Experimental determination of the structure-amplitude phases

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On the basis of a modified geometry of a three-wave diffraction a procedure is proposed, and implemented, for an experimental determination of the phase invariants of the x-ray diffraction reflections. This procedure is used in experiments with silicon single crystals.

The determination of the phases of the structure amplitudes has been, and is now, the key factor in determining the atomic structure of crystals from x-ray, neutron, and electron diffraction data. In the case of x-ray diffraction analysis, the integral intensities of the diffraction reflections, $I_{\mathbf{H}}$, measured experimentally, are scaled to the moduli of the Fourier coefficients $F_{\mathbf{H}}$ of the corresponding expansion of a periodic electron density distribution $\rho(\mathbf{r})$ in the crystal,

$$\rho(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{H}} |F_{\mathbf{H}}| \exp[-i(2\pi \mathbf{H}\mathbf{r} - \alpha_{\mathbf{H}})], \tag{1}$$

where $\mathbf{H} \equiv (h,k,l)$ are integer indices of the diffraction reflections, $\alpha_{\mathbf{H}}$ are the phases of the structure amplitudes, and V is the volume of the unit cell of the crystal. The strides that have recently been made in the solution of the phase problem can be attributed to the use of stochastic methods of estimating the phase invariants of the type $\phi = -\alpha_{\mathbf{H}_1} + \alpha_{\mathbf{H}_2} + \alpha_{\mathbf{H}_3}$, where $\mathbf{H}_1 = \mathbf{H}_2 + \mathbf{H}_3$, on the basis of the analysis of the experimental distributions of the structure-amplitude moduli. The American crystallographers H. A. Hauptman and J. Karle have been awarded the 1985 Nobel prize in chemistry for the development of these methods. In protein crystallography the phase problem is solved by measuring the diffraction patterns from a series of crystals of a protein with heavy-atom tags which is to be studied.

The basic possibility of an experimental determination of the structure-amplitude phases was pointed out long ago.[1–3] This possibility is based on the interaction of x–ray diffraction reflections in the case of multiple-wave diffraction. More recent encouraging attempts to obtain a practical solution to this problem[4–7] have identified some serious difficulties stemming from the masking of the corresponding interference patterns by stronger effects.

Let us assume that the crystal in the primary x-ray beam is oriented in such a way that there is a diffraction scattering from a system of planes which is characterized by the reciprocal-space vector $\mathbf{H}_1$. Turning the crystal relative to this vector, which is directed normal to the reflecting systems of planes, we can place one more system of planes, characterized by the vector $\mathbf{H}_2$, in the reflecting position, without violating the diffraction conditions. The experimental arrangement described below is incorporated into a three-crystal x-ray diffractometer,[8] in which the primary beam is monochroma-

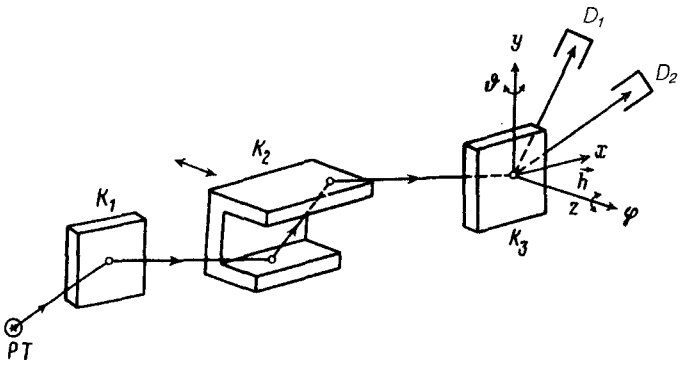

FIG. 1. An arrangement for a diffraction experiment for determining the structure-amplitude phases. *PT* — x-ray source; K_1 and K_2—crystal monochromators; K_3—the crystal to be analyzed; D_1 and D_2—detectors.

tized according to the scheme shown in Fig. 1 in two mutually perpendicular planes. The divergence of the primary beam in the horizontal and vertical directions is 0.5 and 8 arcsec, respectively, which allows us to study in a single experiment the spatial distribution of the intensity in the diffraction reflection by independently scanning the sample at φ and ϑ angles (see Fig. 1). This particular circumstance has made it possible for us to find a way to eliminate the effects that obscure the relationship between the phases.

This procedure can be explained in its simplest form by using a specific example of three-wave diffraction. As the candidate for analysis we chose a silicon single crystal. We measured three reflections with the indices 202, 422, and 220 in a symmetrical Bragg geometry. The reflection curve peaks $R_{202}(\vartheta)$ and $R_{422}(\varphi)$, which are measured independently far from the three-wave point when there is virtually no interaction between the diffraction waves $\mathbf{E}_1$ and $\mathbf{E}_2$, are twice as large as the corresponding values obtained by simultaneously reflecting these reflections (Fig. 2). In the case of

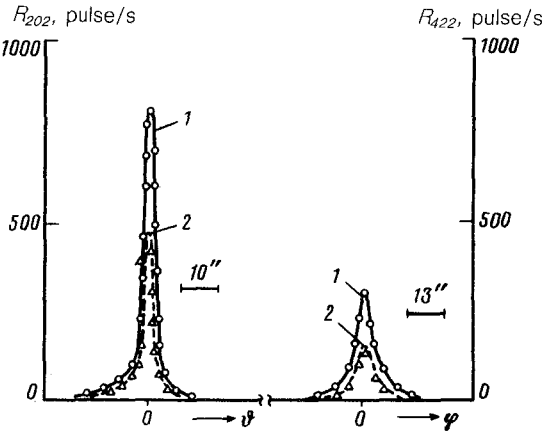

FIG. 2. Profiles of diffraction reflections $R_{202}(\vartheta)$ and $R_{422}(\varphi)$ measured far from the three-wave point (curve 1) and in the case of simultaneous reflection (curves 2).

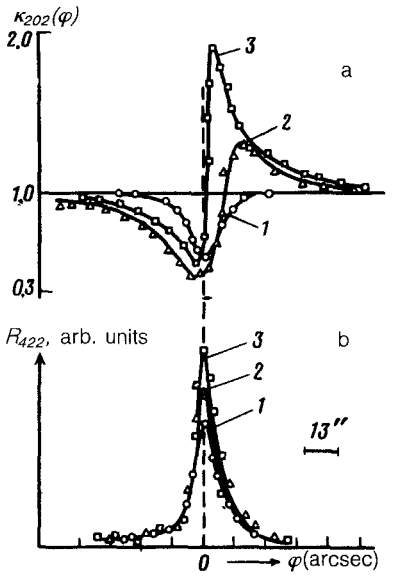

FIG. 3. (a) Normalized profiles $\kappa_{202}(\varphi)$ and (b) total profiles $R_{422}(\varphi)$ of the diffraction reflections at different divergence angles $\delta\vartheta_{202}$. 0″—Curves 1; 3″—curves 2; 12″—curves 3.

strong diffraction reflections, like the 202 and 422 reflections in silicon, such a reduction in intensities due to a three-ray diffraction is a typical reduction which is caused by extinction. Because of this strong effect, only one extinction minimum [curve 1 in Fig. 3(a)] is clearly identifiable at the three-wave point on the curve of the normalized intensity of the reflection 202 versus the angle φ. This minimum has virtually no information on the phases of the structure amplitudes. To identify the phase relationships, we must avoid the dominating influence of the extinction at the three-wave point. This problem can be solved simply and effectively by plotting the curves for the intensity of scattering of the reflection 202 versus the scanning angle φ in a geometry in which the system of planes is deflected by a small angle $\delta\vartheta$ from the exact Bragg position characterized by the angle ϑ. Figure 3 reproduces a series of $\kappa_{202}(\varphi)$ curves which are normalized to the intensity of two-wave diffraction and which are plotted for different values of the divergence angle $\delta\vartheta_{202}$. An angular displacement of the system of planes $\mathbf{H}_1$ from the exact position of the Bragg reflection naturally causes the intensity of the wave $\mathbf{E}_1$ to fall and the interaction of the waves $\mathbf{E}_0$ with $\mathbf{E}_1$ with $\mathbf{E}_1$ and $\mathbf{E}_2$ to weaken. In the latter case, the weak wave $\mathbf{E}_1$ has virtually no effect on the wave $\mathbf{E}_2$, and the strong wave $\mathbf{E}_2$ will affect $\mathbf{E}_1$ even in the case of weakened coupling.A departure of the reflection from the exact reflecting position complicates the behavior of the normalized $\kappa_{202}(\varphi)$ curves which acquire a clearly defined shape of the dispersion curves with maxima and minima. On these curves the transitions between the extreme points corresponds to the maximum of the reflection 422. The $\kappa(\varphi)$ curves can be calculated in the two-wave approximation of the dynamic theory of diffraction of x-rays by crystals. On the basis of this approximation we derive expressions for the Bragg amplitudes with σ- and π-polarized radiation, respectively

$$_1/E_{\sigma 0}) = (-1/2\xi_1)[p_\sigma \chi_{1-0} + c_2 \chi_{1-2}(E_{\sigma 2}/E_{\sigma 0})_{1,2}], \quad (2)$$

$$(E_{\pi 1}/E_{\pi 0}) = (-1/2\xi_1)\{p_\pi \chi_{1-0} + \chi_{1-2}[c_5(E_{\pi 2}/E_{\pi 0})_{1,2} + c_4(E_{\sigma 2}/E_{\sigma 0})_{1,2}]\},$$

where $p_\sigma = 1$, $p_\pi = \cos 2\vartheta$ [1], the polarization coefficients c_i are calculated from the geometry of the three-wave diffraction, and $2\xi_1$ is the resonance error in the excitation of the wave $\mathbf{E}_1$ in the dynamic theory of scattering. The Bragg amplitudes $(E_{\sigma 2}/E_{\sigma 0})_{1,2}$ and $(E_{\pi 2}/E_{\pi 0})_{1,2}$ are the solution of the dynamical problem, in which the interaction of these amplitudes is taken into account, and χ_{i-j} are the Fourier coefficients of the polarizability of the crystal for $\mathbf{H}_i - \mathbf{H}_j = \mathbf{H}_{i-j}$ reciprocal-lattice vectors. In the case of a parallel-plane plate of finite thickness, under appropriate boundary conditions the solutions can be obtained in the Bragg geometry and also in the Laue geometry. We see from (2) that the normalized $\kappa(\varphi)$ curves show direct evidence of intereference due to the interaction of waves of the direct and circumventing excitation. The phase of the sum wave is determined by the resultant phase of the three diffraction waves and is directly related to the phase invariant of the corresponding structure amplitudes with the indices $\mathbf{H}_1 = \mathbf{H}_2 + \mathbf{H}_3$.

In the case of crystals with an inversion center, the structure-amplitude phases can have only two values: 0 or π, and the problem involving the phases reduces to the signs. In this case the invariant is the sign of the triple product $S_{\mathbf{H}_1} S_{\mathbf{H}_2} S_{\mathbf{H}_3}$, which is determined simply by the order in which the minimum and the maximum appear on the $\kappa(\varphi)$ curve. In determining the signs from curves such as 2 and 3 in [Fig. 3(a)], account must be taken of the fact that when the crystal rotates through an angle φ, the reciprocal-lattice site $\mathbf{H}_2$ may pass the reflecting position, leaving the Ewald sphere or entering it. Accordingly, the $\kappa(\varphi)$ curve becomes inverted.[9] This circumstance must be taken into account in determining the sign (phase) of the structure invariant.

If in describing the diamond-like structure of silicon the coordinate origin is placed at the symmetry center, the signs of the structure amplitudes with the indices 202 and 220 will be negative (the phases are equal to π) and the sign of the amplitude 422 will be positive (the phase is zero). Accordingly, the phase of the structure invariant $\varnothing = -\alpha_{202} + \alpha_{422} + \alpha_{220}$, which does not depend on the choice of the coordinate origin, is zero, as is clearly and uniquely indicated by the shape of curves 2 and 3 in [Fig. 3(a)].

In the study of crystals without a symmetry center, when the structure-amplitude phases can have any values from zero to 2π, the phases cannot be determined without an accurate measurement of te entire profile of the $\kappa(\varphi)$ curves and the corresponding computer calculations of these curves. Our experiments have shown that at the maximum the normalized $\kappa(\varphi)$ curves can have a value of 2 or 3 if there is an asymmetric Bragg diffraction. We can therefore assert that the suggested diffraction geometry, with the introduction of the divergence angle $\delta\vartheta$, will give us an efficient and accurate method for experimental determination of the structure-amplitude phases.

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