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Low-frequency dielectric response of the charge-density wave in orthorhombic TaS_3

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We have studied the dielectric response of the charge-density wave (CDW) in orthorhombic TaS_3 in the frequency range 5 Hz to 5 MHz as a function of ac signal amplitude, and at temperatures between 73 and 128 K. The CDW response is strongly dependent on signal amplitude for rms signals greater than 10% of the threshold voltage for nonlinear transport. Divergent dielectric constants at low frequency are observed for relatively large signal amplitudes. The small signal response reveals the dramatic disappearance of a low-frequency relaxation between 115 and 65 K.

For a number of anisotropic materials, charge transport by means of a moving charge-density wave (CDW) has been observed under the application of small electric fields.[1] The materials most studied in this class are $K_{0.3}MoO_3$ (the "blue bronze"), $NbSe_3$, and TaS_3. One of the unusual phenomena observed is an enhanced ac conductivity for the CDW-bearing material in the pinned CDW state. The first interpretations of the enhanced ac conductivity were in terms of the relaxation of a rigid CDW with no internal degrees of freedom: i.e., the whole CDW system relaxed in response to an applied field at a single relaxation time.[2] In a careful analysis of the ac conductivity in $K_{0.3}MoO_3$ in terms of complex dielectric constants we showed that the relaxation of the CDW occurs with a distribution of times, indicating that the CDW does not act as a rigid body but in fact displays significant internal degrees of freedom.[3] These degrees of freedom are associated with the population of metastable states as the CDW relaxes to equilibrium, which have been studied by many workers in many experiments.[1]

The dielectric response of a system with a single degree of freedom was first derived by Debye.[4] This description, which is equivalent to an overdamped oscillator formalism[2] is inadequate to describe the response of a system with a distribution of relaxation times. A general empiricial modification of the Debye expression has been developed to describe the relaxation of a system which may have a different distribution of relaxation times for times longer and shorter than the mean time τ_0:[5]

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

where $\epsilon(\omega)$ is the complex dielectric constant at frequency ω, ϵ_0 and ϵ_{HF} are the dielectric constants at frequencies much lower and much higher than the mean frequency of the relaxation, τ_0 is the mean relaxation time ($\omega_0=1/\tau_0$), and the exponents α and β characterize the width and skewness of the distribution of times about τ_0. With this expression one can describe the conventional single relaxation response ($\alpha=0$, $\beta=1$), the symmetrical distribution of relaxation times about $\tau_0(\alpha\neq 0,\ \beta=1)$, and a general, asymmetric distribution ($\alpha\neq 0$, $\beta\neq 1$) of times.

By analyzing ac conductivity data via expression (1) we were able to characterize the dynamics of the CDW relaxation in $K_{0.3}MoO_3$ in some detail.[3,6] We also found that the expression describes very well the enhanced ac conductivity in $NbSe_3$. For othorhombic TaS_3 (CDW onset temperature ~220 K), the $\sigma(\omega)$ data at high temperatures have previously been approximated by the single oscillator description[7] with a relaxation time, at 210 K, for instance, of 9.9×10^{-10} sec ($\omega_0/2\pi=160$ MHz). The data reported for $\sigma(\omega)$ for temperatures less than 120 K, however, cannot be described by expression (1). The detailed report[8] on the data at 120 K found a power-law behavior for $\sigma(\omega)$, $\sigma(\omega)=A(i\omega)^{\alpha}$, with $\alpha=0.87$. This surprising result indicates that both $\epsilon'(\omega)$ and $\epsilon''(\omega)$ diverge at low frequencies, with the same power $[\epsilon(\omega)=\sigma(\omega)/i\omega]$. Whereas a slowly diverging $\epsilon'(\omega)$ might be observed over a limited frequency range for a system obeying expression (1), for a low-frequency relaxation with a broad distribution of times $\epsilon''(\omega)$ will decrease on the low-frequency (long time) side of the characteristic frequency, and is therefore not divergent. A slowly diverging $\epsilon'(\omega)$ at low temperatures in TaS_3 has also been reported by another group,[9] who pointed out the consistency with Eq. (1), but the frequency dependence of $\epsilon''(\omega)$ was not reported. The study on TaS_3 reported here was undertaken in an attempt to attain further insight into the unusual behavior reported for the low-frequency ac conductivity in orthorhombic TaS_3 at low temperatures.

The crystals of orthorhombic TaS_3 were grown by vapor transport from stoichiometric mixtures of the elements, sealed in evacuated quartz tubes and heated in a gradient of 600 °C (charge) to 550 °C(crystals) for two weeks. Relatively long crystals (3–5 mm) were selected for study so that the applied ac signal level could be small with respect to the threshold voltage (V_T) for nonlinear CDW transport. The complex admittance of the samples was measured between 5 Hz and 5 MHz by a Hewlett Packard HP4192A impedance analyzer (at constant voltage) at 20 points per frequency decade under computer control. Dielectric constants were extracted from the conductivity data by the relations $\epsilon'(\omega)=\sigma''\omega$, and $\epsilon''=[\sigma'(\omega)-\sigma_{\mathrm{dc}}]/\omega$, where σ_{dc} was determined at low frequencies where $\sigma'(\omega)$ was independent of ω. Crystals were mounted in two-probe measurement configuration, with current flow parallel to the needle axis. The quality of the contacts was determined by analysis of the data in the impedance plane,[3] and only samples with negligible contact resistance and capacitive coupling at the contacts were employed for further study. Unlike the case for $K_{0.3}MoO_3$, we found silver paint contacts to be of good quality for TaS_3. Samples were mounted on sapphire substrates which were glued to the cold finger of a closed cycle helium refrigerator. Temperature control was better than ±0.05 K.

Two sets of experiments were performed on each of the four TaS_3 crystals studied. In the first set, the dielectric response was studied at fixed temperature as a function of applied ac signal level. The smallest signals which could be applied were on the order of 3% (rms) of V_T. For comparison with the earlier published data on TaS_3, we performed the measurements at 118 K. All four crystals showed the same behavior, that is, that the dielectric response of the CDW was apparently independent of ac signal level for small signals (less than 8–10% of V_T) but was strongly signal dependent for large amplitudes. In the second set of experiments, complex admittance data at a fixed signal level were obtained on heating samples from 73 to 128 K, with a 30-min equilibration time at each temperature prior to data collection. In this temperature range, at small signal levels, we found the dielectric response of the CDW to be described well by Eq. (1). As in the case of $K_{0.3}MoO_3$ we found the characteristic frequency of the relaxation of the CDW to be sample dependent, and the temperature dependence displayed by all samples to be generally the same. In this report we describe in detail the results for one crystal whose distribution of relaxation times was relatively narrow, and whose characteristic frequencies were within our accessible range in the temperature range studied. The threshold field (E_T) of the sample at 120 K was 500 mV/cm. None of the four samples studied displayed measurable narrow-band noise in response to a dc field greater than E_T. Current-voltage hysteresis loops, similar to those resulting from metastable states in $K_{0.3}MoO_3$,[10] were seen in all TaS_3 samples.

The results of the measurements of the dielectric response at a fixed temperature of 118 K as a function of applied ac signal amplitude are summarized in Figs. 1 and 2. The data are presented as a complex conductivity in Fig. 1 to facilitate comparison with results presented in Ref. 8. We find for all crystals studied that for small signal levels the dielectric response is independent of signal level and is consistent with the behavior expected from a CDW relaxation obeying Eq. (1). A dielectric response similar to that reported in Ref. 8 is obtained for the four crystals studied only for relatively large signal amplitudes. The CDW response can be more clearly understood in terms of the complex dielectric constants, which are presented in Fig. 2 for the same data presented in Fig. 1. For small signal levels—for this crystal less than 8% of V_T—the response is characteristic of a CDW relaxation whose distribution of relaxation times is essentially independent of signal amplitude. For larger signals $\epsilon''(\omega)$ is very strongly affected. The behavior is very similar to that we reported for $K_{0.3}MoO_3$ (Ref. 6) which could be described as being due to the occurrence of an increasing proportion of long time relaxations with increasing ac signal level, as the CDW relaxed from a large proportion of metastable states further from its equilibrium configuration in response to the large ac field. Finally, in orthorhombic TaS_3, for large signal levels (but still smaller than V_T), $\epsilon''(\omega)$ becomes apparently divergent, in agreement with the results in Ref. 8. The rate of the apparent divergence of $\epsilon'(\omega)$ and $\epsilon''(\omega)$ is dependent on ac signal amplitude, and we did not generally observe them to diverge with the same power law, although we do observe the divergence of $\epsilon''(\omega)$ to be at first at a lower rate than that of $\epsilon'(\omega)$ and then at a higher rate as signal level is increased beyond the levels presented in Figs. 1 and 2. For comparison with Ref. 8, where at 120 K $\omega\epsilon'(\omega)$ and $\omega\epsilon''(\omega)$ both diverge at $\alpha = 0.87$, we observe, at 118 K for an rms signal amplitude of 33% of V_T, low-frequency divergences of $\omega\epsilon'(\omega)$ and $\omega\epsilon''(\omega)$ of $\alpha \cong 0.90$ and $\alpha \cong 0.94$, respectively. We note that for one of the crystals studied we observed a significant deviation of the dielectric response from the small signal response at a signal level of 6% of V_T.

We found the small signal ac response at low frequencies to be well described by a CDW relaxation behaving according to Eq. (1). We studied the temperature dependence of

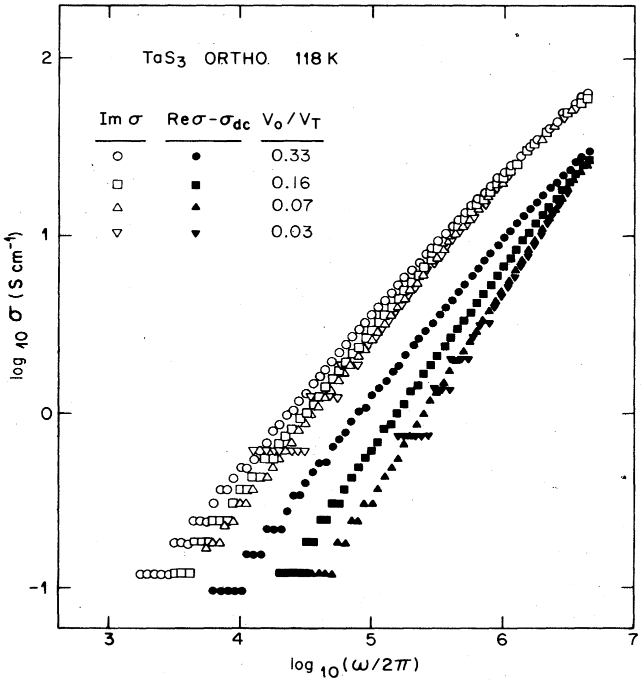

FIG. 1. Low-frequency conductivity of orthorhombic TaS_3 at 118 K as a function of ac signal level (rms). Open symbols imaginary σ; closed symbols real $\sigma - \sigma_{dc}$.

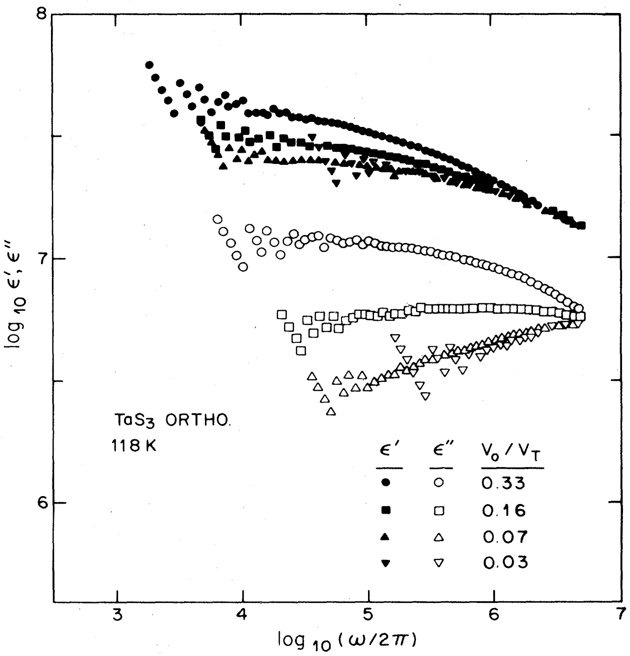

FIG. 2. Low-frequency dielectric response of orthorhombic TaS_3 at 118 K as a function of ac signal level (rms). Open symbols: $\epsilon''(\omega)$, closed symbols: $\epsilon'(\omega)$.

TABLE I. Parameters describing the low-frequency dielectric relaxation in orthorhombic TaS_3.[a]

T (K)	ϵ_0	ϵ_{HF}	α	β	τ_0 (sec)	$\omega_0/2\pi$ (Hz)	Agreement[b] R (%)
128	2.75×10^7	· · ·	0.61	1.35	1.10×10^{-8}	1.45×10^7	2.4
123	2.75×10^7	· · ·	0.58	1.35	1.40×10^{-8}	1.14×10^7	1.2
118	2.78×10^7	· · ·	0.58	1.35	1.90×10^{-8}	8.38×10^6	1.8
113	2.75×10^7	2.5×10^6	0.57	1.35	3.65×10^{-8}	4.36×10^6	2.1
108	2.43×10^7	4.1×10^6	0.50	1.35	5.00×10^{-8}	3.18×10^6	1.6
103	2.21×10^7	4.1×10^6	0.50	1.35	6.10×10^{-8}	2.61×10^6	1.4
93	1.74×10^7	5.2×10^6	0.50	1.35	1.30×10^{-7}	1.22×10^6	1.4
83	1.12×10^7	5.49×10^6	0.50	1.35	2.25×10^{-7}	7.07×10^5	0.6
78	8.67×10^6	5.39×10^6	0.50	1.35	2.40×10^{-7}	6.63×10^5	0.8
73	6.91×10^6	5.32×10^6	0.50	1.35	2.50×10^{-7}	6.37×10^5	0.7

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

[b] $R=\sum_\omega\{[|\epsilon'_{obs}(\omega)-\epsilon'_{calc}(\omega)|+|\epsilon''_{obs}(\omega)-\epsilon''_{calc}(\omega)|]/[\epsilon'_{obs}(\omega)+\epsilon''_{obs}(\omega)]\}$ all fits to 90 ± 5 ϵ',ϵ'' points between 10–30 kHz and 5 MHz.

the dielectric response of the sample characterized in Figs. 1 and 2 at ten temperatures between 73 and 128 K (signal level 7% of V_T at 120 K). The parameters of the fits to Eq. (1) of approximately 90 $\epsilon'(\omega)$ and $\epsilon''(\omega)$ points as a function of temperature are presented in Table I. The low agreement indices indicate fits of good quality. For the three highest temperatures studied the data did not extend to high enough frequencies such that ϵ_{HF} could be determined, and it was excluded from the fits. As we found for doped blue bronzes,[11] the distribution of relaxation times for orthorhombic TaS_3 is very broad, and for this sample, the distribution is insensitive to temperatures below approximately 110 K. The same insensitivity of the distribution of times to temperature was observed in some of the doped bronzes. The distribution of relaxation times was significantly broader in some of the other crystals of orthorhombic TaS_3 which we studied. The characteristic frequencies which we observe for the CDW relaxation in TaS_3 are significantly higher than those for the pure blue bronze in the same temperature range but are comparable to those found for some of the doped bronzes. The high static dielectric constants $\epsilon_0\sim10^7$ are similar to those observed for the blue bronzes and $NbSe_3$. Examples of the data at three representative temperatures and the calculated dielectric constants from fits to Eq. (1) are presented in Fig. 3.

The dielectric relaxation at low frequencies in orthorhombic TaS_3 shows some very interesting behavior in the temperature range studied. The behavior is best illustrated by considering the mean relaxation time τ_0 and the strength of the dielectric relaxation $\epsilon_0-\epsilon_{HF}$ as a function of temperature (Fig. 4). At the highest temperatures, between approximately 130 and 100 K, the relaxation time is thermally activated, as we have observed in the blue bronze, with an activation energy of approximately 400 K. At low temperatures, however, the relaxation time is apparently saturating

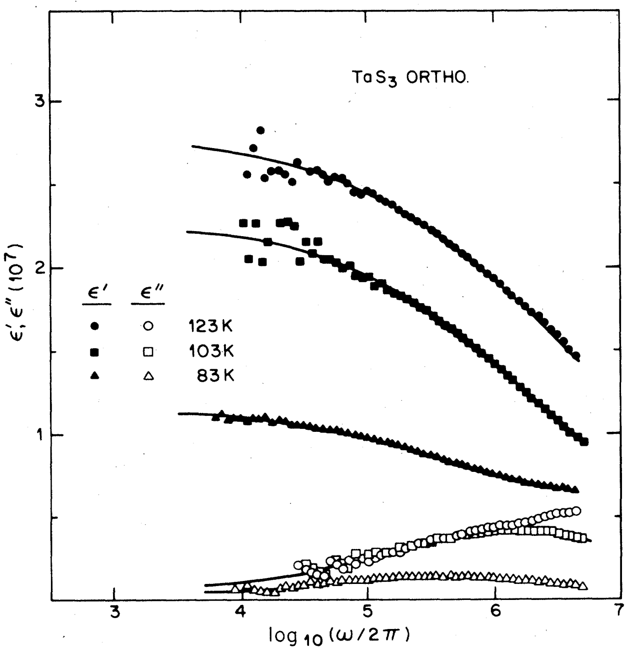

FIG. 3. Low-frequency dielectric response of orthorhombic TaS_3 at three representative temperatures. Solid lines are from fits of Eq. (1) to the data.

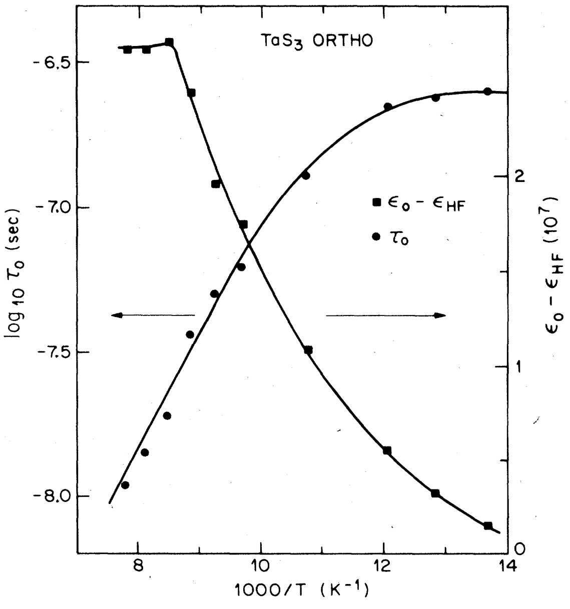

FIG. 4. Temperature dependence of the logarithm of the mean relaxation time τ_0, and the dielectric strength of the low-frequency relaxation $\epsilon_0-\epsilon_{HF}$ in orthorhombic TaS_3 between 128 and 73 K.

to a maximum value of about 2.5×10^{-7} sec. In the same temperature interval there is a dramatic change in the strength of the relaxation. It is approximately constant from 128 to 118 K but then drops quickly until the relaxation has almost completely disappeared by 75 K. At the rate of decrease shown in Fig. 4 we expect the low-frequency relaxation to be completely gone by 65 K. This behavior is also clearly illustrated in Fig. 3. Although the low-frequency relaxation disappears, there remains a large high-frequency dielectric constant ($\epsilon_{\mathrm{HF}}\approx5.3\times10^{6}$ at 73 K) which must be due to an additional high oscillator strength process which should relax at higher frequencies. This higher-frequency process, reflected through ϵ_{HF}, is apparently beginning to decrease in oscillator strength as the temperature is lowered from approximately 80 K.

As we have also found for $K_{0.3}MoO_3$, the low-frequency relaxation of the CDW in orthorhombic TaS_3 is strongly dependent on ac signal amplitude for applied signals greater than approximately 10% of V_T. For the four samples of TaS_3 we studied at 118 K, $\epsilon''(\omega)$ shows divergence at low frequencies for applied signals larger than 25%–35% of V_T. The dependence of the CDW dielectric response on signal amplitude is likely to be due to the occurrence of metastable states in the CDW configuration as it relaxes to equilibrium. Even for very low ac signal amplitudes the observed distribution of relaxation times, as obtained by fits to Eq. (1), is likely to be due to a distribution of metastable CDW configurations very near in energy to the equilibrium configuration. We have now observed similar behavior for both $K_{0.3}MoO_3$ and orthorhombic TaS_3: the proportion of long time relaxations from metastable states increases as the driving of the CDW from its equilibrium configuration by large ac signals increases. For large enough signals, there are a large number of very long time relaxations present and $\epsilon'(\omega)$ and $\epsilon''(\omega)$ are divergent at low frequencies; e.g., the CDW polarization appears to be frozen. In fact, a step-function-type distribution of relaxation times which is large down to $\omega=0$ ($\tau=\infty$) has been proposed to account for the divergences in $\epsilon'(\omega)$ and $\epsilon''(\omega)$ in TaS_3 observed in Ref. 8.[12] Our data suggest that this is a nonequilibrium set of relaxations present due to the perturbation of the CDW far from equilibrium. This nonequilibrium dielectric response can apparently occur for signals as low as 10% of V_T.[8] Results similar to ours on the signal dependence of the dielectric response have also recently been observed in orthorhombic TaS_3 by another group,[13] and our small signal data are in good agreement with another recent report.[14]

The dramatic disappearance of the low-frequency CDW relaxation between approximately 115 and 65 K is of interest as it occurs in a temperature interval where several other properties have been reported to change significantly for orthorhombic TaS_3. Thermopower measurements[15,16] have found an increasing thermopower in the CDW state on cooling from onset ($\sim$220 K) which reaches a maximum value at approximately 105 K, and then decreases quickly to become negative at temperatures below approximately 65 K. A dramatic anomoly in the stress dependence of the resistance of TaS_3 (in the pinned state) disappears on cooling below 66 K.[17] Further, hysteresis has been reported in the behavior of the dielectric constant,[14] thermoelectric power,[15] and the dc resistivity[18] on thermal cycling between approximately 60 and 200 K. The threshold field for nonlinear conductivity increases below 100 K,[18,19] and the nonlinear CDW current for fields greater than E_T decreases drastically as the temperature is decreased below 130–120 K.[20,21] Electron diffraction measurements suggest that the CDW locks into commensurate values of wavelength in the vicinity of 80 K along the crystallographic b^* and c^* directions, but its characteristics along a^* have apparently not yet been determined.[22] It seems to us that the most straightforward interpretation of the low-frequency relaxation we have observed in orthorhombic TaS_3 is that it is due to the relaxation of discommensurations. The static dielectric constant due to the relaxation of the discommensurations increases with decreasing temperature in a thermally activated manner between 220 and approximately 120 K (Ref. 14) when it then begins to drop. The disappearance of the relaxation between 120 and 65 K suggests that the number of discommensurations is decreasing and finally disappearing as temperature is lowered. This suggests to us, as it has suggested to others, that the nonlinear current in TaS_3 is carried primarily by discommensurations in the temperature interval between 120 and 70 K.

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