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Study of crystalline structures via physical determination of triplet phase invariants

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Abstract

In this article, we report a practical application of physical-phasing X-ray crystallography to access specific information about the electron-density distribution on an III–V semiconductor. The objective is to demonstrate that physical measurements of phase invariants can also be useful as an alternative method for studying crystalline structures. Here, evidences are given of their sensitivity to non-spherical charge distribution around atomic sites.

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Keywords: Multiple-wave X-ray diffraction; Phase invariants; Anomalous dispersion; Chemical bond charges

1. Introduction

During the last two years, several experiments have been carried out at the Brazilian Synchrotron Light Laboratory (LNLS) to inspect the feasibility of studying crystalline structures by measuring triplet phase invariants (or just phase unless specified). Physical determination of phase invariants is possible via interference of diffracted X-ray waves, for instance, when several Bragg reflections are simultaneously excited in a single crystal. The three-beam X-ray diffraction (3BD) phenomenon is the most suitable case of multiple-wave diffraction for phase measurements [1,2]. Although, exploitation of the linear polarization of synchrotron radiation is necessary to improve accuracy [3], phase determination is not just a question of data collection. For a given model used to interpret the experimental data, previous assumption on the square moduli of structure-factors and on

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crystalline perfection can severely compromise the accuracy and reliability on the measured phase values. Under the framework of the second-order approach of the 3BD [4,5], after some modifications [3], relevant points for developing data analysis procedures were outlined [6] and, based on these points, an analytical algorithm has been written [7]. In this article, we report the application of the phasing procedure [6,7] for extracting a specific information of a crystalline structure; in this case the formation and positioning of chemical bonding charges in a semiconductor crystal. In other words, it is been investigated if such phasing procedure has enough sensitivity to evidence non-spherical charge distribution around atomic sites. Since accuracy also depends on the phase values, the experiments were carried out near absorption edges. Anomalous dispersion does produce significant changes in the atomic scattering factor of a particular atom and, consequently, changes in the reflection phases (phases of the structure-factors), as well as in the triplet phases [5]. It is a well-known phenomenon already exploited in complex protein X-ray crystallography. Here, by tuning the energy across the Ga edge in a GaSb crystal, the interference profiles of several 3BDs have been monitored.

2. Results and discussions

The GaSb crystal is a 550 μm thick wafer with (0 0 1) polished surfaces. In the ϕ rotation of this crystal around the diffraction vector of the $\bar{2}\,2\,6$ reflection, the 3BD cases generated by the $\bar{3}\,\bar{1}\,3+1\,3\,3$ (**A**), $\bar{3}\,\bar{1}\,1+1\,3\,5$ (**B**), $\bar{1}\,\bar{1}\,3+\bar{1}\,3\,3$ (**C**), and $\bar{3}\,1\,3+1\,1\,3$ (**F**) *Umweg* reflections have been investigated – the *Umweg* terminology is commonly used to indicate sequence of consecutive reflections responsible for scattering the secondary waves in the same direction of the primary one, which is generated by the $\bar{2}\,2\,6$ reflection. The interference profiles (ϕ-scans) shown in Fig. 1 were collected as a function of both the polarization angle, χ [8], and photon energy, E, below and above the Ga edge at 10,370 eV.

Relative strength and phase difference between secondary and primary waves depend upon,

$$W(E) = |W(E)|e^{i\delta_T(E)} = \frac{F_S F_R}{F_P} = \frac{|F_S||F_R|}{|F_P|} e^{i(\delta_S+\delta_R-\delta_P)}, \quad (1)$$

where F_G is the structure-factor of reflection G, whose diffraction vector is $\boldsymbol{G}$. P stands for the primary $\bar{2}\,2\,6$ reflection, responsible for the primary wave, and the S + R reflection provides the secondary wave. In terms of *hkl* reflection indexes, the structure-factors are given by

$$F_{hkl} = 4f_A(E) + 4f_B(E)e^{i\frac{\pi}{2}(h+k+l)} + f_{bc}\left[e^{i\frac{\pi}{2}x(h+k+l)} + e^{i\frac{\pi}{2}x(h-k-l)} + e^{i\frac{\pi}{2}x(-h+k-l)} + e^{i\frac{\pi}{2}x(-h-k+l)}\right], \quad (2)$$

where $f_{A,B}(E) = f^{(0)}_{A,B} - \Delta f_{A,B} + f'_{A,B}(E) + i f''_{A,B}(E)$, $f_{bc} = (\Delta f_A + \Delta f_B)/4$, and x stands for the location of the bond-charge in-between the A–B atomic sites. The atomic scattering factors, $f^{(0)}$, were obtained from the Cromer–Mann coefficients, and their respective anomalous dispersion corrections, f' and f'', calculated according to Cromer and Liberman theory [9]. Fig. 2 shows the theoretical behaviors of $|W(E)|$ and $\delta_T(E)$ for two GaSb model structures: with ($\Delta f_{Sb} = 5$ and $\Delta f_{Ga} = 3$) and without ($\Delta f_{Sb} = \Delta f_{Ga} = 0$) covalent bonds placed at $x = 0.5$. The A sites are occupied by Sb atoms.

The expected qualitative behaviors of the ϕ-scans in Fig. 1, as function of E, can be inferred from the theoretical $|W(E)|$ and $\delta_T(E)$ values (Fig. 2). It is possible by written $\boldsymbol{D}_P = D_0\boldsymbol{v}_P$ and $\boldsymbol{D}_{SR}(\phi) = D_0 W(E) f(\phi)\boldsymbol{v}_{SR}$ as the amplitude of the primary and secondary waves, respectively. $\boldsymbol{v}_{P,S} = \hat{\boldsymbol{k}}_{P,S} \times (\hat{\boldsymbol{v}}_0 \times \hat{\boldsymbol{k}}_{P,S})$ and $\boldsymbol{v}_{SR} = \hat{\boldsymbol{k}}_P \times (\boldsymbol{v}_S \times \hat{\boldsymbol{k}}_P)$ are polarization factors, $\boldsymbol{k}_G = \boldsymbol{G} + \boldsymbol{k}_0$ is the wavevector of the diffracted beam G (G = 0, P, or S), and $\hat{\boldsymbol{v}}_0$ is the polarization direction of the incident beam. The primary intensity modulation due to the excitement of the secondary wave is

$$I(\phi) = |\boldsymbol{D}_P + \boldsymbol{D}_{RS}|^2 = |D_0\boldsymbol{v}_P|^2[1 + R^2|f(\phi)|^2 + 2\xi R|f(\phi)|\cos(\Omega + \delta_T)], \quad (3)$$

where $\xi = 1$ in the standard second-order formalism [4], $R = W(E)|\boldsymbol{v}_{SR}|/|\boldsymbol{v}_P|$ and $|f(\phi)|^2$ is a Lorentzian function of unit weight, i.e. $|f(\phi_0)|^2 = 1$ at maximum of the *Umweg* reflection ($\phi = \phi_0$). In

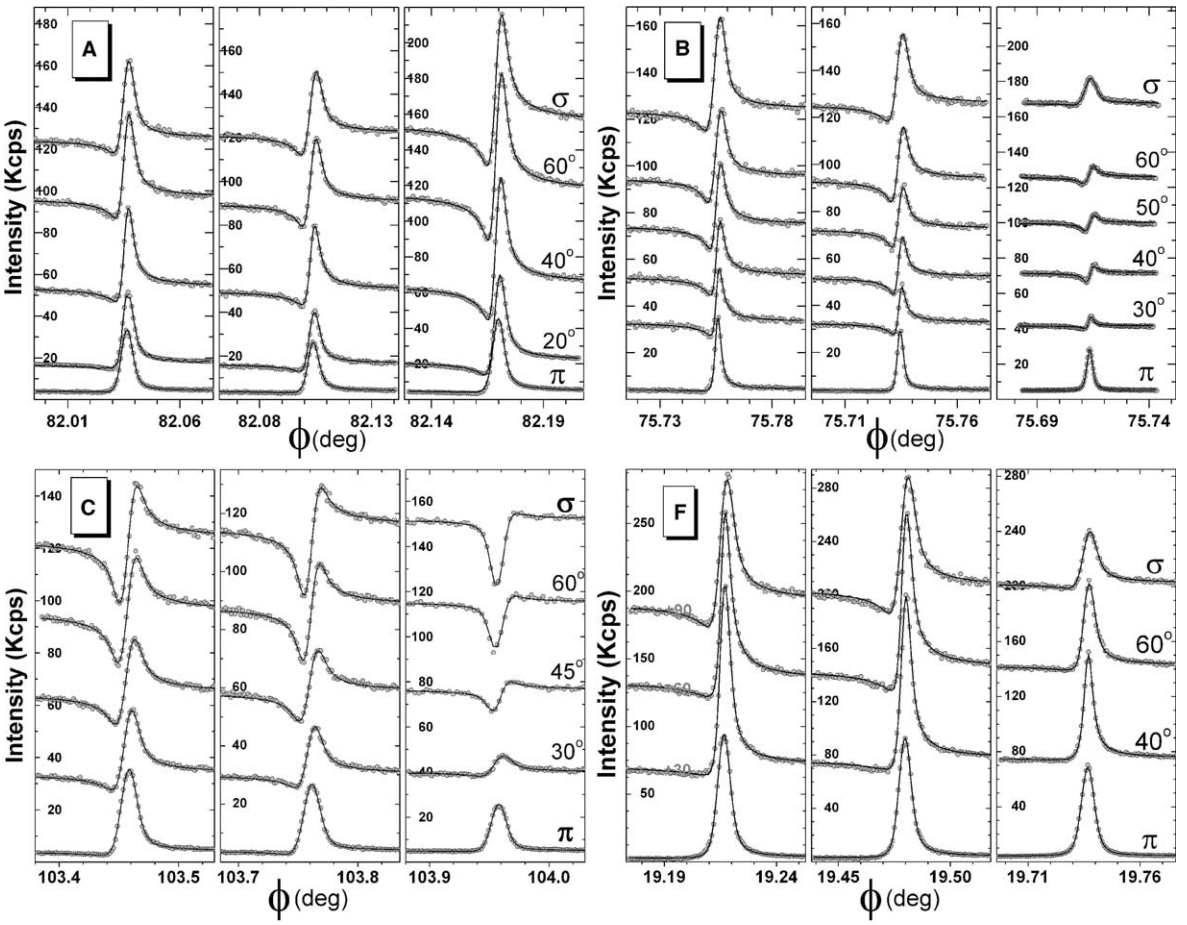

Fig. 1. Experimental (circles) and simulated (solid lines) interference profiles, ϕ-scans, of the $\bar{3}\,\bar{1}\,3+1\,3\,3$ (**A**), $\bar{3}\,\bar{1}\,1+1\,3\,5$ (**B**), $\bar{1}\,\bar{1}\,3+\bar{1}\,3\,3$ (**C**), and $\bar{3}\,1\,3+1\,1\,3$ (**F**) *Umweg* reflections; primary reflection: $\bar{2}\,2\,6$; Crystal: GaSb (0 0 1); X-ray photon energies: 10,300 eV (left), 10,350 eV (middle), and 10,400 eV (right). Polarization angle χ is shown at the right of each scan where π and σ stand for $\chi = 0$ and $\chi = 90°$, respectively. Simulation and fitting procedures, based on Eq. (3), are described in more details elsewhere [5], as well as other instrumental details [8].

the measured 3BD cases, the dynamical phase shift Ω, varies from 180° to 0 across $\Omega = 90°$ at ϕ_0. It determines the following *well-known* 3BD characteristic interference profiles [1,2,5]: (i) for $\delta_T \approx 0$, $I(\phi < \phi_0) \approx I_0(1 - R|f|)^2$ and $I(\phi > \phi_0) \approx I_0(1 + R|f|)^2$, and an asymmetric profile should be observed, with destructive interference at the left-hand side of the peak and constructive interference on the other side; (ii) for $\delta_T = -90°$, $I(\phi \leqslant \phi_0) = I(\phi \geqslant \phi_0) \approx I_0(1 + R|f|)^2$, a symmetric peak is observed, i.e. a constructive interference; and (iii) for $\delta_T = +90°$, $I(\phi \leqslant \phi_0) = I(\phi \geqslant \phi_0) \approx I_0(1 - R|f|)^2$, asymmetric dip should be observed, i.e. a destructive interference. As extensively discussed somewhere else [6], the coherence between the diffracted waves is affected by imperfections of the crystalline lattice, and the ξ parameter artificially accounts for coherence loss effects in the profiles. It implies that, destructive interference is attenuated by partial levels of coherence ($0 < \xi < 1$) and, therefore, observation of symmetric peaks are inconclusive since they can either occur for coherent waves ($\xi = 1$) with $\delta_T = -90°$ as well as for incoherent ones ($\xi = 0$) with any phase

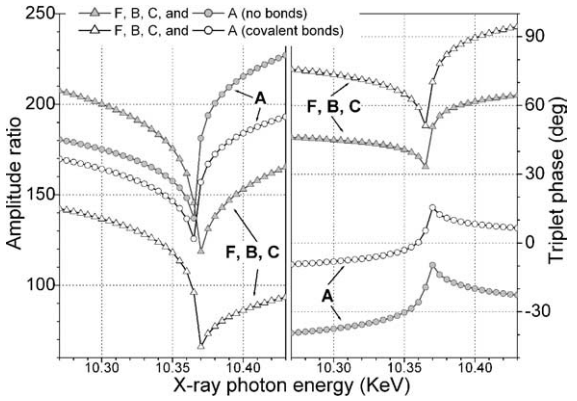

Fig. 2. Theoretical behaviors of $|W(E)|$ and $\delta_T(E)$, Eq. (1), for the **A**, **B**, **C**, and **F** *Umweg* reflections as a function of the X-ray photon energy, E, across the Ga edge at 10,370 eV. The curves were calculated for two GaSb model structures: with (open symbols) and without (gray symbols) covalent bonds, as defined in Eq. (2).

value. Any mosaicity in the crystal is responsible for some coherence losses. Instrumental broadening and mosaicity are taken into account by convolution of Eq. (3) with a gaussian function [2,6,7].

For a given 3BD, the maximum intensity of the ϕ-scans at π-polarization ($\chi = 0$) provides information on the relative $|W(E)|$ variation across the Ga edge. At other polarization angles, the amplitude of the primary intensity modulation provides the same qualitative information, although it is compromised by changes in the phase values. For the **B**, **C**, and **F** *Umweg* reflections the $|W(E)|$ values seem to decrease across the Ga edge, as predicted in Fig. 2. The opposite behavior is observed for **A**, as also predicted (see Fig. 2). Note that very similar behavior of $|W(E)|$ are predicted for both structures, with and without covalent bonds. On the other hand, ϕ-scans at higher polarization angles are sensitive to the phase values, and for the structure with covalent bonds, the **B**, **C**, and **F** cases have δ_T very close to 90° above the Ga edge, and a dip should be observed for these reflections. However, the total destructive interference may have been partially suppressed by crystalline imperfections; only the **C** reflection does appear as a dip for $E =$ 10,400 eV, as clearly observed in Fig. 1. In the case of the *Umweg* **B**, the profiles for $E = 10{,}400$ eV present an interesting behavior that could not be explained under the second-order approximation.

The phase analysis of the **A** and **C** *Umweg* reflections in Fig. 3 provide relatively accurate phase values, $\delta_T = 30° \pm 20°$ (**A**) and $\delta_T = 85° \pm 5°$ (**C**), above the Ga edge in agreement with the model structure where $2e^-$ bonding charges are placed midway between the Sb–Ga bonds. However, to explain quantitatively all intensity data reported in Fig. 1, a more complex model structure seems to be necessary, as well as a more elaborated diffraction theory accounting for higher-order interference terms. The major concern in using the n-beam dynamical diffraction theory [1,2] relies

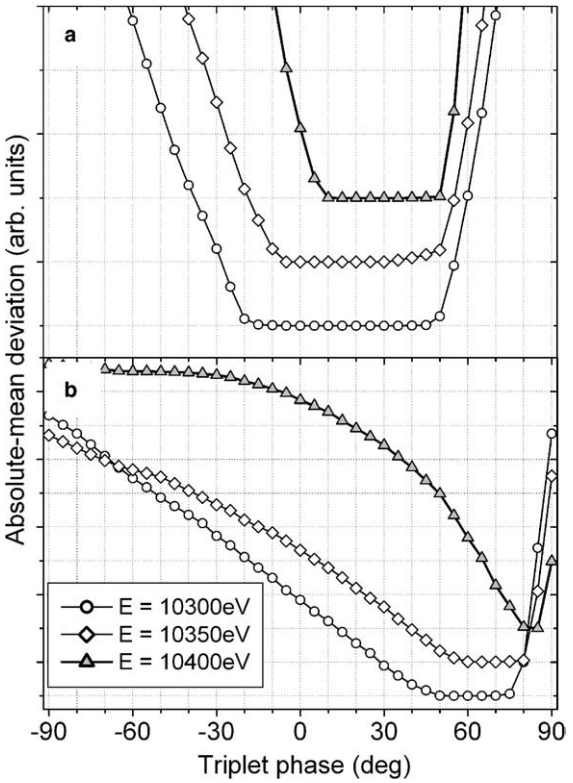

Fig. 3. Phase analysis of interference profiles (in Fig. 1): (a) **A** and (b) **C** *Umweg* reflections. The analysis is based on minimization of as a function of the triplet phase, δ_T. It shows the sum of absolute-mean deviations, from all scans in each data set. For visualization purposes, the curves are normalized by their respective minimum and their ordinates displaced by small amounts. Details on phasing procedures are given elsewhere [5,6].

on its intrinsical assumption of total coherence among the diffracted wavefields; it still has to be validated against polarization-dependent sets of ϕ-scans, as those reported in Fig. 1. Other phasing methods, such as Friedel partners measurements [5], could also be performed to assure the reliability of the phasing procedure used here, or vice-versa.

3. Conclusions

Although, the GaSb crystal model with localized bond charges is quite simple, it provides a better agreement with the measured triplet phases than the model with spherical charge densities centered only at the atomic sites. The exploratory work presented here is an example of physical-phasing X-ray crystallography where information on the electron density is obtained without resolving the whole structures by conventional structure determination methods. The advantage may reside on the resolution with the desired information is obtained.

Acknowledgements

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