X-ray multiple-wave coherent interaction in a quasi-two-dimensional material NbSe$_2$-2H

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The first observation of the X-ray multiple-wave interaction in an incommensurate charge-density-wave (CDW) modulated structure at low temperatures is reported for an example of a quasi-two-dimensional material, NbSe$_2$-2H. Via the coherent interaction between the X-ray waves propagating in the CDW-modulated structure and the host structure, the phase-dependent intensity variations of a CDW reflection were detected. In accord with a centrosymmetric structure, the phases of the structure-factor triplets of two CDW reflections and a Bragg reflection of the host structure were determined to be either 0 or 180°, and not to vary with temperature. Relative phase differences of the two CDW reflections are also deduced.

1. Introduction

Determining the phases of the reflected X-rays from a substance has long been a key issue for understanding crystal structure in condensed-matter physics, materials science and crystallography, because the phases contain important information on the electron-density distribution in a crystalline material. There are many techniques developed to serve this purpose (Hauptman, 1989; Schenk, 1991; Hendrickson, 1991; Woolfson & Fan, 1995; Chang, 1998; and references therein). In most cases, these techniques are used to provide the phase information of a crystal that usually produces relatively strong Bragg reflections. However, the technique may not be phase sensitive if the crystal undergoes a lattice modulation or the electron density around each atom is not spherically symmetric because of the appearance of some weak satellite reflections or nearly forbidden reflections. The use of highly brilliant X-rays and resonant X-ray scattering has made possible the detailed study of the phases and physical properties relating to the electron-density modulation. Recent reports on the determination of the spectral distribution of resonance phases of GaAs near the Ga K and As K absorption edges (Stetsko et al., 2001) and the measurement of the phases of the forbidden 600 and 222 reflections of germanium (Lee et al., 2001), both employing three-wave resonance diffraction, are examples. For the latter, the hybridization of p and d atomic states in Ge has been demonstrated theoretically to result in an additional phase shift at resonance (Elfimov et al., 2002).

In contrast to the resonance of Bragg reflections, either allowed or forbidden, of perfect crystals like Ge and GaAs, the inhomogeneous distributions of the charge or spin density as a result of electron–phonon or electron–electron interactions can also produce modulations accompanying a phase transition at the transition temperature, and therefore introduce additional phase factors to the electron or spin densities as well as to X-ray reflections. For example, density-wave modulations (charge- or spin-density waves) have been commonly observed in low-dimensional materials and exhibit unusual transport phenomena (Hutiray & Sólyom, 1985; Thorne, 1996). Even in the recently discovered colossal magnetoresistance manganites (CMR), high-T_c superconductor cuprates and nickelates, the charge, orbital and spin stripes also form modulated structures and have been demonstrated to dominate the transport behaviour (Murakami et al., 1998; Elfimov et al., 1999; Du, Ghazi et al., 2000). The question arises, from the structure point of view, what is happening if the waves propagate in a system possessing a modulation and how can the resultant phases of the system be measured?

In a system involving the instability of the CDWs, the electronic ground state can be written as

$$\rho = \rho_0 \left[1 + \sum_i P_i \cos(2\pi \mathbf{Q}_i \cdot \mathbf{r} + \varphi_i) \right], \qquad (1)$$

where ρ_0 is the undistorted electron density, P_i is the distorted amplitude, $\mathbf{Q}_i$ is the wavevector of the CDW and φ_i is the phase (Overhauser & de Graaf, 1968; Overhauser, 1978). It has been demonstrated that the phase φ_i governs the propagation of the CDWs and is responsible for the occurrence of unusual physical phenomena, such as pinning and memory effects, and

sliding behaviour. The importance of the phases of the density waves has been recognized, but its study has, so far, relied only on the theoretical models and the indirect probe from transport measurements. In practice, according to the definition of the structure factor for diffraction from a polyatomic CDW system [see equation (2) below], it is not possible to separate the phase of the CDW from the (collective) phase of the structure factor of the whole system. As an alternative, the relations in the collective phases between CDW (fractional) reflections and the Bragg (integer) reflections are investigated in this paper using multiple-wave X-ray diffraction. The relative phase differences between two fractional reflections are also determined.

The structure factor of a CDW reflection Q' of a polyatomic system, hereinafter also called fractional reflection, is defined as (Overhauser & de Graaf, 1968; Overhauser, 1978; Giuliani & Overhauser, 1982; Giacovazzo, 2002)

$$F(\mathbf{Q}) = \sum_{j=1}^{N} f_j(\mathbf{Q}') \exp(2\pi i \, \mathbf{Q}' \cdot \mathbf{R}_j^0) J_m(2\pi \, \mathbf{Q}' \cdot \mathbf{A}_{0j})(-1)^m$$
$$\times \exp(-2\pi i \, \mathbf{Q} \cdot \mathbf{R}_j^0) \exp(im\varphi_j), \qquad (2)$$

where $\mathbf{Q}' = \mathbf{G} + m\mathbf{Q}$, m being an integer, $J_m(x)$ is a Bessel function of the first kind, $\mathbf{G}$ is a reciprocal-lattice vector of an integer Bragg reflection G from the undistorted structure, and

$$\mathbf{R}_{ij} = \mathbf{R}_j^0 + \boldsymbol{\tau}_i + \mathbf{A}_{0j} \sin[\mathbf{Q} \cdot (\mathbf{R}_j^0 + \boldsymbol{\tau}_i) + \varphi_{0j}] \qquad (3)$$

is the distorted position vector of the jth ion due to the CDW for the lattice point i with respect to the origin of the unit cell, $\mathbf{R}_j^0$ being the equilibrium position of the jth ion in the basis, $\boldsymbol{\tau}_i$ being the position vector of lattice point i within the unit cell, with $\mathbf{A}_{0j}$ the amplitude of the distortion proportional to the distorted amplitude of the CDW (Giuliani & Overhauser, 1982; Chapman & Colella, 1985; Giacovazzo, 2002). The phase of $F(\mathbf{Q}')$ depends not only on φ_{0j} but also on the phase shifts caused by each ionic displacement. The phase of $F(\mathbf{Q}'_i)$ is therefore the relative collective phase, which is defined as that reported by Chapman & Colella (1985).

X-ray scattering is an ideal probe for studying the modulations; however, it can only provide the magnitudes directly, not the phases, of the static structure factors. It is known that using X-ray multiple-wave diffraction could lead to direct phase determination (Colella, 1974; Post, 1977; Chapman et al., 1981; Juretschke, 1982; Chang, 1982, 1984, 1998; Shen, 1986, 1998; Hümmer et al., 1989; Weckert & Hümmer, 1997; Chang et al., 1998; Avanci et al., 1998, 2000; Stetsko et al., 2001; Lee et al., 2001; and others). Therefore, here we adopt this diffraction technique to investigate the phase problem of the CDWs in a quasi-two-dimensional material, NbSe₂-2H. From the multiple-wave experiment reported below, the coherent interaction of the X-ray waves between the CDW reflections and the integer reflections was detected, and the relative phases between two CDW reflections were therefore determined.

2. Multiple-wave experiment

In a three-wave diffraction experiment, the crystal was first aligned for a reflection G, the so-called primary reflection, and was then rotated around the reciprocal-lattice vector $\mathbf{g}$ of the reflection G, the azimuthal ψ rotation, in order to make a secondary reflection L also satisfy Bragg's law. That is, 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 the intensity variation I_G of the primary reflection as a function of the azimuthal angle ψ. According to the above-mentioned references, the asymmetry of the profile of the intensity variation can be used for the direct estimation of the phase,

$$\delta_3 = -\delta_G + \delta_L + \delta_{G-L}, \qquad (4)$$

of the structure-factor triplet, $F_L F_{G-L}/F_G$, provided that the effect of anomalous dispersion is negligibly small. G–L is the coupling between the G and L reflections.

The experiment was carried out on beamline BL12B2 (Tang et al., 2001) at the SPring-8 synchrotron facility. The incident photon energy was selected to be 12.398 keV (wavelength $\lambda = 1.0$ Å) by an Si (311) cut sagittal double-crystal monochromator. A mirror coated with Si was used to reject the high-order contaminations and refocus vertically the incident beam. The beam size was set by slits to be 0.51×1 mm at the sample position. With this configuration, the beam divergences were measured to be 0.0033° (vertical) and 0.0025° (horizontal) at the centre of the diffractometer. σ polarization was chosen for the incident beam.

A thick NbSe₂-2H single crystal with a hexagonally shaped surface ($\sim 4 \times 5$ mm), parallel to the (0001) planes, was used for this study. NbSe₂-2H is a quasi-two-dimensional material and has a hexagonal layer structure with space group $P6_3/mmc$ and lattice parameters $a = b = 3.45$ and $c = 12.54$ Å. It undergoes a phase transition to a CDW state at $T_{\mathrm{CDW}} \simeq 32.5$ K; upon cooling, it becomes a superconductor at $T_c \simeq 7.2$ K, while the CDW remains incommensurate down to 5 K (Moncton et al., 1977). Our previous study on this crystal using high-resolution X-ray scattering (Du, Lin et al., 2000) demonstrated that the CDW satellite reflections were not influenced by the application of magnetic fields up to 10 T and exhibited an unusual critical scattering. The crystal was aligned at room temperature in such a way that the scattering plane was in the $b^* \times c^*$ reciprocal plane, and was then cooled to 16 K. The satellite reflection caused by the formation of the CDW was located at a position around $(\frac{1}{3} 0\, 9)$ with an intensity of about 1300 counts s⁻¹. The peak widths (rocking curves) of $(0\, 0\, 8)$ and $(\frac{1}{3} 0\, 9)$ were measured to be 0.03° and 0.15°, respectively, by transverse scans. At the peak position of $(\frac{1}{3} 0\, 9)$, an azimuthal ψ scan around the reciprocal-lattice vector of this reflection was performed to generate many

multiple-wave diffractions. A scintillation counter was used to monitor the intensity variation of the primary $(\tfrac{1}{3}\,0\,9)$ reflection.

3. Results and discussion

It is possible to generate a large number of multiple-wave diffractions but only those with 'strong' integer reflections, being either secondary or coupling reflections, have appreciable intensities. This situation is similar to that for macromolecular crystals (see, for example, Chang *et al.*, 1991, 2002; Chao *et al*, 2002). Fig. 1 shows a portion of a multiple-wave diffraction pattern of the $(\tfrac{1}{3}\,0\,9)$ reflection, which was obtained with a ψ scan of 0.005° per step. The ψ angle was measured counterclockwise from the [010] direction. For convenience of representation, the relatively intense peaks and dips are denoted in the figures with the Miller indices of only the secondary reflection L. At the same time, in the text we use a more detailed designation for multiple-wave diffraction, namely $(L)/(G{-}L)$, to stress the cases with fractional or integer coupling $G{-}L$ reflections. The IN and OUT positions are also indicated in the figures. The rather noisy background arises from the presence of many weak fractional reflections.
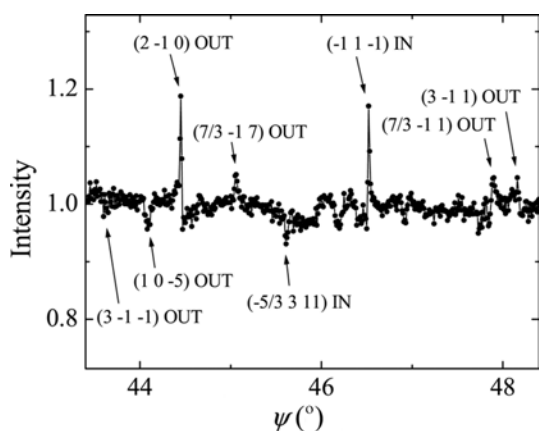

Figure 1
ψ-scan multiple-wave diffraction diagram for a CDW satellite $(\tfrac{1}{3}\,0\,9)$ primary reflection at $T = 16$ K. Intensity has been normalized with respect to the two-wave intensity of primary reflection.
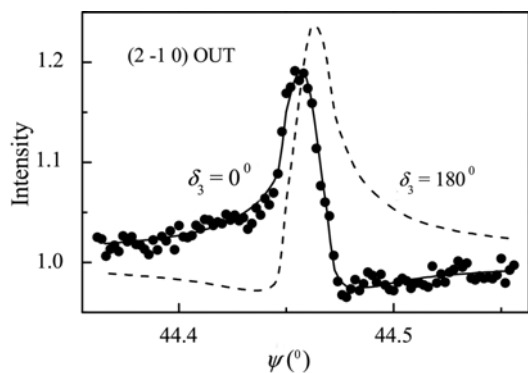

Figure 2
The experimental (solid circles) and calculated (lines) three-wave $(2\,{-}1\,0)$ profiles at $T = 16$ K. The solid line is for $\delta_3 = 0°$ and the dashed line for $\delta_3 = 180°$.

Obviously, the peak-type (*Umweganregung*) profiles $(2\,{-}1\,0)/(-\tfrac{5}{3}\,1\,9)$ in Fig. 2 and $(-1\,1\,{-}1)/(\tfrac{4}{3}\,{-}1\,10)$ in Fig. 3(*b*), and the dip-type (*Aufhellung*; see, for example, Chang, 1984) profiles $(-\tfrac{5}{3}\,2\,10)/(2\,{-}2\,{-}1)$ in Fig. 3(*a*) have distinct asymmetry. This asymmetry profile showing the phase effect on the multiply diffracted intensity is readily seen.

Triplet phases δ_3 were analysed based on the measured profiles for a centrosymmetric crystal, because the host structure of NbSe$_2$-2H at 16 K retains the same point symmetry as that at 297 K and the formation of CDWs does not affect the symmetry (Moncton *et al.*, 1977). Since the phase's δ values are either 0 or 180°, only the sign of $\cos\delta$ matters (see for example Chang, 1984, 1998; Weckert & Hümmer, 1997; and references therein). From the measured asymmetry of the profiles shown in Figs. 2 and 3, and the IN and OUT positions on the ψ-scan diffraction diagrams, the triplet phases are determined as $\delta_3 = -\delta(\tfrac{1}{3}\,0\,9) + \delta(2\,{-}1\,0) + \delta(-\tfrac{5}{3}\,1\,9) = 0°$, $\delta_3 = -\delta(\tfrac{1}{3}\,0\,9) + \delta(-\tfrac{5}{3}\,2\,10) + \delta(2\,{-}2\,{-}1) = 180°$, and $\delta_3 = -\delta(\tfrac{1}{3}\,0\,9) + \delta(-1\,1\,{-}1) + \delta(\tfrac{4}{3}\,{-}1\,10) = 0°$, respectively. In Fig. 3(*a*), an additional dip shows up on the higher angle side owing to the presence of a neighbouring diffraction. Yet the profile asymmetry as a whole is still observable. In Fig. 2, the solid line and the dashed line are the profiles of direct dynamical calculations (Stetsko & Chang, 1997) for $\delta_3 = 0$ and 180°, which are in agreement with the above qualitative phase estimation. The calculation for profile fitting to the experimental data was performed by varying the magnitudes of the structure factors of the 'weak' fractional primary $(\tfrac{1}{3}\,0\,9)$ and the coupling $(-\tfrac{5}{3}\,1\,9)$ reflections relative to that of the known 'strong' integer $(2\,{-}1\,0)$ reflection, without changing the triplet phase value $\delta_3 = 0°$ (the solid curve in Fig. 2). For
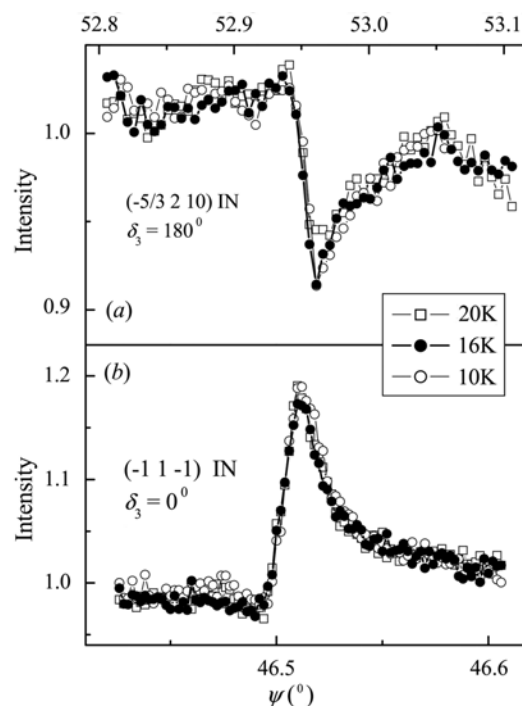

Figure 3
Experimental three-wave (*a*) $(-\tfrac{5}{3}\,2\,10)$ and (*b*) $(-1\,1\,{-}1)$ profiles at $T = 10$, 16 and 20 K.

comparison, the dashed curve shows the usual inversed asymmetry of peak profile for $\delta_3 = 180°$. In addition, it was noticed that the calculation also demonstrated that the shape of the multiple-wave profile depends mainly on the ratio between the structure factors of 'weak' fractional reflections, while the width of the profile relies mostly on that of 'strong' integer reflections.

Although the phase δ_Q of the CDW cannot be separated from the phase δ_G of the integer reflection in δ_3, the relative phases, $\Delta\delta(hkl) = \delta(hkl) - \delta(\frac{1}{3}09)$, of the fractional reflections hkl with respect to the $(\frac{1}{3}09)$ reflection can still be determined by using the known phases of 'strong' integer reflections. Since $\delta(2-10) = \delta(-11-1) = \delta(2-2-1) = 0°$, the relative phases derived from the corresponding δ_3 are thus $\Delta\delta(-\frac{5}{3}19) = \Delta\delta(\frac{4}{3}-110) = 0°$ and $\Delta\delta(-\frac{5}{3}210) = 180°$. These relative phases are also the collective phases of the CDW reflections along the given $[hkl]$ directions with respect to that of the $[\frac{1}{3}09]$ direction.

Several multiple-wave diffractions were measured at $T = 10$, 16 and 20 K; however, the profiles do not exhibit a temperature dependence in this low-temperature region. Fig. 3 shows the measured three-wave profiles normalized with the two-wave intensities of the $(\frac{1}{3}09)$ reflection for the corresponding temperatures. In each case, all the three normalized profiles coincide with one another.

The observation of the relative phase of CDW relies on the preservation of the coherent interaction of X-ray waves between the CDW reflections and the integer ones in the multiple-wave diffraction process. Although the peak widths (about $0.15°$) of CDW reflections are broad, the integer reflection with a sharp profile of about $0.03°$ ensures that the coherent interaction occurs in a narrow angular range. In other words, through the coupling reflection, the diffracted waves of a fractional reflection from some CDW domains (Burk *et al.*, 1992; Du *et al.*, 2004) are still able to propagate along the same direction as that of an integer reflection, and interact with each other coherently, although the mosaic spread of the CDW domain structure is large. This situation resembles the interference of surface in-plane waves diffracted from a thin film and a substrate crystal (Huang *et al.*, 2001). On the other hand, the broad CDW peak profiles indicate that the CDW is short-range ordered and forms a domain structure (Du *et al.*, 2004). Consequently, the diffraction intensity contains average information about these domains. At the static state, *i.e.* without the application of an external driving force, CDWs are pinned by the imperfections in the crystal and CDWs do not undergo a phase transition at low temperatures. The average triplet phase over the domains is therefore expected not to change with changing temperature. The variation of triplet phase is expected to happen when CDW sliding occurs. This fact makes the multiple-wave diffraction method a potentially ideal probe of the dynamic behaviour of CDW and related systems.

As is known, for a system possessing density-wave modulations, the order parameters contain both the amplitude and phase terms of the density waves, and only the latter dominate the physical properties at low temperature because the amplitude excitations are expected to be frozen out at low temperature. Based on this study, we believe that solving the dynamic phase problem, in which the phases are driven by applied electric fields exceeding a threshold value, is achievable. Experimentally, by measuring the profiles of the CDW satellite reflections under the application of electric fields exceeding the threshold value, the deformation of a CDW state has been observed and was ascribed to result from the disordering of the phases of the CDWs (Zhang *et al.*, 1993*a*,*b*). Such distorted phases can be directly studied in detail using X-ray multiple-wave diffraction. Moreover, combining X-ray multiple-wave diffraction and resonant X-ray scattering in the study of the modulations caused by charge, orbital and spin ordering, as observed in CMR materials, cuprates and nickelates, and related materials, should be able to provide further information about the electronic structures.

4. Conclusions

In conclusion, we have demonstrated the fundamental possibility of the X-ray multiple-wave interaction in CDW-modulated structures, specifically for a quasi-two-dimensional material $NbSe_2$-$2H$. The coherent dynamical interaction between CDW fractional reflections and integer reflections of the host structure in the multiple-wave diffraction processes provides phase information about structure-factor triples. The values of the triplet phases of the $NbSe_2$-$2H$ CDW-modulated centrosymmetric structure are determined to be either 0 or $180°$, and do not vary with temperature.

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