Direct Determination of X-Ray Reflection Phases

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A practical method is described for the phase determination of x-ray reflections from single crystals. Considerations on the dynamical interaction in multiple diffraction and on the relative rotation of the crystal lattice with respect to the Ewald sphere reveal both experimentally and theoretically the phase dependence of the reflected intensity. Applications can be made for a direct experimental determination of phases without carrying out the complicated dynamical calculation.

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The phase of a scattered radiation cannot be determined from intensity measurement of a simple two-beam (the incident and the scattered beams) reflection, especially when incoherent radiations, such as x rays, are used. This fact constitutes the well-known physically unsolved phase problem in x-ray optics as well as in crystallography. The existing mathematical methods, using a huge collection of intensity data for phase determination, do not, however, provide a direct solution to this problem.

The coherent dynamical interaction in x-ray multiple diffraction was thought[1-3] to lead to a direct determination of the reflection phases. In multiple-diffraction experiments, one of the diffracted beams can be treated as a reference for the other beams. The relative phase differences among them modulate the diffracted intensity of the reference beam. Information about the relative phases can therefore be extracted from these intensity variations. Efforts have been made to prove this point by using a three-beam *Pendellösung* effect,[4] three-beam Borrmann diffractions,[5] and two overlapped *Umweg* reflections.[6] In Ref. 5, a difficulty arises when crystal thickness has a major effect on the diffracted intensity. In Ref. 6, the involved triplet and quartet phase relations in a four-beam reflection cannot be resolved. The asymmetry of diffraction-line profile alone provides no correct phase information. No actually practical ways for a direct phase determination have been reported in the literature so far.

In this Letter, I present a practical procedure for the phase determination. I consider the effects of crystal rotation and of the phase on the line profile of multiple diffracted beams by using both the diffraction geometry and the dynamical theory of x-ray diffraction. I newly consider the rotation situation whether the additional reciprocal-lattice point is entering or leaving the Ewald sphere. This previously unreported rotation effect on the diffracted line profile is shown below.

Figure 1 shows a systematical way of obtaining a multiple diffraction. A crystal is first aligned to have a simple two-beam Bragg reflection, the primary reflection, with the reflection vector $\vec{P}$. In a symmetric reflection geometry, the crystal surface is perpendicular to $\vec{P}$. The crystal is then rotated around the vector $\vec{P}$, without disturbing the setting of $\vec{P}$. Thus additional reciprocal-lattice points, e.g., with a reflection vector $\vec{H}$ (the secondary reflection), are brought onto the surface of the Ewald sphere, and multiple diffraction occurs. θ is the Bragg angle for the primary reflection and ϕ is the azimuthal rotation angle.

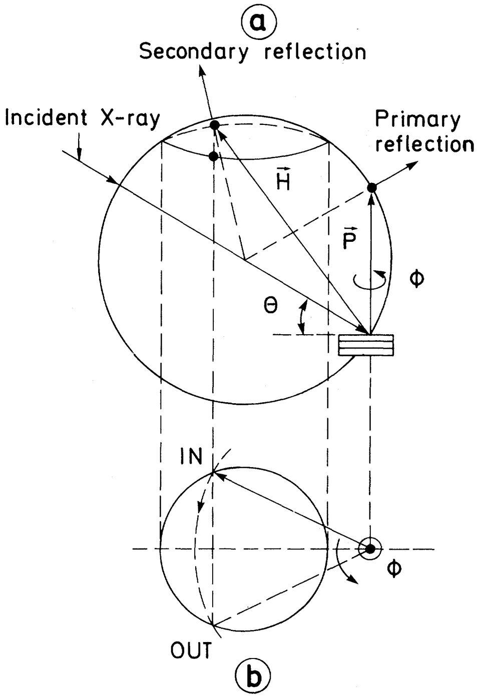


FIG. 1. Geometry of multiple diffraction in reciprocal space: (a) an overall view and (b) a projection of (a) on the plane perpendicular to the plane of incidence.

As a consequence of the rotation, the additional reciprocal-lattice point can either enter (incoming) or leave (outgoing) the Ewald sphere. This is illustrated in Fig. 1(b). The sense of rotation, either "incoming" or "outgoing," and the phases will apparently affect the line profile of the multiple diffraction. It has been shown[5] that in a three-beam Borrmann diffraction, the triplet phase product of structure factors affects the dispersion surface and hence the diffracted intensity. I have considered this fact for three-beam Bragg reflections. Let us define $S_{P,T}$ as the sign of the triplet phase product obtained theoretically from the structure factors of reflections $-P$, H, and $P-H$. It is shown that for a positive $S_{P,T}$, the intensity on one side of the multiple diffraction peak is higher than that on the other side at the incoming situation. The line profile is reversed if $S_{P,T}$ is negative or the diffraction is at its outgoing position. Because of the limited space permitted, the detailed theoretical consideration will be reported elsewhere. The rotation dependence of the line profile is demonstrated in Fig. 2 both experimentally [Fig. 2(a)] and theoretically [Fig. 2(b)] for the *Aufhellung*[7] case, (000)(111)($\bar{1}\bar{1}1$), where (000) is the direct reflection and (111) and ($\bar{1}\bar{1}1$) are the primary and the secondary reflections, respectively. The coupling reflection is (220). $S_{P,T}$ is positive. A [111]-cut germanium crystal and Cu $K\alpha_1$ radiation are used. The incident beam has an angular divergence of about 3′. The calculation is based on Laue's treatment of the dynamical theory[8] together with the consideration of the number of modes of wave propagation for the cases involving Bragg reflections.[9] Every point on the calculated curve, Fig. 2(b), represents the intensity integrated over ϕ and $\Delta\theta$, the angular deviation from θ. The line profile relative to the azimuth ϕ clearly depends on whether the reciprocal-lattice point of the secondary reflection is incoming or outgoing. For the incoming situation, the integrated intensity, for increasing ϕ, first increases above the (111) two-beam intensity level and drops abruptly and then recovers rather slowly towards its two-beam level. For the outgoing position, the sense of the line profile is reversed as shown in the same figure.

The phase effect is another important factor of reversing the sense of line profile. For illustration, two *Umweg* cases are considered: (1) (000)(222)($\bar{1}\bar{1}1$)/(331) and (2) (000)(222)(113)/($11\bar{1}$)

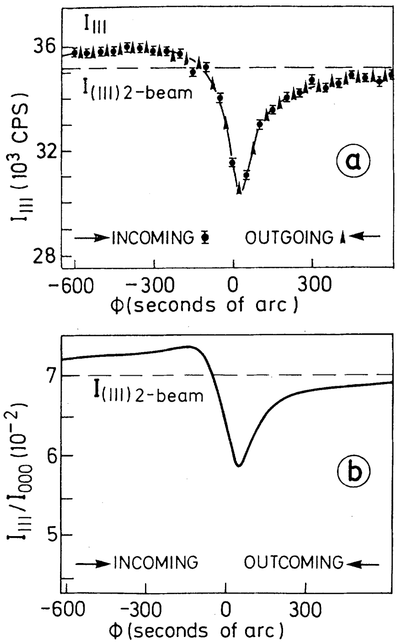


FIG. 2. (a) Measured intensity of Ge (111) reflection for Cu $K\alpha_1$ in the vicinity of three-beam (000)(111)($\bar{1}\bar{1}1$) *Aufhellung*. The solid line is a guide to the eye. Incoming and outgoing indicate the sense of crystal rotation. (b) Calculated intensity for the same geometry.

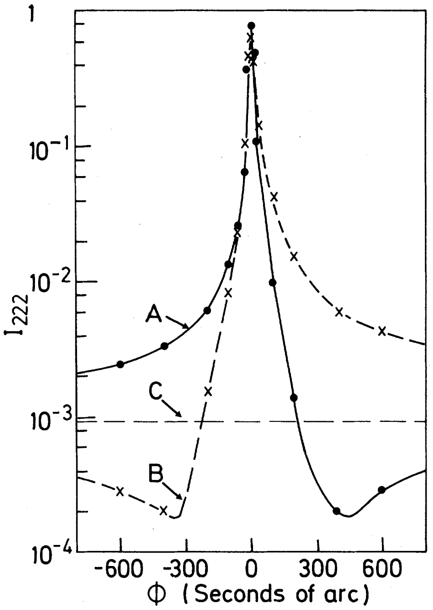


FIG. 3. Calculated Ge (222) reflected intensity profiles for a simple two-beam reflection (line C), and for two three-beam *Umwegs*: (000)(222)(113)/($11\bar{1}$) with a negative relative phase (curve A); and (000)(222)($\bar{1}\bar{1}1$)/(331) with a positive relative phase (curve B). Incoming positions and Cu $K\alpha_1$ radiation are used. The sense of crystal rotation is from positive φ to negative φ.

of Ge for Cu $K\alpha_1$, where (222) is the primary reflection and $(\bar{1}\bar{1}1)$ and (113) are the secondary reflections. The Miller indices behind the slashes stand for the interaction reflection, $\bar{P}-\bar{H}$, i.e., the coupling between the primary and secondary reflections.

For centrosymmetric crystals, such as germanium and silicon, reflections possess phases equal to either 0 or π, provided that the origin of the crystallographic unit cell is placed at the center of symmetry. $(\bar{2}\bar{2}\bar{2})$ has a zero phase angle.[10] In case (1), $S_{P,T}$ is positive, while $S_{P,T}$ for case (2) is negative. As shown in Fig. 3, the calculated intensities do exhibit the line-profile reversal due to this phase change. Both cases are at their incoming positions.

By combining the effects of rotation and phases on the multiple-diffraction line profile, the sense, S_L, of the profile (whether the intensity is stronger on one side of the peak than that on the other side, or vice versa) can be determined as a product of $S_{P,T}$ and S_R, where S_R is the sense of rotation of the reciprocal-lattice point of the secondary reflection. S_R is positive for incoming and negative for outgoing positions. $S_{P,T}$ is positive or negative, depending whether the triplet phase is equal to 0 or π, respectively. The S_L are defined in Table I for *Umweg* peaks for both a well-collimated (or strong reflections) and a rather divergent incident beam (or weak reflections). For *Aufhellung* dips[7] (see also in Fig. 2), Table I should be read upside down.

For an experimental determination of the phases, $S_{P,E}$, the relation can be deduced from the above consideration as

$$S_{P,E}=S_L S_R \; . \qquad (1)$$

S_L can be obtained experimentally and S_R can be determined from the rotation geometry.[11] An asymmetric portion of the multiple-diffraction pattern of germanium (222) for Cu $K\alpha_1$ is shown in Fig. 4(a). The strong reflection peaks are indexed and enlarged in Fig. 4(b) and 4(c). The experimentally determined signs $S_{P,E}$, using Eq. (1), and the theoretical $S_{P,T}$ are summarized in Table II. The exact agreement between $S_{P,E}$ and $S_{P,T}$ is seen. The observed symmetry of the *Umweg* peaks with respect to $\phi=0^0$ (corresponding to $[1\bar{1}0]$) and to $\phi=30^0$ (corresponding to $[1\bar{2}1]$) is consistent with the rotation and phase dependences of the line profile. Further support for the procedure presented here is obtained from the multiple-diffraction data of various crystals.[12]

Although the (222) reflection is very weak, the multiple diffractions discussed above still involve strong or moderately strong secondary and coupling reflections. Clearly, the phase dependence of the reflected intensity is not a kinematical but a dynamical effect. This fact is, however, not

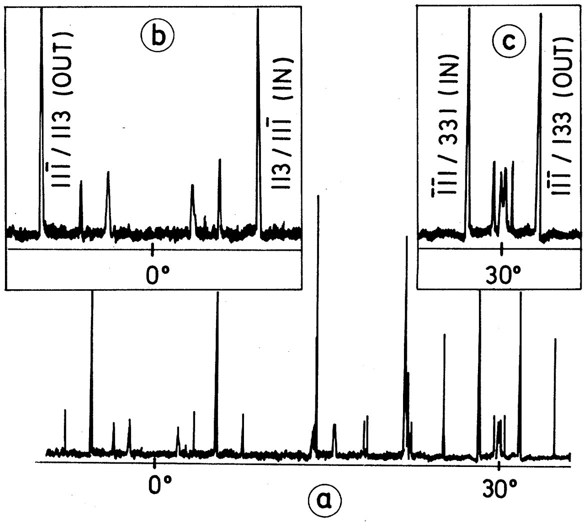


FIG. 4. A 30° asymmetric portion of the multiple diffraction pattern of Ge (222) for (a) Cu $K\alpha_1$, and the details near (b) $\varphi=0°$, and (c) $\varphi=30°$.

TABLE I. Definition for S_L of line profiles obtained by using a well-collimated (convergent) and a rather divergent incident beam (divergent).

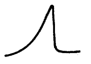
Line Profile		S_L
Convergent	Divergent	
		+
		—

TABLE II. Summary of the experimentally determined phases.

Reflection					
Secondary	Coupling	S_R	S_L	$S_{P,E}$	$S_{P,T}$
$11\bar{1}$	113	−	+	−	−
113	$11\bar{1}$	+	−	−	−
$\bar{1}\bar{1}1$	331	+	+	+	+
$1\bar{1}\bar{1}$	133	−	−	+	+

harmful to the applicability of this method to cases involving mosaic crystals, since mosaic crystals are composed of many tiny perfect crystal blocks. Strong primary or secondary reflections are still suitable for phase determinations from mosaic crystals. Application of this method has recently been applied to the monoclinic crystal of $Cs_{10}Ga_6Se_{14}$. The determination of this structure has been attempted by the ordinary direct method, for example, the MULTAN program,[12] but without success. By use of the present method, fourteen phase angles were obtained from fourteen triplet phase relations via Eq. (1). By treating these phase angles as the starting phases for the program MULTAN74 , we were able to determine the relative positions of Cs, Ga, and Se in the unit cell. This is the first application of multiple diffraction to crystal-structure determination. For more complicated, for example, noncentrosymmetric crystals, Eq. (1) will still be valid. However, S_L for random phases, between 0° and 360°, will be more complicated and more difficult to handle than the centrosymmetric cases.

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Anomalous Behavior of Surface Acoustic Waves in Cu/Nb Superlattices

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Brillouin-scattering measurements show an anomalous dip in the elastic constants of Nb/Cu superlattices for superlattice wavelengths of $\lesssim 100$ Å. This dip is correlated with changes in the electrical resistivity of the samples giving the first evidence that electronic effects are responsible for phonon softening in these materials.

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The production of crystallographically coherent layered structures of two different materials has led to the development of a whole new class of materials called superlattices. The components can be either metals or semiconductors and the superlattices are grown by either thermal evaporation or sputtering. These materials have very interesting properties which can be different from those of either of the constituents. The general interest in these new materials has been motivated both by the potential for discovery of new and as yet unknown physical properties, as well as by possible applications in such diverse fields as x-ray and neutron-beam monochromators, lasers, and microwave electronics. However, since these structures are produced in the form of thin films many conventional techniques (e.g., ultrasonics and neutron scattering) are not readily applicable to their study.

In the present work we have made the first light-scattering measurements of the elastic properties of metallic superlattices. The results show a remarkable anomaly in the velocity of surface acoustic waves as a function of layer thickness in Nb/Cu layered ultrathin coherent structures (LUCS). This anomaly is correlated with changes in the temperature coefficient of resistivity of the material. At the thickness at