Stretched-Exponential Dielectric Relaxation in a Charge-Density-Wave System

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(Received 22 January (1986)

The relaxation of the electric polarization is investigated in the charge-density-wave compound $K_{0.3}MoO_3$. Direct measurements of discharge current in the time interval of 10^{-5} to 10^3 s reveal a stretched exponential law for the time decay of polarization: $P=P_0\exp[-\{t/\tau(T)\}^{1-n}]$, where both the initial polarization, P_0, and the exponent $(1-n=0.7)$ are temperature independent. The time scale of the process indicates temperature activation with an activation energy equal to the single-particle Peierls gap. The glassy relaxation of randomly pinned charge-density waves is compared with recent theories and experiments on spin-glasses.

PACS numbers: 77.40.+i, 72.15.Nj

Considerable efforts have been devoted to the understanding of the general features of dynamics in random systems. Until recently spin-glasses have been the most studied solids. The first clear evidence for a "weak" relaxation process was provided by the observation of unusual time dependence in the spin correlation function in *Cu*-Mn spin-glasses.[1] Investigation of magnetization and complex susceptibility[2] in $Eu_{0.2}Sr_{0.8}S$ glasses also suggests a wide distribution in relaxation times. By accurate measurements extending over four orders of magnitude in time it was shown that the time decay of remanent magnetization in *Cu*-Mn and *Ag*-Mn glasses can be characterized by a stretched exponential form[3] [see Eq. (3)].

This time dependence, often referred to as the Williams-Watts-Kohlrausch relaxation law, is described by recent theories of spin-glasses. New dynamic scaling hypotheses applied for percolation clusters[4]; assumption of hierarchy in relaxation levels[5]; estimation of survival probability of a random-walking particle in the presence of a static distribution of random traps[6]—each microscopic model can explain a stretched exponential decay.

A general description of glassy relaxation was suggested by Ngai.[7] Recognizing the high similarities of relaxation processes in rather different random systems—glasses, spin-glasses, polymers, viscous fluids, disordered dielectrics—he found that the common origin of the universal behavior is the coupling of the relaxing modes to low-energy excitations showing infrared divergence.

In quasi-one-dimensional Peierls-Fröhlich systems, like $NbSe_3$, TaS_3, or blue bronzes, scientific interest arises from the observation of sliding charge-density-wave (CDW) conduction[8] appearing above an unusually low threshold field, E_T. Although the collective excitation of CDWs is highly coherent,[9] recent investigations revealed the importance of inherent degrees of freedom. Weak relaxation (of the form of $\log t$ or $t^{-\alpha}$) in the Ohmic conductivity observed following an abrupt change in temperature,[10] as well as the frequency dependence of the complex dielectric constant,[11] indicated that physical properties—even at low electric fields $(E<E_T)$ or at low frequencies—are strongly effected by the rearrangement of pinned CDW configurations. A possible relation between glassy systems and charge-density waves (which develop in perfect crystals) is the randomness of the pinning centers. In high-quality crystals CDW pinning arises from impurities of concentration in the parts-per-million level.[12]

In this Letter direct measurements of the relaxation of CDW polarization[13] are presented. We investigated the time decay of polarization current, $I(t)=(1/l)dP(t)/dt$, where the initial polarization $P_0=P(t=0)$ is the maximal charge separation that can be reached by application of electric field, and l is the length of the sample.

Measurements on a $K_{0.3}MoO_3$ single crystal (dimensions $l=2.2$ mm, $A=2.3\times0.43$ mm^2) were carried out well below the Peierls transition temperature ($T_p=180$ K), in the range 25 K $<T<$ 65 K. At these temperatures we observed a nearly temperature-independent threshold field $E_T=0.03$ V/cm, and an activated resistivity corresponding to a single-particle Peierls gap $E_g=0.079$ eV.

CDWs were polarized by application of high electric field, E_p. We found that the amplitude of depolarization current measured after switching off of the field saturates above $E_p\approx0.5$ V/cm. In the present work we discuss depolarization curves for which initially the polarization is saturated. For this the polarization was created by a field $E_p=1$ V/cm at all temperatures. We verified that for this field Joule heating effects are negligible.

The depolarization current was detected by the sensor coil of a SQUID magnetometer. It served as a zero-input-resistance nanoammeter with high long-time stability. For short times and/or high signal levels a current amplifier (K 427) and a transient recorder were applied.

Figure 1 shows the time dependence of the depolarization current at different temperatures. The time is measured from the switching-off edge of the polarization field pulse. On the log-log plot of Fig. 1 it is easy

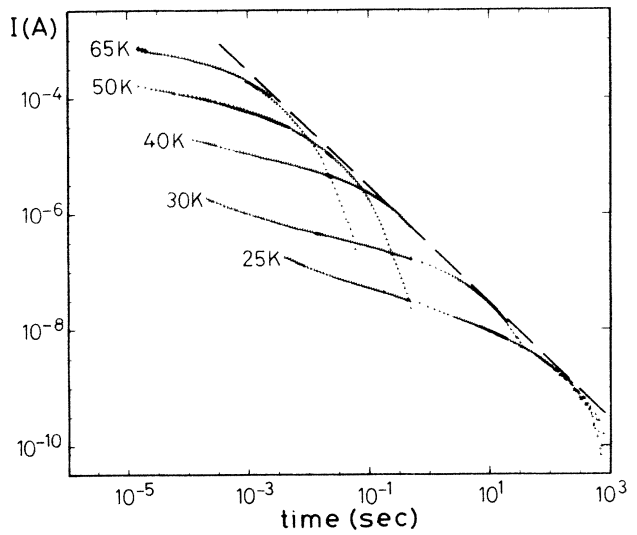

FIG. 1. Time dependence of depolarization current at different temperatures. Dashed line has a slope -1.

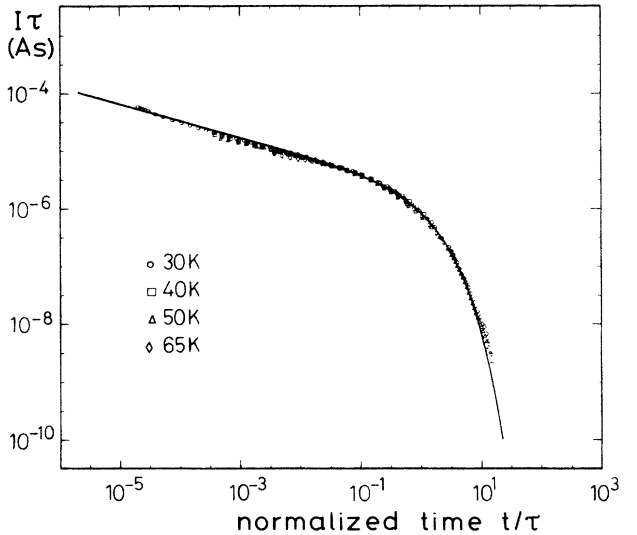

FIG. 2. Relaxation curves of Fig. 1 plotted on normalized time and current scales. Solid line corresponds to a stretched exponential behavior.

to recognize the high similarity of curves measured at different temperatures T. In fact, all curves coincide if shifted appropriately along a line of slope -1. From this a simple scaling law follows for the time decay of polarization,

$$P(t,T)=P_0 f(t/\tau(T)), \tag{1}$$

and for the current,

$$I(t,T)=(P_0/l)[1/\tau(T)]g(t/\tau(T)), \tag{2}$$

$$g(x)=df(x)/dx,$$

where f is a universal function independent of temperature if time is measured in appropriate units $\tau(T)$. In other words, on lowering of the temperature the current is reduced by the same factor as the "time unit" is increased.

Figure 2 shows the relaxation-current curves normalized by appropriate scale factors $\tau(T)$ deduced from the shifts along the line of slope -1 of Fig. 1. This way the temperature dependence of the "time unit" can be determined apart from a universal constant factor. This empirical $\tau(T)$ vs T is indicated by circles in Fig. 3.

We searched for an analytic description of the time decay of the CDW polarization in the form of a stretched exponential function:

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

in which the temperature dependence is reflected in $\tau(T)$ only in accordance with Eq. (1). The measured current is the derivative of the polarization:

$$I(t)=\frac{P_0}{l}\frac{1}{\tau(T)}\left[\frac{t}{\tau(T)}\right]^{-n}\exp\left\{-\left[\frac{t}{\tau(T)}\right]^{1-n}\right\}. \tag{4}$$

For short times the asymptotic behavior is $I\propto t^{-n}$. This power-law decay corresponds to a straight line on the log-log plot of Fig. 2, as observed for the first four orders of magnitude in t/τ. The initial slope gives $n=0.3$, and by use of this value the expected time dependence of Eq. (4) can be drawn for longer times as well. The two other parameters of the expression, P_0 and τ, are scale factors, and thus they do not change the shape of the curve on a log-log plot. One can again choose an appropriate shift to cover the measured points, and this gives the time scale of $\tau(T)$ in

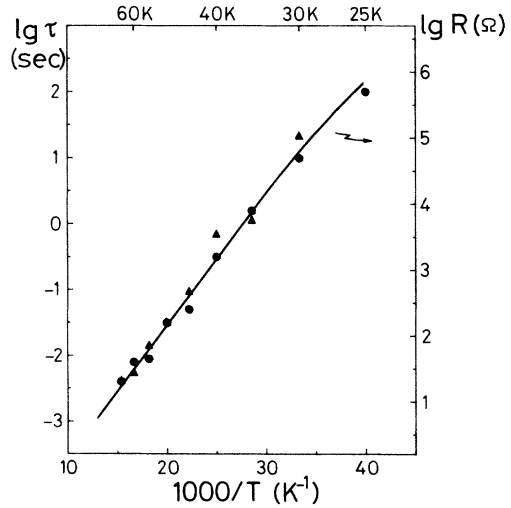

FIG. 3. Temperature dependence of the time scale of the relaxation process. Circles: τ determined from the scaling rule of Eq. (2). Triangles: τ obtained from stretched exponential fits. Solid line is the variation of the Ohmic resistance.

seconds and the absolute value of the initial polarization P_0; $P_0/l = 1.6\ \mu$C independent of temperature.

The agreement observed over several orders of magnitude in time is the first clear evidence for stretched exponential relaxation in a CDW system. We stress that to obtain the universal curve of Fig. 2 only one parameter, $\tau(T)$, was fitted at each temperature, while $n = 0.3$ and $P_0/l = 1.6\ \mu$C are temperature-independent values.

The temperature dependence of the time unit $\tau(T)$ is shown in Fig. 3. The $4\frac{1}{2}$ orders of magnitude change in τ between 25 and 65 K reflects the strong temperature dependence of the phenomenon. The "transient response" to a pulse, appearing as a peak on a high-frequency oscilloscope, is the same effect as the slowly decaying current measured at 40 K below by dc technique.

For τ we find an activated behavior

$$\tau(T) = \tau_0 e^{\Delta/T}. \tag{5}$$

For comparison, in Fig. 3 we plotted the temperature dependence of the low-field Ohmic resistivity measured on the same crystal by four-probe method. The average single-particle activation energy characteristic of this temperature range agrees (within experimental error) with the one determined for Δ from expression (5): $E_g/2 = 460$ K, $\Delta = 450 \pm 30$ K.

As shown by Figs. 2 and 3, the stretched exponential decay of polarization according to Eqs. (4) and (5) is valid over a wide time and temperature range. If, however, the measurements are extended a further 2 orders of magnitude above τ, a continuous transition from the stretched exponential decay to a Debye relaxation with a single time constant is observed. This is illustrated in Fig. 4, where data of a $T = 38$ K measurement are plotted on both a linear and a logarithmic time scale. The solid curve corresponds to the stretched exponential relaxation with $\tau = 0.45$ sec, while the dashed line describes an exponential decay with a time constant $\tau_D = 14$ sec. The Debye form is the asymptotic behavior for a polarization level below $0.08P_0$ and for long times ($t > 20$ sec at 38 K):

$$P \propto e^{-t/\tau_D}, \quad t \gg \tau, \quad P \ll P_0. \tag{6}$$

In the discussion first we treat the role of one-electron excitations. Single-particle contributions to the current cease with a time constant $\tau_{sp} = \epsilon_{sp}\rho$. Estimating the static dielectric constant as $\epsilon_{sp} = \frac{2}{3}(\omega_p/\Delta)^2$ with a plasma frequency[14] $\omega_p = 2.7$ eV and with the measured resitivity ρ, one gets $\tau_{sp} \approx 0.05$ nsec at $T = 65$ K and $\tau \approx 7\ \mu$sec at $T = 25$ K, well below the time interval investigated. Thus, we believe that the weak relaxation observed in the range of $10^{-5} < t < 10^3$ sec reflects the rearrangements of the CDW.

The absolute value of the initial polarization is also too high to arise from one-electron excitations. If blue bronze were a simple semiconductor, an electric field around 1500 kV/cm should be applied to reach the measured polarization. The total charge involved in the process, $P_0/l = 1.6\ \mu$C, is a saturated value observed at fields as low as 500 mV/cm.

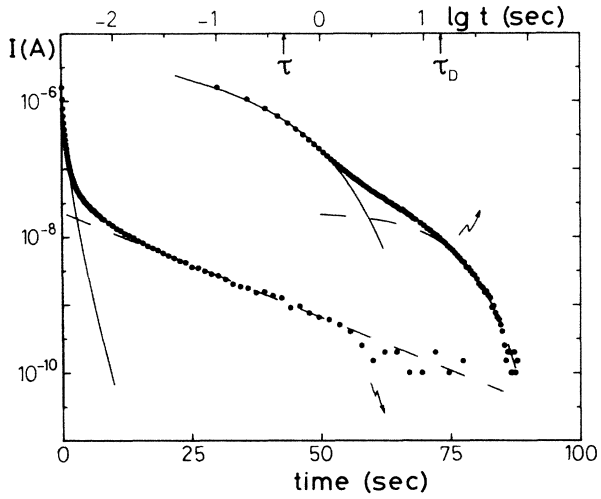

FIG. 4. Asymptotic behavior of depolarization current plotted on linear and logarithmic time scales. Solid line corresponds to the stretched exponential law; dashed line represents Debye relaxation. (Parameters: $\tau = 0.45$ sec, $\tau_D = 14$ sec, $T = 38$ K.)

Based on the above arguments a natural assumption is that the temperature-independent initial state is a polarized state of CDWs. Decay of this polarization follows a universal stretched exponential law. The only temperature-dependent parameter is the time scale.

The time scale strongly varies with temperature. Since $\tau(T)$ is activated with the single-particle gap, the relaxation of CDW polarization is obviously related to one-electron excitations. This observation makes questionable the validity of the general view that the collective and one-electron excitations are completely independent. Rather, it seems that rearrangement of pinned CDW configuration needs intermediate one-electron states and the temperature dependence is the consequence of the variation of the population in these intermediate states. Relaxation of pinned configurations occurs through breaking up and restoring of the CDW condensate.

Direct application of theories worked out for spin-glasses would need an elaborate microscopic picture for pinned CDW systems, still missing. A computer simulation of the Fukayama-Lee Hamiltonian[15] has led to a stretched exponential time dependence of the polarization in presence of an electric field,[16] but thermal relaxation of CDWs was not investigated.

The general idea of Ngai seems to explain both the

observed time and temperature dependence. Randomness in the pinning forces may lead to a linear CDW energy-level spacing distribution function for small energies, playing a crucial role in the theory. If the primary relaxation is the CDW rearrangement governed by thermally induced CDW → normal and normal → CDW transformations, one expects a Debye relaxation with a time constant reflecting activation with $\Delta = E_g/2$. As a result of the coupling of CDW–normal-electron conversion to the low-energy excitations, in Ngai's theory the simple exponential relaxation is transformed to a stretched exponential one. The variation of the characteristic time, τ, of the stretched exponential function with temperature is still Arrhenius type but with a slightly different activation energy; Δ is replaced by $\Delta^* = \Delta/(1-n)$. This value does not contradict our measurements (Fig. 3).

It is a common feature of all the models of glassy relaxation that for extremely long times a single relaxation time dominates (see, e.g., Refs. 4–6). To our knowledge, Fig. 4 presents the first experimental observation of this sort of transition.

In conclusion, we have shown that the decay of the CDW polarization is accurately characterized by a stretched exponential function. While the initial state—the saturated polarization of CDWs—is temperature independent, the time scale of the relaxation process shows activation with the single-particle gap. This strong temperature dependence indicates that CDW rearrangements involve intermediate states determined by normal-electron population. Time and temperature dependence have been discussed in terms of the theory of Ngai, based on low-energy excitations.

Discussions with A. Jánossy and L. Mihály are gratefully acknowledged. This work was supported by the Hungarian Academy of Sciences Grant No. TPB-KKFA-ATA 85-1-099.

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