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A NOVEL SWITCHING PHENOMENON IN QUENCHED $NbSe_3$

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We have induced switching in nominally pure crystals of $NbSe_3$ by heating and quenching. The quenched switching samples display a number of novel characteristics including switching at temperatures up to 57K, a linear dependence of the threshold field on temperature, large statistical fluctuations of the threshold fields and long switching times on the order of a few ms. We propose that the quenched samples contain a large concentration of lattice defects, that these defects act as "ultrastrong pinning centers", and that the unusual aspects of switching in quenched samples are due to an unusally large concentration of these centers.

1. Introduction

The quasi one-dimensional conductor $NbSe_3$ undergoes Peierls distortions at 144 and 59K to form incommensurate charge density waves (CDWs).[1] Below the transitions the dc conductivity displays strong nonlinearities if a well-defined threshhold field E_T is exceeded, causing the CDW to slide. Most CDWs depin in a smooth manner. Many electronic properties of these conventional samples have been understood in terms of models which consider the dynamics of the CDW phase only.[2] Less well understood is the phenomenon of switching in selected crystals of $NbSe_3$.[3-6] Switching crystals are thought to contain "ultrastrong" pinning centers.[3] The CDW can slide past these centers only when the CDW amplitude collapses, nucleating a phase slip center. A model of switching CDW conduction has been proposed which considers both the amplitude and phase dynamics of the CDW.[4] Many experimentally-observed features of CDW dynamics are qualitatively reproduced, but much work remains to be done to understand pinning, avalanche depinning and chaos[6] that have been observed in switching CDWs.

The nature of the ultra strong pinning centers responsible for switching has been unclear. In this paper, we report that switching may be reproducibly induced in nominally pure samples of $NbSe_3$ by heating and quenching. Switching in the quenched samples occurs at unusually high temperatures. The switching times are two to three orders of magnitude longer than previously reported in unquenched switching samples. It is likely that a large number of lattice defects are frozen into the crystal during the quench. We conclude that lattice defects can cause switching. We attribute the unusual temperature and time dependence of switching in quenched samples to the large number of defects induced.

2. Experiment

High purity crystals of $NbSe_3$ were prepared by direct reaction of the elements. The original batch used for all experiments displayed threshold fields on the order of $E_T \approx 20mV/cm$ at T=48K and no switching samples were found. This was expected because the crystals had been grown more than two years before the testing, and switching samples are generally found only in recently grown batches[3]. Six batches were prepared by heating $NbSe_3$ to 570,620 or 670 C for four minutes and quenching with water or liquid nitrogen. The cooling rates averaged over the first 200 degrees were 12.6°K/s for water and 10.4°K/s for liquid nitrogen. To avoid oxidation of the $NbSe_3$, the samples were contained in a quartz tube that was evacuated to a pressure of P<2mTorr and continuously-pumped during the heat treatment. Prior to the heating, the quartz tubes were repeatedly washed with soap, methanol and nitric acid and were baked at 700 C in a vacuum for several hours. The difference in heat treatments did not seem to have any effect on either the temperature dependence of the switching threshhold fields or on the sizes of the switches. This might be because in our configuration the cooling rates for quenching with either water or liquid nitrogen are similar for the uppermost 200 degrees. Using the quenching procedure outlined above, switching was induced in more than 97% of the samples tested.

Quenched samples were mounted in two-probe configurations for the I-V measurements. Current leads were attached to single crystals using fine gold wires and conducting silver paint. Typical crystal dimensions were 1μm×5μm×4mm. A calibrated diode, located close to the sample, monitored temperature. The temperature was stable to within ±1mK. Current driven as well as voltage driven

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experiments were performed.

Fig. 1 examines the temperature-dependence of switching in quenched samples of $NbSe_3$. Fig. 1a shows a sequence of current-driven I-V curves measured at various temperatures in the switching regime. At 58.3K, just below the 60K Peierls transition temperature, the CDW depins smoothly. The 58.3K I-V curve has a sharp "knee" at E_T, a feature that is a precursor to switching.[7] As the temperature is lowered to 56.5K, two small switches appear. Multiple switches are common in switching CDWs and indicate the presence within the sample of serially arranged domains that depin at different electric fields.[3,8] We define the threshold field for the nth switch as E_{Cn}. Both the height of the switches and the switching threshold fields E_{C1} and E_{C2} grow as the temperature is lowered below 56.5K in Fig. 1a. The switch heights reach a maximum at T = 50.5 K and then begin to decrease. The switching thresholds continue to increase as temperature is lowered. Fig. 1b plots the temperature-dependence of the lowest critical fields E_{C1} in two different samples. The threshold fields are normalized to their minimum values. The normalized critical field E_{C1} depends linearly on temperature in the switching regime with a sample-independent slope. Near 40 K, the CDW depinned smoothly. Below 25K, the threshold field E_T, if it existed, was well in the heating region of the crystal ($E_T >$ 300 mV/cm).

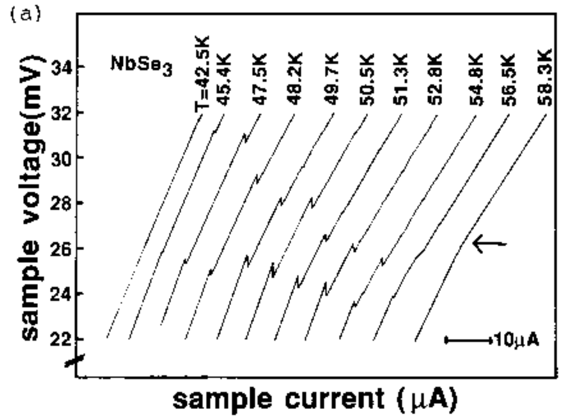

Figure 1a: dc I-V characteristics for a $NbSe_3$ crystal at several temperatures (current driven,increasing current). The arrow shows the threshold field at which the CDW has depinned for the trace at T=58.3K.

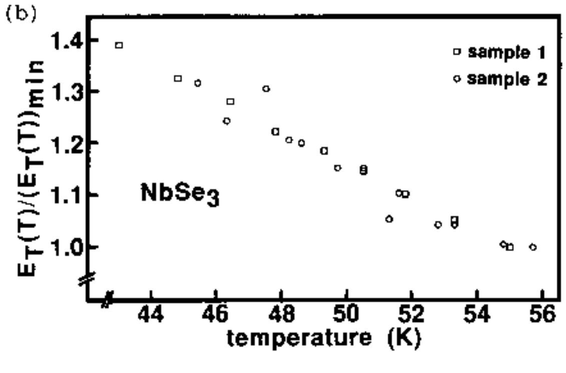

Figure 1b: Temperature-dependence of the lowest critical field EC1 for two switching samples of NbSe3. Each data set has been normalized to its minimum.

The I-V curves in Fig. 1a are typical of quenched samples. Multiple switches were present in all the quenched samples that we tested. Switches ranged in height from ΔVs ≈ 0.1mV to ΔVs ≈ 2.5mV and were strongly hysteretic. The lowest switching threshold fields E_{C1} varied between 25mV/cm and 100mV/cm at T=48K.

We have also investigated time delays associated with switching in quenched samples. When I-V traces are recorded for very slow current sweeps (as in Fig. 1), the switches at E_{Cn} appear to be instantaneous. Fig. 2 shows a single depinning event recorded on a digital oscilloscope. The current was swept at dI/dt=560μA/s, considerably faster than the sweep speeds used in Fig. 1. The voltage was sampled every 10μs. The switch does not occur instantaneously on this time scale. The CDW begins to depin at a well-defined voltage, indicated by the arrow. The CDW reaches the high-conductivity depinned state only after an unusually long time $\tau \approx 3$ms.

The switching process in quenched samples is also highly unpredictable. The threshold field E_{Cn} for each switch in the I-V curve, and even the number of switches in the I-V curve, varies significantly from run to run. In order to collect statistics on the probability distribution of the lowest critical field E_{C1} in a particular sample, 100 I-V traces were recorded on a digital oscilloscope. All experimental conditions were identical for each trace. Fig. 3 is a histogram showing the probability distribution of critical fields E_{C1} extracted from the 100 I-V traces. The normalized range of observed threshold fields is R=0.3 in Fig. 3 ($R = [E_{C1\,max} - E_{C1\,min}]/\langle E_{C1}\rangle$, where $E_{C1\,max}$, $E_{C1\,min}$, and $\langle E_{C1}\rangle$ are the maximum, minimum and mean of the ensemble of measured E_{C1}'s). The normalized range of threshold fields appears to be larger for samples with larger values of $(\Sigma_n \Delta V_n)/\langle V_C\rangle$, where ΔV_n is the voltage drop at the nth switch in a single I-V curve, and $\langle V_C\rangle$ is the average $1/N(\Sigma_n V_{Cn})$ where N is the total number of switches. The range of critical fields evident in Fig. 3 is roughly one order of magnitude larger than the range observed in other quenched samples.

3. Analysis

In conventional (nonswitching) CDWs, the CDW is pinned by relatively weak impurities. These are sufficiently strong to pin the phase of the CDW, but do not significantly distort its amplitude.[2] Thus most classical[2] and quantum-mechanical[9] models of sliding CDW conduction treat only

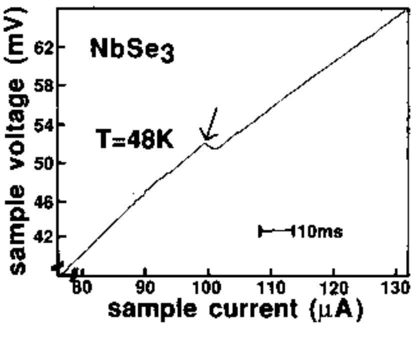

Figure 2: I-V characteristic (current driven, increasing current) for a $NbSe_3$ crystal in which the current was ramped at dI/dt=560μA/s. The voltage was sampled at 10μs intervals with a digitizer.

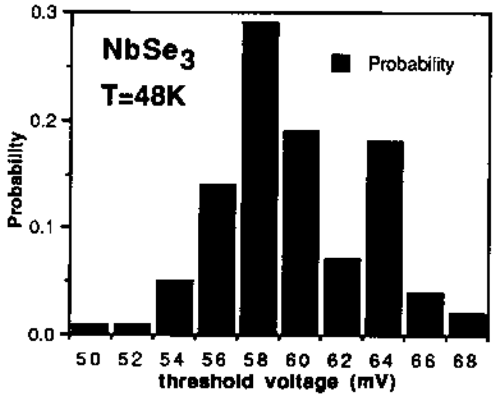

Fig. 3: Distribution of switching threshhold voltages for a $NbSe_3$ crystal. Current was swept at $dI/dt=560\mu A/s$ and the I-V characteristics (current driven, increasing current) were recorded with a digitizer. Statistics are based on 100 measurements of V_T.

the phase of the CDW as a dynamical variable. The amplitude of the CDW is assumed to be constant.

In switching samples, the CDW appears to be pinned by "ultrastrong pinning centers" in addition to conventional weak impurities.[3] The assumption of a constant CDW amplitude has been shown to be invalid in switching CDWs. Within a single dc-biased switching sample, segments of sliding CDW have been observed separated by less than 10 μm from segments of pinned CDW.[10] Periodic slippage of the CDW phase must occur at the interface between a pinned and sliding CDW segment. Thus, the interface must contain a "phase-slip center" (analogous to phase-slip centers observed in superconductors) in which the CDW amplitude is periodically driven to zero. A dynamical model of a CDW with a single phase-slip center has been proposed and qualitatively explains many features of switching CDW conduction, such as a hysteretic depinning transition, a period-doubling route to chaos, and inductive ac conductivity in the sliding state.

The response of switching CDWs to current pulses and to dc plus low-frequency ac electric fields suggest that switching CDWs depin via an avalanche of many ultrastrongly-pinned domains. When a pulse with $I>I_C$ is applied to an unquenched switching sample, Zettl and Grüner[11] found that the CDW remains pinned for a time τ_{wait} (a random variable with a Lorentzian probability distribution) after the beginning of the pulse, and then depins in a shorter time τ_{switch}. For pulse height $I=1.01\ I_C$, the average τ_{wait} was 100 μsec, and the switching time τ_{switch} was of the order of 10 μsec. Unquenched switching samples of $NbSe_3$ driven repeatedly through the switch in the I-V curve by dc plus low-frequency ac electric fields show "ac switching noise",[6] which is 10dB larger than conventional broad-band noise in a depinned switching CDW. The ac switching noise has been attributed to repeated avalanches, with the stochasticity arising from the unpredictability of each avalanche.

The results of Zettl and Grüner have been modeled by Joos and Murray[12] as arising from an avalanche-like process. Although the Joos-Murray model cannot explain many experimental results on switching (e.g., inductive ac conductivity in the sliding state, period-doubling route to chaos in the mode-locked state), it is a model that considers the statistical nature of depinning in switching CDWs. The CDW is treated as a two-dimensional ribbon of identical domains (the physical origin of the domains and their couplings are not specified in the Joos-Murray model). When an electric field exceeding threshold is applied to the crystal, each domain is assigned a probability per unit time of depinning. Once a single domain is depinned, it can trigger depinning of neighboring domains, thus setting off a "depinning wave" or avalanche. The depinning wave travels at a fixed velocity v_0 in the Joos-Murray model. The model reproduces the results reported by Zettl and Grüner, including the distribution of waiting times.

Strogatz et. al. [13] have recently proposed a mean-field model of switching. Switching delays arise in their model because of the finite time necessary to build up coherence between the phases of the CDW domains. Predictions have been made for the scaling of the switching delay times with $(E-E_C)$. However, it is not clear at this time how to relate the parameters of the Strogatz et. al. model to microscopic parameters of the CDW. Thus we will not use their model to compare the dynamics of quenched and unquenched samples.

Prior to our work, switching in nominally-pure $NbSe_3$ was observed primarily in freshly-grown samples. [3] (Switching is also observed in iron-doped $NbSe_3$, but these samples will not be discussed in this paper.) The temperature-dependence, switching delay times and range of threshold fields observed for quenched switching samples of $NbSe_3$ differ dramatically from the analogous properties of unquenched switching samples. In unquenched samples, switching is a relatively rare phenomenon. In some unquenched batches of $NbSe_3$ no samples switch, whereas in other batches, over 50% of the samples switch.[3] Switching was observed in over 97% of quenched samples. Unquenched samples of $NbSe_3$ show switching only for temperatures[3,7] less than 30K. Quenched samples show switching between 42K and 57K. Unquenched samples show switching times[11] of the order of $\tau_{switch} \approx 1\text{-}10$ μsec, compared with $\tau_{switch} > 1$ msec for quenched samples. No fluctuations in the critical field have been observed for unquenched switching samples. Critical fields for quenched samples fluctuate up to 30% from run to run.

In our heat treatment, $NbSe_3$ crystals were quenched from near the formation temperature. At high temperatures, the equilibrium density of defects is relatively large. During the rapid quench, many defects such as dislocation lines must freeze into the crystal. We have notice that Se begins to dissociate from $NbSe_3$ above T=500K, and thus some Se vacancies were also induced in our heat treatment. We propose that lattice defects form ultrastrong pinning centers that cause switching in quenched samples. The hypothesis that ultrastrong pinning centers in nominally-pure (as opposed to iron-doped) switching samples are lattice defects is consistent with the observation that switching seems to occur more frequently in recently-grown batches of $NbSe_3$. Nonequilibrium lattice defects can be expected to heal over long time scales, reducing the number of ultrastrong pinning centers and hence the incidence of switching. We attribute the difference between quenched and unquenched samples to the high density of defects in the former. The high incidence of switching in quenched samples is then attributed to the large number of ultrastrong pinning centers in each sample.

In order to attribute to a high density of ultrastrong pinning centers the 2-3 order of magnitude difference in switching times between quenched and unquenched samples, a small modification to the Joos-Murray model appears necessary. We assume that the domains in the Joos-Murray model correspond to a domain of CDW pinned by an ultrastrong pinning center. In the Joos-Murray model, the velocity of the depinning wave is assumed to be independent of the density of defects. The switching time cannot exceed the time required for a depinning wave to traverse a sample. Joos and Murray estimated a depinning velocity of 17m/sec from the data of Zettl and Grüner[11] on an unquenched sample. For a sample of the order of 5 mm long, this yields a maximum switching time of the order of 300μsec, an order of magnitude smaller than the time we observed. Thus, in order to be consistent with the Joos-Murray model, the velocity of the depinning wave must be at least an order of magnitude slower in quenched than in unquenched samples (in the switching temperature range of each sample). Since switching in quenched samples occurs at higher temperatures than in unquenched samples, the difference in velocity of the depinning wave could be attributed to a temperature-dependent velocity for the depinning wave. However, it would also be possible to modify the Joos-Murray model to make the velocity of the depinning wave depend explicitly on the density of domains. If one assumes that a fixed delay is required for a sliding domain to trigger a static neighboring domain, the velocity of a depinning wave would be proportional to the density of domains. The main results of the Joos-Murray model would still hold, (for instance, delay and switching times in response to an electric field pulse). However, the maximum switching time and delay times would become extensive quantities, proportional to the number of longitudinal domains in a sample of fixed size.

We have shown that heating nonswitching, nominally-pure $NbSe_3$ to near its formation temperature and then rapidly quenching it induces switching with near unit efficiency. The switching induced in quenched samples is quite different from switching in unquenched samples. In quenched samples, switching occurs at higher temperatures, the switching times are longer, and there is large scatter in the switching thresholds E_C for a given sample. We propose that a high density of lattice defects is frozen into the quenched samples, and that these defects form ultrastrong pinning centers, and that the high density of ultrastrong pinning centers is responsible for the unusual observed properties. An independent measurement of the density and type of defects in switching samples (e. g. , using transmission electron microscopy) is being attempted by one of us (MSS). This will enable a direct correlation of defect type and density with electronic properties, opening the door to a microscopic structural understanding of switching and amplitude dynamics in charge-density-wave conductors.

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