Field-Induced Charge-Density-Wave Deformations and Phase Slip in $NbSe_3$

D. DiCarlo,[1] E. Sweetland,[1] M. Sutton,[2,a] J. D. Brock,[2] and R. E. Thorne[1]
[1]*Laboratory of Atomic and Solid State Physics and Materials Science Center, Cornell University, Ithaca, New York 14853*
[2]*School of Applied and Engineering Physics and Materials Science Center, Cornell University, Ithaca, New York 14853*
(Received 28 September 1992)

We report x-ray diffraction measurements of the effects of electric fields on charge-density-wave (CDW) structure in $NbSe_3$. For fields exceeding the CDW depinning field E_T, the $(0\,1+Q\,0)$ CDW superlattice peak shifts along b^*. The shift increases rapidly with decreasing temperature, is largest near the electrical contacts, and is in opposite directions in the two halves of the crystal. We show that the observed CDW deformations are consistent with those required for phase slip and CDW-to-normal carrier conversion at the contacts. From the magnitude of these deformations, we determine the CDW elastic constant.

PACS numbers: 72.15.Nj

Quasi-one-dimensional metals such as $NbSe_3$ are unstable to formation of a charge-density wave (CDW), in which the electron density exhibits a periodic modulation [1]. This modulation is accompanied by a lattice distortion of the form $u(\mathbf{r})=u_1\cos[\mathbf{Q}\cdot\mathbf{r}+\phi(\mathbf{r},t)]$, where $|\mathbf{Q}|=2k_F$ is the CDW wave vector and ϕ is the phase of the CDW order parameter. In a perfect crystal, a CDW with $\mathbf{Q}$ incommensurate to the reciprocal lattice would have no preferred phase ϕ. The CDW could then "slide" freely through the crystal, resulting in collective charge transport and a current $I_c \propto d\phi/dt$. Real crystals contain impurities and other defects which pin the phase, and the CDW lowers its energy by elastically deforming. CDW sliding thus occurs only for electric fields greater than a threshold field E_T.

Electrical contacts must play a crucial role in determining the structure of the sliding CDW state. Since $E=0$ beyond the contacts, the CDW always remains pinned there. CDW current flow thus requires a mechanism for adding or removing CDW wave fronts at the contacts, and for converting between collective current and single-particle current. As in superconductors and superfluids, this mechanism is provided by phase slip [2–5], and is driven by gradients in the phase ϕ of the order parameter. Unlike these other systems, however, the gradients are determined not by the flow velocity but by boundary conditions [3,4]. As illustrated in Fig. 1, depinning between the contacts is expected to produce compression of the CDW near one contact and expansion near the other. The phase slip rate at the contacts, and thus the time-averaged CDW velocity between the contacts, is determined by the magnitude of these compressions and expansions [4].

Here we report high-resolution x-ray scattering measurements which provide direct evidence for phase-slip-related CDW deformations in $NbSe_3$. We observe longitudinal shifts of the CDW wave vector which depend strongly upon electric field and temperature. Most importantly, we observe a systematic position dependence, which establishes that the shifts are due to boundary conditions. These results are in excellent agreement with prediction [4] based upon recent electrical measurements of phase slip, and allow a novel, model-insensitive estimate of the CDW elastic constant.

The scattering measurements were performed on the A-2 experimental station at the Cornell High Energy Synchrotron Source (CHESS). A double-bounce Si(111) monochromator selected a wavelength of 1.5 Å, and a flat quartz mirror suppressed harmonics. The second monochromator crystal was sagittally bent to focus the x-ray beam in the out-of-scattering-plane direction. Ta slits produced a spot size at the sample of approximately 0.8 mm×3 mm, containing 4×10^{10} phonons/sec at a ring current of 100 mA. Scattered x rays were collected using a Si(111) analyzer crystal and a NaI(Tl) detector.

$NbSe_3$ has a monoclinic unit cell with reciprocal lattice constants of $a^*=0.6658$ Å^{-1}, $b^*=1.806$ Å^{-1}, $c^*=0.4264$ Å^{-1}, and $\beta=70.53°$ (Ref. [6]). Independent CDWs form at $T_{P_1}=145$ K and $T_{P_2}=59$ K, the former

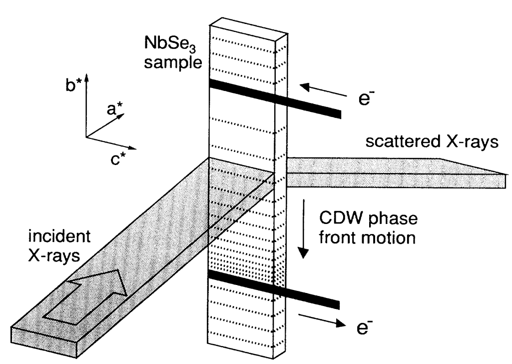

FIG. 1. Schematic illustration of the configuration used in the x-ray scattering experiments. Current injected through the contacts (black) leads to motion of the CDW phase fronts (dotted lines) between the contacts. The x-ray beam width along the b^* direction was 0.8 mm, and the contact separation was 4.5 mm.

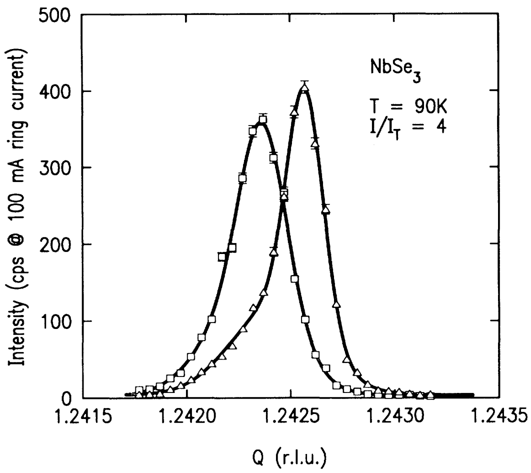

FIG. 2. Typical scans along the b^* direction through the $(0\,1+Q\,0)$ CDW superlattice peak at $T=90$ K and $z=1$ mm for $I/I_T=4$. Triangles and squares indicate data obtained for positive and negative currents, respectively. Error bars represent counting statistics. The solid lines are guides to the eye.

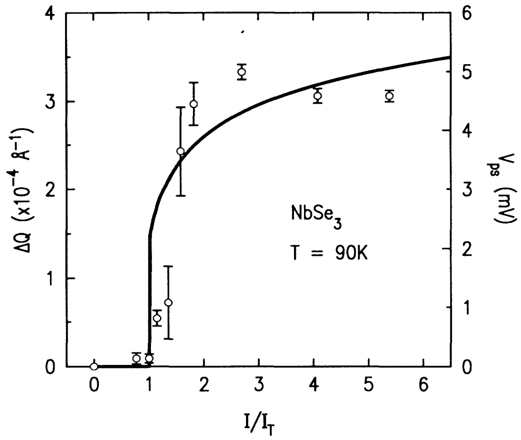

FIG. 3. Shift in CDW peak position $\Delta Q=\frac{1}{2}[Q(+|I|)-Q(-|I|)]$ at $z=1$ mm (circles) and phase slip voltage V_{ps} (solid line, from Ref. [14]) vs I/I_T at $T=90$ K. Error bars represent a doubling of χ^2.

having a wave vector $\mathbf{q}_1=(0,Q,0)$ with $Q\approx 0.243$. We chose to study the $(0\,1+Q\,0)$ CDW superlattice reflection of the T_{P_1} CDW because it is nearest to the nondispersive diffraction condition for our Si(111) monochromator. The resulting resolution (FWHM) of our diffractometer at $(0\,1+Q\,0)$ is $\delta q=2.8\times10^{-4}$ Å^{-1}.

Two high-purity (residual resistivity ratio > 300) $NbSe_3$ single crystals were examined. Sample 1 had dimensions of 8 mm (along b^*)$\times$40 μm$\times$7 μm, a θ rocking width [7] for the (020) peak of 0.008°, a threshold field $E_T(T=90$ K) of 42 mV/cm, a threshold current $I_T(T=90$ K) of 1.3 mA, and a current contact separation of $L=4.5$ mm. Sample 2 had dimensions of 8 mm$\times$190 μm$\times$11 μm and a width of 0.03°. The samples were mounted using silver paint on an alumina substrate, which contained a 3.5 mm hole to permit transmission of x rays. Sample cooling with a temperature stability of 0.1 K was provided by a closed-cycle helium refrigerator. To avoid Ohmic heating, sample currents were pulsed at 100 Hz with a duty cycle of 1%. All data presented here are for sample 1, although similar results were obtained for sample 2.

Figure 2 shows scans along b^* through the CDW superlattice peak at $T=90$ K, for two pulsed currents of equal magnitude $|I|=4|I_T|$ and opposite direction. Here, I is the total current, equal to the sum of the CDW current I_c and the single-particle current I_n. 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 [8,9]. 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 [10,11]. These results indicate that the CDW peak shifts are due only to changes in CDW structure. Furthermore, CDW peaks obtained using x rays collected during the current pulses and those obtained during the ~10 msec between pulses were identical. Because of this metastability, the current-induced states could be characterized using x rays collected during the full period of the current wave form. Significant relaxation of the current-induced states occurred only on a time scale of tens of seconds. The relaxed ($I=0$) state was reproducible, but was different from the zero-field-cooled state. The $I>I_T$ peaks were also completely reproducible and history independent.

Because the peak shifts are small, we define $\Delta Q=\frac{1}{2}[Q(+|I|)-Q(-|I|)]$, in order to avoid systematic errors [10]. Figure 3 shows this ΔQ vs I/I_T at $T=90$ K. The mean CDW wave vectors were obtained by fitting

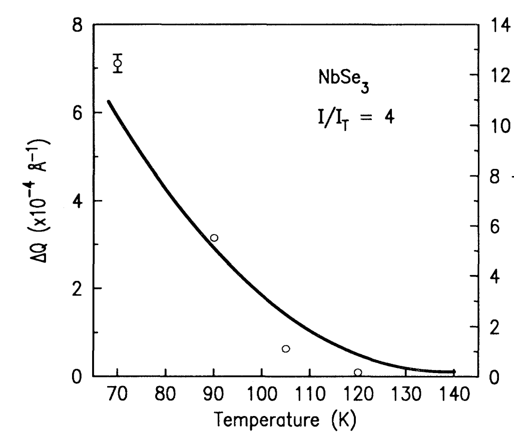

FIG. 4. Shift in CDW peak position ΔQ at $z=1$ mm (circles) and phase slip voltage V_{ps} (solid line, from Ref. [14]) vs temperature for $I/I_T=4$.

the CDW peaks with a pseudo-Voigt line shape using a nonlinear least-squares algorithm. The shift is negligible for $|I| < |I_T|$ and increases rapidly just above I_T. The shift either increases or decreases slightly as I is increased further, depending upon the portion of the sample illuminated. Similar behavior was observed at all temperatures studied.

Figure 4 shows the longitudinal wave-vector shift ΔQ versus temperature for $I/I_T=4$. The shift increases strongly with decreasing temperature. Figure 5 shows ΔQ at $I/I_T=4$ measured by illuminating different positions z along the sample. We define $z=0$ to be midway between the contacts [12], and positive z to be in the direction of the contact which has positive polarity when $+|I|$ is applied. The wave-vector shift varies monotonically with position, and has opposite signs in the two halves of the crystal.

Field-dependent changes in CDW structure are expected as a consequence of impurity pinning [1,13]. However, variations of the average structure or CDW wave vector on macroscopic length scales are not predicted.

One interpretation is that the observed wave-vector changes are associated with the CDW phase slip necessary for CDW-to-normal carrier conversion at the contacts. In a simple 1D model [3,4], the CDW wave vector varies between the contacts according to

$$\Delta Q(z)=\frac{\partial \phi}{\partial z}=\frac{e\rho_c}{QK_z}V_{\mathrm{ps}}\left(\frac{z}{L}\right). \quad (1)$$

Here z is the position measured from the midpoint between the contacts, L is the contact separation, $e\rho_c$ 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 needed to overcome pinning forces) required to produce this wave-vector variation; its magnitude determines the phase slip rate and CDW current. As indicated by the solid line in Fig. 5, this linear wave-vector variation provides a good qualitative description of the data. Since the CDW compresses ($\Delta Q > 0$) near the positive contact, the CDW's charge must be negative, as expected.

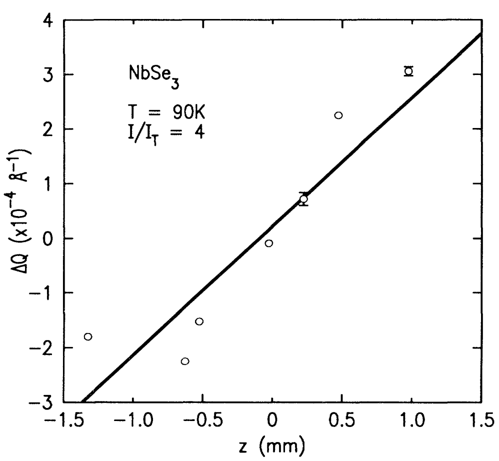

FIG. 5. Shift in CDW peak position ΔQ vs the position of the x-ray beam on the crystal (z) for $I/I_T=4$ at $T=90$ K. The solid line indicates the fit of Eq. (1).

Detailed electrical measurements of the phase slip process in $NbSe_3$ have recently been reported by Maher *et al.* [14] using a method introduced by Gill and by Monceau *et al.* [15]. The variation of the CDW current I_c (proportional to the phase slip rate) with the phase slip voltage V_{ps} and temperature was found to be consistent with the predictions of Ramakrishna *et al.* [4] for CDW phase slip by dislocation loop nucleation. If the CDW deformations observed here are due to phase slip, then Eq. (1) implies that the ΔQ-I_c relation should have the same form as the V_{ps}-I_c relation. The solid line in Fig. 3 indicates a fit to the data of Maher *et al.* for $NbSe_3$ at $T=90$ K. The qualitative agreement with the x-ray data is very good. The solid line in Fig. 4 indicates the data of Maher *et al.* for the temperature dependence of V_{ps} at $I/I_T=4$. The strong increase in V_{ps} with decreasing temperature (attributed to the thermal activation of the phase slip) [4,15] is also in good agreement with the behavior of the wave-vector shift. These results provide compelling evidence that the observed CDW deformations are associated with phase slip.

The effects of electric fields upon CDW structure have been investigated in several previous studies [16–19]. The implicit focus of these studies has been structural changes related to impurity pinning. In the first such study, using $NbSe_3$, Fleming *et al.* [16] did not observe any field-dependent effects. Using $K_{0.3}MoO_3$, Tamegai *et al.* [17] found broadenings and shifts of the CDW diffraction peaks *transverse* to the CDW wave vector for applied fields above threshold. These effects depended upon both the direction and the magnitude of the field, and persisted long after the field was reduced below E_T. Similar effects, as well as a longitudinal broadening, have been observed in $K_{0.3}MoO_3$ by Mihaly, Lee, and Stephens [18] and by Zhang *et al.* [19]. Interpretation of $K_{0.3}MoO_3$ experiments is difficult because, unlike $NbSe_3$, electric fields and current densities within this material tend to be highly inhomogeneous; Tamegai *et al.* [17] showed that these inhomogeneities were responsible for most of the structural changes they observed. However, based upon some similarities with the behavior described here, we suggest that phase-slip-related deformations may have played an important role in these previous experiments as well.

The present results allow a model-insensitive estimate of the CDW elastic constant K_z in $NbSe_3$. This is a crucial parameter in all theories of CDW pinning and dynamics, and no reliable experimental estimate is currently available. From Eq. (1), the elastic constant determines the magnitude of the wave-vector shift produced by a given applied voltage V_{ps}. Thus, using measured values of $\partial(\Delta Q)/\partial z = (2.8 \pm 0.3) \times 10^{-4}$ Å^{-1}/mm and $V_{ps} = 4.9$ mV at $I/I_T = 4$ and $T = 90$ K together with $\rho_c = 1.9 \times 10^{21}$ cm^{-3} yields $K_z \approx (1.7 \pm 0.25) \times 10^{-2}$ eV Å^{-1} [20]. This value is roughly 5 times larger than that obtained from mean field theory, but is consistent with the estimates of McCarten *et al.* [21] based upon a weak pinning analysis of transport measurements.

In conclusion, we have observed electric-field-induced deformations of the CDW state in $NbSe_3$. We have shown that these deformations are a consequence of boundary conditions, and are consistent with present models for CDW phase slip and current conversion at contacts.

We wish to thank W. Podulka and T. Adelman for technical assistance, M. P. Maher for providing electrical measurement data, and J. McCarten, S. Ramakrishna, and V. Ambegaokar for fruitful discussions. M.S. acknowledges the hospitality of Cornell's Materials Science Center and Applied Physics Department during the 1991–1992 academic year. This work was supported by the Materials Science Center (NSF Grant No. DMR-88-1858-A02). R.E.T. acknowledges additional support provided by the Alfred P. Sloan Foundation and by the NSF (Grant No. DMR-89-58515.) CHESS is supported by the NSF (Grant No. DMR-90-21700).

[a]Permanent address: Department of Physics, McGill University, Montreal, PQ, Canada H3A 2T8.

[1] For comprehensive reviews of CDWs, see P. Monceau, in *Electronic Properties of Quasi-One-Dimensional Materials* (Reidel, Dordrecht, 1985), Pt. II, p. 139; G. Grüner, Rev. Mod. Phys. **60**, 1129 (1988).

[2] P. A. Lee and T. M. Rice, Phys. Rev. B **19**, 3970 (1979); N. P. Ong, G. Verma, and K. Maki, Phys. Rev. Lett. **52**, 663 (1984).

[3] D. Feinberg and J. Freidel, in *Low-Dimensional Electronic Properties of Molybdenum Bronzes and Oxides*, edited by C. Schlenker (Kluwer, Dordrecht, 1989), p. 407.

[4] S. Ramakrishna, M. P. Maher, V. Ambegaokar, and U. Eckern, Phys. Rev. Lett. **68**, 2066 (1992).

[5] For a comprehensive review of previous work on CDW phase slip, see F. Ya. Nad', in *Charge Density Waves in Solids*, edited by L. P. Gor'kov and G. Grüner (Elsevier, Amsterdam, 1989), p. 189.

[6] J. L. Hodeau, M. Marezio, C. Roucau, R. Ayroles, A. Meerschaut, J. Rouxel, and P. Monceau, J. Phys. C **11**, 4117 (1978).

[7] The diffractometer was run in a mode which kept a^* and b^* in the scattering plane.

[8] The precise origin of the observed broadenings is unclear. Possible mechanisms include the following: the beam sampling regions of the sample where the wave vector is different; inhomogenous CDW current due to sample thickness variations; and inhomogenous CDW current due to field fringing at contacts.

[9] Low-resolution scans indicate that the integrated peak intensity is independent of I.

[10] Our sensitivity to peak position shifts is $\sim 3 \times 10^{-5}$ Å^{-1}, which is $\sim 10\%$ of the line width (FWHM).

[11] S. Hoen, B. Burk, A. Zettl, and M. Inui, Phys. Rev. B **46**, 1874 (1992), observed changes in the length of TaS_3 crystals when the CDW was depinned. The changes they observed correspond to (020) shifts of $\sim 4 \times 10^{-6}$ Å^{-1}, which were not resolvable in our experiment.

[12] Because of the finite current contact widths, the uncertainty in the position of the midpoint between contacts is approximately 0.5 mm.

[13] A. Middleton and J. McCarten (private communication).

[14] M. P. Maher, T. L. Adelman, S. Ramakrishna, J. P. McCarten, D. A. DiCarlo, and R. E. Thorne, Phys. Rev. Lett. **68**, 3084 (1992).

[15] J. C. Gill, J. Phys. C **19**, 6589 (1986); Physica (Amsterdam) **143B**, 61 (1986); P. Monceau, M. Renard, J. Richard, and M. C. Saint-Lager, Physica (Amsterdam) **143B**, 64 (1986).

[16] R. M. Fleming, D. E. Moncton, and D. B. McWhan, Phys. Rev. B **18**, 5560 (1978); R. M. Fleming, D. E. Moncton, J. D. Axe, and G. S. Brown, *ibid.* **30**, 1877 (1984).

[17] T. Tamegai, K. Tsutsumi, S. Kagoshima, Y. Kanai, M. Tani, H. Tomozawa, M. Sato, K. Tsuji, J. Harada, M. Sakata, and T. Nakajima, Solid State Commun. **51**, 585 (1984); T. Tamegai *et al.*, *ibid.* **56**, 13 (1985); see also R. M. Fleming, R. G. Dunn, and L. F. Schneemeyer, Phys. Rev. B **31**, 4099 (1985).

[18] L. Mihaly, K.-B. Lee, and P. W. Stephens, Phys. Rev. B **36**, 1793 (1987).

[19] J. Zhang, J. F. Ma, S. E. Nagler, and S. E. Brown, Bull. Am. Phys. Soc. **37**, 110 (1992).

[20] If the effects of field fringing near the contacts is included, the K_z estimate is reduced by roughly a factor of 2. See S. Ramakrishna *et al.* (to be published).

[21] J. McCarten, D. A. DiCarlo, M. P. Maher, T. L. Adelman, and R. E. Thorne, Phys. Rev. B **46**, 4456 (1992).