Structure and kinetics of the sliding Q_1 CDW in NbSe_3

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Abstract: Using crystallographically perfect single crystal whiskers of NbSe_3 and the synchrotron x-ray scattering facilities at CHESS, we have performed detailed high resolution measurements of the structure of a sliding CDW. We observe the longitudinal strain of the CDW associated with the phase slip necessary to convert between normal and collective current at the electrical contacts. Using a stroboscopic x-ray scattering technique, we have extended these measurements into the time domain and studied the evolution of the structure of the sliding CDW as it responds to a reversal of the direction of an applied d.c. electric field. The time constant characterizing this structural evolution is on the order of milliseconds for fields well above threshold. Near threshold the CDW splits into two components; one component is pinned and the other is sliding. As the electric field strength is increased, the fraction of the CDW which remains pinned decreases monotonically.

1 Introduction

X-ray scattering is frequently the technique of choice for quantitative structural studies of materials for two reasons. First, the intensity and collimation associated with modern synchrotron x-ray sources allow extremely high resolution measurements of scattered line shapes from very weakly scattering structures. Typical uncertainties in the magnitude of the scattered wave vector, $\frac{\delta q}{q}$, are on the order of $10^{-4} \rightarrow 10^{-5}$. Second, in most x-ray scattering measurements, the scattered intensity is directly proportional to the spatial Fourier transform of the *instantaneous* or *equal-time* electronic density-density correlation function, $G(\vec{r}, t) = \langle \rho(\vec{0}, t) \rho(\vec{r}, t) \rangle$. Thus, experimenters are able to make quantitative measurements of the correlation lengths, susceptibilities and critical exponents of physical systems which can be directly compared to theoretical predictions. During the past twenty years, x-ray scattering measurements of the correlations found near phase transitions in physical systems have both driven and confirmed the theoretical development of equilibrium critical phenomena. As a result, the statistical physics of systems in thermal equilibrium is, more or less, a solved problem. Consequently, many physicists are now turning their attention to non-equilibrium systems. In particular, systems which are so far out of equilibrium that standard near-equilibrium techniques do not apply are attracting considerable interest, largely due to their technological importance. We have been studying two classes of non-equilibrium systems:

- systems which evolved in the presence of quenched randomness[1],[2], and
- systems which evolve in response to a time dependent field[3],[4].

Several of the quasi-one-dimensional charge density wave (CDW) systems are appealing material systems in which to study these fundamental problems. In particular, crystallographically perfect whiskers of NbSe_3 can be grown and reliably doped with tantalum over a large range of concentrations. Thus, quenched random disorder can easily be introduced and characterized. Additionally, the Q_1 CDW in NbSe_3 has been extensively characterized by IV transport measurements. It is well known that it can be depinned by modest

electric fields, exhibits sample size dependent effects, and exhibits transient behaviors on widely varying time scales. In this paper, we will report on our recent work on the time-dependent structure of a sliding CDW.

2 Review of Basic Theoretical Ideas

2.1 Phase Slip & CDW Strain

In simple one-dimensional lattice models[5], the CDW state consists of a periodic modulation of the conduction electron density and a periodic longitudinal lattice distortion of the form $u(\vec{r}) = u_1 \cos[\vec{Q} \cdot \vec{r} + \phi(\vec{r}, t)]$ where $|\vec{Q}| = 2k_F$ is the CDW wave vector, ϕ is the phase of the CDW order parameter and k_F is the Fermi wave number. In an ideal crystal, there is no energetically favored location for a CDW whose wave number incommensurate with the reciprocal lattice. The absence of a preferred position implies that there is no elastic restoring force. Thus, a vanishingly small electric field can push a CDW through the crystal *rigidly*, producing a collective current[6]. Real crystals, of course, contain impurities and other defects which will provide an energetically preferred location for the CDW and pin the phase. *Sliding* of the CDW occurs only for electric fields greater than a threshold field, E_T .

The boundary conditions imposed at the electrical contacts play a crucial role in determining the structure of the sliding CDW state. Since $E = 0$ in the regions outside of the contacts, the CDW always remains pinned there. Collective current flow requires a mechanism for inserting or extracting CDW phase fronts at the contacts, and for converting between collective current and single-particle current. As in superconduc-

Figure 1: Schematic illustration of the experimental configuration used in these experiments. Current is injected through the contacts and leads to a motion of the CDW phase fronts in the region between the contacts. The width of the x-ray beam in the b^* direction was 0.8 mm. The distance between the electrical contacts was 4.5 mm.

tors and superfluids, this mechanism is provided by phase slip[7], and is driven by spatial gradients in ϕ . Unlike these other systems, however, the gradients are determined by the boundary conditions rather than the flow velocity. As illustrated in the Fig. 1, depinning between the contacts is expected to produce an expansion of the CDW near one electrode and a compression of the CDW near the other [8],[9].

2.2 X-ray Scattering

The usefulness of x-ray scattering as a structural probe is, in large part, due to the absence of significant multiple scattering. Therefore, *kinematic* scattering theory accurately describes the scattered line shapes. In the *kinematic approximation*, the differential scattering cross section is proportional to the *static structure factor*, $\mathcal{S}(\vec{q})$, the spatial Fourier transform of the *equal-time* electronic density-density correlation function[10].

$$\mathcal{S}(\vec{q}, t) \sim \int d\vec{r}_1 d\vec{r}_2 e^{i\vec{q} \cdot (\vec{r}_1 - \vec{r}_2)} \langle \rho(\vec{r}_1, t) \rho(\vec{r}_2, t) \rangle = \langle |\rho_{\vec{q}}(t)|^2 \rangle$$

Here, $\rho(\vec{r}, t)$ is the electronic charge density, and $\hbar\vec{q}$ is the momentum transferred in the scattering process. The angular bracket indicates an ensemble average over the allowed states of the system.

2.3 X-ray Scattering from CDW's

The essential physics required to understand the scattering from an incommensurate CDW is illustrated by considering the scattering from a simple incommensurate lattice distortion wave in a monatomic crystal[11]. At $T = 0$, the density of an ideal crystal is given by $\rho(\vec{r}) = \sum_j \rho_A(\vec{r} - \vec{R}_j)$ where $\rho_A(\vec{r})$ is the density of an atom at the origin and $\vec{R}_j$ is the equilibrium position of the j^{th} atom. The lattice distortion wave is introduced by letting $\vec{R}_j \rightarrow \vec{R}_j + \vec{u} \sin(\vec{Q} \cdot \vec{R}_j + \phi(\vec{R}_j))$. We then proceed, ignoring amplitude fluctuations, to calculate $\langle |\rho_{\vec{q}}|^2 \rangle$, arriving at the expression[12]

$$S(\vec{q}, t) \sim |F(\vec{q})|^2 \left[|J_0(\vec{q} \cdot \vec{u})|^2 \sum_j e^{i\vec{q} \cdot \vec{R}_j} + |J_1(\vec{q} \cdot \vec{u})|^2 \sum_j e^{i(\vec{q} \pm \vec{Q}) \cdot \vec{R}_j} \langle e^{i[\phi(\vec{R}_j, t) - \phi(\vec{R}_j, t)]} \rangle + \dots \right].$$

Here, $|F(\vec{q})|^2$ is the atomic form factor and $J_n(x)$ is the n^{th} order Bessel function. The first sum inside the square brackets produces the Bragg peaks associated with the undistorted crystal lattice. The second sum creates satellite peaks at $\pm \vec{Q}$ from each Bragg peak. The line shape of these CDW satellite peaks is given, independent of the microscopic model, by the spatial Fourier transform of the *equal-time-phase-phase* correlation function.

3 Steady State Measurements

The scattering measurements were performed on the A-2 and F-2 wiggler beam lines at the Cornell High Energy Synchrotron Source (CHESS). A double-bounce Si(111) monochromator selected 8.25 keV x-rays from the white wiggler beam. A flat mirror located inside the hutch rejected higher harmonics in the x-ray beam. The sagittally bent second monochromator crystal focused the x-ray beam in the out-of-scattering-plane direction at the sample position. A set of tantalum slits immediately before the sample limited the size of the x-ray beam at the sample to a spot approximately $0.8 \text{ mm} \times 3 \text{ mm}$, which contained 4×10^{10} photons/second/100 mA of storage ring current. The scattered x-rays were analyzed and collected using a triple bounce, channel cut Si(111) analyzer crystal and a NaI(Tl) scintillation detector.

All of the data presented here were taken using high-purity (residual resistivity ratio > 300) NbSe₃ crystals. Typical sample dimensions were $20 \mu\text{m} \times 2 \mu\text{m} \times 5 \text{ mm}$. The NbSe₃ whiskers were mounted using silver paint onto an alumina substrate, which contained a 3.5 mm hole to permit transmission of the x-rays. Sample cooling with a temperature stability of 0.1 K was provided by a closed-cycle helium refrigerator.

NbSe₃ has a monoclinic unit cell with reciprocal lattice constants $a^* = 0.6658 \text{ \AA}^{-1}$, $b^* = 1.806 \text{ \AA}^{-1}$, $c^* = 0.4264 \text{ \AA}^{-1}$, and $\beta = 70.53^\circ$ [13]. Two independent CDWs form at $T_{P_1} = 145 \text{ K}$ and $T_{P_2} = 59 \text{ K}$. The former has the wave vector $\vec{q}_1 = (0, Q, 0)$ with $Q \sim 0.243$. We chose to study the $(0, 1 + Q, 0)$ superlattice reflection because it is very near to the non-dispersive diffraction condition of our Si(111) monochromator. The resulting resolution (FWHM) of our diffractometer at $(0, 1 + Q, 0)$ is $\delta q = 2.8 \times 10^{-4} \text{ \AA}^{-1}$. The sample was oriented with the a^* and b^* reciprocal lattice vectors in the scattering plane.

One of the attractive materials properties of NbSe₃ is its metallic character at low temperatures. The electronic transport is dominated by normal carriers and the samples cannot support much polarization due to imperfect electrical contacts. On the other hand, Ohmic heating is definitely a concern in these very small whiskers. To avoid structural changes due to Ohmic heating, sample currents were pulsed at 100 Hz with a duty cycle of 1%. Figure 2 shows scans along b^* through the CDW superlattice peak at $T = 90 \text{ K}$, for two pulsed currents of equal magnitude and opposite direction. Relative to the zero field-cooled-state, the peaks in the current carrying state are slightly broader and are shifted along b^* , the direction of the shift depending upon the direction of the current. When the current was turned off, the peak recovered on a time scale of minutes. The shift between the positive and negative current-carrying states of the $(0, 1 + Q, 0)$ peak is opposite to that of the $(0, 1 + Q, 0)$ peak. In contrast, currents do not produce any broadening or shift of the (020) Bragg peak. Thus, the CDW peak shifts are due to changes in the CDW structure. A simple one-dimensional model[9] predicts a linear relationship between ΔQ and the position in the sample, $\Delta Q(z) = \frac{e\rho_c}{QK_z} V_{ps} \left(\frac{z}{L} \right)$, where z is the position measured from the midpoint between the contacts, L is the distance between the contacts, $e\rho_c$ is the CDW charge density, and K_z is the CDW elastic constant. The phase slip voltage V_{ps} is the additional voltage (beyond that required to overcome pinning forces) required to produce this wave number variation. Figure 2b illustrates this linear variation[1].

Figure 2: (a) Typical scans along the b^* direction through the $(0, 1 + Q, 0)$ CDW superlattice peak, approximately 1 mm from the center of the contacts. Triangles and squares indicate data obtained for positive and negative currents, respectively. Error bars represent counting statistics. (b) Shift in the CDW satellite peak position $\Delta Q = \frac{1}{2}[Q(I_+) - Q(I_-)]$ vs position on the sample.

4 Time-Resolved Measurements

Utilizing a stroboscopic detection technique[14], standard x-ray scattering measurements can be extended into the time domain. A periodic voltage wave form is applied to the sample, as shown in the inset to Figure 3a. A multi-channel scalar records the scattered x-rays which are detected in a given time bin. The scalar advances to the next time bin at each clock pulse. At the end of the current wave form, the scalar returns to the first bin. A signal averaging memory unit adds together x-rays detected in different current cycles. The experiment proceeds point by point in reciprocal space, acquiring a complete time series before moving on to the next reciprocal space point. A typical data set (summed over 10^4 sweeps/ q -point) is shown in Figure 3(a). To eliminate periodic structural effects due to heating, we used bipolar current wave forms, which

Figure 3: (a) Contour plot of intensity as a function of time and scattering vector $(0, q, 0)$. Lines are lines of constant scattered intensity. (b) Best fit peak position as a function of time. The solid line is the best fit to an exponential decay. $I/I_T \sim 1$ for this sample.

keep the sample heating constant. The sample temperature was estimated by both measuring the sample resistance and by measuring $|\vec{Q}|$ [15]. The data set can now be analyzed to determine the peak position, peak width and integrated intensity as a function of time. Figure 3b illustrates typical peak position vs time results.

At low driving fields, the behavior is very rich. For example Figure 4(a) shows data taken just above threshold. The peak splits into two pieces with one portion remaining stationary while the other peak

Figure 4: (a) Scans along b^* as a function of time. Each scan is offset for clarity. $I/I_T \sim 1$ and $T = 70\text{K}$ (b) Fraction of the total integrated intensity contained in the stationary peak vs I . $I_T \sim 20 \text{ mA}$.

moves back and forth. Line shape analysis reveals that, although the peak widths vary with time, the integrated intensity under each peak is constant and the integrated intensity of the moving peak decreases monotonically as the applied field strength is increased.[4] That is, near threshold, only a portion of the CDW slides, the rest remains pinned. Well above threshold, the entire CDW slides. At all currents, the time constants describing the structural evolution were on the order of milliseconds. These measurements support Gill's explanation of many of the memory effects in terms of lattice strains.[16] The time constant to get into the sliding state is much shorter than that characterizing the relaxation towards the pinned state. Thus, the sliding state is metastable.

5 Discussion & Future Directions

The extension of standard kinematic scattering theory from the equilibrium case to the time-dependent case is straight forward. We write down the form of $\mathcal{S}(\vec{q}, t)$ and explicitly write out the average indicated by the angular brackets.

$$\frac{d}{dt}\mathcal{S}(\vec{q}, t) \sim \int d\vec{r}_1 d\vec{r}_2 e^{i\vec{q} \cdot (\vec{r}_1 - \vec{r}_2)} \int \mathcal{D}\{\phi(\vec{r})\} e^{i\phi(\vec{r}_1)} e^{-i\phi(\vec{r}_2)} \frac{d}{dt} P[\phi(\vec{r}), t]$$

Here $\mathcal{D}\{\phi(\vec{r})\}$ indicates a functional integration and $P[\phi(\vec{r}), t]$ is the probability distribution functional. All of the time dependence of $\mathcal{S}(\vec{q}, t)$ is contained in the time dependence of $P[\phi(\vec{r}), t]$.

The problem can now be mapped onto theories of the kinetics of first order phase transitions, in which one develops an equation of motion for $\mathcal{S}(\vec{q})$. The key step is to develop an equation of motion for the probability distribution $P[\phi]$ over the space of configurations $\{\phi\}$. This is typically done by beginning with a Langevin equation for ϕ [17]. A one-dimensional Langevin equation of motion for ϕ has been developed using microscopic arguments [18],[9].

$$\gamma \frac{\partial \phi(x, t)}{\partial t} = K_z \Delta^2 \frac{\partial^2 \phi(x, t)}{\partial x^2} + \frac{e\rho_c}{2k_F} E + F_{imp}(\phi) + \eta(x, t)$$

Here Δ is the magnitude of the CDW order parameter, $F_{imp}(\phi)$ is the quenched random pinning force and $\eta(x, t)$ is a *noise* field. We hope to study this and possibly other Langevin equations by isolating the behaviors due to the various terms in the equation by, for example, using field strengths well above threshold so that V_{ps} and η are unimportant or by watching the evolution of the system from the sliding to the pinned state where $E = 0$ and V_{ps} should control the behavior.

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