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Dependence of the dielectric response of the charge-density wave in $K_{0.3}MoO_3$ on ac signal amplitude

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We have measured the dielectric response of the charge-density wave (CDW) in $K_{0.3}MoO_3$ at 77 K for ac signal amplitudes between 2% and 18% of the threshold field (E_T) for CDW transport. For ac signal levels less than approximately 10% of E_T the intrinsic relaxation of the CDW is probed. For larger ac levels the response is nonlinear as the CDW is driven into metastable states with longer relaxation times. The mean relaxation time increases for large ac signal levels as the proportion of long-time processes increases.

The "blue bronze" $K_{0.3}MoO_3$ displays a phase transition at 181 K below which it has a charge-density wave (CDW) which is pinned to the lattice at threshold fields (E_T) less than a few hundred mV/cm.[1] In a recent study of the frequency-dependent conductivity in the frequency range 5Hz–13MHz, at temperatures between 60–100 K, we found[2] that response of the pinned CDW to the applied signal was that of a single dielectric relaxation process with a distribution of relaxation times. The response was fit to an excellent approximation by a semiempirical generalization of the Debye[3] description of dielectric relaxation which includes a distribution of relaxation times associated with a single process:[4]

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

where $\epsilon(\omega)$ is the frequency-dependent dielectric response, τ_0 the characteristic relaxation time, ϵ_0 the static dielectric constant ($\omega << 1/\tau_0$), ϵ_{HF} the high-frequency dielectric constant ($\omega >> 1/\tau_0$), and α and β characterize the width of the distribution of relaxation times and the skewness, respectively. Equation (1) describes a general relaxation process where $\epsilon(\omega)$ behaves differently for $\omega\tau_0 < 1$ and $\omega\tau_0 > 1$, going as $\epsilon(\omega) \sim \epsilon_0[1-\beta(i\omega\tau_0)^{1-\alpha}]$ and $\epsilon(\omega) \sim \epsilon_0(i\omega\tau_0)^{-\beta(1-\alpha)}$, respectively. The relaxation times we found to be surprisingly long, on the order of 10^{-5}–10^{-7} sec. The mean relaxation time and the static dielectric constant (which is on the order of 10^6–10^7) show Arrhenius temperature dependence in the temperature range studied. Both α and β were also found to be functions of temperature: with decreasing temperature, the distribution of relaxation times became broader; long-time processes became more widely distributed (α increased), but short-time processes were unchanged [$\beta(1-\alpha)=\text{const}$].

The measurement of $\epsilon(\omega)$ for small ac signals probes the relaxation of the CDW about its equilibrium state. If metastable states for the CDW exist below E_T, nonlinear response of the CDW to ac signals which are a significant fraction of E_T can occur as metastable states relatively far from equilibrium are populated in significant amounts. Metastable states below E_T have been demonstrated to exist in several materials[5] and are predicted in theoretical models[6,7] and their influence on the bias-dependent response of the CDW in $K_{0.3}MoO_3$ has been observed by us.[2] In this experiment we have measured $\epsilon(\omega)$ in a crystal[8] of $K_{0.3}MoO_3$ at 77 K for ac signal amplitudes between approximately 2% and 18% of E_T. We have found that nonlinear CDW response becomes significant for ac signal amplitudes on the order of 10% of E_T. The nonlinear response is reflected in an increasing proportion of long-time (low-frequency) relaxations, which effectively increase the mean relaxation time. Short-time (high-frequency) CDW relaxations are not significantly subject to nonlinearity.

The sample (7) was an electrochemically grown platelet of $K_{0.3}MoO_3$ of dimension $0.14\times0.014\times0.33$ cm^3 mounted on a sapphire substrate and immersed in liquid nitrogen. Current flow was along the crystallographic b axis. Ultrasonic indium leads were applied to freshly cleaved crystal surfaces in a two-probe configuration and $\sigma(\omega)$ was measured with an Hewlett Packard 4192A impedance meter at 131 frequencies between 5 Hz and 13 MHz. The ac signal amplitude was measured at 300 KHz, the approximate frequency of the CDW relaxation. We have previously shown that the measurement of $\sigma(\omega)$ at low frequencies in $K_{0.3}MoO_3$ is strongly affected by the quality of the leads, which, when capacitively coupled to the sample, give rise to an additional low-frequency arc in the complex impedance plane.[2] The current sample was selected from a larger batch for study because of the absence of that low-frequency arc. The threshold field for nonlinear conductivity was 130 mV/cm at 77 K, a threshold voltage of 43 mV. The onset of nonlinear conduction was sharp, and the sample displayed "switching"[9] at E_T, but to a lesser degree than the sample previously studied for $\epsilon(\omega)$.[2]

The results of the study are presented in Table I, where the parameters from Eq. (1) are presented as a function of ac signal amplitude. Parameters are obtained by a minimization of an average agreement index in fits to $\epsilon'(\omega)$ and $\epsilon''(\omega)$ obtained from $\sigma(\omega)$ by the relations: $\epsilon'(\omega)=\text{Im}\sigma(\omega)/\omega$ and $\epsilon''(\omega)=[\text{Re}\sigma(\omega)-\sigma_{dc}]/\omega$ where σ_{dc} was obtained from the measured frequency-independent Reσ at low frequencies. Parameters τ_0, ϵ_0, α, and β were varied in the fits to 114$\epsilon'(\omega)$ and $\epsilon''(\omega)$ points. As found previously, ϵ_{HF} is less than 0.5% of ϵ_0 and is, therefore, not included in the fits. Estimates of the errors are ±0.01 for α, between ±0.01 and ±0.02 for β, $\pm2\%$ for ϵ_0, and $\pm3\%$ for τ_0. The agreement values, which are between 1% and 2%, indicate the excellent quality of the fits. Figure 1 presents observed and calculated dielectric constants for small and large ac signals. The fits indicate that the CDW relaxation parameters change by only a few percent for ac signal levels less than approximately 5%–10% of the threshold voltage (V_T). At the highest investigated ac signal level, 18% of V_T, ϵ_0, τ_0, and α have increased by 40%, 20%,

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TABLE I. Parameters describing the relaxation of the charge-density wave in $K_{0.3}MoO_3$ at 77 K as a function of ac signal level.[a]

Signal level V_S (mV)[b]	V_S/V_t[c]	ϵ_0	α	β	$\beta(1-\alpha)$	τ_0 (sec)	$\omega_0/2\pi$ (Hz)	Agreement (R,%)[d]
1.0	0.023	4.31×10^6	0.26	1.01	0.75	5.02×10^{-7}	3.17×10^5	1.3
2.0	0.047	4.35×10^6	0.27	1.02	0.74	5.04×10^{-7}	3.16×10^5	1.6
3.0	0.070	4.47×10^6	0.28	1.04	0.75	5.12×10^{-7}	3.11×10^5	1.4
4.0	0.093	4.57×10^6	0.30	1.07	0.75	5.16×10^{-7}	3.08×10^5	1.3
5.0	0.116	4.84×10^6	0.33	1.12	0.75	5.29×10^{-7}	3.01×10^5	1.2
6.2	0.144	5.20×10^6	0.37	1.19	0.75	5.42×10^{-7}	2.94×10^5	1.4
7.4	0.172	5.60×10^6	0.40	1.27	0.76	5.53×10^{-7}	2.87×10^5	1.7
7.8	0.181	6.04×10^6	0.43	1.31	0.75	6.03×10^{-7}	2.64×10^5	1.9

[a] $\epsilon(\omega)=\epsilon_0/[1+(i\omega\tau_0)^{1-\alpha}]^{\beta}$.

[b] $V=V_S\cos(\omega t)$.

[c] $V_T=43$ mV.

[d] $$R=\frac{\sum_{\omega}[|\epsilon'_{\rm obs}(\omega)-\epsilon'_{\rm calc}(\omega)|+|\epsilon''_{\rm obs}(\omega)-\epsilon''_{\rm calc}(\omega)|]}{\sum_{\omega}[\epsilon'_{\rm obs}(\omega)+\epsilon''_{\rm obs}(\omega)]}\ .$$

and 65%, respectively, while the product $\beta(1-\alpha)$, which describes the short-time relaxations, is independent of signal amplitude. The variation of ϵ_0, τ_0, and α with signal amplitude is presented in Fig. 2. The characteristics of the CDW relaxation at the lowest ac level are comparable but not identical to those measured on the previous sample,[2] where $E_T=113$ mV/cm. At 77 K the characteristic frequency $(\omega_0/2\pi)$ of the relaxation is higher, 317 vs 76 kHz, the static dielectric constant (ϵ_0) somewhat lower, 4.31×10^6 vs 8.47×10^6, the distribution of relaxation times significantly broader $\alpha=0.26$ vs 0.18, and the high-frequency behavior approximately the same, $\beta(1-\alpha)=0.75$ vs 0.71.

The results of this study indicate that for ac signal levels less than approximately 10% of the threshold field, the intrinsic CDW relaxation in the neighborhood of its equilibrium configuration is probed for $K_{0.3}MoO_3$. The nonlinear response of the CDW is dramatically reflected in the change of the distribution of relaxation times and the static dielectric constant as the CDW is displaced further from its equilibrium configuration by larger ac amplitudes. The high-frequency, short-time relaxations are not significantly

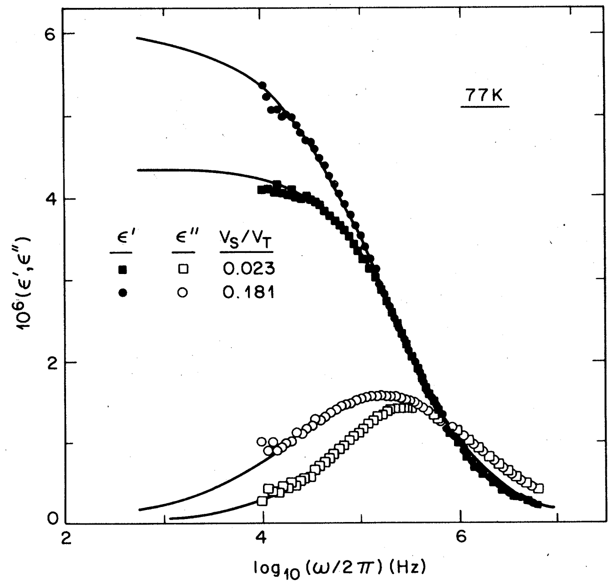

FIG. 1. Observed and calculated real (closed symbols) and imaginary (open symbols) parts of the dielectric constant at 77 K for signal amplitudes of 2% (■) and 18% (●) of the threshold voltage for CDW transport. Solid lines, calculated from Eq. (1) with parameters from Table I.

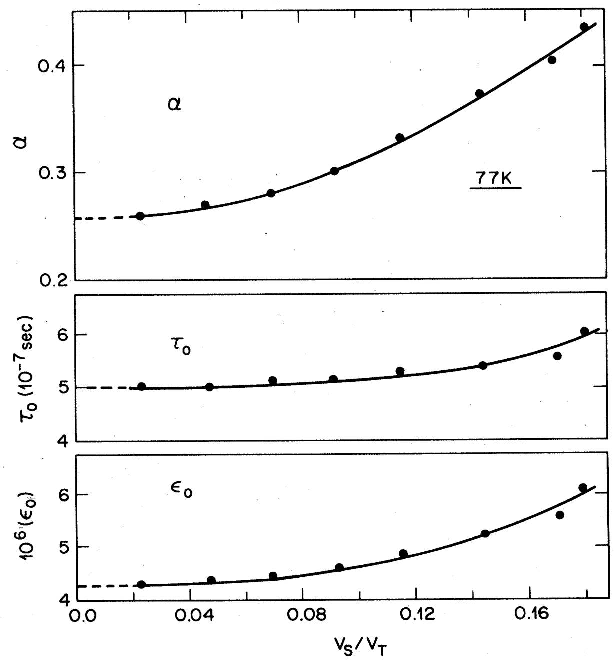

FIG. 2. Variation of shape of relaxation distribution function (α), mean relaxation time (τ_0), and static dielectric constant (ϵ_0) with ac signal amplitude.

nonlinear: they are unaffected by the ac amplitude. [$\beta(1-\alpha)=\text{const}$ in Table I]. This can be seen in the equivalence of the $\epsilon(\omega)$ plots in Fig. 1 for $\omega > \omega_0$. Long-time processes, however, are significanlty nonlinear: as the ac amplitude is increased, more long-time relaxations occur, reflecting relaxations of the CDW from metastable states far from equilibrium, which take longer to relax to the equilibrium configuration. The shift of the mean relaxation time to longer times with increasing ac signal amplitude reflects this increased proportion of long-time processes. The increasing rate of change of α, ϵ_0, and τ_0 with increasing ac signal indicates an increasing nonlinearity due to the availability of a greater number and variety of long relaxation time metastable states for the CDW as its displacement from equilibrium configuration is increased.

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