

# Charge Density Modulation in 2H-NbSe<sub>2</sub> Using Multiple X-ray Diffraction

*We learn from solid state physics that the Fourier transform of the density function gives rise to the structure factor,  $S(\mathbf{Q}, \omega)$  where  $\mathbf{Q}$  and  $\omega$  are the wavevector and energy transfers, characterizing the static and dynamic properties of materials. For the cases without the distortions the static structure factor  $S(\mathbf{Q})$ , i.e.,  $\Delta\omega = 0$ , produces the Bragg reflections with the wavevector  $\vec{G} = \vec{Q} = h\vec{a} + k\vec{b} + l\vec{c}$ , where the  $h$ ,  $k$ , and  $l$  are integers, in the reciprocal space, which can be probed by x-ray, neutron or electron beams. This is the case that the density function describes a homogeneous and spherical distribution of electron densities of the material, but this is always not the case that we deal with in the material science. Most of the cases, the structure factor could produce the weak satellite reflections in addition to the Bragg reflections, namely the modulated structure, so that the wavevector must be expressed as  $\vec{G}' = \vec{Q} + m\vec{q}$ , where  $m$  is not an integer and  $\vec{q}$  the modulated wavevector. The concomitant of a modulation is usually the occurrence of the abnormal physical properties at or below the transition temperature, such as the non-linear conductivity, the frequency dependent conductivity, the metastability and memory effects.*

There are many causes that are responsible for the formation of the modulations, for instance the soft mode distortion as that observed in SrTiO<sub>3</sub>, the displacement distortion of the ions in alloy compounds, or the occurrence of the inhomogeneous or anisotropic density distribution of either the charge or spin. The latter results in the so-called charge-density wave (CDW) or spin-density wave (SDW) modulation. As a consequence of the redistributions, the modulated electron-density can be expressed as  $\rho(\vec{r}) = \rho_0 + p \cos(\vec{q} \cdot \vec{r} + \phi)$ , where  $\rho_0$  is the non-modulated density,  $p$  the modulated amplitude,  $\vec{q}$  the modulated wave-vector, and  $\phi$  the phase. It therefore produces a so-called CDW modulated structure with a wavevector  $\vec{q}$  in the host lattice.

It has been demonstrated that the phase  $\phi$  governs the propagation of the CDWs and is responsible for the occurrence of the unusual physical phenomena, such as the pinning and memory effects and sliding behavior. The importance of the phases of the density waves has been recognized, but its study has been, so far, relied only on the theoretical models and the indirect probe from transport measurements. For the conventional scattering experiment, one can directly obtain the changes in the order parameters, the modulated wave-vector  $\vec{q}$  and the modulated amplitude  $p$ , but the information regarding the phase  $\phi$  is lost because the measured intensity,  $I$ , is proportional to the square of the structure factor.

Multiple x-ray diffraction has been known as an ideal technique for solving the phase problem in

crystallography. In a multiple-wave diffraction experiment, for instance the three-wave case, the crystal was first aligned for a reflection  $G$ , the so-called primary reflection, and was then rotated around the reflection  $G$ , i.e., the azimuthal  $\psi$  rotation, to bring a secondary reflection  $L$  to also satisfy Bragg's law. Namely, the reciprocal lattice points of the  $G$  and  $L$  reflections are brought onto the surface of the Ewald sphere simultaneously. During the azimuthal rotation, the same three-wave ( $O$ ,  $G$ ,  $L$ ) diffraction occurs at the two positions, denoted as IN and OUT, at which the reciprocal lattice point  $L$  enters and leaves the Ewald sphere, respectively. The interaction among the diffracted waves inside the crystal gives rise to intensity variation  $I_G$  on the primary reflection as a function of the azimuthal angle  $\psi$ . By analyzing the asymmetry of the profile of the intensity variation, the phase of the structure-factor triplet can be expressed as

$$\delta_3 = -\delta_G + \delta_L + \delta_{G-L},$$

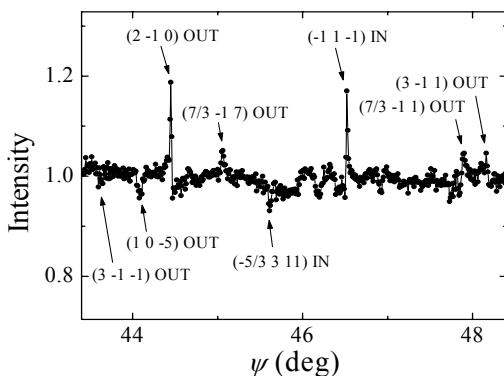
providing that the effect of anomalous dispersion is negligibly small. The  $G$ - $L$  is the coupling between the  $G$  and  $L$  reflections.

In order to tackle this problem, i.e., directly probing the phases of CDWs, a thick 2H-NbSe<sub>2</sub> single crystal with a hexagonally shaped surface ( $\sim 4 \times 5 \text{ mm}^2$ ) being parallel to the (0001) planes was used for this study. 2H-NbSe<sub>2</sub> is a quasi-two-dimensional material, and has a hexagonal layer structure with a space group P6<sub>3</sub>/mmc and lattice

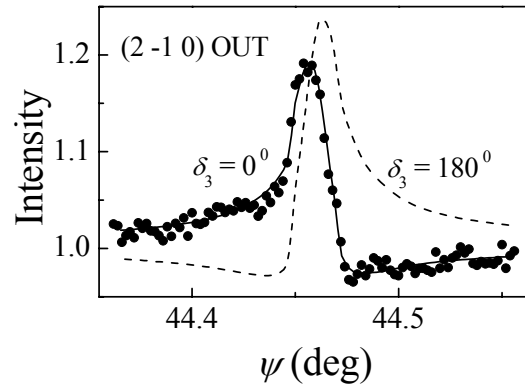
parameters  $a = b = 3.45 \text{ \AA}$  and  $c = 12.54 \text{ \AA}$ . It undergoes a phase transition to a CDW state at  $T_{CDW} \approx 32.5 \text{ K}$ ; upon cooling it becomes a superconductor at  $T_c \approx 7.2 \text{ K}$  while the CDW remains incommensurate down to  $5 \text{ K}$ .

The experiment was carried out on the beamline BL12B2 at the SPring-8 synchrotron facility. The incident photon energy was selected to be  $12.398 \text{ keV}$  (wavelength  $\lambda = 1.0 \text{ \AA}$ ) by a Si (311) cut sagittal double-crystal monochromator. The crystal was aligned at room temperature in such a way that the scattering plane was in the  $b \times c$  reciprocal plane, and then was cooled down to  $16 \text{ K}$ . The satellite reflection due to the formation of CDW was located at position around  $(1/3 \ 0 \ 9)$  with intensity of about  $1300 \text{ counts/sec}$ . The peak widths of (008) and  $(1/3 \ 0 \ 9)$  were measured to be  $0.03^\circ$  and  $0.15^\circ$  by transverse scans, respectively. At the peak position of  $(1/3 \ 0 \ 9)$ , the azimuthal  $\psi$ -scan around the reciprocal lattice vector of this reflection was performed to generate many multiple-wave diffractions.

Figure 1 shows a portion of a multiple-wave diffraction pattern of  $(1/3 \ 0 \ 9)$  reflection, which was obtained with a  $\psi$ -scan of  $0.005^\circ$  per step. The  $\psi$  angle was measured counterclockwise from the [010] direction. For convenience of representation the relatively intense peaks and dips are denoted in figure with the Miller indices of only the secondary reflection  $L$ . At the same time in the text we use more detailed designation for multiple-wave diffraction, namely  $(L)/(G-L)$ , to stress on cases with fractional or integer coupling  $G-L$  reflections. The IN and OUT positions are also indicated in figure. The rather noisy background is because of the presence of many weak fractional reflections.



**Fig. 1:** Multiple diffraction pattern.  $\psi$ -scan was taken on a CDW satellite  $(1/3 \ 0 \ 9)$  reflection at  $T = 16 \text{ K}$ . Intensity is normalized with the two-wave intensity of  $(1/3 \ 0 \ 9)$ .



**Fig. 2:** The experimental (solid circles) and calculated (lines) three-wave  $(2 \ -1 \ 0)$  profiles at  $T = 16 \text{ K}$ . The solid line is for the  $\delta_3 = 0^\circ$  and the dash line for  $\delta_3 = 180^\circ$ .

Triplet phases  $\delta_3$  were analyzed based on the measured profiles for a centrosymmetric crystal, because the host structure of  $2H\text{-NbSe}_2$  at  $16 \text{ K}$  retains the same point symmetry as that at  $297 \text{ K}$  and the formation of CDWs does not affect the symmetry. From the measured asymmetry of the profiles shown in Figs. 2 and the IN and OUT positions on the  $\psi$ -scan diffraction diagrams, the triplet phases are determined as  $\delta_3 = -\delta(1/3 \ 0 \ 9) + \delta(2 \ -1 \ 0) + \delta(-5/3 \ 1 \ 9) = 0^\circ$ ,  $\delta_3 = -\delta(1/3 \ 0 \ 9) + \delta(-5/3 \ 2 \ 10) + \delta(2 \ -2 \ -1) = 180^\circ$  and  $\delta_3 = -\delta(1/3 \ 0 \ 9) + \delta(-1 \ 1 \ -1) + \delta(4/3 \ -1 \ 10) = 0^\circ$ , respectively.

In conclusion, we have demonstrated that the correlative phases of the CDWs can be directly probed in a quasi-two-dimensional material  $2H\text{-NbSe}_2$  using x-ray multiple diffraction. With this finding, we are stepping further to observe the dynamic behaviour caused by the sliding CDWs. As the CDW being in a static state, its phase is pinned by the imperfections, and the dynamic behaviour occurs as the phases de-pinned from the imperfections by the external field. The understanding of the changes of the relative phases under the application of the electric fields is therefore helpful to grasp the dynamic phenomena of the CDWs. Recently, we have observed the dynamic phases transitions, showing the CDWs undergoing a successive transition from the pined state  $\rightarrow$  creeping  $\rightarrow$  plastic flow  $\rightarrow$  moving solid, as the applied electric fields approaching to and exceeding the threshold value.

**BEAMLINE**

SP12B Biostructure and Materials Research beamline

**EXPERIMENTAL STATION**

X-ray Scattering end station

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