

Thermally Stimulated Depolarization of the Charge-Density Wave in $K_{0.3}MoO_3$

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We have found that $K_{0.3}MoO_3$ acts as a current source on heating after the charge-density wave has been frozen into a metastable state by cooling to 4.2 K in the presence of small electric fields. The current emitted is dependent on the magnitude of the field applied on cooling, reflecting differences in the frozen-in metastable states. The relaxation of the charge-density wave from its metastable state is thermally activated and occurs with a distribution of relaxation times.

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The study of charge-density waves (CDW's) has resulted in the observation of many interesting and often initially surprising physical phenomena.¹ The phenomena are all associated with a CDW which can move in either a dc electric field in excess of a threshold (E_T) or in a small amplitude, low-frequency ac field. The ac response of the CDW for field amplitudes much less than E_T is strongly overdamped. In the case of $K_{0.3}MoO_3$, which has a CDW onset at 180 K,² the frequency-dependent complex conductivity is characteristic of a CDW relaxation with a distribution of relaxation times.³ The dielectric response is described to an excellent approximation by the expression⁴

$$\epsilon(\omega) = \epsilon_{HF} + (\epsilon_0 - \epsilon_{HF})/[1 + (i\omega\tau_0)^{1-\alpha}]^\beta, \quad (1)$$

where τ_0 is the mean relaxation time, ϵ_{HF} is the dielectric constant for $\tau \ll \tau_0$, ϵ_0 is the static dielectric constant for $\tau \gg \tau_0$, and α and β characterize the shape of the distribution of relaxation times. The mean relaxation times for the CDW in $K_{0.3}MoO_3$ are on the order of 10^{-4} to 10^{-7} sec between 60 and 100 K, and follow an Arrhenius behavior in that temperature range. If the thermal activation of the CDW relaxation is maintained to low temperatures, then the CDW in $K_{0.3}MoO_3$ might be expected to "freeze" at temperatures below 20 K, where the relaxation time would be on the order of years.

In this Letter we show that the frozen CDW metastable state does occur in $K_{0.3}MoO_3$ at low temperatures. Moreover, we show that a sample with a frozen polarized metastable state acts as a temperature-dependent current source when heated to temperatures where the relaxation time of the CDW is finite. Currents of approximately 10^{-9} A are generated by a sample of volume approximately 10^{-3} cm³. The CDW is raised to a metastable state by the application of small electric fields (0.03 to 1.0 V/cm, where $E_T = 130$ mV/cm at 77 K) at tem-

peratures where the relaxation times are short. The material is then cooled in the presence of the field to 4.2 K, where the CDW is unable to relax into its equilibrium configuration. The electric field is removed and the current released from the sample on heating is measured with a sensitive ammeter. The current peaks strongly at about 30 K and is present for applied fields both below and above E_T . Current is released on heating when the CDW polarization is thermally relaxed and is neutralized by the flow of electrons in the external circuit.

The sample employed⁵ was a $K_{0.3}MoO_3$ crystal of dimension $0.33 \times 0.14 \times 0.014$ cm³ on a sapphire substrate mounted on a brass block in a He flow cryostat. Two indium leads were applied ultrasonically to freshly cleaved surfaces. Current flow was along the crystallographic b axis. The quality of the leads was tested at 77 K, through the observation of a single arc in the impedance plane [$Z(\omega)$] for frequencies between 5 Hz and 13 MHz.³ The relaxation of the CDW (in its equilibrium state) at 77 K was described by Eq. (1) with $\tau_0 = 5.02 \times 10^{-7}$ sec ($\omega_0/2\pi = 317$ kHz), $\alpha = 0.26$, $\beta = 1.01$, and $\epsilon_0 = 4.31 \times 10^6$ ($\epsilon_{HF} \ll \epsilon_0$). The electric field was applied with a constant voltage source, at 60 K, and the sample was cooled to 4.2 K at 50 K per minute in the presence of the field. After removal of the field, the sample was connected in series with a Keithley 616 electrometer to measure the emitted current (a short circuit), and heated at rates between 5.9 and 1.7 K per minute. The magnitude of the thermally stimulated depolarization (TSD) current and the temperature were recorded on a chart recorder.

Figure 1 presents the TSD spectra for the $K_{0.3}MoO_3$ sample polarized at 1 V/cm and heated at various rates from 4.2 K. The TSD peak is present at low temperatures when the sample has been cooled in the field [Figs. 1(a)–1(c)] but is absent [Fig. 1(d)] when the sample has been cooled in

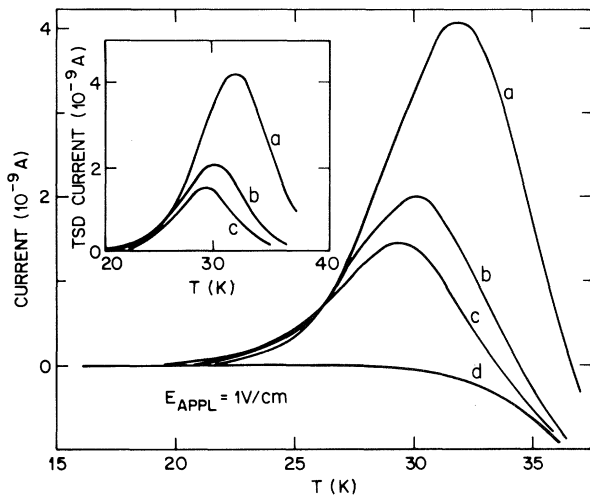


FIG. 1. Current released on heating $K_{0.3}MoO_3$ from 4.2 K after cooling from 60 K in the presence of 1-V/cm electric field with heating rates of (a) 5.9 K/min, (b) 2.5 K/min, and (c) 1.7 K/min. (d) Background current for sample heated in zero field. Inset: total TSD current, background subtracted, for the three heating rates.

zero field. The background, Fig. 1(d), is an apparent current from the feedback loop of the electrometer present because the sample impedance is relatively low at temperatures greater than 32 K. It is also present for a resistor of the same impedance. The actual TSD current is obtained by subtraction of the background, and is shown in Fig. 1 in the inset. The current rises as the polarization begins to relax at about 22 K, reaches a peak at about 30 K, and then drops when the polarization has been exhausted.

As expected for a thermally stimulated current originating from the relaxation of polarization within the sample,⁶ the maximum in the current occurs at higher temperatures at faster heating rates, as the relaxation rate of the polarization is not insignificant compared to the heating rate. For any purely electronic process that might be postulated to occur without relaxation of the CDW, a heating-rate dependence of the TSD current maximum would not occur, because of the relatively short electronic relaxation times (estimated from ρ and ϵ_{HF} to be approximately 10^{-6} sec). The total charge released during the depolarization of the CDW is the same for all heating rates, and is approximately 3.5×10^{-7} C. On the basis of the crystal volume (approximately 5×10^{17} crystallographic unit cells), and estimating 1 electron/cell in the CDW, approximately 5×10^{-6} of the total available charge has been released through the external cir-

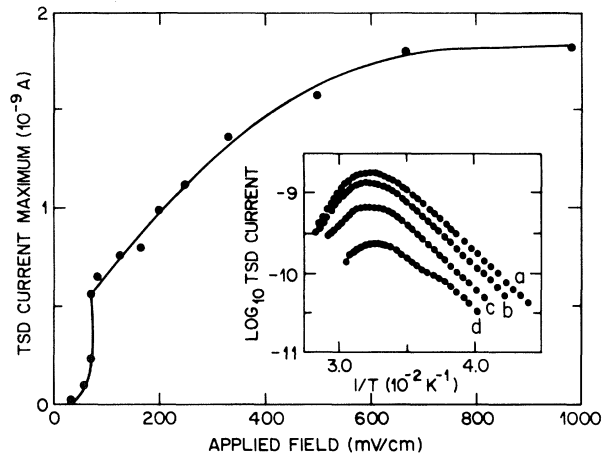


FIG. 2. Maximum TSD current released on heating at 2.4 K/min for sample cooled in applied fields of different magnitudes. Inset, logarithm of the TSD current vs $1/T$ for representative applied fields (a) 1 V/cm, (b) 330 mV/cm, (c) 83 mV/cm, and (d) 70 mV/cm.

cuit during the depolarization. This is consistent with our expectation that polarization relaxation in the interior of the sample will be accommodated by the redistribution of the carriers within the sample itself, as $K_{0.3}MoO_3$ is not an insulator over much of the temperature range of the depolarization. Two experiments were performed that showed that the CDW was indeed "frozen" at 4.2 K. First, after cooling in a field of 1 V/cm to 4.2 K the sample was short circuited externally for 1 h, and then heated. The TSD current was identical to that obtained in the usual heating run which indicated that the polarization could not be relaxed at 4.2 K. Second, a sample cooled in zero field to 4.2 K was placed in a 1-V/cm field for 1 h at 4.2 K. On heating, no TSD current was observed as the CDW was frozen in a nonpolarized state and could not respond to the field.

Figure 2 summarizes the results of experiments in which the sample was cooled in the presence of constant electric fields between 30 and 1000 mV/cm and heated at 2.4 K/min. The maximum value of the TSD current, proportional to the amount of polarization frozen into the sample, is plotted against applied field. The TSD current is present for low applied fields, displays a discontinuous increase at approximately 75 mV/cm, and saturates at applied fields on the order of 1 V/cm. For fields below 75 mV/cm, the CDW was apparently not depinned during cooling. At 77 K, $E_T = 130$ mV/cm (in the dc $I-V$ trace), and indicates a sharp onset of nonlinear conductivity. E_T decreases to

approximately 90 mV/cm at 30 K where the non-linearity is very weak, in agreement with previous measurements.^{2,7} The increase in the maximum released TSD current with increasing applied electric field above 75 mV/cm indicates that the CDW is frozen into a nonunique metastable state of increasing polarization until the applied field is on the order of 1 V/cm. The nonuniqueness of the frozen-in CDW state for fields above 75 mV/cm may be due to either differences in the sliding CDW state at different fields, or differences in the CDW state that occur during the thermal freezing process. The observation of nonzero TSD current for applied fields below 75 mV/cm indicates that metastable CDW states below E_T may also be frozen. The existence of such metastable states below E_T has been indicated by theoretical models^{8,9} and several experimental studies.^{3,10}

The inset in Fig. 2 presents representative TSD current data for three applied fields above and one field below 75 mV/cm. For applied fields in excess of 75 mV/cm [Figs. 2(a)–2(c)] the temperature at which the maximum current is emitted is independent of applied field (for a particular heating rate). Further, the emitted current at low temperatures has an Arrhenius behavior, indicating that the relaxation of the CDW from its metastable to its equilibrium state is thermally activated. The relaxation rate is independent of applied field above 75 mV/cm, with an apparent activation energy of approximately 330 K. Thus, although the CDW is frozen into a nonunique metastable state for fields above 75 mV/cm, its relaxation to the equilibrium state is via the same process. For the relaxation of metastable states frozen in at applied fields below 75 mV/cm the behavior is more complex. The data suggest that an additional relaxation process may be occurring with a maximum TSD current several degrees lower in temperature. All relaxations appear to have the same activation energy. Further, more detailed, TSD measurements for fields below E_T would be necessary to clarify this behavior.

The results of partial TSD experiments are presented in Fig. 3. The sample was cooled in the presence of a field of 1 V/cm and then heated to an intermediate temperature (27.1 K), where a significant amount of current had been released. It was then rapidly cooled, without applying a field, and reheated at the original rate. For a single Debye relaxation (no distribution of relaxation times), and a slowly varying ϵ_0 with temperature, the slope of the logarithm of the TSD current versus $1/T$ at low temperature is simply the activation energy of the relaxation process.⁶ For a depolarization occurring

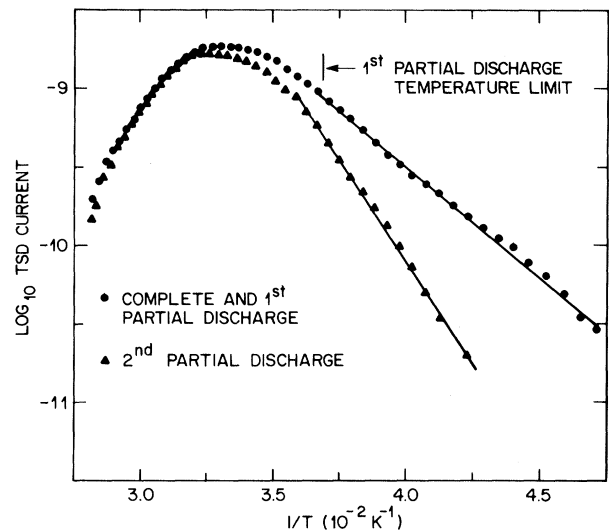


FIG. 3. Logarithm of TSD current vs $1/T$ for sample cooled in presence of a field of 1 V/cm and heated at 2.4 K/min. First partial discharge (circles) on heating from 4.2 to 27.1 K, and second partial discharge (triangles). Straight lines indicate activation energies of 330 K (circles) and 600 K (triangles) respectively.

with a distribution of relaxation times, the slope is less than that for a single relaxation, because of the depolarization at low temperatures of relaxations in the short-time region of the relaxation distribution function. Such short-time relaxations exist for the CDW near its equilibrium configuration in $K_{0.3}MoO_3$.³ The partial TSD measurements indicate that a distribution of relaxation times is also present for relaxation from metastable CDW states. During the first depolarization, the short-time processes discharge preferentially, and the apparent activation energy is 330 K. For the second discharge, short-time processes have already relaxed. The activation energy during the second depolarization has changed dramatically to approximately 600 K, and is the apparent activation energy of the mean relaxation. We expect that the relaxation process of the CDW from its frozen metastable state to its equilibrium state is related but not identical to the relaxation process of the CDW near its equilibrium state (as measured in dielectric-constant measurements). The temperature at which the TSD maximum occurs (~ 30 K) is near that expected from extrapolation of the relaxation time of the CDW near its equilibrium state to a few seconds. The apparent activation energy for relaxation of the CDW from its metastable to equilibrium states (600 K) is on the same order as those mea-

sured³ for ϵ_0 (334 K), τ_0 (829 K), and conductivity (350 K).

Detailed interpretation of the TSD measurements is complicated by the existence and temperature dependence of the distribution of relaxation processes, exponential temperature dependence of ϵ_0 , and a complex microscopic relationship between finite conductivity and relaxation process. Presently available theoretical models provide several alternative explanations for the origin of the polarized CDW state, such as frozen vortices,¹¹ discommensurations,¹² or metastable-phase pinned states,^{8, 13, 14} but none have addressed the thermal behavior of CDW states in a manner which allows a detailed microscopic picture to be applied to the interpretation of our data. This microscopic picture may be elaborated in further experimental studies and theoretical models.

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¹For reviews of the literature see, for instance, N. P. Ong, *Can. J. Phys.* **60**, 757 (1982) or G. Grüner, *Comments Solid State Phys.* **10**, 183 (1983).

²J. Dumas, C. Schlenker, J. Marcus, and R. Buder, *Phys. Rev. Lett.* **50**, 757 (1983).

³R. J. Cava, R. M. Fleming, P. Littlewood, E. A. Rietman, L. F. Schneemeyer, and R. G. Dunn, *Phys. Rev. B* **30**, 3228 (1984).

⁴S. Havriliak and S. Negami, *J. Polym. Sci.* **C14**, 99 (1966).

⁵The identical sample has been employed by R. M. Fleming *et al.* in the study of voltage oscillations in response to a current step, and by R. J. Cava *et al.* in the study of ac signal amplitude dependence of dielectric response; both studies are to be published.

⁶J. van Turnhout, *Thermally Stimulated Discharge of Polymer Electrets* (Elsevier, Amsterdam, 1975).

⁷R. M. Fleming, L. F. Schneemeyer, and D. E. Moncton, to be published.

⁸D. Fisher, *Phys. Rev. Lett.* **50**, 1486 (1983).

⁹P. Littlewood, unpublished.

¹⁰G. Mahály and L. Mihály, *Phys. Rev. Lett.* **52**, 109 (1984).

¹¹P. A. Lee and T. M. Rice, *Phys. Rev. B* **19**, 3970 (1980).

¹²T. M. Rice, S. Whitehouse, and P. Littlewood, *Phys. Rev. B* **24**, 2751 (1981).

¹³P. B. Littlewood and T. M. Rice, *Phys. Rev. Lett.* **48**, 44 (1982).

¹⁴H. Matsukawa and H. Takayama, *Solid State Commun.* **50**, 283 (1984).