

## Aging Effects and Nonexponential Energy Relaxations in Charge-Density-Wave Systems

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Low-energy excitations between charge-density-wave metastable states are revealed in low-temperature specific-heat measurements in quasi-one-dimensional materials as an excess contribution (to the lattice one) following a  $C_p = T^\nu$  law with  $\nu < 1$ . In the same temperature range the energy relaxation is not exponential but follows a stretched-exponential variation. Aging effects are also demonstrated. Analogies and differences with other glassy materials are briefly discussed.

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The dynamical properties of charge-density waves (CDW's) in pseudo-one-dimensional conductors such as NbSe<sub>3</sub>, TaS<sub>3</sub>, (TaSe<sub>4</sub>)<sub>2</sub>I, (NbSe<sub>4</sub>)<sub>10</sub>I<sub>3</sub>, or K<sub>0.3</sub>MoO<sub>3</sub> have been intensively studied in the last years.<sup>1</sup> The more common model for explaining CDW sliding has been derived by Fukuyama, Lee, and Rice<sup>2</sup> (FLR) in which the elastic deformation of the CDW competes with the pinning energy provided by randomly distributed impurities. In the nonlinear regime, i.e., for electric fields higher than the threshold value  $E_T$ , the CDW phase is found to be unique which means that the average CDW velocity is identical in all parts of the sample, which accounts for the spectacular long-range coherence effects.<sup>3</sup> But for  $E < E_T$  because of the random pinning the CDW remains in a metastable state out of its equilibrium position. It was shown by numerical simulations of the 1D FLR model<sup>4</sup> that a metastable state is characterized by local deformations of the pinned CDW phase which induces a macroscopic polarization. CDW metastable states have essentially been revealed by the long-time relaxation (following a stretched-exponential variation<sup>5</sup>) of the depolarization current when a current pulse above threshold is applied and switched off, and by the thermally stimulated depolarization current of frozen dipole moments when a CDW sample is cooled down under an electric field  $> E_T$ .<sup>6</sup> The normal conductivity has also been shown to follow logarithmic time dependence when an electric pulse higher than  $E_T$ ,<sup>7</sup> or a heat pulse,<sup>8</sup> (for compounds in which the CDW distortion vector is temperature dependent as in TaS<sub>3</sub> or K<sub>0.3</sub>MoO<sub>3</sub>) is applied. Finally the real part of the dielectric constant shows a cusp<sup>9,10</sup> at low frequency which indicates a broad distribution of relaxation times extending to infinite time. These properties show that the pinned CDW ground state is strongly disordered and that CDW's behave as other glassy materials such as structural glasses, spin-glasses, or polymers.

In this Letter, we report on our investigations of meta-

stable states by thermodynamic measurements. The CDW compound is cooled down through the Peierls transition temperature without application of any electric field. The disordered nature of the CDW state is revealed by an excess contribution to the specific heat at low temperatures following a  $C_p \sim T^\nu$  law with  $\nu < 1$ . Energy relaxation is then shown to be not exponential, the involved time constants being strongly dependent on the time at which the energy flux is applied. These aging phenomena, observed for the first time in a CDW, resemble those recently reported on spin-glasses.<sup>11,12</sup>

We have measured the specific heat of NbSe<sub>3</sub>,<sup>13</sup> TaS<sub>3</sub>,<sup>14</sup> (TaSe<sub>4</sub>)<sub>2</sub>I and (NbSe<sub>4</sub>)<sub>3</sub>I,<sup>15</sup> and K<sub>0.3</sub>MoO<sub>3</sub>,<sup>16</sup> between 0.1 and 8 K in a dilution refrigerator with a transient heat-pulse technique. The specific heat  $C_p$  is calculated from the increment of temperature  $\Delta T_0$  after a heat pulse (duration 0.1 to 0.9 s,  $\Delta T_0/T_0 \sim 5\% - 10\%$ ) by using the exponential decay of the temperature increase  $\Delta T(t) = \Delta T_0 \exp(-t/\tau)$ , with the time constant  $\tau = C_p R_l$ ;  $R_l$  is the thermal resistivity of the thermal link to the regulated cold sink, the temperature  $T_0$  of which can be stabilized within  $5 \times 10^{-4}$  over several hours.

However, in *all* the CDW conductors that we have measured, there is a deviation from an exponential decay without any possibility of fit by an exact exponential in the whole time range. This deviation observed at low  $T$  ( $T \leq 0.3$  K) is clearly related to the CDW state as can be seen in Fig. 1 where we have plotted  $\Delta T(t)$  at the same minimum temperature of 0.11 K in structurally similar compounds: (NbSe<sub>4</sub>)<sub>3</sub>I without CDW transition and (TaSe<sub>4</sub>)<sub>2</sub>I with a CDW transition. In this low-temperature range we determine a "short-time" heat capacity from the initial exponential decay after the heat pulse, as drawn in Fig. 1(b). The analysis of  $C_p$  defined in this way is then consistent with an excess heat capacity following a  $T^\nu$  variation with  $\nu < 1$ :  $\nu = 0.22$  in (TaSe<sub>4</sub>)<sub>2</sub>I between 0.1 and 0.25 K,<sup>15</sup>  $\nu = 0.6$  in our recent measurements on blue bronze between 0.1 and 0.5

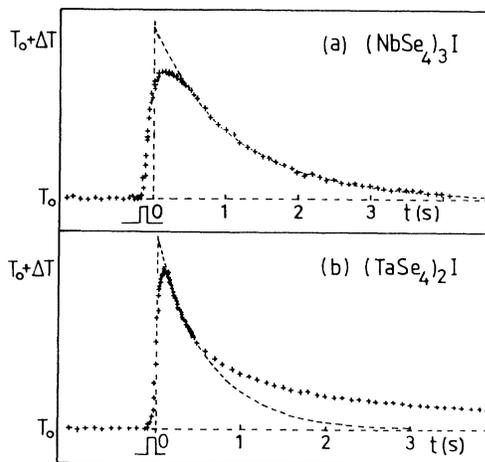


FIG. 1. Time dependence of the temperature after a heat pulse of duration 0.1 s has been applied to the sample (the reference temperature  $T_0$  is 0.11 K and  $\Delta T_0/T_0 \sim 10\%$ ) showing (a) an exponential decay in the case of the compound  $(\text{NbSe}_4)_3\text{I}$  exhibiting no Peierls transition (the time constant  $\tau = 1.15$  s), and (b) a deviation of the exponential decay in the case of the CDW  $(\text{TaSe}_4)_2\text{I}$  compound. In the latter case the specific heat is calculated from the initial exponential decay as indicated by the dashed lines (with  $\tau = 0.60$  s).

K,<sup>16</sup>  $\nu \sim 1$  in  $\text{NbSe}_3$ ,<sup>13</sup> where we have reanalyzed<sup>14</sup> the linear term as resulting from metastable excitations rather than from electronic contribution, and  $\nu = 0.32$  in  $\text{TaS}_3$ ,<sup>14</sup> between 0.1 and 2 K. Some other values of  $\nu$  have also been reported:  $\sim 1$  in  $\text{K}_{0.3}\text{MoO}_3$ <sup>17</sup> and in  $(\text{TaSe}_4)_2\text{I}$ <sup>18</sup>; but for this latter compound, measurements have not been performed at low enough temperatures and the pseudolinear term is only a crossover between two different temperature-dependent regimes. Notice that a time-dependent specific heat has previously been indicated in  $(\text{TaSe}_4)_2\text{I}$ <sup>18</sup> and in  $\text{K}_{0.3}\text{MoO}_3$ <sup>17</sup> but without analysis.

Deviation from the simple exponential decay reveals very long-time relaxation which leads us to consider energy relaxation in CDW compounds in the same frame as for other disordered systems.<sup>19</sup> A characteristic feature of glassy materials is aging properties,<sup>20</sup> as recently demonstrated in spin-glasses<sup>11,12</sup> when the response of the system after the switch off of a perturbation depends on the time this perturbation has been applied. We may wonder whether such effects exist in CDW's. So we have performed some appropriate experiments on  $\text{TaS}_3$  because the temperature range in which the excess specific heat is observed is the largest.<sup>21</sup> Then we have recorded the time dependence (up to  $2 \times 10^4$  s) of the temperature decrease in three different conditions as schematically shown in the inset of Fig. 2(b) after (a) a short pulse duration of 0.9 s is applied, or when the power flux is kept constant (b) for 5 h, or (c) for 13 h. Figure 2(a) shows  $\Delta T(t)$  in a semilog plot with the same

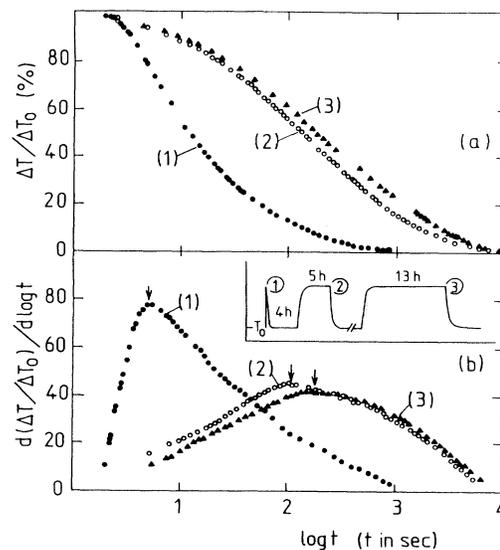


FIG. 2. (a) Variation of the normalized temperature decrease  $\Delta T/\Delta T_0$  as a function of  $\log t$  for a  $\text{TaS}_3$  sample with  $T_0 = 0.165$  K and  $\Delta T_0/T_0 \cong 8\%$  in all three conditions as schematically drawn in the inset of (b): after a heat pulse of duration of 0.9 s is applied ( $\bullet$ ); after the heat flow has been applied for 5 h and switched off ( $\circ$ ); and applied for 13 h and switched off ( $\blacktriangle$ ). (b) Time dependence of the relaxation rate  $d(\Delta T/\Delta T_0)/d \log t$  with  $T_0 = 0.165$  K for the same three conditions of applied heat flow as in (a).

$\Delta T_0/T_0$  for the three measurements. Aging effects are clearly demonstrated with energy relaxation at longer time when the perturbation  $\Delta T$  has been applied longer. Similarly to spin-glass experiments, this time plays the role of "waiting time" as we will call it below.

A simple fashion to understand the waiting time effects is to assume a wide relaxation time distribution  $g(\tau)$  for the energy of metastable states due to randomness in pinning centers. In general one has<sup>11</sup>  $\Delta T(t)/\Delta T(0) = \int_{\tau_0}^{\infty} g(\tau) \exp[-(t/\tau)] d \ln \tau$  where  $\tau_0$  is a short-time cutoff. It has also been shown<sup>11</sup> that the partial derivative of the above quantity with respect to  $\ln t$  reflects the form of  $g(\tau)$ . Figure 2(b) shows  $\partial \Delta T(t)/\partial \log t$  for the three waiting times: For a given waiting time  $t_w$ ,  $g(\tau)$  shows a peak at  $t$  of the order of  $t_w$  and the peak is shifted towards long time for longer  $t_w$ . Following results on spin-glasses, it is important to distinguish different time scales, one associated with polarization (or magnetization) relaxation and one corresponding to energy (or temperature) relaxation. In general the first is longer than the second one because of the differences between the explored regions in phase space. Indeed it is much easier to stabilize the energy in a metastable well remaining far away from equilibrium than for the polarization, for instance. This property has been shown, in particular, in homogeneous systems such as Ising ferromagnets.<sup>22</sup>

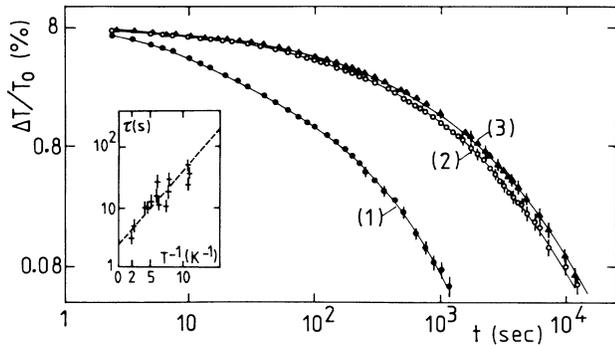


FIG. 3. Variation of  $\Delta T/T_0$  as function of time in a log-log plot with  $T_0=0.165$  K for a  $\text{TaS}_3$  sample with the same conditions of heat flow as in the inset of Fig. 2(b). The fits correspond to Eq. (1) (see the text for the values of parameters  $\tau_p$ ,  $\alpha$ , and  $\beta$  giving the best fits). Inset: The temperature dependence of the time constant  $\tau_p$  in the case of pulse heat flow, indicating a thermally activated behavior.

In glassy materials relaxation is often analyzed by the product of a power law by a stretched exponential.<sup>12</sup> The deep nature of the stretched variation has led to a long debate but it is now recognized<sup>12</sup> that the stretched variation superposes on the power-law decay as reflecting only the aging effect during the interval of time in which the experiment is performed. Then the dynamic equilibrium behavior will be only reached for an infinite age of the system (waiting time plus observation time), i.e., for extrapolation at short times. In Fig. 3 we have drawn  $\Delta T(t)$  in a log-log plot for the three different waiting times at the same temperature. A simple stretched exponential cannot fit the data especially for short times. The curves in Fig. 3 correspond to the following fits:

$$\Delta T \propto (t/\tau_p)^{-\alpha} \exp[-(t/\tau_p)^\beta], \quad (1)$$

with  $\tau_p=28$  s,  $\alpha=0.14$ , and  $\beta=0.4$  for the shorter waiting time (transient heat pulse);  $\tau_p=260$  s,  $\alpha=0.04$ , and  $\beta=0.42$  for a waiting time of 5 h;  $\tau_p=350$  s,  $\alpha=0.035$ , and  $\beta=0.43$  for a waiting time of 13 h. The curves for the shorter waiting time [ $\Delta T_1(t)$ ] and for 5 h waiting time [ $\Delta T_2(t)$ ], for instance, can be superposed by a horizontal shift in the log-log plot such as  $\Delta T_1(t) = \Delta T_2(at)$  with  $a \sim 10$ , except for initial times. This result means that all the characteristic times in the energy relaxation should be multiplied by 10 when the waiting time has been as long as 5 h. For short-time observation, however, one reaches the stationary regime in which the relaxation follows a power law  $t^{-\alpha}$  with  $\alpha=0.04$ .

We have also studied the temperature dependence of the energy relaxation time using the transient heat-pulse method. Except for initial times,  $\Delta T(t)$  can be accurately analyzed with the only stretched-exponential variation  $\exp[-(t/\tau_p)^\beta]$ . The coefficient  $\beta$  is measured by the slope of  $\log |d \ln \Delta T / dt|$  as drawn in Fig. 4 for different temperatures. The temperature dependence of  $\beta$  is plot-

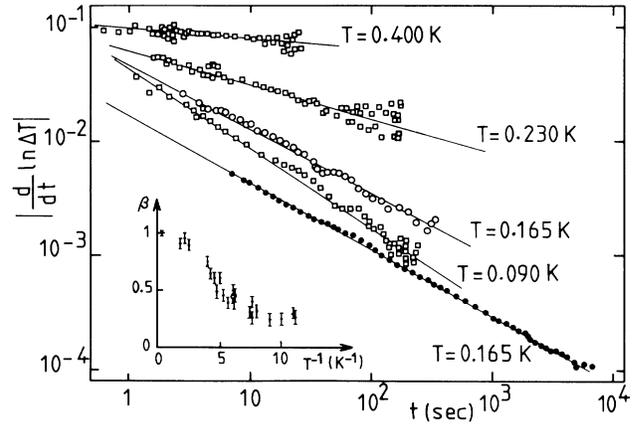


FIG. 4. Variation of  $|d \ln \Delta T / dt|$  as a function of time in a log-log plot for  $\text{TaS}_3$  for several temperatures in the case of pulse heat flow. The slope fixes the coefficient  $\beta$  of Eq. (1). Inset: The variation of  $\beta$  as a function of  $T^{-1}$ .

ted in the inset of Fig. 4:  $\beta=0.3$  at the lowest temperatures and increases up to  $\sim 1$  at  $T=0.5-0.6$  K. Finally the average relaxation time  $\tau_p$  can be estimated from the value of  $|d \ln \Delta T / dt|$  extrapolated at 1 s.  $\tau_p$  is plotted in the inset of Fig. 3 as a function of  $1/T$ . In spite of a large uncertainty,  $\tau$  shows an Arrhenius variation with an activation energy of 0.3–0.4 K.

The picture which emerges from the measurements of energy relaxation of CDW systems at low temperatures is the very broad distribution for relaxation processes. The CDW metastable states can be described as a frozen landscape of potential wells and hills with some height and depth for inhibiting the evolution of the system in phase space. The time necessary for the system to jump from a given metastable state to another is shown to be thermally activated as

$$\tau_p = \tau_0 \exp(W/kT).$$

The small activation energy reflects the very small energy difference between the well and the hill of the potential, i.e., a very small barrier height. A very small perturbation in energy (as small as  $10^{-6}$  eV) allows the system to explore many neighboring states. One might think that at very low temperature the minima of nearly equal energy would be separated by high barriers through which tunneling would take place. Our results show that thermally activated processes dominate and *not tunneling states* as in structural glasses. This is confirmed by the absence of any electric echo in  $\text{K}_{0.3}\text{MoO}_3$  as recently reported.<sup>23</sup>

In conclusion, all the CDW compounds with nonlinear transport properties have a strongly disordered CDW state: Excitations between these metastable states yield an extra contribution to the specific heat with a  $T^\nu$  law with  $\nu < 1$ . Then the energy relaxation extends to very long times, exhibiting aging effects. We have shown that

the energy relaxation follows the power law for short times. These results are consistent with recent theoretical studies by Littlewood and Rammal<sup>24</sup> for the glassy relaxation of the polarization in a CDW, and may also probably be described by an extension of the recent model of Feigel'man and Vinokur<sup>25</sup> of a one-dimensional random walk in a random force field. As for spin-glasses,<sup>19</sup> thermodynamic measurements reveal thermal hopping over a large distribution of barriers between CDW metastable states with an arbitrarily low height.

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