

A Practical Application of Experimentally Determined X-ray Phases Applied to the Direct Method

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Abstract

The experimental method for the direct determination of phases, proposed by Chang [*Appl. Phys.* (1981), A26, 221–226; *Phys. Rev. Lett.* (1982), 48, 163–166], utilizing the coherent interaction of diffracted X-ray beams according to the dynamical theory in a three-beam multiple Bragg reflection, is applied to the crystal structure of diamond by using an irregularly shaped crystal on a conventional four-circle single-crystal diffractometer. The phases of three reflections can be derived from the signs of three triplet-phase products which are obtained experimentally from three multiple-reflection line profiles. Using these phases as a starting set for the direct method, the phases of other reflections are obtained. The computing time for the *MULTAN* program is therefore drastically reduced.

1. Introduction

Reflection phases cannot be determined from the intensity measurement of a two-beam reflection. The coherent interaction among diffracted beams in multiple-diffraction experiments was, however, thought to lead to a direct determination of the phases (Lipscomb, 1949; Eckstein, 1949; Fankuchen, 1949). Investigations have been carried out by Hart & Lang (1961), Post (1977) and Chapman, Yoder & Colella (1981) for X-rays and Miyake & Kambe (1954), Kambe (1957), Madsen & Cotterill (1978) and many others for electron diffraction, but with limited success. In all these investigations, the rotation of the crystal relative to the Ewald sphere was not exploited. In fact, the crystal rotation plays a role as important as the phase effect on the diffracted intensity.

Recently, Chang (1981) considered the effects of the crystal rotation and of the phases on the diffracted

intensity profile of a three-beam Bragg reflection. It was proposed (Chang, 1981, 1982a) that the sign, S_p , of the triplet-phase products is

$$S_p = S_L S_R, \quad (1)$$

where S_L is the sign obtained from the intensity profiles for both *Aufhellung* (Wagner, 1920; also quoted by Moon & Shull, 1964) and *Umweganregung* (Renninger, 1937) multiple diffractions (Table 1). The sign, S_R , concerning the rotation of the crystal lattice relative to the Ewald sphere in multiple-diffraction experiments, is determined in the following way:

In a multiple-reflection experiment (Fig. 1), a crystal is first aligned to have a simple two-beam Bragg reflection, the primary reflection, with the reflection vector \mathbf{H}_1 . Usually, a symmetric Bragg reflection is chosen as the primary reflection. θ is the Bragg angle of \mathbf{H}_1 reflection. The crystal is then rotated around the vector \mathbf{H}_1 to bring other reciprocal-lattice points with a reflection vector \mathbf{H}_2 (the secondary reflection) onto the surface of the Ewald sphere, and multiple reflection occurs. The vector $\mathbf{H}_1 - \mathbf{H}_2$ represents the coupling reflection between \mathbf{H}_1 and \mathbf{H}_2 . The interaction among the diffracted beams generates peaks (the *Umweganregung*) and dips (the *Aufhellung*) on the intensity

Table 1. Definition for S_L of line profiles for strong reflections (or a well collimated incident beam) and weak reflections (or a divergent beam), as recorded by a rolling chart

	LINE PROFILE		S_L
	STRONG REFLECTION (CONVERGENT BEAM)	WEAK REFLECTION (DIVERGENT BEAM)	
UMWEG			—
			+
AUFHEL.			—
			+

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background of the primary reflection. As a consequence of the rotation, the reciprocal-lattice points of the secondary reflections can either enter (incoming) or leave (outgoing) the Ewald sphere. According to Cole, Chambers & Dunn (1962), multiple diffraction peaks or dips can be indexed and the incoming and outgoing situations can be distinguished. By considering equations (7) and (8) of the paper (Cole, Chambers & Dunn, 1962), S_R is defined as the sign of the derivative:

$$S_R = S \left[-\frac{\partial(1/\lambda)}{\partial\varphi} \right], \quad (2)$$

where λ and φ are the wavelength used and the rotation angle. S_R is therefore positive for the incoming and negative for the outgoing situations (Chang, 1981a,b).

Equation (1) was confirmed by multiple-diffraction line-profile measurement using a setup similar to the one reported by Renninger (1937). Dynamical calculations, based on von Laue's (1931) treatment together with the consideration of the number of effective modes of wave propagation by Chang (1979) gives further support on theoretical grounds. Comparisons with the experiments given by Hart & Lang (1961), Post (1977) and Chapman, Yoder & Colella (1981) are discussed in detail by Chang (1982b).

The purpose of the experiments described in this paper is to test the applicability of the method mentioned above for practical crystal-structure determination by using a four-circle diffractometer. A

discussion on the number of multiple reflections necessary for an unambiguous phase determination is given below.

2. Practical consideration

For a three-beam multiple reflection, involving reflections \mathbf{H}_1 , \mathbf{H}_2 , and $\mathbf{H}_1 - \mathbf{H}_2$ as the primary, secondary and coupling reflections, the sign of the triplet-phase product is defined as

$$S_p = S_{-\mathbf{H}_1} S_{\mathbf{H}_2} S_{\mathbf{H}_1 - \mathbf{H}_2}, \quad (3)$$

where $S_{-\mathbf{H}_1}$, $S_{\mathbf{H}_2}$ and $S_{\mathbf{H}_1 - \mathbf{H}_2}$ are the signs of the structure factors of $-\mathbf{H}_1$, \mathbf{H}_2 , and $\mathbf{H}_1 - \mathbf{H}_2$ reflections. S_p can be obtained experimentally from (1). The determination of the phase of each individual reflection requires several phase relations, like (3), to be fulfilled. In practice, a convenient way of obtaining these required relations is to have three multiple diffractions with a common primary reflection \mathbf{H}_1 . For determining each individual reflection phase, the involved reflections should form a cycle or should be symmetrically related to each other. In other words, the obtained phase relations must be one of the following two sets:

(i) Set A:

$$S_1 = S_{-\mathbf{H}_1} S_{\mathbf{H}_2} S_{\mathbf{H}_1 - \mathbf{H}_2}, \quad (4)$$

$$S_2 = S_{-\mathbf{H}_1} S_{\mathbf{H}_3} S_{\{\mathbf{H}_2\}}, \quad (5)$$

$$S_3 = S_{-\mathbf{H}_1} S_{\{\mathbf{H}_3\}} S_{\{\mathbf{H}_1 - \mathbf{H}_2\}}. \quad (6)$$

(ii) Set B:

$$S_1 = S_{-\mathbf{H}_1} S_{\mathbf{H}_2} S_{\mathbf{H}_1 - \mathbf{H}_2}, \quad (4)$$

$$S_2 = S_{-\mathbf{H}_1} S_{\mathbf{H}_3} S_{\{\mathbf{H}_2\}}, \quad (5)$$

$$S_3 = S_{-\mathbf{H}_1} S_{\mathbf{H}_4} S_{\{\mathbf{H}_4\}}. \quad (7)$$

\mathbf{H}_4 serves as an auxiliary reflection. $\{\mathbf{H}\}$ represents a symmetry-related reflection of \mathbf{H} . $\{\mathbf{H}_2\}$ is equal to $\mathbf{H}_1 - \mathbf{H}_3$ in (5) and $\{\mathbf{H}_4\}$ is equal to $\mathbf{H}_1 - \mathbf{H}_4$ in (7). $\{\mathbf{H}_1 - \mathbf{H}_2\}$ in (6) is equal to $\mathbf{H}_1 - \mathbf{H}_3$. The phase relations between the symmetry-related reflections can be easily determined from the space group of the crystal. S_1 , S_2 and S_3 are the experimentally obtained signs from (1).

Utilizing either set A or set B of these relations, two groups of the individual phases $S_{-\mathbf{H}_1}$, $S_{\mathbf{H}_2}$, $S_{\mathbf{H}_3}$, and $S_{\mathbf{H}_1 - \mathbf{H}_2}$ are obtained. These two groups are, however, equivalent and are related to each other by a translation of the origin of the unit cell. By fixing the origin from one of the individual signs, the corresponding phase group may be used as a starting set for the direct method [e.g. MULTAN74; Main, Woolfson, Lessinger, Germain & Declercq (1974)]. (For a different crystal system, the number of equivalent groups of the individual phases is different.) The case studied here will be demonstrated in § 4 as an example.

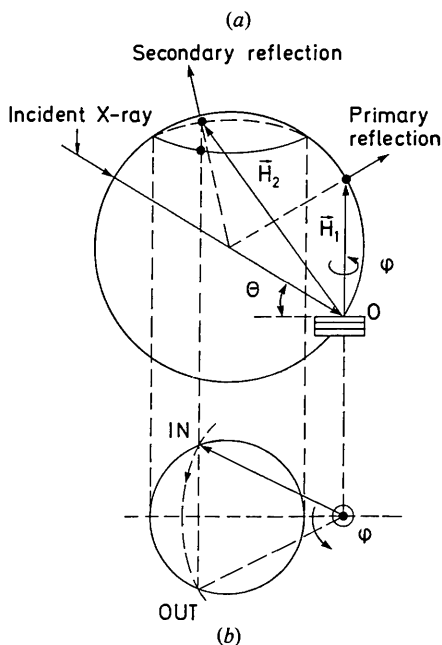


Fig. 1. Geometry of multiple diffraction in reciprocal space. (a) An overall view; (b) a projection of (a) on the plane perpendicular to the plane of incidence.

3. Experiments

An irregularly shaped diamond crystal of size approximately $0.1 \times 0.1 \times 0.1$ mm is mounted on a four-circle single-crystal diffractometer. A fine-focus Mo tube and a graphite monochromator provide an incident beam with $6'$ angular divergence. The line profiles of multiple diffraction peaks are obtained by the rotation around 222, the ψ scan, at a speed of $0.05^\circ \text{ min}^{-1}$, in the vicinities of the pre-calculated peak positions (Cole, Chambers & Dunn, 1962) for cases having strong secondary and/or coupling reflections. A scintillation counter is used to monitor the 222 reflected intensity, which is recorded on a rolling chart. The intensities of many two-beam reflections are also collected in the usual way as for routine crystal-structure determination.

4. Results and discussion

Fig. 2 shows the line profiles for multiple reflections: (i) $131/1\bar{1}\bar{1}$, (ii) $1\bar{1}\bar{1}/131$, (iii) $313/\bar{1}\bar{1}\bar{1}$, and (iv) $13\bar{1}/1\bar{1}\bar{3}$. The primary reflection is 222. The Miller indices in front of and behind the slashes are the secondary and coupling reflections, respectively. Cases (i) and (ii) are symmetric about $[1\bar{1}0]$, *i.e.* $\varphi = 0$. The peak positions, line profiles, and the experimentally determined S_p are listed in Table 2.

From the fourth relation in Table 2, S_{222} is positive since $S_{13\bar{1}}S_{1\bar{1}\bar{3}}$ is positive. This leads to $S_{313} = S_{\bar{1}\bar{1}\bar{1}}$ and $S_{1\bar{1}\bar{1}} = -S_{131}$, according to the second and the third relations of Table 2. Thus, $S_{\bar{1}\bar{1}\bar{1}} = S_{313} = -S_{131}$. Fixing the origin of the unit cell by $S_{\bar{1}\bar{1}\bar{1}} = +1$, the signs of the reflections 313 and 131 are determined as positive and negative, respectively. Accordingly, the phase angles, β , of 111, 113, and 331 are 180° , 180° , and 360° . Using these three phases as starting phases in the *MULTAN74* program, the correct phases of all reflections whose intensities have been measured are determined with certainty. They are listed in Table 3.

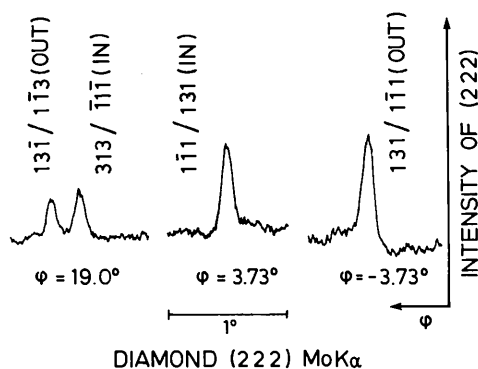


Fig. 2. Experimentally obtained multiple diffraction line profiles of 222 diamond for Mo $K\alpha$ as a function of the azimuthal angle φ .

Table 2. Summary of the experimentally determined phases, S_p

Diamond ($H_c = 222$) MoK α							
REFLECTION		φ (DEG)	ROTATION	PROFILE	S_R	S_L	S_P
H_2	H_1-H_2						
131	$1\bar{1}\bar{1}$	-3.73	OUT	\downarrow	-	+	-
$1\bar{1}\bar{1}$	131	3.73	IN	\uparrow	+	-	-
313	$\bar{1}\bar{1}\bar{1}$	18.96	IN	\downarrow	+	+	+
$13\bar{1}$	$1\bar{1}\bar{3}$	19.19	OUT	\uparrow	-	-	+

Table 3. The phase angles, β , ($^\circ$) of the reflections of diamond

Reflection	β	Reflection	β	Reflection	β
111	180.	220	180.	311	180.
331	360.	333	360.	400	180.
422	360.	440	360.	444	180.
511	360.	531	360.	533	180.
551	180.	620	360.	711	360.

The 222 reflection has a zero phase angle. The computing time for phase determination is reduced by a factor of four in comparison to that in usual *MULTAN* calculation involving no experimental phases.

The experiment on the simple diamond structure reported here serves as an example of how to use the method proposed by Chang (1981, 1982a) for crystal-structure determination. We expect that more complicated structures, which cannot be solved by the ordinary direct method, may become accessible using a large set of experimentally determined starting phases, which play an important role in the phase determination by the direct method. Further experiments along these lines are under way in this laboratory.

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Coordinated Use of Isomorphous Replacement and Layer-Line Splitting in the Phasing of Fiber Diffraction Data

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Abstract

In order to calculate electron density maps from fiber diffraction patterns, the terms which superimpose because of cylindrical averaging of the pattern must be separated and their phases determined. This can be done using a technique analogous to the isomorphous replacement method of protein crystallography, but large numbers of heavy-atom derivatives are required. Because of the cylindrical averaging, the number of derivatives increases with increasing resolution. This paper describes a method for measuring the fine splitting of layer lines which occurs when a helical structure repeats approximately, but not exactly, in a given number of turns, and for using this as a source of phase information. The amount of phase information obtainable from each heavy-atom derivative is theoretically doubled since differences in both layer-line intensity and apparent layer-line position can be used, and this substantially increases the resolution attainable with a limited number of derivatives. The method is used to calculate an electron density map of tobacco mosaic virus at 6.7 Å resolution using only two derivatives instead of the four which would have been required using previously available methods.

Introduction

Structure determination using fiber diffraction is complicated by the fact that fiber diffraction data are cylindrically averaged. This is because the particles (such as rod-shaped viruses or helical nucleic acid molecules) that make up a fiber diffraction specimen are randomly oriented about their long axes. Model building, that is, the construction of models and the refinement of their parameters against the observed data, has been an effective way of determining structures such as nucleic acids and polysaccharides, but the great complexity of the macromolecular subunits in such systems as helical viruses and rod-shaped intracellular assemblies limits the value of this approach. Stubbs & Diamond (1975) showed that the information lost by cylindrical averaging can be recovered by a technique analogous to the isomorphous replacement method of protein crystallography, but this method requires the preparation of a large number of heavy-atom derivatives. For example, to solve the structure of tobacco mosaic virus (TMV) at a resolution of 4 Å, six derivatives were required (Stubbs, Warren & Holmes, 1977). The number of derivatives increases with resolution, and at 3 Å