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# X-ray-scattering study of the charge-density-wave structure in $NbSe_3$ in high magnetic fields

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An upper bound of $\Delta q/q \leqslant 2.5\times 10^{-3}$ on the magnetic-field-induced shift of the wave vector of the low-temperature charge-density wave in $NbSe_3$ is established by high-resolution x-ray diffraction in magnetic fields up to 10 T. The charge-density-wave order parameter is also magnetic-field independent, to within 10%. These limits are discussed in the context of magnetotransport experiments on $NbSe_3$ as well as theoretical models that had predicted a magnetic-field dependence of the charge-density-wave structure. [S0163-1829(98)05403-4]

## I. INTRODUCTION

The crystal structure of $NbSe_3$ consists of three pairs of inequivalent prismatic chains. Band-structure calculations[1] show that the states at the Fermi level originate mainly from two types of chains. Two successive structural transitions at 145 and 59 K (Ref. 2) have been shown to be associated with the formation of essentially independent charge-density waves (CDW's) on these two chains.[3] In spite of the CDW transitions, $NbSe_3$ remains semimetallic down to the lowest temperatures. Electronic-structure calculations[4] have attributed this behavior to imperfect nesting; the charge-density wave does not remove the entire Fermi surface.

The magnetic-field dependence of the charge-density-wave structure has been of interest since the discovery of a very large positive magnetoresistance below the 59-K transition (up to a factor of 4 for $H=22$ T with the field applied perpendicular to the conducting chains).[5,6] Measurements as a function of electric field showed that this behavior was not caused by CDW motion. On the basis of subsequent narrow-band noise[7] and thermopower[8] measurements in transverse magnetic fields, it was attributed to a substantial increase in the number of carriers participating in collective CDW transport, lowering the density of normal carriers in ungapped pockets of the Fermi surface. This would correspond to an increase in the CDW order parameter induced by the magnetic field.

Theoretically, this behavior can be understood by considering the orbital response of the electrons to the magnetic field.[9] The transverse field constrains the electronic motion thereby improving the nesting properties of the quasi-one-dimensional Fermi surface and enhancing its propensity for CDW formation. Models in the same spirit have also been proposed to account for the field-induced spin-density-wave phenomenon in quasi-one-dimensional organic conductors.[10] However, in contrast to the organics, the electronic structure of $NbSe_3$ is very complex, and quantitative predictions using a realistic band structure have thus far not been attempted.

Both the experiments of Refs. 7 and 8 and the theoretical interpretation were subsequently challenged. More exhaustive measurements indicated only a very small magnetic-field-induced enhancement of the narrow-band noise,[11] inconsistent with the earlier experimental reports. The thermopower is magnetic-field dependent also for a field applied parallel to the conducting chains, which the improved-nesting model cannot account for.[12] The CDW transition temperature increases only by 0.5 K, or less, in a field in excess of 20 T.[6] Finally, measurements of the Hall effect[13] were found to be inconsistent with a substantial decrease in the density of normal carriers. The conjecture was made[11] that the large magnetoresistance could be explained simply by considering the response of normal carriers in the complex Fermi-surface geometry created by the 59-K transition. Again, quantitative estimates of such effects have not been reported.

Finally, it was found that the threshold electric field $E_c$ for depinning the low-temperature CDW is strongly magnetic-field dependent.[14] This effect was explored in detail as a function of temperature, and two distinct regions in the $(H,T)$ phase diagram were identified according to the response of the CDW to the electric field.[15,16] It was speculated that this behavior reflects the Zeeman response of the electron gas which shifts the CDW wave vector, perhaps causing a lock-in transition due to interactions with the CDW on the other set of chains. However, the magnetic-field-induced reduction of $E_c$ was found to depend strongly on the crystallographic direction in which $H$ was applied, suggesting that orbital effects also play a role. This observation has led to more recent theories that consider both CDW and spin-density-wave correlations of the electron gas.[17]

This decade-old discussion has unfolded entirely on the basis of transport data. Similar experiments on other CDW systems have also resulted in suggestions of a magnetic-field dependence of the CDW structure, although these effects were explored in much less detail.[18–20]

Clearly, in light of these results, measurements with an equilibrium probe are highly desirable. Of particular interest is a possible shift of the CDW wave vector induced by a magnetic field. We have chosen x-ray diffraction because the CDW amplitude and periodicity are measured directly, and high-momentum resolution can be achieved.

## II. EXPERIMENTAL DETAILS

$NbSe_3$ has a monoclinic unit cell with room-temperature lattice parameters $a = 10.009$ Å, $b = 3.480$ Å, $c = 15.629$ Å, and $\beta = 109.47°$ (the angle between the $a$ and $c$ directions).[21] The $b$ direction is along the conducting chains. The approximate dimensions of the single-crystal sample used in this study were several $\mu$m × 1 mm × 0.2 mm. The crystal had two domains about 0.5° apart, each with a mosaicity of about 0.1°.

The measurements were carried out on beamline X22B at the National Synchrotron Light Source, using 8-keV x rays monochromated by a flat Ge(111) monochromator and reflected from a focusing Ni mirror. As in previous x-ray-scattering experiments on $NbSe_3$,[22,23] one end of the crystal was glued onto a piece of aluminum foil using silver paint in order to minimize thermal strains. The foil was then mounted on a stepper motor-driven rotator inside a vertical-field superconducting magnet with x-ray transparent windows. The entire magnet assembly was mounted on a two-circle goniometer. The scattered x rays were analyzed by a Ge(111) crystal and detected by a magnetically shielded scintillation detector. In the geometry chosen, momentum transfers of the form $(h, k, h)$ were accessible in the (horizontal) scattering plane, and the magnetic field is applied perpendicular to the most conducting $b$ direction (as in the transport experiments). The sample rotator allows limited adjustments of the scattering geometry.

## III. RESULTS

The goal of the experiment was to determine the presence or absence of a magnetic-field-induced shift in the position of superlattice reflections with reduced wave vector $\mathbf{q} = (0.5, 0.26, 0.5)$, which correspond to the low-temperature CDW. A complication arises from magnetic-field-induced sample motion due to the anisotropic susceptibility of the very thin crystal. Even in zero field the angular positions of the Bragg reflections were observed to drift slowly, presumably due to relaxation of residual thermal strains. The high angular resolution made it necessary to recenter the sample frequently. After changing the magnetic field, the sample was therefore carefully realigned by optimizing the intensities of the main crystallographic Bragg reflections.

Longitudinal scans through two such reflections in zero field and in an applied field of 10 T are shown in Fig. 1. (The peak position in a longitudinal scan is sensitive only to changes in the magnitude of the wave vector, and not to small differences in angular alignment of the sample.) The slight asymmetry of the profiles presumably originates from the irregular mosaic structure of our sample. The $Q$ positions of the main Bragg reflections do not change with magnetic field, providing reassurance that the magnetic-field dependence of the CDW periodicity can be extracted from the measurements, despite the sample motion.

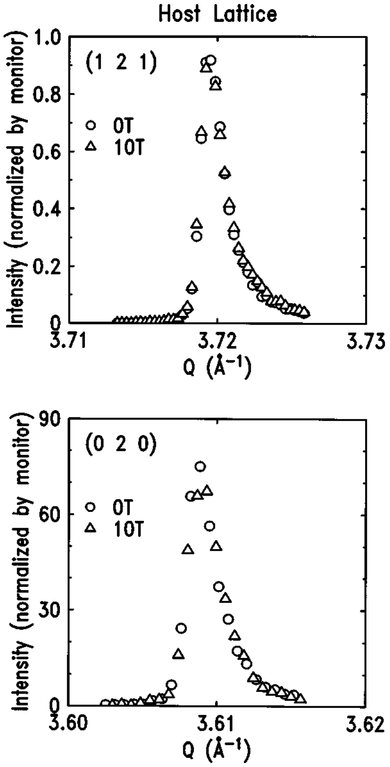

FIG. 1. Longitudinal scans through the (121) and (020) Bragg reflections of the host lattice, in magnetic fields of 0 and 10 T. The temperature is 5 K.

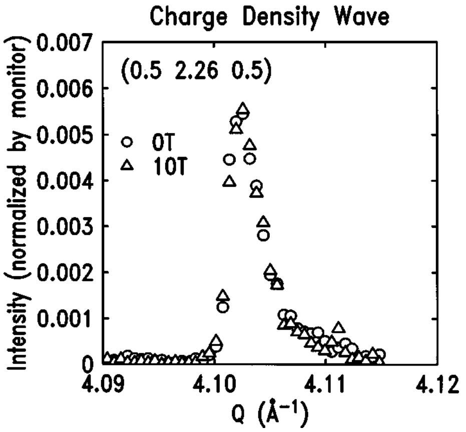

FIG. 2. Longitudinal scans through the (0.5, 2.26, 0.5) superlattice reflection whose intensity is proportional to the square of the order parameter of the low-temperature charge-density wave, in magnetic fields of 0 and 10 T. The temperature is 5 K. Presumably due to a subtle sample motion, the intensities before and after setting the field to 10 T are somewhat different (though the peak positions are identical). The $H = 0$ T scan shown is an average of scans taken before and after the field was set to 10 T. The magnetic-field dependence of the peak amplitude was determined by the low-resolution measurements of Fig. 3.

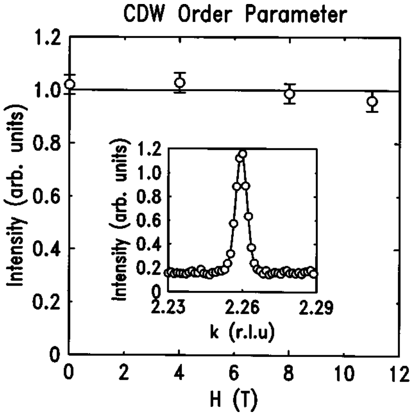

FIG. 3. Magnetic-field dependence of the intensity of the (0.5, 2.26, 0.5) superlattice reflection, extracted from Gaussian fits to profiles measured with low-momentum resolution. A typical scan (at $H=0$ T, $T=5$ K) in the $b$ direction along the conducting chains is shown in the inset, together with the result of a fit (solid line). The reciprocal lattice coordinate $k$ is measured in reciprocal lattice units (r.l.u), that is, in units of $b^*$.

Figure 2 shows longitudinal scans through the (0.5, 2.26, 0.5) superlattice reflection, at a temperature of 5 K where the CDW order parameter is saturated. The scan direction subtends an angle of only 6.5° with $b^*$, so that the peak position measures the wave vector along the conducting chains. Evidently, the wave vector of the CDW is not affected by a magnetic field of 10 T, to within our resolution. The wave-vector resolution at the (0.5, 2.26, 0.5) position is about 0.0011 $\text{Å}^{-1}$ (half width at half maximum), comparable to previous high-resolution synchrotron x-ray-diffraction measurements on this sytem.[22] Since a wave-vector shift equal to the resolution would have been easily observable, a conservative upper limit of $\Delta q_b/q_b \leqslant 2.5\times10^{-3}$ on the shift of the CDW wave vector in a magnetic field of 10 T may be set ($q_b=0.26b^*=0.469$ $\text{Å}^{-1}$ is the $b$ component of the reduced wave vector).

The data of Figs. 1 and 2 are also inconsistent with an appreciable change in the CDW order parameter with magnetic field. In order to place quantitative limits on any amplitude changes, the germanium analyzer was removed, and studies were carried out in a lower resolution mode, thus minimizing the possible effects of small differences in angular alignment on the peak amplitude. The resulting resolution was ~0.005 $\text{Å}^{-1}$ (half width at half maximum). A typical scan through the (0.5, 2.26, 0.5) reflection is shown in the inset of Fig. 3. The data were fitted to resolution limited Gaussians, and the peak amplitudes extracted from the fits are plotted in Fig. 3 as a function of magnetic field. Very conservatively, these data are inconsistent with a change in peak amplitude of more than 20%. The peak width is resolution limited in all directions and does not change with field, so that the peak intensity is proportional to the integrated intensity and thus to the square of the order parameter. The 20% limit on the change in peak amplitude therefore corresponds to an upper bound of 10% on the variation of the magnitude of the CDW order parameter in a magnetic field of 10 T. A ~30% enhancement of the order parameter in a 7.5-T field claimed by Hall, Hundley, and Zettl[7] is ruled out by these data, thus supporting the transport experiments of Tritt *et al.*[11]

## IV. CONCLUSIONS

One further consideration must be made in comparing the x-ray and magnetotransport data. Both the transport experiments and the theoretical interpretation in terms of the orbital response of the electron gas require the magnetic field to be perpendicular to the $b$ axis, as in our experiment. However, in the transport experiments an $a$-$c$ anisotropy was also observed. The magnetoresistance anisotropy is modest [~50% larger along $c$ than perpendicular to $c$ (Ref. 6)], but the anisotropy found in the nonlinear transport studies is more pronounced.[15,16] The magnetic-field-induced reduction in CDW depinning field $E_c$ is maximum when the field is applied perpendicular to the $b$-$c$ plane, and very small when it is applied parallel to this plane.

In our experiment, application of the field perpendicular to the $b$-$c$ plane is incompatible with the constraints of vertical field and horizontal scattering plane, and with the extremely thin sample dimension perpendicular to $b$. Rather, the field was applied at an angle of 26.5° with respect to the $b$-$c$ plane. Fortunately, detailed transport measurements[16] indicate that in this geometry the suppression of $E_c$ is already substantial (~75% of the suppression in the optimal geometry). Moreover, the magnetic field applied in our experiment is much larger than 2.5 T, the critical magnetic field above which suppression of $E_c$ is first observed at low temperatures. We thus believe that our x-ray study is a meaningful complement to these nonlinear transport measurements, as well as to the numerous other magnetotransport studies that have been reported on $\text{NbSe}_3$.

The limit of $\Delta q_b/q_b \leqslant 2.5\times10^{-3}$ on the shift of the CDW wave vector in a 10-T magnetic field was obtained by using a high-resolution scattering configuration at a synchrotron. (With special care and crystals with very low mosaic spreads, further improvements in resolution have been achieved in some zero-field experiments.[23]) Unfortunately, none of the theoretical models proposed to explain the magnetotransport experiments[6,9,15] allow for quantitative estimates of $\Delta q_b/q_b$ or the order-parameter variation to which our upper bounds can be compared. A quantitative analysis will have to await more elaborate calculations using a realistic Fermi surface and electron-phonon interaction.

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