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X-ray scattering and electric field studies of the sliding mode conductor $NbSe_3$

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X-ray scattering studies of $NbSe_3$ show the formation of two independent, incommensurate charge-density waves (CDW) with wave vectors $\vec{q}_1 = (0,0.243,0)$ and $\vec{q}_2 = (0.5,0.263,0.5)$ at $T_1 = 144$ K and $T_2 = 59$ K, respectively. Electric fields that suppress the resistive anomaly associated with the lower-temperature CDW have no measurable effect on either the CDW amplitude or wave vector. The field required for suppression appears to scale roughly with the defect concentration as measured by the residual-resistance ratio. These results are consistent with the Fröhlich sliding-CDW model with impurity pinning.

Studies of transport properties of the chainlike trichalcogenide, $NbSe_3$, have revealed two phase transitions at 144 and 59 K that give rise to large resistive anomalies.[1] Unlike similar phenomena in transition-metal dichalcogenides[2] and in other quasi-one-dimensional systems,[3] the anomalies in $NbSe_3$ are remarkably sensitive to an applied electric field, and can be completely suppressed with fields on the order of 10 V/cm.[4] Models have been proposed[4,5] in which the conduction electron system develops a charge-density wave (CDW). In support of these speculations, electron-diffraction measurements near 144 K have demonstrated the presence of incommensurate, periodic latttice distortions characteristic of a Fermi-surface driven CDW.[6,7]

Two key questions have not been experimentally resolved. These concern the nature of the 59-K phase transition and the origin of the highly nonlinear conductivity. It might be anticipated in analogy with both one-dimensional[3] (1-D) and two-dimensional (2-D) systems that the 59-K transition is associated with a locking of the CDW wave vector to a commensurate superlattice. It has also been speculated[4,5] that the nonlinear conductivity may result from electric field breakdown (Zener tunneling) across the CDW gaps. In this paper we show that both of these hypotheses are incorrect. We find that the 59-K transition is associated with an entirely new CDW that is independent of the first. X-ray-diffraction studies of this CDW show that there is no change in its wave vector or amplitude with an applied electric field, indicating that electric field breakdown does not occur. Preliminary data indicate that the field required to suppress the associated resistive anomaly may scale with the defect concentration as measured by the residual-resistance ratio. This suggests that $NbSe_3$ is the first example of a "sliding mode" conductor, originally suggested by Fröhlich.[8] As anticipated by Lee, Rice, and Anderson,[9] these sliding modes will be pinned by impurities in the absence of electric field, but at high fields they may be depinned and carry current.

X-ray diffraction and four-lead resistivity measurements were performed simultaneously. Sample dimensions were determined with both an optical and a scanning electron microscope. The x-ray diffraction apparatus consisted of a 50-kW rotating anode generator in which Cu $K\alpha$ x-rays were focused on the specimen with a vertically bent pyrolytic graphite (PG) monochromator. A flat PG analyzer was used in the diffracted beam to decrease background from stray radiation.

The single crystals of $NbSe_3$ used in this experiment were from the same batch of specimens described in Ref. 10, and have resistance ratios $R_{300\,\mathrm{K}}/R_{4.2\,\mathrm{K}} \approx 200$. The crystal structure is monoclinic ($P2_1/m$),[6,7,11] with niobium chains parallel to the $\vec{b}$ axis. The crystals grow as ribbon-shaped needles (typically $20 \times 0.2 \times 0.01$ mm) with the needle axis along $\vec{b}$ and the plane of the ribbon parallel to $\vec{c}$. The low-temperature superlattice reflections were studied by tilting the crystal out of either the ($hk0$) or the ($0kl$) zones to give ($hk\alpha k$) or (βkkl) zones, respectively. In order to study the (0.5, 2.263, 0.5) reflection, zones with $\alpha = \beta = 0.5/2.263 = 0.221$ were used.

At $T_1 = 144$ K, a phase transition to an incommensurate CDW state produces superlattice diffraction peaks that are separated from the main peaks by the reduced wave vector $\vec{q}_1 = \pm(0, 0.243 \pm 0.005, 0)$. We also note the presence of the second harmonic with a reduced wave vector of $2\vec{q}_1 = \pm(0, 0.486, 0)$. Although the intensity of the second harmonic was too low to permit a detailed study of its temperature dependence, the presence of harmonics indicates the importance of considering nonsinusoidal CDW ground states. CDW's with substantial harmonic content have also been seen in $2H$-$TaSe_2$,[12] and are the subject of a number of theoretical investigations.[13]

At $T_2 = 59$ K, a second set of superlattice peaks develop with reduced wave vector $\vec{q}_2 = (0.5, 0.263 \pm 0.005, 0.5)$, indicating the formation of a second incommensurate CDW. Scans through the (1, 2.243, 0) and the (0.5, 2.263, 0.5) peaks shown in Fig. 1 demonstrate the distinct difference between the chain-axis periodicity of the two CDW's. The inset to Fig. 1 shows the relevant region of reciprocal space and the location of the two CDW superlattice peaks. Within the limit of our ability to detect changes in the peak positions ($\pm 0.005 b^*$), there is no measurable temperature dependence of either CDW wave vector.

The temperature dependence of the square of the CDW order parameter may be obtained from the integrated superlattice peak intensity, as shown for both superlattices in Fig. 2. Both transitions are second order, with some evidence of critical scattering near the transition temperature. We note no indication of the 59-K transition in the intensity data for the 144-K CDW.

We now consider our studies of the CDW behavior in an electric field. As shown in Fig. 2, the order parameter for the lower-temperature CDW remains unchanged in an applied electric field that produces a current density of 11.6 A/mm^2,[14] and suppresses approximately 60% of the resistive anomaly. The resistivity data taken during the order-parameter measurements are shown in the inset to Fig. 2. At high currents a temperature gradient was present between the sample and the thermometer. Assuming (i) that the transition temperature is field independent,[4,5] and (ii) that the sample is heated uniformly, the temperatures associated with the high-current data in Fig. 2 were scaled by the power dissipation. This procedure is not entirely sufficient for the resistivity, since these measurements are sensitive to nonuniform heating at the contacts. However, it is adequate for the x-ray data since only a small central region of the sample is irradiated.

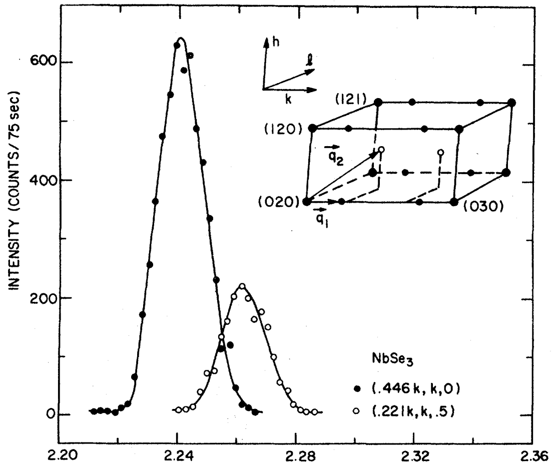

FIG. 1. Scans of the (1, 2.24, 0) and the (0.5, 2.26, 0.5) superlattice peaks at $T = 30$ K. The component of the CDW wave vector along b^* is clearly different for the two CDW's. The inset illustrates the location of the peaks in the reciprocal lattice (not to scale).

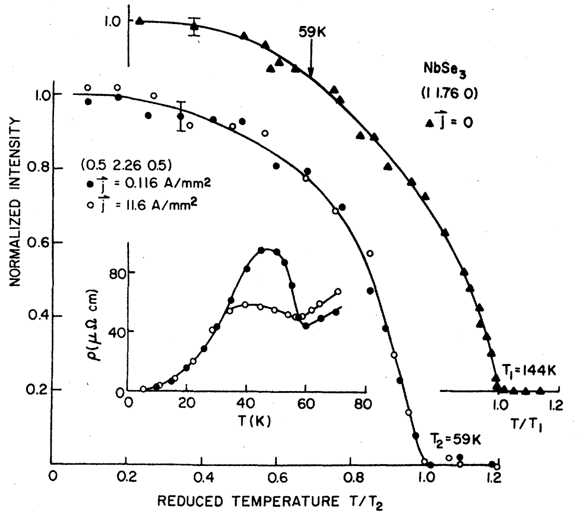

FIG. 2. Temperature dependence of the integrated peak intensity for both CDW superlattices. The solid lines are guides for the eye. The inset shows the results of a simultaneous measurement of the sample resistivity.

Overall, these results show that an electric field has no measurable effect on either the CDW amplitude or wave vector, since a change in either would directly affect the measured intensity. Because of the similarity of the two phase transitions, it is likely that the upper transition will also be unaffected by an electric field. Attempts to perform such measurements were precluded by more pronounced heating effects.

Our experiments show that the resistive anomalies in NbSe$_3$ are each the result of separate CDW instabilities. They further indicate that the unusual electric field suppression of the anomalies is not a result of Zener breakdown as previously suggested,[4,5] but probably results instead from moving CDW's. The possibility of moving CDW's was included in a group of models of the nonlinear conductivity by Ong and Monceau.[5] This conclusion is supported by the measurement of the nonlinear resistivity of a second specimen with a resistance ratio of about 40. The data can be fit to a function of the form[4,5] $\sigma - \sigma_0 \propto e^{-E/E_0}$, where E_0 is the characteristic field required to suppress the anomaly. We find for the second specimen that $E_0 \approx 0.052$ V/cm at 47.5 K, as compared with $E_0 \approx 0.027$ V/cm for the first sample (resistance ratio ≈200). These preliminary data suggest that the characteristic field E_0 scales with the number of defects. We therefore conclude that $NbSe_3$ is the first example of a Frölich "sliding mode" conductor[8] with CDW pinning at defect or impurity sites.

In the investigation of phase transformations in systems with reduced structural dimensionality, it is important to determine the anisotropy exhibited in various properties. It is already known from Fermi-surface studies[10,15] that $NbSe_3$ is not extremely one dimensional. Furthermore, the fact that the CDW transitions do not remove all the Fermi surface, as in TTF-TCNQ (tetrathiafulvalenium-tetracyanoquinodimethanide),[3] also supports this lack of dominant one dimensionality. To probe further the anisotropy in $NbSe_3$, measurements of diffuse scattering were made along $\vec{a}^*$ and $\vec{b}^*$. These directions correspond to the longest and shortest average Nb-Nb distances. As shown in Fig. 3 for both transitions, the longitudinal widths are almost entirely accounted for by the finite spectrometer resolution, and it is not possible to extract precise quantitative information. From the slight excess width that is observed, one can estimate lower limits for the correlation length: $\kappa_{\parallel}^{-1}(160\ \mathrm{K}) > 50$ Å for the upper CDW, and $\kappa_{\parallel}^{-1}(62\ \mathrm{K}) > 100$ Å for the lower CDW. In the transverse direction the instrumental width including mosaic spread effects is small compared to the observed widths. For the upper CDW we obtain $\kappa_{\perp}^{-1}(160\ \mathrm{K}) \approx 12$ Å, and for the lower CDW $\kappa_{\perp}^{-1}(62\ \mathrm{K}) \approx 30$ Å. Corrections for the poor resolution of our instrument perpendicular to the diffraction plane (0.1 Å^{-1}) could increase the quoted correlation lengths up to 40%; however, they do not affect our qualitative conclusion. Although the phase transitions in $NbSe_3$ involve substantial anisotropy, $\kappa_{\perp}/\kappa_{\parallel}$ on the order of 5, they are not in the class of systems with extreme anisotropy.[16,17] Although Tsutsumi *et al.*[6] have reported 1-D precursor scattering in $NbSe_3$, recent studies by Hodeau *et al.*[7] indicate that 1-D sheets are not present, in agreement with our results.

The coexistence of two independent CDW's is similar to the cases of the layered compounds 4*Hb*-$TaSe_2$[16] and 4*Hb*-TaS_2,[18] where CDW's with different wave vectors develop in alternating layers with different bonding configurations. The crystal structure of $NbSe_3$ (Refs. 7 and 11) contains six chains that may be separated into two classes based on Se-Se bond lengths and the number of Nb-Se bonds at the apexes of the prisms. We speculate that the two CDW's are associated with these two classes of chains. With this model, one can conceive of an interchain phase ordering scheme that gives the observed transverse wave-vector components for each CDW: however, it is premature to develop this model further in the absence of structural data.

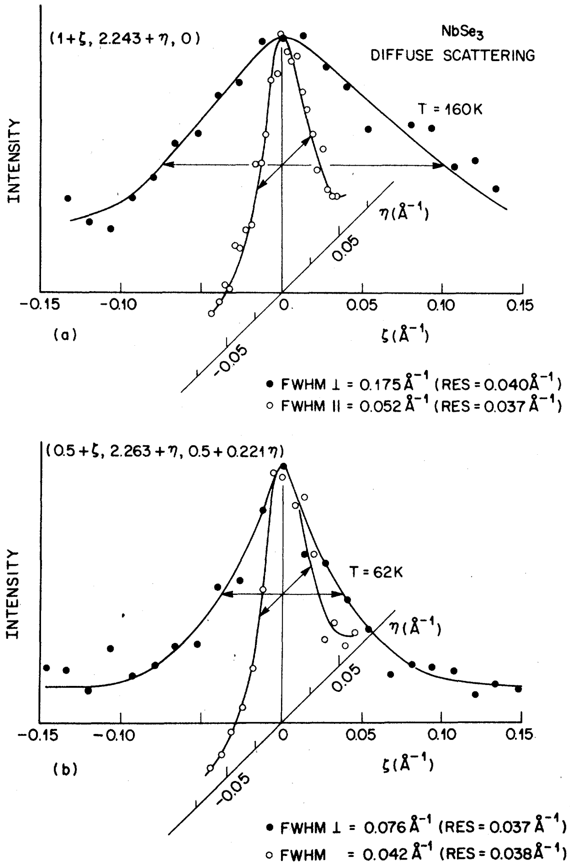

FIG. 3. Diffuse scattering at temperatures above the two phase transitions. The widths of the peaks may be compared with the spectrometer resolution indicated.

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