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Direct Determination of the Phases of X-ray Structure Amplitudes in Crystals Irradiated by Laser Beam

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Abstract

A new method to determine the phases of X-ray reflections by laser irradiation excitation of the coherent optical phonons in crystals is proposed. This method can be applied to both dynamically and kinematically scattering crystals.

1. Introduction

Detection of the intensities of reflections in X-ray diffraction experiments on crystals makes it possible to measure only the magnitude of X-ray structure amplitudes. To obtain full information about crystal structure one also needs to know the phases of these amplitudes. Determination of the reflection phases is one of the most important problems in the physics of X-ray diffraction in crystals.

There are several direct methods of solving this problem, such as isomorphic replacement, anomalous dispersion, multiwave diffraction and virtual Bragg scattering (see Budo, Dintris, Kendrew & Wyckhoff, 1959; Collela, 1982; Mössbauer, Parak & Hoppe, 1981; Chang, 1984, and references therein). Each of the above methods has limitations: several different heavy-atom derivatives are necessary; X-rays with wavelengths above and below the *K*- (or *L*- *etc.*) absorption edges of the atoms of the media must be used; perfect dynamically scattering objects must exist. However, there is a method of direct X-ray structure and phase determination that does not involve growing new crystals or varying the X-ray wavelength and that can be applied to both dynamically and kinematically scattering crystals.

The new method to determine the phases of X-ray reflections is described in the present paper. The main aim of this method is the determination of the phases of the X-ray scattering amplitudes for each atom in the unit cell of a crystal.

2. The theoretical background

Irradiation by laser beam can result in coherent excitation of optical photons in the media and Raman scattering of X-rays (Baryshevsky, 1982; Born & Huang, 1954). In a recent experiment (Chapman, Hsiesh & Collela, 1984) on the effect of infrared radiation on X-ray diffraction in quartz it was shown that coherent excitation of the transversal optical phonons in crystals affected the process of diffraction, resulting in an increase of the intensity of X-ray reflections. The theory of X-ray diffraction in such a crystal can be developed by analogy with the theory of X-ray diffraction in crystals subjected to high-frequency acoustic waves (see, for example, Polikarpov & Skadorov, 1987, 1988). In this situation, the increase of the X-ray integral reflection coefficient in Laue geometry for the slightly absorbing crystal can be written in the form

$$\Delta R^s = R_0^s \sum_{l=-\infty}^{+\infty} |\chi_\tau^l|/|\chi_\tau| \qquad (1)$$

where

$$R_0^s = \pi|\chi_\tau| C_s/[2\beta^{1/2} \sin(2\theta_b)]$$

is the integral reflection coefficient of a stationary crystal;

$$\begin{aligned} \chi_\tau &= -(\omega_l^2/\omega^2) \exp[-W(\tau)]|F(\tau)| \exp(i\varphi); \\ \chi_\tau^l &= -(\omega_l^2/\omega^2) \exp[-W(\tau)]|F_l(\tau)| \exp(i\varphi_l) \\ |F(\tau)| \exp(i\varphi) &= \sum_{i=1}^{N} f_i \exp(i\boldsymbol{\tau} \cdot \mathbf{r}_i); \\ |F_l(\tau)| \exp(i\varphi_l) &= \sum_{i=1}^{N} J_l(\boldsymbol{\tau} \cdot \mathbf{a}_i) f_i^* \exp(i\boldsymbol{\tau} \cdot \mathbf{r}_i); \end{aligned} \qquad (2)$$

ω_l is the Langmuir frequency of the scattering media, ω is the X-ray frequency; $\exp[-W(\tau)]$ is the Debye-Waller factor; $C_s = 1$ ($\cos 2\theta_b$) for σ (π) polarization; f_i is the X-ray scattering amplitude for the ith atom; $\mathbf{r}_i$ is its position in the unit cell of a crystal; $\mathbf{a}_i$ is the projection of the forced oscillation amplitude of the ith atom on the scattering plane; $\boldsymbol{\tau}$ is the reciprocal-lattice vector; N is the number of atoms in the unit cell of the crystal; $J_p(x)$ is the pth-order Bessel function.

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It follows from (1) that

$$\sum_{l=-\infty}^{+\infty}\left|\sum_{i=1}^{N}\left\{J_l(\tau\cdot\mathbf{a}_i)f_i'(\omega+l\Omega)\left[J_l(\tau\cdot\mathbf{a}_i)f_i'(\omega+l\Omega)+2\sum_{j=i+1}^{N}J_l(\tau\cdot\mathbf{a}_j)\{f_j'(\omega+l\Omega)\cos[\tau\cdot(\mathbf{r}_i-\mathbf{r}_j)]-f_j''(\omega+l\Omega)\sin[\tau\cdot(\mathbf{r}_i-\mathbf{r}_j)]\}\right]\right\}\right|^{1/2}=C_n \quad (3)$$

where

$$C_n=\Delta R^s\omega^2/\omega_l^2\exp[-W(\tau)].$$

Equation (3) is a system of nonhomogeneous equations with variable coefficients with respect to the functions $\cos(\tau\cdot\mathbf{r}_i)$ and $\sin(\tau\cdot\mathbf{R}_i)$. Therefore, to determine the values of $\cos(\tau\cdot\mathbf{r}_i)$ and $\sin(\tau\cdot\mathbf{r}_i)$ one must have $N(N-1)$ independent equations. In other words, to determine the phases of the X-ray scattering amplitude for the ith atom, the relative increase of the integral reflection coefficients for $N(N-1)$ different values of oscillation amplitudes $\mathbf{a}_i$ must be measured. The values of $\mathbf{a}_i$ can be easily varied by changing the strength of the electric field E of the laser beam or its projection on the scattering plane. The phase of the X-ray reflection φ can be easily derived using the phases of the atomic scattering amplitudes.

It should be noted that a similar method can be used in the case of kinematic diffraction of X-rays. Then the system of equations for the determination of the phases of the X-ray scattering amplitude for the ith atom has the form

$$\sum_{l=-\infty}^{+\infty}\sum_{i=1}^{N}\left\{J_l(\tau\cdot\mathbf{a}_i)f_i'(\omega+l\Omega)\left[J_l(\tau\cdot\mathbf{a}_i)f_i'(\omega+l\Omega)+2\sum_{j=i+1}^{N}J_l(\tau\cdot\mathbf{a}_j)\{f_j'(\omega+l\Omega)\cos[\tau\cdot(\mathbf{r}_i-\mathbf{r}_j)]-f_j''(\omega+l\Omega)\sin[\tau\cdot(\mathbf{r}_i-\mathbf{r}_j)]\}\right]\right\}=B_n \quad (4)$$

where

$$B_n=\Delta R^s\omega^4/\omega_l^4\exp[-2W(\tau)].$$

Clearly (4) permits one to determine the values $\tau\cdot(\mathbf{r}_i+\mathbf{r}_j)$. For their determination one needs to have $N(N-1)$ measurements of the relative integral reflection coefficient of the crystal. Equations (3) and (4) allow one to determine the forced oscillation amplitudes $\mathbf{a}_i$ of the atoms in the crystal with known structure which is very important for several problems of nonlinear optics (Shen, 1984). In this situation, the reciprocal-lattice vector τ is also a variable parameter.

3. Concluding remarks

The optimization of the experimental conditions in the experiment of Chapman, Hsiesh & Collela (1984) (laser irradiation focusing and changing of crystal orientation) allows one to increase the projection of the electric field strength **E** on the reciprocal-lattice vector τ by at least one order of magnitude. Thus the method proposed seems to be easily realized experimentally.

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A Crystal-Chemical Model of Atomic Interactions. 6. Intermetallic Phase Structures

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Abstract

Commonly occurring structures are considered from the point of view of a crystal-chemical model of atomic interactions. It is shown that these structures sometimes contain coordination polyhedra distinct from Platonic, Archimedean and Zalgaller's polyhedra. These polyhedra have two or more groups of

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