Spontaneous Decay of Metastable States in Orthorhombic TaS_3

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High-accuracy, long-time dc conductivity measurements were performed at fixed temperatures. The conductivity corresponding to a metastable state created by a quick heat treatment was found to be time dependent on the time domain of $10-10^5$ sec. A logarithmic expression describes the time dependence in the entire temperature range investigated ($100\text{ K} < T < 150\text{ K}$). A simple model, based on the analogy with spin-glasses, is proposed. The possible role of low-energy excitations and infrared divergences is also discussed.

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New transport properties, associated with the collective response of charge density waves (CDW's), have been studied in a number of materials exhibiting the Peierls transition.[1] Orthorhombic TaS_3 is an excellent model system, where the nonlinear conductivity, the highly frequency-dependent ac conductivity, and the coherent current oscillations in the nonlinear regime have been investigated extensively.[2] Two phenomenological models, differing in the basic assumptions, were proposed to account for the above phenomena. In the tunneling model of Bardeen the CDW's are treated as quantum mechanical objects.[3] Grüner, Zawadowski, and Chaikin constructed a simple, classical model.[4] At certain points these attempts achieved a remarkable success in spite of the neglect of the internal degrees of freedom of the CDW's.

Recent investigation of the response to high-field pulses[5] and accurate measurements of the Ohmic conductivity[6,7] have shown the presence of metastable states in the material. Theoretical works on a classical, deformable medium demonstrated that a sharp threshold for the nonlinear conduction is possible for random pinning strengths and it was claimed that metastable states may evolve in this system.[8]

In this Letter we report results on the spontaneous relaxation of the metastable Ohmic conductivity in orthorhombic TaS_3. Although in earlier experiments[6,7] time dependence has not been found, the authors made only careful statements, taking into account the limited time domain available in experiments not especially planned for this type of studies. On theoretical grounds the system with random pinning strengths shows a slight similarity to spin-glasses, where the time dependence of magnetization and susceptibility have been thoroughly investigated.[9] Therefore we made special efforts to expand the accuracy and duration of the measurements in order to detect the expected weak (e.g., t^ν, $\nu\sim 0$, or $\log t$) time dependence.

Standard four-probe samples of high-purity TaS_3 (transition temperature $T_p = 222$ K, threshold field $E_T = 0.5$ V/cm) were prepared using 7-μm-diam annealed gold wires and silver glue. Setting of the sample current and voltage, current and time measurements were coordinated by a Hewlett-Packard model HP85 calculator. The temperature stability during the measurement was better than 0.05 K and He exchange gas improved the thermalization.

At a given temperature T the conductivity of the sample can always be brought to a unique, well defined value $\sigma_0(T)$ by application of conditioning pulses, i.e., electric field E high enough to depin the whole CDW condensate ($E > 4E_T$).[6] In the temperature range of $50\text{ K} < T < 190\text{ K}$, a metastable state can be created by a simple heat treatment.[6,7] The conductivity in the metastable state, σ, differs from σ_0 and $\Delta\sigma = \sigma - \sigma_0$ can be relaxed to zero in a few microseconds by conditioning.

For the investigation of a weakly time-dependent $\Delta\sigma(t)$ it is essential to cover several orders of magnitude in the time scale. The requirement of long-time temperature stability set an upper limit for the duration of the measurement; therefore we tried to expand the time scale to shorter times. Reliable measurements for short t are possible only if the thermalization after the heat treatment is quick enough. To reach the metastable state we directly heated the samply by a large current pulse. As the current pulse ceases the few-microgram mass of the sample is quenched in the He gas to the fixed, stable temperature of the sample holder.

Figure 1(a) shows the variation of the current during heating pulses of different magnitude. For the pulse of 2 V the conductivity of the sample is far in the nonlinear regime but there is no considerable temperature change. The increase of the magnitude of the pulses leads to the pulse shape characteristic of heating. The quenching process was monitored by small-amplitude measuring pulses [Fig. 1(b)]. The quick cooling results in a current decrease in the first few milliseconds. From the change in the current one can estimate a temperature change $\Delta T \sim 50$ K, i.e., $\Delta\sigma(\Delta T)$ is certainly in the saturation regime.[6] Application of conditioning pulses results in $\sigma \to \sigma_0$ relaxation similar to that observed after a conventional heat treatment.

The registration of $\Delta\sigma(t)$ was started ~10 sec after the quenching in order to be sure that no thermal transients are present. Protecting capacitors were connected to the current and potential leads to avoid unwanted conditioning by external noise. The electric field in the sample was kept below $E_T/20$. The small and time-independent thermopower contribution to the measured voltages was subtracted by current inversion. The accuracy of the conductivity measurements was better than 5×10^{-4}.

In Fig. 2 the time dependence of $\Delta\sigma/\sigma_0$ is plotted for different temperatures. To our knowledge this is the first evidence for the spontaneous decay of metastable states in a CDW system. The formula $\Delta\sigma/\sigma_0 = -A \log t + B$ fits the measured data with $A = 3\times 10^{-3}$ independent of temperature. The parameter B is temperature dependent, according to earlier observations.[6] Corresponding to this expression the conditioned value of the conductivity (i.e., $\Delta\sigma = 0$) would be reached in several thousand years, but for extremely long (and short) times the logarithmic time dependence is certainly not valid. Plotting $\log \Delta\sigma$ vs $\log t$ shows that $\Delta\sigma/\sigma_0 \sim t^{-\nu}$ cannot be excluded and the exponent is in the range of $0<\nu<0.1$. We would like to emphasize that conventional heat treatments result in the same time-dependent $\Delta\sigma(t)$, but the first two decades on the time scale are lost because of the thermal inertia of the sample holder.

Discussing the results we assume that the single-particle gap Δ is sensitive to the presence of metastable CDW states. A possible mechanism is that the pinning centers prevent the temperature-dependent[10] wave numbers of the CDW's from reaching their equilibrium value after a heat treatment and the frozen wave number results in a nonequilibrial gap.[11] The deviation $\delta = (\Delta - \Delta_0)/\Delta_0$ (where Δ_0 corresponds to the conditioned, stable state) manifests itself in the conductivity $\sigma \sim \exp(-\Delta/kT)$. The relative change in the conductivity for small δ is $\Delta\sigma/\sigma_0 = (\Delta_0/kT)\delta$. Another phenomenological assumption is that the CDW's relax to the equilibrium by thermally

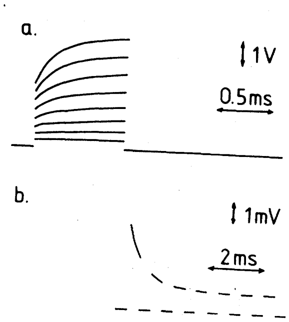

FIG. 1. Voltage measured on 1.6-kΩ reference resistor (a) for heating pulses of different magnitudes and (b) for sample current during the cooling process. Highest heating voltage was 9 V; other traces correspond to voltages decreased in steps of 1 V. To monitor the cooling (b) the oscilliscope was triggered at the end of the heating pulse of 9 V and pulses of 0.09 V were applied. Total sample length was 5 mm (threshold voltage ~ 0.25); temperature of sample holder T=110 K.

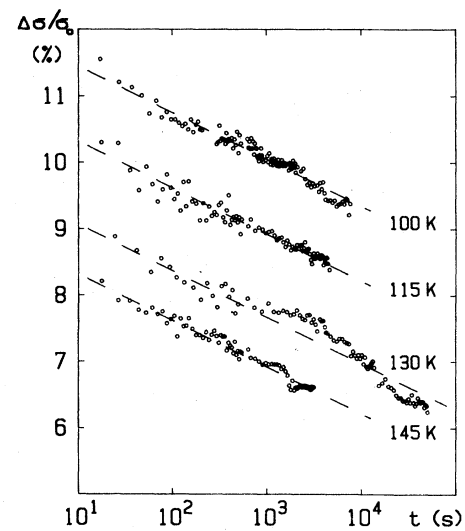

FIG. 2. Time dependence of conductivity σ after quenching at $t=0$. $\Delta\sigma = \sigma(t) - \sigma_0$, where σ_0 is the conditioned, stable value. Decrease of $\Delta\sigma$ corresponds to the spontaneous decay of metastable states. The distance between potential contacts is 3 mm; the cross section of the sample is 10 μm $\times$ 15 μm.

activated processes. The relaxation rate γ depends on the temperature and on the local pinning strength h in the form $\gamma = (1/\tau)\exp(-h/kT)$ where $1/\tau$ can be related to the phonon frequency. We suppose a wide distribution $P(h)$ for the pinning strengths and express the quantity characteristic of the decay of metastable states as $I(t) = \int_0^\infty dh\, P(h)\exp[-\gamma(h)t]$. This idea was originally applied for spin glasses by Ma.[9] The deviation in the gap is proportional to this quantity $\delta = \alpha I$. From the $t=0$ limit, $\delta = \alpha \int P(h)dh = \alpha$, one can estimate an upper bound to α since the deviation in the gap is probably not higher than a few percent. On the other hand at short times we observed $\Delta\sigma/\sigma \sim 10\%$ which corresponds to $\delta > 1\%$. Therefore we take $\alpha = 0.02$ as a rough estimate.

In case of flat distribution of pinning energies, i.e., if $P(h) = 1/D$ is constant for a range of h wider than kT the integral can be evaluated[9] and we get $\Delta\sigma/\sigma_0 = -\alpha(\Delta_0/D)\log t + B$ where B contains τ and other parameters characteristic of $P(h)$. We note that for uniform distribution D is the magnitude of the strongest pinning energy.

The above expression, obtained from the spin-glass analogy, describes the observed logarithmic time dependence. A crucial assumption was the random distribution of the individual pinning strengths. Fisher has shown[8] that this does not contradict the presence of a sharp threshold field for the nonlinear conduction. The slope $\alpha\Delta_0/D$ is independent of the temperature in agreement with the measurement (Fig. 2). Using the estimated value of α we can calculate the highest pinning energy from the measured slope as $D = \alpha\Delta_0/A \approx 0.5$ eV. Charged impurities, considered as strong pinnings by Lee and Rice,[12] lead to interaction energies of this magnitude.

Although with some reasonable assumptions we got a consistent picture, the model described above is not the only way to account for the observations. A wide variety of materials, including ceramics, ionic conductors, polymers, amorphous semiconductors, and electrochemical and biological systems, show anomalous long-time relaxation in response to different excitations (mechanical stresses, external electric fields, photocurrents, etc.). In a recent review, Ngai and Lin have proposed[13] a unified theory claiming that infrared (IR) divergences are responsible for these phenomena. The best known examples are the bremsstrahlung in quantum electrodynamics and the x-ray absorption-edge problem in solid state physics. The sudden application of a potential or a sudden change in the Hamiltonian and the availability of low-energy excitations (LEE's) are the common features to systems exhibiting IR divergences. As the equilibrium is approached the relaxation rate changes because of the presence of LEE's. In a Peierls system LEE's (e.g., long-wavelength acoustic modes of the deformable CDW's) are quite probably coupled to the rearrangement of CDW's. From this point our dc conductivity measurement is a sensitive but indirect tool to examine the internal state of the material. More detailed investigations on the frequency-dependent dielectric response may help to clarify the situation.

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