Towards Equilibrium Ground State in Charge-Density-Wave Systems

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We present a study of energy relaxation in two representative charge-density-wave compounds: TaS_3 and $NbSe_3$ below $T=0.5$ K. The evolution of the relaxation indicates a crossover between a nonequilibrium state and the thermodynamical equilibrium state when the system has been allowed to age. In the equilibrium state the relaxation is thermally activated with an activation energy of ~1 K. We interpret these results as long-time dynamics in the network of charge-density-wave dislocations with a critical temperature close to 0 K.

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Anomalous slow relaxations have been actively studied for many years in a wide variety of materials, such as polymers, ionic conductors, amorphous semiconductors, and spin glasses, in response to different excitations [1] (mechanical stresses, external electric and magnetic fields, etc.). Recent experiments show that charge-density-wave (CDW) compounds [2] can be included in this broad class of physical systems [3,4]. The CDW ground state formed below the Peierls transition results from the competition between elastic deformations of the CDW and pinning potentials caused by randomly distributed impurities. In its pinned state due to randomness and disorder, the CDW exists in many metastable states characterized by local deformations of its phase. Indeed the signature of CDW low-energy excitations (LEE) was recently found [5–7] at very low temperature, as a contribution to the specific heat additional to that of phonons, in the family of inorganic CDW compounds TaS_3, $(TaSe_4)_2I$, $NbSe_3$, and $K_{0.3}MoO_3$. Moreover, in this temperature range the energy relaxation shows an anomalous long-time response with, in addition, "aging" effects [8]. This term, borrowed from the terminology used in the study of amorphous materials and spin glasses, means that the relaxation-time dependence of the energy relaxation depends on the time duration (waiting time) of the application of the thermal perturbation.

In this Letter we report on energy relaxation measurements for two representative CDW systems, i.e., TaS_3 and $NbSe_3$ in the temperature range 0.1–1 K and in the time window 1–10^5 s. The relaxation rate clearly shows a crossover between a nonequilibrium state (with waiting-time effects) and the thermodynamic equilibrium state beyond a temperature-dependent waiting time. The time for reaching the ground state increases when T is reduced and is well described by an Arrhenius law with an activation energy of ~1 K. We propose that the barriers dominating the relaxation originate from the dynamics between the defects in the CDW superstructure: phase slips or dislocation loops interacting with impurities. By analogy with dynamical properties in random systems in which a hierarchical procedure governs the time evolution, the nonexponential character of the relaxation and the activated behavior of the relaxation rate at equilibrium may indicate that the critical temperature of CDW glassy systems is ~0 K.

We have studied the energy relaxation between 0.08 and 8 K in a dilution refrigerator after cooling the sample through the Peierls transition (210 K in TaS_3; 145 and 59 K for $NbSe_3$) without application of any electric field. We used two different types of heat perturbation: a heat pulse no longer than 1 s and a heat flow with a duration (playing the role of a waiting time) of a few tens of seconds to longer than a day. The relaxations, in terms of the observation time after switching off the perturbation (at $t=0$), have a nonexponential time dependence [9] which can in general be fitted for $0.05 < \Delta T(t)/\Delta T_0 < 0.95$ by a stretched-exponential function $\Delta T(t)/\Delta T_0 = A\exp[-(t/\tau_p)^\beta]$, where β is temperature dependent [8]. We wish now to study the evolution of the distribution of relaxation times in terms of the temperature and of the waiting time. We assume that $\Delta T(t)/\Delta T(0)$ may be expressed in terms of a distribution of relaxation times $g(\ln\tau)$ as $\Delta T(t)/\Delta T(0) = \int_{\tau_{co}}^{\infty} g(\ln\tau)\exp(-t/\tau)\,d\ln\tau$, where τ_{co} is a short-time cutoff; $g(\ln\tau)$ can be obtained from the partial differentiation of the relaxation function with respect to $\ln t$: $d[\Delta T(t)/\Delta T(0)]/d\ln t \simeq g(\ln\tau)$ [10]. For a fixed waiting time of 20 min, the time dependence of $\Delta T(t)$ as a function of $\log_{10} t$ is shown in Fig. 1(a) for orthorhombic TaS_3 at four different temperatures below 0.5 K. The logarithmic derivative of $\Delta T(t)$ drawn in Fig. 1(b) shows a peak in the relaxation rate at τ_p. The distribution of relaxation times, especially at lower temperatures, is smeared out over a few orders of magnitude in time, reflecting the wide spectrum of relaxation times τ and its correlation with t_w. The pronounced increase of the aging effect when T is decreased is clearly presented in Fig. 2 where the relaxation rate $g(\log\tau)$ at different temperatures is shown in the limits of two extreme waiting times, the shortest one (1 s) and the longest one (10 h): At $T=0.4$ K, τ_p increases by a factor ~2 between

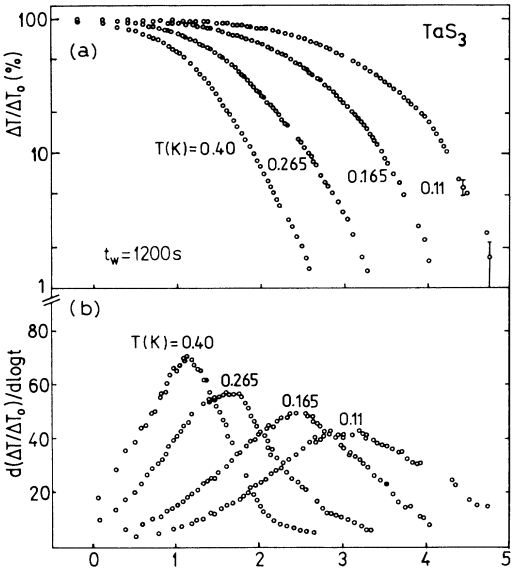

FIG. 1. (a) Variation of $\Delta T(t)/\Delta T_0$ as a function of time in a log-log plot for TaS₃ at four temperatures (in all the figures, logarithms are base 10). A heat flow has been applied through the sample during a time $t_w = 1200$ s; the origin of time starts when this heat flow is switched off. ΔT_0 is a few percent ($< 8\%$) of the reference temperature. (b) Time dependence of the relaxation rate $d(\Delta T/\Delta T_0)/d\log t$ for the same conditions as in (a).

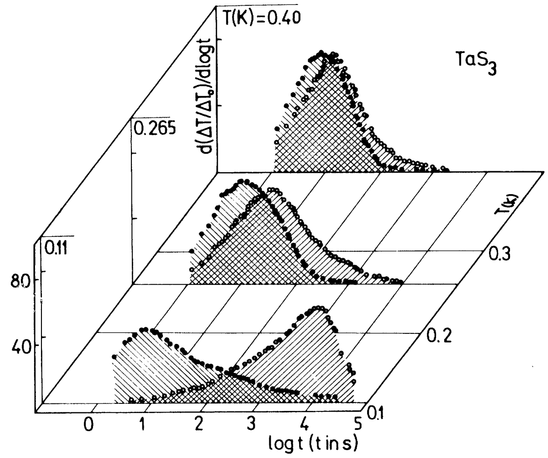

FIG. 2. Time dependence of the relaxation rate $d(\Delta T/\Delta T_0)/d\log t$ of TaS₃ at $T = 0.4$, 0.265, and 0.11 K in the limit of two extreme waiting times (see text): ●, heat pulse of 1 s; ○, heat flow of ~10 h. In both thermal perturbations the maximum ΔT_0 is a few percent of the reference temperature.

$t_w = 1$ s and 10 h, whereas at $T = 0.1$ K the increase of τ_p under the same conditions is larger than 10^3. The change in the shape of the relaxation rate as a function of the waiting time is also very remarkable.

Figure 3 shows how the position τ_p of the peak in the relaxation rate depends on the waiting time t_w; in Fig. 3(a) for TaS₃ and in Fig. 3(b) for NbSe₃: τ_p increases with t_w but saturates at a maximum value $\tau_{\max}$ for longer t_w indicating that the system *has reached its thermodynamical equilibrium.* The nonequilibrium properties reflected in the aging effect are much more pronounced in TaS₃ than in NbSe₃. Aging effects appear in NbSe₃ only below 150 mK. At $T = 0.075$ K, equilibrium in NbSe₃ is reached after $\tau_{\max} \sim 10$ min, whereas in TaS₃ at $T = 0.1$ K, $\tau_{\max}$ is of the order of the longest waiting time, i.e., ~10 h [dashed line in Fig. 3(a)].

Nonexponential relaxation and aging effects as exhibited by CDW compounds are known to occur in disordered systems such as glassy polymers [11] or spin glasses [12–14]. For these latter systems different models have yielded different predictions for the divergence of the relaxation time at the phase-transition temperature T_c. For a finite T_c, in the hypothesis of critical slowing down, τ diverges as

$$\tau/\tau_0 \sim (1 - T_c/T)^{-z\nu} = \xi^z, \qquad (1)$$

where ν is the critical exponent for the correlation length ξ and z the critical dynamical exponent. Acceptable fits for TaS₃ would give very small T_c ($T_c \lesssim 0.03$ K) and huge $z\nu$ ($z\nu > 30$) and respectively $T_c \lesssim 0.01$ K and $z\nu \gtrsim 25$ for NbSe₃. Alternatively an Arrhenius law $\tau = \tau_0 \exp(W/kT)$ gives comparable fits. This is not surprising when viewed in the spirit of Ref. [15], where the argument that expression (1) remains analytic (it can

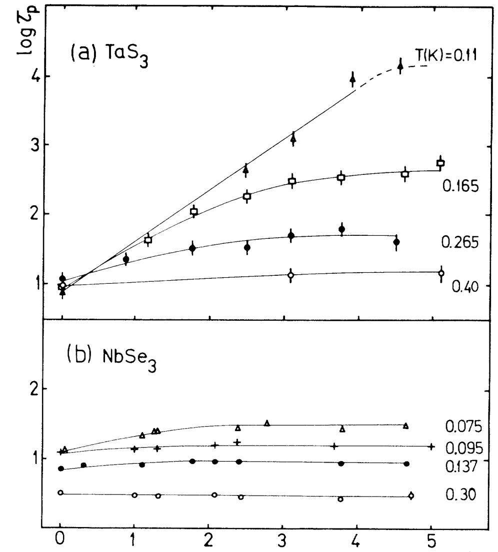

FIG. 3. Variation of the peak in the relaxation rate (as seen in Figs. 1 and 2) as a function of the waiting time t_w in a log-log plot at several temperatures for (a) TaS₃ and (b) NbSe₃. The crossover between the nonequilibrium and the equilibrium state occurs when the variation of τ_p flattens with t_w. The dashed line is the saturation of τ_p estimated at $T = 0.11$ K.

be expanded in terms of T_c/T at all temperatures larger than T_c) involves, in the limit of $T > T_c$, that $\tau/\tau_0 \sim 1 + z\nu T_c/T + \cdots$, where $z\nu T_c$ exists and remains finite. Therefore the Arrhenius law is simply the limit of zero critical temperature of Eq. (1) with the activation energy given by $W = z\nu T_c$. Figure 4, where we have drawn the variation of $\tau_{\max}$ (defined in Fig. 3) as a function of $1/T$, shows that an activated behavior is followed for TaS_3 with $W \sim 0.8$-1 K and $W \sim 0.25$ K for $NbSe_3$. When the system is not allowed to reach equilibrium, for example, for short pulses of 1 s in TaS_3, the activation energy is almost 3 times lower (dashed line in Fig. 4). Thus the effect of aging yields a deepening of the local minima in the energy configuration.

It is worthwhile to compare the aging effects demonstrated above for CDWs with those studied in spin glasses in the same time window (1-10^5 s), such as remanent magnetization [12,13]. When T approaches the freezing temperature T_g, the edge of the relaxation rate drastically increases; i.e., in Ref. [12], $\tau \sim 10^{-3}$ s at $T/T_g \sim 1.05$ and $\tau = 10^3$ s at $T/T_g \simeq 1.01$. Below T_g, relaxation never reaches zero and aging effects appear as a maximum in the relaxation rate at the observation time equal to the waiting time. Aging processes persist until the system has been allowed to age for a time comparable to the longest relaxation time in the system. For a system with a finite T_g, this equilibrium state could be reached only on an astronomic time scale, out of the range of laboratory times (see Fig. 4 in Ref. [12]). However, when the divergence of τ is pushed down to $T_g \to 0$, a broader temperature range is accessible in which the experimental time window for aging effects (1-10^5 s) is in the range of the relaxation time $\tau(T)$ of the compound. Thus for TaS_3 at $T = 0.1$ K (see Fig. 3) the behavior is similar to that of spin glasses where the maximum t_w (10 h) remains smaller than or equal to the longest relaxation time. On the contrary, at slightly higher temperatures, aging stops after a finite t_w, which depends on temperature, when the equilibrium state is reached. To our knowledge this is the first evidence reported in glassy materials for *such a crossover between the nonequilibrium and equilibrium states.*

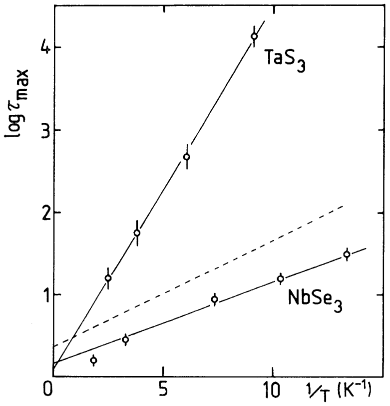

FIG. 4. Variation of $\tau_{\max}$, the saturated value of τ_p in Fig. 3, as a function of $1/T$ of TaS_3 and $NbSe_3$. The dashed line is the variation of the peak in the relaxation rate for a heat pulse of 1 s applied to TaS_3.

A zero-temperature T_c has been experimentally found in 2D spin glasses [16]. $T_c = 0$ also describes the glassy behavior on fractal or percolation structures [17,18]. For these structures, the relaxation is described with a stretched exponential as found in TaS_3 and $NbSe_3$. The coefficient β is temperature dependent. In a recent analysis Castaing and Souletie [15] have associated the hierarchical model of Palmer *et al.* [19] with Kadanoff's renormalization near a phase transition. They showed that, as the renormalization is pushed further, the distribution $g(\ln\tau)$ should tend to a Gaussian. This is sufficient to justify approximate stretched-exponential behavior with $\beta(T)$ which tends to a $\sqrt{T}$ dependence when T_c/T cancels, in the same limit where τ follow Arrhenius behavior [see discussion of Eq. (1)]. Whereas Arrhenius behavior alone is not a proof for critical behavior, it is essential that a sufficient renormalization level and a corresponding coherence-length extension are reached in order to justify a Gaussian shape of $g(\ln\tau)$ [see, e.g., Fig. 1(b) here and Fig. 2 of Ref. [8]] which should otherwise be sample dependent. The universality of the stretched-exponential relaxation therefore is our main argument for claiming critical behavior and, more specifically, a transition with $T_c = 0$ in the present case. On the other hand, in the model of relaxation on percolation clusters, β is expected to vary as $\sim T$ at low T [17]. Although β seems to decrease [8] linearly with T down to 0.1 K ($\beta \simeq 0.3$ at this temperature) in TaS_3, experiments at lower temperatures are in progress to measure the low-temperature dependence of $\beta(T)$.

Below 0.5 K, CDW internal degrees of freedom are still active with an activation energy of ~ 1 K. We will now try to give a description of these low-energy excitations. At higher temperatures, $20 < T < 100$ K, the mean value of the relaxation-time distribution (measured in the relaxation of the polarization [3,20] or deduced from dielectric relaxation measurements [4]) is thermally activated with an activation energy in the range of the Peierls gap (~ 1000 K or more). This is explained with models which only consider elastic deformation of the CDW [3,4]. But this process for relaxation is exhausted at lower temperatures due to the progressive disappearance of the screening of the CDW deformation by normal carriers, and another mechanism should take place to account for our results. We propose that defects in the CDW superstructure, phase slips in 1D and dislocation loops in 3D, are at the origin of the long-time, low-temperature relaxation. These defects are created when the specimen is cooled through the Peierls temperature. Dislocation loops are absolutely necessary at the contacts for current injection [21]. But in the present experiment, because $E=0$, the area of these loops is fixed and their dynamics comes only from their deformation in the situation of frustration between their line tension and their interaction with impurities. One can thus think of a structure of a network of dislocations of nonuniform size similar to the ramified fractal lattice on percolation clusters with similar dynamics. The time constant of these large objects is expected to be high, which may account for the τ_0 value of approximately a few seconds in the Arrhenius behavior (Fig. 4). But more work has to be performed to more firmly establish the correspondence between this model and the CDWs at very low temperatures. The difference in the time scales between $NbSe_3$ and TaS_3 can be explained by the intense Coulomb field in TaS_3 which is insulating at very low temperature whereas $NbSe_3$ still has a small concentration of normal carriers (10^{17} cm^{-3}).

In conclusion, we have shown that CDW compounds [TaS_3, $NbSe_3$, and also $(TaSe_4)_2I$] exhibit long-time energy relaxation at very low temperature. The relaxation rate is a function of the time during which the thermal perturbation has been applied. We found a crossover from nonequilibrium relaxation to equilibrium relaxation beyond a temperature-dependent waiting time, which extends work on random systems to a regime unable to be reached before, for example, in spin glasses. We have proposed that these low-energy excitations originate from deformations in the network of CDW dislocation loops. CDWs can then be considered as test models for relaxation dynamics of random systems with $T_c \sim 0$.

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