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ac response of the charge-density-wave mode in $K_{0.3}MoO_3$

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Frequency-dependent conductivity measurements are reported in the charge-density-wave state of $K_{0.3}MoO_3$ in the micrometer- and millimeter-wave spectral range. The high-frequency mode, the response in the MHz range, and the long-time relaxation processes are analyzed in a wide temperature range. The ac response is suggestive of different relaxation times characterizing different excitations of the charge-density wave.

Considerable progress has been made[1-7] in the exploration of the collective-mode dynamics of charge-density waves (CDW's). One of the most important aspects of this problem is the small-amplitude ac response of the condensate, which appears at frequencies well below the single-particle gap E_g. Previous experiments have indicated that the high-frequency mode, which occurs at the micrometer- and millimeter-wave frequencies,[2] and the response which is observed at radio frequencies[3-6] (below about 100 MHz) may have different origins. Moreover, in semiconducting systems such as TaS_3, $(TaSe_4)_2I$, and $K_{0.3}MoO_3$, the characteristic frequency of the low-frequency mode has been found to be strongly temperature dependent,[3] suggesting the coupling of this mode to the normal carriers. In contrast, the high-frequency mode is only weakly temperature dependent. The above qualitative features can be interpreted by fundamentally different microscopic models.[8-11]

In this Rapid Communication we report experiments on the ac excitations of the incommensurate CDW state of $K_{0.3}MoO_3$ (blue bronze).[12] We find a collective-mode response at millimeter-wave frequencies which becomes progressively sharper as the temperature is decreased. The temperature dependence of the high-frequency mode and the low-temperature long-time relaxation processes[7] are compared to experiments at intermediate frequencies.[3-5] Our analysis provides the first complete experimental mapping of the frequency-dependent CDW response over a broad spectral range and in a wide temperature interval. The experiments can be accounted for by various models, and we discuss those features which should be clearly addressed by a quantitative theoretical interpretation.

The high-frequency experiments have been carried out by using either a bridge configuration or cavity perturbation described earlier.[13] The temperature dependence of the conductivity, measured at various micrometer- and millimeter-wave frequencies, is displayed in Fig. 1. For comparison we also show the dc conductivity measured on crystals from the same preparation batch. We have found that at room temperature the conductivity measured at different frequencies is the same as the dc value, within the experimental error of approximately 30%. Curves shown in Fig. 1 are normalized to this value, $\sigma_{dc}(300\ \mathrm{K}) \simeq 2000\ \Omega^{-1}\mathrm{cm}^{-1}$. The opening of the single-particle gap at the Peierls transition temperature, $T_p = 180$ K, is clearly evident from the dc data. In contrast, the conductivity around $\omega_0/2\pi \simeq 100$ GHz continues to increase as the temperature is decreased, in a fashion expected for a metal. The overall frequency dependence suggests a strong peak centered around ω_0, and the resonance becomes progressively narrower as the temperature is reduced. Figures 2 and 3 clearly demonstrate these features.

In Fig. 2 the CDW conductivity, $\sigma'_{CDW}(\omega) = \sigma'_{total}(\omega) - \sigma_{dc}$, is plotted at different temperatures. Data at the lowest frequencies were obtained by Laplace transformation from real-time charging current measurements, as we will discuss later. The high-frequency peak corresponds to the micrometer- and millimeter-wave results shown in Fig. 1. In the intermediate-frequency range we include the data of Hall, Sherwin, and Zettl[4] and of Reagor and Mozurkewich.[5] The curves overlap within a factor of 2 at $T = 77$ K (the common temperature of their experiments), and agree well with the data of Cava *et al.*,[3] which are also shown in the figure.

Figure 2 indicates that the spectrum of the charge-

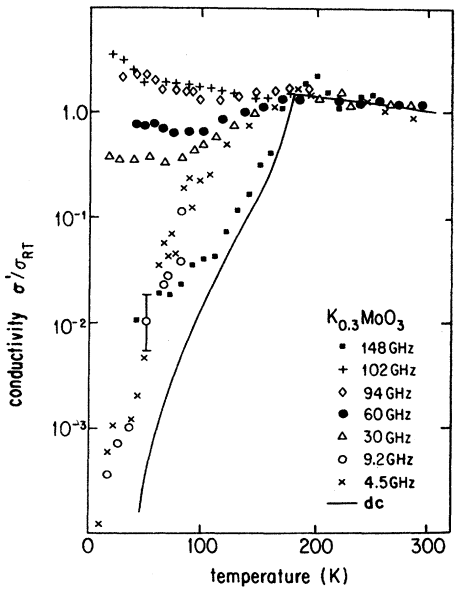

FIG. 1. Temperature dependence of the conductivity of $K_{0.3}MoO_3$ at dc and at various frequencies in the micrometer and millimeter frequency range.

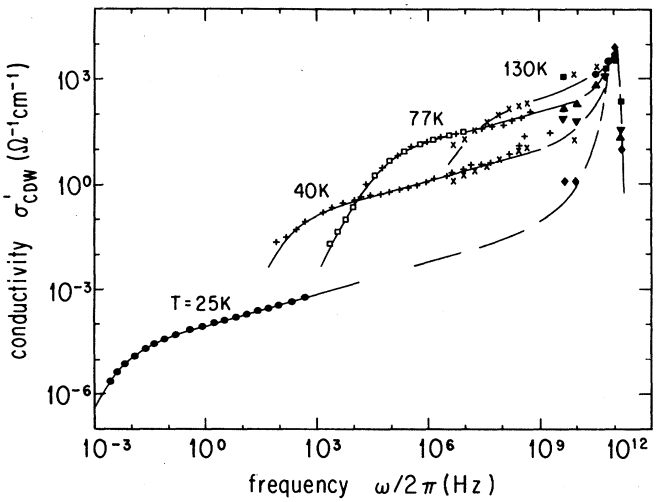

FIG. 2. Frequency dependence of the CDW conductivity at various temperatures. In the intermediate-frequency range, data of Ref. 3 (□), Ref. 4 (+), and Ref. 5 (×) are plotted. The low-frequency data are obtained by Laplace transformation from real-time experiments (Ref. 7). The solid line corresponds to Eq. (3), with $1-n=0.7$, and with τ_n following the temperature dependence of the normal resistivity. The dashed lines are guides to the eye.

density-wave excitations extends over a broad spectral range with considerable dynamics below the GHz frequencies. However, a different representation of the same experimental data reveals that the resonance around $\omega_0/2\pi \simeq 100$ GHz dominates the response. In Fig. 3 $\omega\sigma'_{CDW}(\omega)$ is plotted on logarithmic frequency scales. In this plot the spectrum contains only one narrow peak at ω_0, and no sign of any excitation is apparent at lower frequencies. In this representation the area below the curves corresponds to the oscillator strength:

$$A=\frac{2}{\pi}\int \omega\sigma'(\omega)d(\ln\omega)=\frac{2}{\pi}\int \sigma'(\omega)d\omega .$$

It is evident that most of the oscillator strength, associated with the collective response of the condensate, is due to the high-frequency resonance. The inset of Fig. 3 demonstrates that A is conserved as a function of the temperature, the relatively broad response at 130 K continuously transforms to a narrow, large-amplitude peak. In a simple model, which assumes that the response is that of a harmonic oscillator, the oscillator strength is related to the effective mass of the condensate, $A=n_e e^2/m^*$, and corresponds to a mass enhancement[14] of $m^*/m \simeq 300$ (n_e is the number of electrons condensed into the CDW, m is the free-electron mass). Mass enhancement that is much larger than unity demonstrates the collective nature of the response; the numerical value, however, is only approximate. We note that the narrow peak in $K_{0.3}MoO_3$ corresponds to an *underdamped* resonance, in contrast to $NbSe_3$ and TaS_3 which show an *overdamped* response in the millimeter-wave region.[15]

The high-frequency resonance, which occurs at 100 GHz in $K_{0.3}MoO_3$, is usually associated with the oscillations of the pinned condensate around the equilibrium position. The characteristic relaxation time of this high-frequency mode $1/\tau_{HF} \simeq 50$ GHz around $T=77$ K and τ_{HF} progressively increases as the temperature is lowered. The relaxation process is most probably due to the interaction of the collective mode with phonon or phason excitations, and some of the relevant processes have been examined theoretically.[16] Introducing random pinning leads to a broadened resonance but not to the complex response given in Fig. 2.

The low-frequency part of the spectrum becomes evident in a different representation. Figure 4 shows the imaginary part of the dielectric function, $\epsilon''(\omega)$

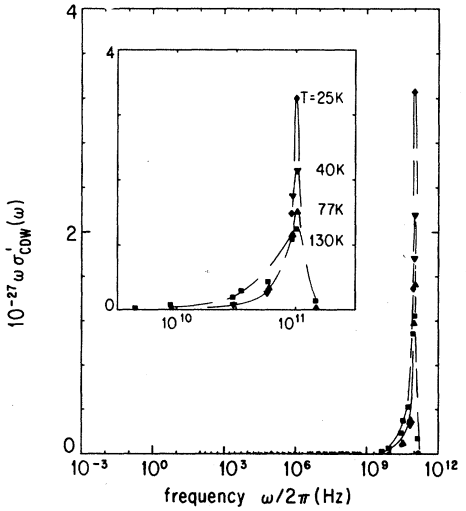

FIG. 3. $\omega\sigma'_{CDW}(\omega)$ vs frequency showing a single peak at ω_0. The inset shows the resonance around 100 GHz. The dashed lines are to guide the eye. (The symbols are the same as in Fig. 2.)

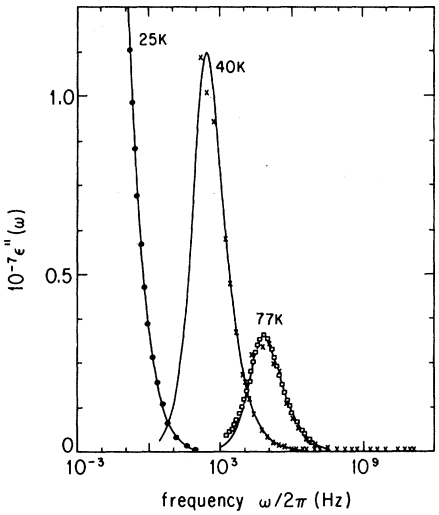

FIG. 4. Imaginary part of the dielectric constant vs frequency. The integrated area gives the static dielectric constant. The solid lines correspond to Eq. (3), with the same parameters as in Fig. 2. (The symbols are the same as in Fig. 2.)

$=4\pi\sigma'(\omega)/\omega$, on logarithmic frequency scales, and this plot emphasizes the low-frequency excitations. The characteristic frequency of ϵ'' dramatically drops with decreasing temperature and the peak shifts from the MHz range to 10^{-2} Hz in the temperature range investigated. According to the Kramers-Kronig relation, the integrated area associated with ϵ'' corresponds to the static dielectric constant:

$$\epsilon'(\omega=0)=\frac{2}{\pi}\int\frac{\epsilon''(\omega)}{\omega}d\omega=\frac{2}{\pi}\int\epsilon''(\omega)d(\ln\omega)\,. \tag{1}$$

Curves shown in Fig. 4 reflect a progressively increasing static dielectric constant. At $T=77$ K, $\epsilon'(\omega=0)=1.1\times10^7$; at 40 K it reaches a value of 4.3×10^7 and the integrated area at 25 K would correspond to $\epsilon'(\omega=0)>10^8$. As the peak of ϵ'' shifts below the experimentally reasonable time scale, the true static value of ϵ' cannot be measured. Figure 4 indicates that an experimental cutoff on the order of 10 s only allows the measurement of about 30% of the static value at $T=25$ K. We found that ϵ_0 continuously increases with decreasing temperature, and it does not saturate[17] or drop[18] at low temperatures.

The low-frequency behavior has been examined by different groups,[3-7] and the strong temperature dependence of the dielectric response has been recognized. The smeared out peak in $\epsilon''(\omega)$, as well as the low-frequency tail in the spectrum, are usually analyzed in terms of phenomenological expressions, derived originally for random systems. One phenomenological description of the results, which has been proposed,[3] is to use the generalized Debye formula of Havriliak and Negami[19]

$$\epsilon(\omega)=\epsilon_\infty+(\epsilon_0-\epsilon_\infty)\frac{1}{[1+(i\omega\tau_m)^{1-\alpha}]^\beta}\,, \tag{2}$$

and to introduce a formal a distribution function[3] of the relaxation times around the mean value τ_m. [Here ϵ_0 and ϵ_∞ are the static and the $\omega\rightarrow\infty$ dielectric constant, α and β are weakly temperature-dependent parameters with $(1-\alpha)\beta=0.7$.] The average relaxation frequency, $\omega_m=1/\tau_m$, was found to be activated,[3] closely following the variation of the normal conductivity. Since the conductivity drops exponentially with decreasing temperature, the relaxation process associated to ω_m slows down rapidly. At low temperatures the same phenomenon may appear as weak relaxation of metastable CDW configurations, a process taking place on the time scale of hours. In fact, the stretched exponential polarization decay,

$$P(t)=P_0\exp[-(t/\tau_n)^{1-n}]\,, \tag{3}$$

observed experimentally[7] in the temperature range of 25–65 K is closely related to the generalized Debye formula applied in the 65–100 K interval.[3] First the characteristic time of this function, τ_n, is also activated and follows the temperature dependence of the normal resistivity.[7] The exponent in the time dependence, $1-n=0.7$, has the same value as $(1-\alpha)\beta$ in Eq. (2). More importantly, we found that the appropriate half-Fourier transformation of Eq. (3),

$$\epsilon(\omega)=\epsilon_\infty+\int p'(t)\exp(i\omega t)dt\,, \tag{4}$$

corresponds to a dielectric function very close to that of Eq. (2) if

$$\tau_n=\tau_m \quad\text{and}\quad 1-n=(1-\alpha)\beta\,. \tag{5}$$

[Here $p'(t)$ is the time derivative of the polarizability, i.e., the charging current following an electric field step of unity.] To show the equivalence of the stretched-exponential relaxation and the generalized Debye formula we have indicated by solid lines the dielectric response corresponding to Eq. (3) in Figs. 2 and 4. The agreement is well within the experimental accuracy. With this fit our aim is not to give a somewhat different phenomenological description of the low-frequency conductivity, but rather to show that the response in the MHz range at 77 K is the same excitation of the condensate as that which appears in glassy behavior on long-time scales below 30 K.[20]

The temperature dependence of τ_m, which follows the variation of the normal conductivity, demonstrates that this relaxation time is governed by screening effects provided by thermally excited electrons. The relevant low-frequency (LF) screening time is given by $\tau_{LF}=\epsilon_0\rho_{dc}$, where ϵ_0 is the background dielectric constant and ρ_{dc} is the dc resistivity. Such screening effects become important when the response of the collective mode involves the gradual buildup of internal deformations, which have to be screened by the uncondensed electrons before further polarization can develop.

Experimental data displayed in Fig. 2 over a broad spectral range clearly demonstrate the complex nature of the frequency-dependent response of the pinned charge-density-wave condensate. On the other hand, Figs. 3 and 4 separate the sharp resonance with a temperature-independent peak frequency at $\omega_0/2\pi\simeq100$ GHz and the smooth response which appears in the MHz range around liquid-nitrogen temperature. Several models attempt to explain the complex behavior we observed, and most of these make a clear distinction between the high-frequency mode, which does not require internal deformations, and the low-frequency response, which proceeds via the development of local charge imbalance.[8-11] Some of the calculations lead to a structure which closely resembles the one displayed in Fig. 2.

Finally, we note that there is a well-defined connection between the structure of $\sigma(\omega)$ and the nonlinear conduction. The strongly damped sliding CDW conduction in the 30–100 K temperature interval is related to the low-frequency response, and obeys the universal relation of $\epsilon_0 E_T=$const. Here E_T is the threshold electric field of the conventional CDW depinning which decreases monotonically with decreasing temperature.[21] Additional evidence that the low-frequency response in $K_{0.3}MoO_3$ is related to the conventional nonlinear conduction was supplied recently by ac-dc interference measurements.[22] In contrast, the narrow peak in the millimeter-wave frequency range is associated with the sharp *I-V* characteristics observed at higher fields and lower temperatures.[14] At liquid-helium temperature, where the low-frequency mode is frozen out, the threshold field is related to the "static" dielectric constant arising solely from the high-frequency mode. The unusually low damping of the sliding mode is consistent with the small dielectric loss in ac response of the pinned mode. We believe that the existence of two basically

different types of CDW conduction is reflected both in the field- and frequency-dependent excitations.

In conclusion, we have examined the frequency-dependent response of the pinned condensate in $K_{0.3}MoO_3$. The response is suggestive of different relaxation effects which progressively separate with decreasing temperature. Internal deformations are important for low-frequency processes, but they do not play a role for the high-frequency response. The various relaxation times which characterize the frequency-dependent charge-density-wave excitations are related to the nonlinear dc response of the condensate.

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