Solving the Phase Problem with Multiple-Beam Diffraction and Elliptically Polarized X Rays

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Interference among Bragg beams and effects of polarization-state mixing in a multiple-beam diffraction process leads to a new method of determining noncentrosymmetric phases when an elliptically polarized x-ray beam is used. This idea is proposed for the first time, based on the perturbation theory of scattering, and is demonstrated by an experiment on a GaAs single crystal.

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X-ray resonant scattering phenomena, such as anomalous scattering[1] and magnetic scattering[2] near an atomic absorption transition, have revealed many interesting features. These include enhancement and suppression of scattering cross sections near the resonance, complex dependence of the scattered photons on incident polarizations, and mixing of the polarization states in the scattering process. An analog to these energy resonance phenomena can occur for a normal Bragg-diffracted x-ray beam in the vicinity of a multiple-beam excitation point, which may also exhibit constructive and destructive interferences on both sides of the multiple-beam point, and mixing of the polarization states. Indeed, it is due to this similarity that the interference effect in multiple-beam diffraction has been termed virtual Bragg scattering[3] or spatial resonance phenomenon.[4,5] This multiple-beam interference effect can be used to retrieve the lost phase information in the diffracted intensity, and may lead to a physical solution of the famous "phase problem" in diffraction physics and crystallography.[3-9] As realized by several authors,[9-11] the interference effect in the neighborhood of a multiple-beam point contains information only on the *cosine* of the relative phases of the involved structure factors (or the real part of the phase factor), whereas information concerning the *sine* of these phases, which is directly related to the noncentrosymmetry of a crystal, is still lost. Efforts to obtain the complete phase information have been attempted by analyzing the diffracted intensities at the full excitation point of a multiple-beam reflection; however, difficulties arise from complications of kinematic and extinction effects that exist when comparing relative peak or integrated intensities in an experiment with dynamical or kinematical calculations.[12-14] It is the purpose of this paper to show that the noncentrosymmetric phase information can be obtained directly from the enhancement and the suppression of the diffracted intensity in the vicinity of a multiple-beam point, if a circularly polarized (or complex polarization) component exists in the incident x-ray beam. This is a direct consequence of polarization mixing during the multiple-beam spatial resonance, and effectively is very similar to the introduction of a complex atomic scattering factor in an anomalous scattering process.

A convenient way of achieving a multiple-beam diffraction condition is to rotate the diffracting crystal around the scattering vector, described by the azimuthal angle ψ, while always keeping one Bragg reflection **H** excited.[15,16] When the crystal is in an orientation such that another reciprocal node **L** is on the sphere of reflection, a multiple-beam diffraction occurs and it usually gives rise to a secondary peak in the intensity of the **H** reflection. The interference effect in the multiple-beam diffraction process refers to the intensity enhancement and suppression in reflection **H** on the wings of the multiple-beam diffraction peak. It can be fully explained both by the n-beam dynamical theory of x-ray diffraction[6] and by the perturbational approaches using an effective two-beam structure factor.[10,11,13] Using the second-order Born approximation, it can be shown[11] that the diffracted wave field for reflection **H** is perturbed by the presence of the extra reciprocal node **L** close to its excitation point, and the normalized perturbed wave field $\mathbf{D}_H$ is given by

$$\mathbf{D}_H=\hat{\mathbf{k}}_H\times\left\{\hat{\mathbf{k}}_H\times\left[\mathbf{D}_0-\Gamma\left|\frac{F_{H-L}F_L}{F_H}\right|e^{i\delta_{HL}}\frac{\mathbf{k}_L\times(\mathbf{k}_L\times\mathbf{D}_0)}{k_0^2-k_L^2}\right]\right\}. \tag{1}$$

In this expression, $\Gamma=r_e\lambda^2/\pi V_c$, λ is the x-ray wavelength, V_c is the unit-cell volume, and r_e is the classical radius of an electron, $F_H=|F_H|e^{i\alpha_H}$, $F_L=|F_L|e^{i\alpha_L}$, and $F_{H-L}=|F_{H-L}|e^{i\alpha_{H-L}}$ are the structure factors involved in the three-beam diffraction process, $\delta_{HL}=\alpha_{H-L}+\alpha_L-\alpha_H$ is the relative phase between them, and θ is the Bragg angle for the **H** reflection. The incident wave vector is $\mathbf{k}_0$, while $\mathbf{k}_H=\mathbf{k}_0+\mathbf{H}$ and $\mathbf{k}_L=\mathbf{k}_0+\mathbf{L}$ are the diffracted wave vectors for the **H** and **L** reflections, respectively, and $\hat{\mathbf{k}}_H=\mathbf{k}_H/k_0$. The first term in Eq. (1) is the usual two-beam diffracted wave field in the kinematic theory and the second term represents the three-beam perturbation to the two-beam field. To calculate the in-

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tensity, the cross product between the two terms gives rise to the constructive and the destructive interference effects in the neighborhood of the three-beam excitation point $k_0=k_L=k_H$, depending upon the relative phase difference δ_{HL}. When the anomalous dispersion in a crystal is negligible, it can be seen that for a linearly polarized or an unpolarized incident beam (i.e., $\mathbf{D}_0$ is real) the single complex term $e^{i\delta_{HL}}$ in Eq. (1) can only lead to the phase dependence on $\cos\delta_{HL}$ and results in lost information about the noncentrosymmetry $\sin\delta_{HL}$ of the reflections.

It is interesting to note the fact that the sign of the phases of the structure factors is reversed under a spatial-inversion symmetry operation, whereas the polarization states of the linearly or unpolarized x-ray photons remain unchanged. It is therefore reasonable to expect that a circularly polarized component in the incident x-ray beam, which would change its circular handedness under a spatial inversion, may be used to obtain the lost noncentrosymmetric phase information. Indeed, from Eq. (1) it is straightforward to show that when the incident beam is elliptically polarized (i.e., $\mathbf{D}_0=\hat{\boldsymbol{\sigma}}_0+ib\hat{\boldsymbol{\pi}}_0$, where b is the ratio of the $\hat{\boldsymbol{\pi}}$ component to the $\hat{\boldsymbol{\sigma}}$ component) the perturbed wave fields for reflection $\mathbf{H}$, resolved into components normal ($\hat{\boldsymbol{\sigma}}=\hat{\boldsymbol{\sigma}}_0$) and parallel ($\hat{\boldsymbol{\pi}}$) to the plane defined by $\mathbf{k}_0$ and $\mathbf{k}_H$, are given by

$$D_H^{\sigma}=1+\Gamma\left|\frac{F_{H-L}F_L}{F_H}\right|e^{i\delta_{HL}}\frac{k_L^2-(\mathbf{L}\cdot\hat{\boldsymbol{\sigma}})^2-ib(\mathbf{L}\cdot\hat{\boldsymbol{\sigma}})(\mathbf{L}\cdot\hat{\boldsymbol{\pi}}_0)}{k_0^2-k_L^2},$$

$$D_H^{\pi}=ib\left[\cos2\theta+\Gamma\left|\frac{F_{H-L}F_L}{F_H}\right|e^{i\delta_{HL}}\frac{k_L^2\cos2\theta-(\mathbf{k}_L\cdot\hat{\boldsymbol{\pi}})(\mathbf{L}\cdot\hat{\boldsymbol{\pi}}_0)+i(\mathbf{L}\cdot\hat{\boldsymbol{\sigma}})(\mathbf{k}_L\cdot\hat{\boldsymbol{\pi}})/b}{k_0^2-k_L^2}\right]. \tag{2}$$

It can be seen from Eq. (2) that the intensities $|D_H^{\sigma}|^2$ and $|D_H^{\pi}|^2$ depend on both $\cos\delta_{HL}$ and $\sin\delta_{HL}$ because of the extra complex terms that come from the mixing of the $\hat{\boldsymbol{\sigma}}$ and $\hat{\boldsymbol{\pi}}$ states in the multiple-beam diffraction process. In fact, the interference term in the intensity expressions is proportional to $\cos(\delta_{HL}+\beta)$, with

$$\beta=\begin{cases}\arctan[-b(\mathbf{L}\cdot\hat{\boldsymbol{\sigma}})(\mathbf{L}\cdot\hat{\boldsymbol{\pi}}_0),\ k_L^2-(\mathbf{L}\cdot\hat{\boldsymbol{\sigma}})^2] & \text{for } |D_H^{\sigma}|^2,\\ \arctan[(\mathbf{L}\cdot\hat{\boldsymbol{\sigma}})(\mathbf{k}_L\cdot\hat{\boldsymbol{\pi}})/b,\ k_L^2\cos2\theta-(\mathbf{L}\cdot\hat{\boldsymbol{\pi}}_0)(\mathbf{k}_L\cdot\hat{\boldsymbol{\pi}})] & \text{for } |D_H^{\pi}|^2,\end{cases}$$

where $\arctan(y,x)$ defines an angle $\arctan(y/x)$ in the quadrant specified by the signs of the x and y values. Although there is still a degeneracy in the cosine of the sum angle $\delta_{HL}+\beta$, the phase δ_{HL} can be obtained unambiguously because the degeneracy can be resolved in one of two ways: One is to measure $\hat{\boldsymbol{\sigma}}$ and $\hat{\boldsymbol{\pi}}$ polarizations separately in the diffracted beam, and the other is to make two measurements with two different incident polarizations b, e.g., left-elliptical and right-elliptical beams.

This idea has been confirmed by a recent measurement on a noncentrosymmetric crystal, GaAs, performed at a bending magnet beam line, the D-1 station at the Cornell High Energy Synchrotron Source (CHESS). In the experiment, the three-beam diffraction intensity profiles for the GaAs (442)/(151) reflection were measured using the synchrotron radiation emitted above and below the storage-ring orbital plane, where opposite senses of elliptical polarization are accessible. The profiles were obtained by measuring the integrated intensities of the (442) rocking curves, collected at a series of azimuthal angles ψ in the neighborhood of the multiple-beam diffraction peak $\mathbf{L}=(151)$. In order to minimize the background and the standing-wave effect[17] on the fluorescence, the wavelength of the incident beam was chosen to be $\lambda=1.3$ Å, so that the energy is well below the Ga and As K edges. The monochromatic x rays were produced by a pair of silicon (111) perfect crystals diffracting in the vertical plane.

Two sets of data were collected, one using the synchrotron radiation at 0.11 mrad above the orbital plane, Fig. 1(a), and the other 0.11 mrad below, Fig. 1(b). As shown in Fig. 1, clear differences were observed (squares) on the three-beam profiles when the sense of circular polarization was reversed. The curves in the figure are the perturbation-theory calculations using Eq. (2) for $\delta_{HL}=0°$, 90°, 180°, and −90°, respectively. All curves are convoluted with a Gaussian instrumental width function with a standard deviation of 18″. The ellipticity of the incident beam is assumed to be $b=0.45$ at 0.11 mrad above and $b=-0.45$ at 0.11 mrad below the orbital plane. This assumption is consistent with the theoretical prediction[18] for synchrotron radiation (at the CHESS D-1 station) based on the vertical size (~0.75 mm) of the positron beam in the storage ring, the vertical slit width (~0.25 mm) used in the experiment, and the reduction of the $\hat{\boldsymbol{\pi}}$ polarization in the double-crystal monochromator. The phase triplet $\delta_{HL}=90°$ for the (442)/(151) combination can be uniquely determined by comparing the calculations with the experimental results in Fig. 1, and by the argument that the degenerated phase angle in Fig. 1(a), between 0° and −90°, would yield an asymmetry pattern between the dotted and the dash-dotted lines in Fig. 1(b), very different from that given by $\delta_{HL}=90°$ (solid line).

One may note that the phase sensitivity of the method can be tuned by choosing an optimal elliptical polarization b for a particular range of phase values. As shown in Fig. 1 the elliptical polarization in 1(a) gives better

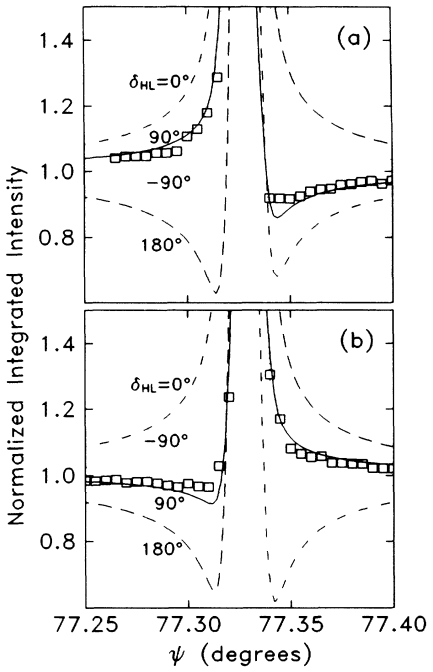

FIG. 1. Azimuthal intensity profiles for the GaAs (442) reflection in the neighborhood of the same multiple-beam excitation $\mathbf{L}=(151)$, using incident radiations with (a) left-handed elliptical polarization (above orbital plane) and (b) right-handed polarization (below orbital plane). The experimental results are given by squares and each point is an integrated intensity over the (442) rocking curve, normalized to the two-beam value obtained far away from any multiple-beam excitations. The zero on the ψ angle corresponds to the reciprocal vector $(\bar{1}10)$ lying on the diffraction plane and with a projection that is antiparallel to the incident wave vector. The four curves in each figure are perturbation-theory calculations described in the text for phase triplet $\delta_{HL}=0°$ (dash-dotted lines), 90° (solid lines), 180° (dashed lines), and $-90°$ (dotted lines), respectively. The elliptical polarization ratio (see text) assumed in all calculations is (a) $b=+0.45$ and (b) $b=-0.45$, and is consistent with the theoretical predictions for the experiment setup.

sensitivity for phase values between $-90°$ and 0° than those between 0° and 90° while the polarization in 1(b) is better suited for the latter. It is also possible to maximize the intensity asymmetry effect by varying the incident polarization. For example, a linearly polarized incident beam gives rise to biggest asymmetry effects for $\delta_{HL}=0°$ or 180°, whereas a pure circularly polarized incident beam should yield greatest asymmetries for $\delta_{HL}=\pm 90°$.

Another important distinction shown in Fig. 1 is between the two curves given by phases of $\pm 90°$ for a single state of elliptical polarization. Such a difference shows that the intensity function $I(\mathbf{H})$ in the neighborhood of a multiple-beam excitation is no longer centrosymmetric as required by Friedel's law which applies to normal two-beam cases with negligible anomalous dispersions. This consequence can be used in the same way that anomalous scattering is used to provide information about the atomic configurations with respect to diffraction geometry for a noncentrosymmetric polar crystal, such as GaAs, and about the handedness of a crystal in an enantiomorphic group, such as quartz. To be more explicit, anomalous scattering, as is well known, makes use of the complex nature of an atomic scattering factor to interfere with the complex geometric structure factor. In our case, with the aid of multiple-beam diffraction, Eq. (2) shows that the complex x-ray polarization plays an equivalent role as the anomalous dispersion by mixing the real and imaginary parts of the structure factor into the two polarization components of the scattered intensity. Therefore additional phase information about handedness and polarity can be obtained even without anomalous dispersion. For the GaAs crystal used in our experiment, the atomic arrangement with the Ga atoms at the $+(\frac{1}{8},\frac{1}{8},\frac{1}{8})$ sites and the As atoms at the $-(\frac{1}{8},\frac{1}{8},\frac{1}{8})$ sites is consistent with the experimental observations on the (442)/(151) asymmetries, because the opposite configuration, Ga at $-(\frac{1}{8},\frac{1}{8},\frac{1}{8})$ and As at $+(\frac{1}{8},\frac{1}{8},\frac{1}{8})$, would have yielded asymmetries given by $-90°$ (dotted lines) in Fig. 1.

In summary, multiple-beam x-ray diffraction with an elliptically or circularly polarized incident beam can provide valuable noncentrosymmetric phase information because of the effects of interference between the phases of the structure factors and the complex components of the incident polarization during the multiple-beam spatial resonance. The physical reason for the ability to distinguish the phases related by a spatial inversion is the introduction of a noncentrosymmetric interaction component between the x-ray photons and the crystal, which is completely analogous to the use of the anomalous dispersions in phase determinations. The increasing worldwide availability of synchrotron-radiation facilities and related circular-polarization sources makes this technique especially promising and useful for diffraction physicists and crystallographers. With a crystal that has a known noncentrosymmetric structure, such as GaAs, the same method can be applied to distinguish circular from unpolarized radiation and to determine the handedness of the elliptical polarization.

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