW deformations. Weakly localized midgap states formed around pinning centers[22] can contribute to the normal conductivity at relatively low frequencies. As far as we know, none of the present microscopic theories of CDW damping suggests power-law dependence.

Finally we comment on the behavior close to the threshold. Equation (1) might seem to correspond to a critical

behavior of CDW drift velocity, suggested recently by Fisher.[12] The exponent is, however, temperature dependent and the analytic form characterizes the moderate and high-field range rather than the $E \to E_T$ limit. Although we do not exclude the possibility of a critical behavior with an universal exponent,[20] we note that it should be present only in a narrow range in the vicinity of the threshold, where the experimental situation is greatly complicated by metastable CDW states.

Laboratoire d'Etudes des Propriétés Electroniques des Solides is "Laboratoire associé au Université Scientifique, Technologique et Médicale de Grenoble, Grenoble, France."

---

*Permanent address: Central Research Institute for Physics, 1525 Budapest, POB 49, Hungary.

†Present address: Department of Physics, University of California at Los Angeles, Los Angeles, CA 90024.

[1]For a review, see G. Grüner and A. Zettl, Phys. Rep. **119**, 117 (1985). For collections of current papers on CDW transport, see Refs. 2–5.

[2]*Electronic Properties of Inorganic Quasi-One-Dimensional Materials,* edited by P. Monceau (Reidel, Dordrecht 1985).

[3]*Charge Density Waves in Solids,* edited by Gy. Hutiray and J. Sólyom, Lecture Notes in Physics, Vol. 217 (Springer-Verlag, Berlin, 1985).

[4]*Proceedings of the Yamada Conference 15 on Physics and Chemistry of Quasi-One-Dimensional Conductors,* edited by S. Tanaka and K. Uchinokura [Physica B **143** (1986)].

[5]*Crystal Chemistry and Properties of Materials with Quasi-One-Dimensional Structures,* edited by J. Rouxel (Reidel, Dordrecht, 1986).

[6]R. E. Thorne, J. H. Miller, W. G. Lyons, J. W. Lyding, and J. R. Tucher, Phys. Rev. Lett. **55**, 1006 (1985).

[7]X. J. Zhang and N. P. Ong, Phys. Rev. Lett. **55**, 2919 (1985), and references therein.

[8]R. M. Fleming, R. J. Cava, L. F. Schneemeyer, E. A. Rietman, and R. G. Dunn, Phys. Rev. B **33**, 5450 (1986).

[9]J. Bardeen, Phys. Rev. Lett. **42**, 1498 (1979); **45**, 1978 (1980); **55**, 1010 (1985); P. A. Lee and T. M. Rice, Phys. Rev. B **19**, 3970 (1979); L. Sneddon, M. C. Cross, and D. S. Fisher, Phys. Rev. Lett. **49**, 292 (1982); H. Matsukawa, J. Phys. Soc. Jpn. **56**, 1522 (1987).

[10]L. Sneddon, Phys. Rev. B **29**, 719 (1984).

[11]S. Abe, J. Phys. Soc. Jpn. **56**, 1532 (1987).

[12]D. S. Fisher, Phys. Rev. B **31**, 1396 (1985).

[13]J. Dumas, C. Schlenker, J. Marcus, and R. Buder, Phys. Rev. Lett. **50**, 757 (1983); C. Schlenker and J. Dumas in Ref. 5, p. 135.

[14]G. Mihály and P. Beauchêne, Solid State Commun. **63**, 911 (1987).

[15]G. Mihály, P. Beauchêne, and J. Marcus (unpublished).

[16]T. Chen, W. P. Beyermann, L. Mihály, D. Reagor, B. Alavi, and G. Grüner (unpublished).

[17]The widely accepted value for blue bronze is $v/j_{CDW} = 1/(2pen_\perp) = 12.5$ kHz cm^2/A ($n_\perp$ is the density of conducting chains, $p = 2$ is the band degeneracy).

[18]H. Mutka, S. Bouffard, J. Dumas, and C. Schlenker, J. Phys. (Paris) Lett. **45**, L729 (1984).

[19]P. Beauchêne, J. Dumas, A. Jánossy, J. Marcus, and C. Schlenker, in Ref. 4, p. 126.

[20]A. Jánossy, G. Kriza, S. Pekker, and K. Kamarás, Europhys. Lett. **3**, 1027 (1987).

[21]A. Jánossy, C. Berthier, P. Segransan, and P. Butaud, Phys. Rev. Lett. **59**, 2348 (1987).

[22]I. Tüttö and A. Zawadowski, Phys. Rev. B **32**, 2449 (1985); I. Tüttö (unpublished).