

# Two-stage dielectric response of charge density waves in TaS<sub>3</sub>

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The kinetics of the polarization of charge density waves has been studied in the quasi-1D conductor TaS<sub>3</sub> over the temperature interval 1.6–20 K and over the time interval from 5  $\mu$ s to 100 s. When a voltage step is applied, the charge density waves become polarized because of thermal activation. There are two clearly defined stages, associated with a contribution from strong-pinning centers (this is the fast stage) and with a polarization of the charge density waves in the case of a weak pinning (the slow stage). © 1995 American Institute of Physics.

The low-temperature properties of quasi-1D conductors have attracted increased interest in recent years because several anomalies have been observed in the kinetics of charge density waves (CDWs).<sup>1</sup> The most interesting temperature region in TaS<sub>3</sub> is below 20 K. Here the activation energy of the linear conductivity decreases, and the current–voltage characteristic changes shape. The idea of a soliton mechanism for conductivity is widely used in interpreting these anomalies.<sup>2–4</sup> It was recently shown that at least certain features of the low-temperature conductivity of CDWs can be explained in terms of a creep of these waves,<sup>5</sup> i.e., without invoking any exotic conductivity mechanisms such as the soliton mechanism. Here the most interesting temperature region is specifically the low-temperature region,  $T \leq 10$ –20 K, in which the activation energy for the nonlinear conductivity has been observed to drop to zero in thin TaS<sub>3</sub> samples. This result has been interpreted as a transition from a thermally activated creep to a quantum-mechanical creep of CDWs.<sup>5</sup> It is natural to suggest that quantum effects may also be responsible for the low-temperature anomalies in samples of ordinary dimensions<sup>2)</sup> (Refs. 6 and 7).

The conductivity of quasi-1D conductors at low temperatures is vanishingly low, and information about the mechanisms for the motion of CDWs can conveniently be obtained by studying their dielectric response. For example, it has been observed<sup>8</sup> that the response to a stepped change in voltage in K<sub>0.3</sub>MoO<sub>3</sub> at comparatively high temperatures,  $T = 25$ –60 K, is described by an extended exponential function

$$Q(T, t) = Q_0 \left( 1 - \exp \left[ - \left( \frac{t}{t_0(T)} \right)^\alpha \right] \right), \quad (1)$$

where  $t_0 \propto \exp(W/T)$ ,  $Q$  is the polarization charge,  $t$  is the time,  $W$  is the activation energy, and  $\alpha \approx 0.3$ . A frequency-dependent maximum in the dielectric constant has been

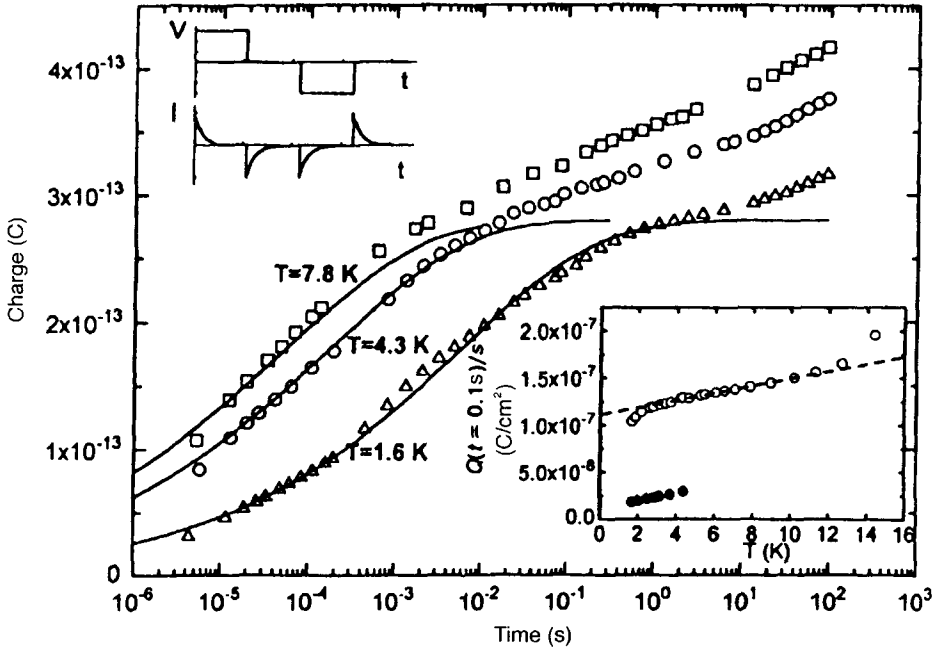


FIG. 1. Response of a pure TaS<sub>3</sub> sample to a single voltage step at various temperatures. Solid curves—Extended exponential dependence [Eq. (1)] with  $\alpha=0.27$ ,  $t_0=\tau \exp(W/T)$ ,  $\tau=1.5 \times 10^{-5}$  s and  $W=10$  K. The inset at the top is a schematic diagram of the train of voltage pulses,  $V(t)$ , and of the corresponding response of the sample,  $I(t)$ . The inset at the bottom shows the temperature dependence of the polarization ( $Q/s$ ) for a pure sample ( $\circ$ ) and a doped sample ( $\bullet$ ). The dashed line corresponds to Eq. (2) with  $\chi=2$ .

observed<sup>9</sup> in TaS<sub>3</sub> at  $T=20\text{--}40$  K. The maximum has been linked with a transition to a glass state. The kinetics of the polarization of CDWs at  $T \leq 4.2$  K was not studied.

In this letter we are reporting a study of the low-temperature kinetics of the polarization of TaS<sub>3</sub> over the time interval from  $5 \mu\text{s}$  to 100 s in the temperature interval 1.6–20 K. The results of this study indicate that there is a *collective* polarization mechanism and that the contribution of *thermal* fluctuations is predominant in the time and temperature intervals studied. The two-stage nature of the polarization relaxation is interpreted as evidence of a transition from strong pinning (short times, low temperatures) to weak pinning (long times, high temperatures).

We studied the dielectric response of TaS<sub>3</sub> samples which arises after the application of a voltage step. For this purpose we measured the polarization current  $I$  as a function of the time  $t$  during the application of an alternating-sign periodic train of voltage pulses (see the inset in Fig. 1). The difference between pairs of  $I(t)$  curves measured at opposite polarities was calculated. The polarization charge  $Q(t)$  was found by integrating the current  $I(t)$ , and it was averaged over a large number of pulses (10–200). Comparing the  $Q(t)$  curves obtained at a zero voltage and a nonzero voltage across the sample, and for various pulse lengths, we can estimate corrections to the polarization charge due to the current flow (at  $V \neq 0$ ) and due to the different histories.<sup>3)</sup> We can then reconstruct the

response of the sample to a *single* voltage step. The lower limit on the time interval of the measurements was set by the time constant of the rf amplifying electrometer (1  $\mu$ s); the upper limit was set by the low-frequency noise of the measurement apparatus and the amplifying electrometer (on the order of  $10^{-16}$  A). An upper limit was imposed on the temperature of the measurements by the onset of a shot noise due to an increase in the conductivity of the samples.

The measurements were carried out using TaS<sub>3</sub> samples with a cross-sectional area  $s = 200\text{--}1500 \mu\text{m}^2$  and a length of 1.2–6 mm. We studied the polarization kinetics in samples of two types, which we call “pure” and “doped.” In the pure samples, the threshold field for the onset of the nonlinear conductivity is  $E_T < 1 \text{ V/cm}$  ( $T = 77 \text{ K}$ ), while that for the doped samples is about 10 V/cm. These figures corresponds to relative impurity concentrations  $< 10^{-5}$  and  $\sim 10^{-3}$ , respectively.

It was established that the magnitude of the polarization charge is an approximately linear function of the amplitude of the voltage step,  $V$ , up to  $V \approx V^*$ , where  $V^*$  is the voltage at which a measurable nonlinear current arises. Nevertheless, in an effort to reduce the error due to the slight nonlinearity of the response, we carried out the measurements at the same pulse amplitude,  $V \leq 0.3V^*$ , at all temperatures.

Figure 1 shows a typical set of  $Q(t)$  curves for one of the pure TaS<sub>3</sub> samples. The polarization relaxation is nonexponential; it continues to the longest times at which measurements were carried out. Two regions can be distinguished on the  $Q(t)$  curves. The first has a comparatively rapid increase in the polarization with the time and a strong temperature dependence of  $Q$  (this is the fast relaxation). In the second region, the time dependence of the polarization charge is approximately logarithmic,  $Q \propto \ln(t)$ , and the temperature dependence of the charge is weak (this is the slow relaxation). As the temperature is lowered, the boundary between the fast and slow relaxation stages shifts to longer times. At all temperatures, however, the region  $Q \leq 2.5 \times 10^{-13} \text{ C}$  belongs to the region of slow relaxation, and  $Q \geq 2.8 \times 10^{-13} \text{ C}$  to the region of fast relaxation.

The inset at the bottom in Fig. 1 shows the temperature dependence of the charge reached by the time 0.1 s for pure and doped TaS<sub>3</sub> samples. The region of slow relaxation corresponds to an approximately linear  $Q(T)$  dependence. The polarization (i.e.,  $Q/s$ ) of the doped sample is nearly an order of magnitude lower than that of the pure sample.

For each value of  $Q$  we can find a set of values of the temperatures and the times at which a given polarization is reached. Figure 2 shows curves of  $\ln t(Q)$  versus  $1/T$  plotted in this manner. The curves are approximately activation laws,  $t(Q) = t_0 \exp(W/T)$ , where  $t_0^{-1}$  represents a frequency of attempts, and  $W = 10\text{--}30 \text{ K}$  represents an effective energy barrier. The frequency of attempts for the slow-relaxation region ( $t_0 \sim 10^{-3} \text{ s}$ ) turns out to be a macroscopic quantity, while in the region of fast relaxation it decreases exponentially rapidly with decreasing  $Q$ . In the region of slow relaxation, an energy barrier thus corresponds to each value of  $Q$ , while the frequency of attempts plays the corresponding role in the fast-relaxation region.

Attempts at polarization relaxation using *macroscopic* frequencies are incompatible with the proposition that the low-temperature properties of TaS<sub>3</sub> are governed by uncorrelated hops of *microscopic* excitations other than electrons (holes) or of phase solitons carrying twice the elementary charge. The most natural assumption is that the CDW itself

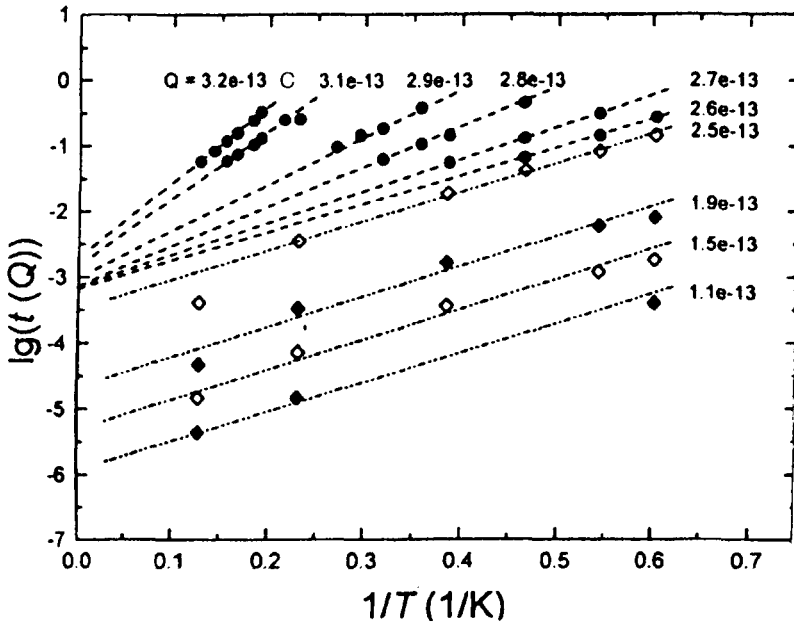


FIG. 2. The time at which a given polarization charge is reached versus the reciprocal temperature.  $\diamond$ —Fast stage;  $\bullet$ —slow stage.

plays the role of the strongly correlated system which is responsible for the polarization and that the observed relaxation is a consequence of a thermally activated *creep* of CDWs.<sup>4)</sup>

The experimental  $Q(T, t)$  dependence in the fast-relaxation region can be described approximately by an extended exponential law as in (1) (the solid lines in Fig. 1). The basic discrepancy stems from the slight temperature dependence of the slope of the curve of  $\ln[t(Q)]$  versus  $1/T$  (Fig. 2). Furthermore, in contrast with the case of blue bronze at high temperatures,<sup>8</sup> in which case the relaxation is observed to stop at  $t = t_{\max} \sim t_0$ , in the case at hand, of TaS<sub>3</sub>, the relaxation process continues even at  $t \gg t_{\max}$ , becoming logarithmic (or an approximately logarithmic power law). In the slow-relaxation region we observe a correspondence between the polarization and the energy barrier  $W$  which must be overcome in order to achieve this polarization. A correspondence of this type is characteristic of disordered systems. It is usually linked with a progressive increase in the size of the polarization regions,  $L$ , which leads to  $W \propto L^\chi$ , where  $1 < \chi < 2$  in the case of 3D pinning.<sup>10</sup> Taking  $Q \propto EL^2$ , we find<sup>10</sup>

$$Q(t) = Q_0 \left( 1 + \frac{T}{T^*} \ln \frac{t}{t_0} \right)^{2\chi}, \quad (2)$$

where  $T^*$  is a typical size of the energy barriers.<sup>5)</sup> In principle, the experimental data (Figs. 1 and 2) in the slow-relaxation region correspond to Eq. (2) with  $\chi = 10$ . In this case, however, the discrepancy between the expected value  $1 \leq \chi \leq 2$  and the value  $\chi = 10$  estimated from the experimental data is nearly an order of magnitude. We can

achieve a reasonable agreement between the experimental results and Eq. (2) by assuming that a logarithmic relaxation begins in the pure samples only after the system has reached a certain initial polarization. The case  $\chi=2$  (the dashed line in the lower inset in Fig. 1) corresponds to an initial polarization of  $2.2 \times 10^{-13}$  C and a value  $Q/s = 1.1 \times 10^{-7}$  C/cm<sup>2</sup>.

In the doped samples we observed only a region of slow (logarithmic) relaxation, which can be described by Eq. (2) with<sup>5)</sup>  $T^* = 10$  K,  $t_0 = 3$  ms, and  $2/\chi \approx 1$ . The value  $\chi \approx 2$  for the doped samples is thus close to the expected value<sup>10</sup>  $1 < \chi < 2$ .

The models of Refs. 10 and 11 have only a single relaxation stage, which can be described by either a logarithmic law or an extended exponential law, but not by the two simultaneously. We therefore believe that *two different* thermally activated relaxation processes occur in succession at low temperatures in TaS<sub>3</sub>. From our point of view, the key to an understanding of the low-temperature behavior of TaS<sub>3</sub> is an analysis of the type of pinning of the CDWs. We know that the pinning of CDWs in TaS<sub>3</sub> is weak at high temperatures. However, we now have more pieces of indirect evidence that at sufficiently low temperatures (apparently at 60–80 K in TaS<sub>3</sub>) there is a transition to strong pinning, due to both a change in the screening of CDWs and a decrease in the role of thermal fluctuations (see, for example, Refs. 5 and 9).

Under the assumption that there are strong-pinning centers in these crystals, we arrive at the following scenario for the polarization of the CDWs. A change in the electric field causes an initial displacement of the CDW as a whole. As a result, a phase slippage of the CDW<sup>6)</sup> at some of the strong-pinning centers (active centers) becomes favorable from the energy standpoint. Each phase-slippage event leads to a change in the sign of the pinning force at that pinning center. As a result, there is a pronounced change in the local configuration of the CDW, which influences the phase slippage at other active centers and which may lead to an extended exponential relaxation.<sup>11</sup> Over times sufficient for the conversion of all active centers into passive centers, the pinning of the CDWs is equivalent to a weak pinning. The subsequent polarization of the CDWs is thus due to a progressive increase in the dimensions and number of regions in which a change in the configuration of the CDW can be observed over the observation time.<sup>10</sup>

With increasing impurity concentration, we would expect a relative increase in the contribution from weak pinning. This result explains why the slow relaxation is predominant in our doped samples. It also explains the circumstance, mentioned above, that Eq. (2) gives a far better description of the slow relaxation in the doped samples than in the pure ones.

In the discussion above we worked from the assumption that the energy of the interaction with the CDWs is approximately the same for all the pinning centers. In a real sample we would expect a variety of strong-pinning centers, differing in energy. Such strong-pinning centers would lead to additional contributions, which would occur in different (and possibly nonoverlapping) time and temperature intervals. If there is a large difference in pinning energies, the relaxation process should be an alternation of fast and slow relaxation stages. Analysis of the energies of the relaxation processes should yield a set of characteristic energies. An increase in polarization at  $T > 12$  K (see the inset in Fig. 1) may be due to a transition to the next fast stage. The slight change in activation energy

with the temperature in the fast-relaxation region (Fig. 2) may be due to either the existence of impurities with approximately equal energies for the interaction with CDWs or the manifestation of a tunneling contribution to the fast relaxation.

In summary, we have observed a two-stage relaxation of the polarization in  $\text{TaS}_3$ . We have shown that this relaxation can be described by existing arguments regarding a thermally activated creep of CDWs; it is not necessary to invoke any exotic conductivity mechanisms in order to explain this relaxation. According to the model discussed here, the answer to the question of what type of pinning is occurring (weak, strong, or mixed) depends on the temperature and the time interval (the frequency), and the two-stage nature of the relaxation is evidence of a transition from one type of pinning to another.

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<sup>2</sup>In the soliton model, the conductivity of  $\text{TaS}_3$  at temperatures below 20 K is interpreted as a hopping conductivity of solitons with a variable hopping length (see, for example, Ref. 3), which is implemented by tunneling.

<sup>3</sup>In the case of a linear response ( $Q \propto V$ ), the overlap of the responses to the leading and trailing edges of the pulse explains the familiar aging effect in disordered systems.

<sup>4</sup>Nevertheless, the decrease in polarizability with increasing impurity concentration contradicts the *soliton* model of creep.<sup>4</sup>

<sup>5</sup>In the case of an activation law  $t_0 = \tau \exp(W/T)$ , Eq. (2) can be used to describe relaxation after we replace  $T^*$  by  $T^*/(W/T^* + 1)$ ,  $Q_0$  by  $Q_0/(W/T^* + 1)^{2\chi}$ , and  $t_0$  by  $\tau$ .

<sup>6</sup>By "phase slippage" of the CDW here we mean a local change in the configuration of the CDW due to a transition between a metastable state and the ground state of the CDW at a pinning impurity.<sup>12</sup>

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