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Wavelength-modulated diffraction: a new method for phase determination

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Abstract

A new diffraction method has been developed in which the intensity of Bragg reflections is measured while changing continually the wavelength of the radiation over a range in the vicinity of the absorption edge of an atom contained in the crystal. It is shown that the intensity gradient with respect to the wavelength of the *hkl* reflection is in a simple relation to the real and imaginary parts of the structure factor of that reflection and, if the positions of the anomalously scattering atoms are known or properly assumed, the phase of $F(hkl)$ can be derived by solving simultaneous linear equations. The procedure is particularly simple when the crystal is centrosymmetric. The method, called the wavelength-modulated diffraction (WMD) method, is free from the problem of intensity scaling encountered in other methods of phase determination. Synchrotron radiation is most suited to WMD measurements. Suggestions on how to measure the intensity gradient are given and the possible errors involved are discussed.

1. Introduction

Determination of the phase (or sign) of the structure factor is a long-standing problem in crystal structure analysis; a number of approaches to its solution have been developed in the past six decades. In recent years, synchrotron radiation has become available for X-ray crystallography; the wavelength tunability combined with the high brightness of such synchrotron sources provide powerful means to overcome the problem. Methods have been developed in which the anomalous-scattering phenomenon has been fully utilized. The multiwavelength anomalous diffraction (MAD) method is one such method that has been successfully applied to macromolecular structure determination (Karle, 1989; Hendrickson, 1991). The fundamental procedure involved in this method is the collection of diffraction intensity data using the radiation of several wavelengths around the absorption edge of an atom contained in a crystal and it is necessary to ensure that the intensity data be obtained exactly on the same scale.

In the present paper, a new method is proposed in which diffraction measurements are made while changing continually the wavelength of the radiation in the vicinity of the absorption edge. What is measured is not an integrated intensity of Bragg reflections but an intensity gradient with respect to the wavelength (or a wavelength profile), which provides information on the phase (or sign) of the structure factor. In this method, called the wavelength-modulated diffraction (WMD) method, only 'one measurement' of the intensity gradient suffices to determine the phase (or sign) and it is therefore free from the problem of intensity scaling.

In the following, a theory of WMD is presented, followed by a suggestion on how to measure the intensity gradient for many Bragg reflections and a discussion on the possible errors involved.

2. Theory

The crystal structure factor is expressed as

$$F(hkl) = \sum_j f_j \exp 2\pi i(hx_j + ky_j + lz_j), \qquad (1)$$

where f_j is the atomic scattering factor of the jth atom and x_j, y_j and z_j are the fractional coordinates of that atom. Intensity of the *hkl* reflection is given by the product of $F(hkl)$ and its complex conjugate $F(hkl)^*$ as

$$I(hkl) = F(hkl)\,F(hkl)^*. \qquad (2)$$

Suppose that the wavelength λ of the radiation to be used for diffraction measurements lies near the absorption edge of an atom contained in a crystal and denote that atom by the symbol H. The atomic scattering factor of this atom is expressed as

$$f_H = f_H^0 + f_H' + if_H''. \qquad (3)$$

It is well known that f_H' changes abruptly to a deep minimum on approaching from both the long- and the short-wavelength sides to the absorption edge, while f_H'' shows a rather gradual variation with λ, except for a sharp discontinuity at the edge. It is convenient to divide the terms in (1) into those including the contribution from atom H and those including the contribution from the other kinds of atoms, which are denoted by the symbol J:

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$$\begin{aligned}F(hkl) &= f_H \sum_H \exp 2\pi i(hx_H + ky_H + lz_H)\\ &\quad + \sum_J f_J \exp 2\pi i(hx_J + ky_J + lz_J). \qquad (4)\end{aligned}$$

We assume that the absorption edge of atom H is far from those of the other kinds of atoms and therefore it is not necessary to take f_J' and f_J'' into account. Rewriting (4), we obtain

$$F(hkl) = A(hkl) + iB(hkl) \qquad (5)$$

with

$$\begin{aligned}A(hkl) &= (f_H^0 + f_H')\Big(\sum_H \cos\vartheta_H\Big) - f_H''\Big(\sum_H \sin\vartheta_H\Big)\\ &\quad + \sum_J f_J^0 \cos\vartheta_J \qquad (6)\end{aligned}$$

and

$$\begin{aligned}B(hkl) &= (f_H^0 + f_H')\Big(\sum_H \sin\vartheta_H\Big) + f_H''\Big(\sum_H \cos\vartheta_H\Big)\\ &\quad + \sum_J f_J^0 \sin\vartheta_J, \qquad (7)\end{aligned}$$

where $\sum_H \cos\vartheta_H$ and $\sum_H \sin\vartheta_H$ represent the sums

$$\sum_H \cos 2\pi(hx_H + ky_H + lz_H)$$

and

$$\sum_H \sin 2\pi(hx_H + ky_H + lz_H),$$

respectively. $\sum_J f_J^0 \cos\vartheta_J$ represents

$$\sum_J f_J^0 \cos 2\pi(hx_J + ky_J + lz_J);$$

the meaning of $\sum_J f_J^0 \sin\vartheta_J$ follows logically.

Next, suppose that diffraction measurements are made while changing continually λ in the small range $\Delta\lambda$ in the vicinity of the absorption edge of the atom H. It is those parts of $I(hkl)$ that contain f_H' and f_H'' which show an appreciable variation with λ. We differentiate $I(hkl)$ with respect to λ in the middle of the range:

$$\partial I(hkl)/\partial\lambda = \partial A^2(hkl)/\partial\lambda + \partial B^2(hkl)/\partial\lambda \qquad (8)$$

with

$$\begin{aligned}&\partial A^2(hkl)/\partial\lambda\\ &\quad = 2(f_H^0 + f_H')(\partial f_H'/\partial\lambda)\Big(\sum_H \cos\vartheta_H\Big)^2\\ &\qquad + 2f_H''(\partial f_H''/\partial\lambda)\Big(\sum_H \sin\vartheta_H\Big)^2\\ &\qquad - \Big\{2\big[f_H''(\partial f_H'/\partial\lambda) + (f_H^0 + f_H')(\partial f_H''/\partial\lambda)\big]\\ &\qquad \times \Big(\sum_H \cos\vartheta_H\Big)\Big(\sum_H \sin\vartheta_H\Big)\Big\}\\ &\qquad + 2\Big[(\partial f_H'/\partial\lambda)\Big(\sum_H \cos\vartheta_H\Big)\\ &\qquad - (\partial f_H''/\partial\lambda)\Big(\sum_H \sin\vartheta_H\Big)\Big]\Big(\sum_J f_J^0 \cos\vartheta_J\Big) \qquad (9)\end{aligned}$$

and

$$\begin{aligned}&\partial B^2(hkl)/\partial\lambda\\ &\quad = 2(f_H^0 + f_H')(\partial f_H'/\partial\lambda)\Big(\sum_H \sin\vartheta_H\Big)^2\\ &\qquad + 2f_H''(\partial f_H''/\partial\lambda)\Big(\sum_H \cos\vartheta_H\Big)^2\\ &\qquad + \Big\{2\big[f_H''(\partial f_H'/\partial\lambda) + (f_H^0 + f_H')(\partial f_H''/\partial\lambda)\big]\\ &\qquad \times \Big(\sum_H \sin\vartheta_H\Big)\Big(\sum_H \cos\vartheta_H\Big)\Big\}\\ &\qquad + 2\Big[(\partial f_H'/\partial\lambda)\Big(\sum_H \sin\vartheta_H\Big)\\ &\qquad + (\partial f_H''/\partial\lambda)\Big(\sum_H \cos\vartheta_H\Big)\Big]\Big(\sum_J f_J^0 \sin\vartheta_J\Big). \qquad (10)\end{aligned}$$

Rearranging terms in (9) and (10), (8) may be written in the form

$$\begin{aligned}\partial I(hkl)/\partial\lambda &= 2\Big[(\partial f_H'/\partial\lambda)\Big(\sum_H \cos\vartheta_H\Big)\\ &\quad - (\partial f_H''/\partial\lambda)\Big(\sum_H \sin\vartheta_H\Big)\Big]A(hkl)\\ &\quad + 2\Big[(\partial f_H'/\partial\lambda)\Big(\sum_H \sin\vartheta_H\Big)\\ &\quad + (\partial f_H''/\partial\lambda)\Big(\sum_H \cos\vartheta_H\Big)\Big]B(hkl). \qquad (11)\end{aligned}$$

Now consider two cases, one in which the crystal is centrosymmetric and the other in which it is noncentrosymmetric. In the first case, $\sum_H \sin\vartheta_H$ and $\sum_J f_J^0 \sin\vartheta_J$ included in the right-hand side of (11) are zero, and (11) reduces to

$$\begin{aligned}\partial I(hkl)/\partial\lambda &= 2\Big[(\partial f_H'/\partial\lambda)\Big(\sum_H \cos\vartheta_H\Big)A(hkl)\\ &\quad + (\partial f_H''/\partial\lambda)f_H''\Big(\sum_H \cos\vartheta_H\Big)^2\Big]. \qquad (12)\end{aligned}$$

On the long-wavelength side of the absorption edge, the product $(\partial f_H''/\partial\lambda)f_H''$ in (12) is very small and the term including it can be neglected. Then we have

$$\partial I(hkl)/\partial\lambda = 2(\partial f_H'/\partial\lambda)\Big(\sum_H \cos\vartheta_H\Big)A(hkl). \qquad (12a)$$

$\partial f_H'/\partial\lambda$ can be obtained from the measurements of f_H' or calculated from numerical tables such as those compiled by Sasaki (1989). Then, (12*a*) suggests that if one measures $\partial I(hkl)/\partial\lambda$, *i.e.* the intensity gradient with respect to the wavelength of the *hkl* reflection, it is possible to obtain $A(hkl)$, provided that the coordinates of the anomalously scattering atoms are known or properly assumed. If the atom H is a heavy atom in a crystal consisting mainly of light atoms and the number of H atoms in a unit cell is not large, it is not difficult to obtain information on x_H, y_H and z_H using various techniques employed in crystal structure analysis. When only the sign of $A(hkl)$ is required, the situation becomes particularly simple and knowing only approximate values of x_H, y_H and z_H suffices to determine the sign as long as $\sum_H \cos\vartheta_H$ has the same sign as that of the corresponding sum for the correct values. The experimental procedure involved is simply to see whether the intensity gradient is positive or negative; there is no need to make quantitative measurements of the intensity gradient.

In the second case, in which the crystal is noncentrosymmetric, the situation is somewhat involved. There are two ways to extract information on the phase of the structure factor. One is to measure the intensity gradient both on the long- and on the short-wavelength side of the absorption edge. The variation of f'_H with λ is nearly symmetrical with respect to the edge: $\partial f'_H/\partial\lambda$ is positive on the long-wavelength side whereas it is negative on the other side. If the sum of the intensity gradients measured on the two sides is taken, the terms including $\partial f'_H/\partial\lambda$ are almost cancelled out and we obtain, neglecting the terms including $\partial f''_H/\partial\lambda$ on the long-wavelength side,

$$\begin{aligned}[\partial I(hkl)/\partial\lambda]_L + [\partial I(hkl)/\partial\lambda]_S &= 2(\partial f''_H/\partial\lambda)_S\Big[-\Big(\sum_H \sin\vartheta_H\Big)A(hkl)_S \\ &\quad + \Big(\sum_H \cos\vartheta_H\Big)B(hkl)_S\Big]. \qquad (13)\end{aligned}$$

On the other hand, the difference of the intensity gradients is expressed as

$$\begin{aligned}[\partial I(hkl)/\partial\lambda]_L - [\partial I(hkl)/\partial\lambda]_S &= 2|\partial f'_H/\partial\lambda|\Big\{\Big(\sum_H \cos\vartheta_H\Big)[A(hkl)_L + A(hkl)_S] \\ &\quad + \Big(\sum_H \sin\vartheta_H\Big)[B(hkl)_L + B(hkl)_S]\Big\} \\ &\quad + 2(\partial f''_H/\partial\lambda)_S\Big[\Big(\sum_H \sin\vartheta_H\Big)A(hkl)_S \\ &\quad - \Big(\sum_H \cos\vartheta_H\Big)B(hkl)_S\Big]. \qquad (14)\end{aligned}$$

In these equations, quantities with the suffix L and S represent those evaluated on the long- and short-wavelength sides, respectively. Setting

$$[A(hkl)_L + A(hkl)_S]/2 = A(hkl)$$

and

$$[B(hkl)_L + B(hkl)_S]/2 = B(hkl)$$

in (14) and replacing $A(hkl)_S$ and $B(hkl)_S$ in (13) and (14) by $A(hkl)$ and $B(hkl)$, respectively, we obtain the approximate relations

$$\begin{aligned}[\partial I(hkl)/\partial\lambda]_L + [\partial I(hkl)/\partial\lambda]_S &= 2(\partial f''_H/\partial\lambda)_S\Big[-\Big(\sum_H \sin\vartheta_H\Big)A(hkl) \\ &\quad + \Big(\sum_H \cos\vartheta_H\Big)B(hkl)\Big] \qquad (15)\end{aligned}$$

and

$$\begin{aligned}[\partial I(hkl)/\partial\lambda]_L - [\partial I(hkl)/\partial\lambda]_S &= 2\Big[2|\partial f'_H/\partial\lambda|\Big(\sum_H \cos\vartheta_H\Big) \\ &\quad + (\partial f''_H/\partial\lambda)_S\Big(\sum_H \sin\vartheta_H\Big)\Big]A(hkl) \\ &\quad + 2\Big[2|\partial f'_H/\partial\lambda|\Big(\sum_H \sin\vartheta_H\Big) \\ &\quad - (\partial f''_H/\partial\lambda)_S\Big(\sum_H \cos\vartheta_H\Big)\Big]B(hkl). \qquad (16)\end{aligned}$$

Now we have two sets of linear equations with $A(hkl)$ and $B(hkl)$ as unknowns. The quantities on the left side are obtained from the measured intensity gradients and, by solving the simultaneous linear equations, it is possible to derive $A(hkl)$ and $B(hkl)$, from which the phase angle $\Phi(hkl)$ of the structure factor is calculated:

$$\Phi(hkl) = \tan^{-1}[B(hkl)/A(hkl)]. \qquad (17)$$

$\Phi(hkl)$ values thus calculated are approximate ones, but it is possible with approximate phase angles to proceed to the first stage of crystal structure analysis, as many experiences show. In practical measurements, the reflection intensity may not be expressed on an absolute scale and $A(hkl)$ and $B(hkl)$ are not in the electron unit. However, this does not raise problems, since what is required for the calculation of $\Phi(hkl)$ is the ratio $B(hkl)/A(hkl)$.

An alternative way of extracting information on the phase of the structure factor is to measure the intensity gradient for the Bijvoet pair of reflections. The intensity gradient for the $\bar{h}\bar{k}\bar{l}$ reflection is written as

$$\begin{aligned}\partial I(\bar{h}\bar{k}\bar{l})/\partial\lambda &= 2\Big[(\partial f'_H/\partial\lambda)\Big(\sum_H \cos\vartheta_H\Big) \\ &\quad + (\partial f''_H/\partial\lambda)\Big(\sum_H \sin\vartheta_H\Big)\Big]A(\bar{h}\bar{k}\bar{l}) \\ &\quad + 2\Big[-(\partial f'_H/\partial\lambda)\Big(\sum_H \sin\vartheta_H\Big) \\ &\quad + (\partial f''_H/\partial\lambda)\Big(\sum_H \cos\vartheta_H\Big)\Big]B(\bar{h}\bar{k}\bar{l}). \qquad (18)\end{aligned}$$

Since f''_H is small on the long-wavelength side, $A(\bar{h}\bar{k}\bar{l}) \simeq A(hkl)$ and $B(\bar{h}\bar{k}\bar{l}) \simeq -B(hkl)$. Then (18) may be rewritten as

$$\begin{aligned}\partial I(\bar{h}\bar{k}\bar{l})/\partial\lambda = {} & 2\Big[(\partial f'_H/\partial\lambda)\Big(\sum_H \cos\vartheta_H\Big) \\ & + (\partial f''_H/\partial\lambda)\Big(\sum_H \sin\vartheta_H\Big)\Big]A(hkl) \\ & + 2\Big[(\partial f'_H/\partial\lambda)\Big(\sum_H \sin\vartheta_H\Big) \\ & - (\partial f''_H/\partial\lambda)\Big(\sum_H \cos\vartheta_H\Big)\Big]B(hkl). \qquad (18a)\end{aligned}$$

It is possible to derive $A(hkl)$ and $B(hkl)$, by solving the two linear simultaneous equations (11) and (18*a*), and calculate the phase angles, as before. Comparison of these equations with (15) and (16) suggests that contrast between the intensity gradients on the long- and short-wavelength sides is higher than the contrast between the intensity gradients of the *hkl* and $\bar{h}\bar{k}\bar{l}$ reflections and therefore the determinancy of $A(hkl)$ and $B(hkl)$ may be higher in the first way (using the long- and short-wavelength sides of the absorption edge). However, there is an advantage in adopting the second way (using the Bijvoet pair); a discussion is given in §4.3 on the choice of the route to phase determination.

The equations derived above are those for obtaining the phase or sign of the structure factor. They suggest that, if the intensity and its gradient are measured on the absolute scale, the magnitude of the structure factor can be calculated from $A(hkl)$ and $B(hkl)$. However, it is preferable to obtain the magnitude of the structure factor from separate integrated-intensity measurements using a conventional X-ray diffraction method, since the accuracy is higher. WMD provides a method for determining the phase or sign of the structure factor, which is attached to $|F(hkl)|$ to perform the Fourier synthesis of the electron density.

3. How to measure the intensity gradient of Bragg reflections

In this section, we consider how to measure the intensity gradient with respect to the wavelength for many Bragg reflections.

It is evident that, owing to its wavelength tunability and high brightness, synchrotron radiation is most applicable to the WMD method. One method to change continually the wavelength of the incident radiation is to rock the monochromator crystal with the position of the monochromated radiation beam kept unchanged. The double-crystal monochromators designed and manufactured for synchrotron X-ray diffraction experiments meet this requirement (see *e.g.* Golovchenko *et al.*, 1981; Matsushita *et al.*, 1986). On the other hand, a method has been proposed by which a radiation beam having a band of wavelengths is produced (Arndt *et al.*, 1982). A monochromator crystal is bent to reflect a diverging X-ray beam at continuously changing Bragg angle and the reflected beam is focused at or near the sample position. This method does not require any movement of the monochromator crystal and provides a radiation beam suitable for WMD experiments. However, the divergence of the radiation beam introduces extra dispersion. In the following, the suggested strategy for the measurements of the intensity gradient is based on the former of the aforementioned methods, but it can easily be extended to include the second method.

In reciprocal space, a continual change in λ is represented by a continual change in the radius of the Ewald sphere. Let the crystal rotate while λ repeats an increase and decrease in the range $\Delta\lambda$. There are chances for a reciprocal-lattice point to intersect the surface of the sphere, the radius of which is, in general, different for successive intersections, except for the case in which the rate of the change in λ is synchronous with the angular velocity of the crystal rotation. If the time of measurement is long enough to allow λ to oscillate many times and the crystal to do a number of rotations, the reciprocal-lattice point intersects the surface of the sphere at all radii included in $\Delta\lambda$, resulting in an 'effective wavelength scan' of the reflection intensity. The intensity gradient with respect to λ can be derived from the intensity profile.

During the combined crystal rotation and λ oscillation, many reciprocal-lattice points intersect the Ewald sphere; we suggest employing an X-ray precession camera or a Weissenberg camera to record the intensity gradient for them. A modification, however, has to be made to the design of the camera so that the position of the layer screen is varied synchronously with the change in λ for the zero-layer pattern. For the upper-layer pattern, additional synchronous variation of the film (or plate) distance is necessary. In the WMD pattern thus obtained, Bragg reflections appear as elongated spots, somewhat like short Laue streaks. The significant difference between the elongated spots and the Laue streaks lies in that the range of λ is definite in the former whereas it is indefinite in the latter. $\Delta\lambda$ is determined by the wavelength of the radiation to be used and the unit-cell size of the crystal. When the intensity gradient is measured both on the long- and on the short-wavelength side of the absorption edge, $\Delta\lambda$ is set to be larger to straddle the absorption edge.

Fig. 1 shows an example of a WMD pattern, recorded using a precession camera. A single crystal of a ferrocene derivative (chemical formula $C_{36}H_{32}O_7Fe$) was used as a sample and $\Delta\lambda$ was set to 1.746–1.824 Å (the *K*-absorption edge of the iron atom is at 1.743 Å). The crystal structure was solved by direct methods (Nakamura & Setodoi, 1998) in space group $P2_1/a$. Table 1 presents a comparison between the signs of the structure factors derived from the measured intensity gradients and the signs calculated from the atomic coordinates determined by the structure analysis. Agreement is found to be good.

Table 1. *Comparison of the sign of the structure factor of a $C_{36}H_{32}O_7Fe$ crystal derived from the observed intensity gradient using equation (12a) and calculated from the atomic coordinates determined by Nakamura & Setodoi (1998)*

hkl	Sign derived using (12*a*)	Sign from atom coordinates	*hkl*	Sign derived using (12*a*)	Sign from atom coordinates
006	−	−	027	−	−
007	−	−	028	−	−
008	−	−	0,2,14	+	+
009	−	−	0,2,15	+	+
0,0,10	−	−	036	+	+
0,0,13	+	+	0,3,11	−	−
0,0,16	+	+	0,3,13	−	−
0,1,10	−	−	042	+	+
0,1,11	−	+	045	−	−
0,1,16	+	+	046	−	−
			047	−	−
			048	−	−

For WMD, the wavelength of the radiation to be used is determined by the absorption edge of the atom contained in the crystal and in some cases it is longer than that usually used for crystal structure analysis. The number of reflections for which the phase or sign is assigned is thus smaller than the number of reflections for which the integrated intensity is measured by means of conventional X-ray diffractometry. However, this is not a fatal drawback of WMD, since knowledge of the phase or sign of a limited number of the structure factors can provide a clue to the solution of the crystal structure.

Note that, when the crystal is centrosymmetric, only 'one measurement' of the intensity gradient suffices to derive the sign of $A(hkl)$ and therefore WMD is free from the problem of intensity scaling. In the case of noncentrosymmetric crystals, the same is true, provided that the Bijvoet pairs of reflections are recorded in one pattern.

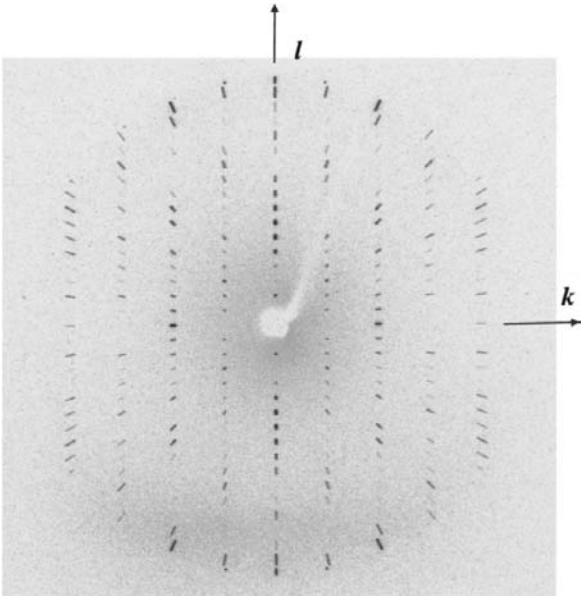

Fig. 1. Wavelength-modulated diffraction pattern of a single crystal of $C_{36}H_{32}O_7Fe$, recorded using an X-ray precession camera on a synchrotron-radiation source at Ritsumeikan University. The continually varied wavelength range was 1.746–1.824 Å, the *K*-absorption edge of Fe being at 1.743 Å. The pattern shows an array of 0*kl*-type reflections, which appear elongated owing to the continual change in the wavelength. (The layer screen used here had an annular aperture of width large enough to allow reflections of varying wavelength to pass; it was not necessary to change continually the position of the layer screen.)

4. Discussion

4.1. *Other factors influencing the intensity gradient of reflections*

The intensity gradient of Bragg reflections has its origin not only in the anomalous scattering of atoms but also in the wavelength dependence of the intensity of the primary radiation beam and in the wavelength dependence of the absorption of the radiation beam by a sample. The spectrum of the synchrotron radiation emitted from the bending magnet is known for each storage ring and can be used for the correction of the observed intensity gradient. It is possible, however, to introduce deformation into the shape of the spectrum by inserting materials in the beam path so that the dependence is very small in the wavelength range under consideration. The wavelength dependence of the sample absorption can be calculated, when measurements are made on the long-wavelength side of the edge, referring to a table such as that compiled by Sasaki (1990). On the short-wavelength side, the absorption is appreciably high and, furthermore, an X-ray absorption fine structure (XAFS) oscillation may appear. It is necessary to make, prior to recording WMD patterns, measurements of the sample absorption to find a wavelength range for which reliable correction can be made.

The wavelength dependence of the Lorentz factor and the polarization factor have to be considered also.

The former is concerned with the rate at which the reciprocal-lattice point passes through the surface of the Ewald sphere. Simple calculation shows that the rate is proportional to $\alpha \sin(2\theta)/\lambda$ (α is the angular velocity of the crystal rotation and θ the Bragg angle) for the reflection for which the axis of rotation is normal to the plane of scattering. Since θ increases with λ according to the Bragg equation, the wavelength dependence of the rate is not appreciable and may be neglected. It should, however, be noted that the Lorentz factor shows an appreciable variation with 2θ in the outer rim region of a precession pattern and has an influence on the intensity profile. The polarization factor depends on λ through the wavelength dependence of the angle of beam deflection and can be calculated. The dependence is not appreciable.

4.2. *Effect of the presence of another anomalously scattering atom*

If there is an atom, say G, whose absorption edge lies not far from that of the H atom, the contribution of f'_G and f''_G cannot be neglected. In this case, the equation of the intensity gradient, corresponding to (11) above, is written as

$$\begin{aligned}
&\partial I(hkl)/\partial\lambda \\
&\quad = 2\Big[(\partial f'_H/\partial\lambda)\Big(\sum_H \cos\vartheta_H\Big) - (\partial f''_H/\partial\lambda)\Big(\sum_H \sin\vartheta_H\Big) \\
&\qquad + (\partial f'_G/\partial\lambda)\Big(\sum_G \cos\vartheta_G\Big) - (\partial f''_G/\partial\lambda)\Big(\sum_G \sin\vartheta_G\Big)\Big] \\
&\qquad \times A(hkl) + 2\Big[(\partial f'_H/\partial\lambda)\Big(\sum_H \sin\vartheta_H\Big) \\
&\qquad + (\partial f''_H/\partial\lambda)\Big(\sum_H \cos\vartheta_H\Big) + (\partial f'_G/\partial\lambda)\Big(\sum_G \sin\vartheta_G\Big) \\
&\qquad + (\partial f''_G/\partial\lambda)\Big(\sum_G \cos\vartheta_G\Big)\Big]B(hkl). \qquad (19)
\end{aligned}$$

This is still in the form of a linear combination of $A(hkl)$ and $B(hkl)$. Two simultaneous equations can be solved, if there is additional information on the coordinates of atom G, to obtain $A(hkl)$ and $B(hkl)$ in a similar way to that described above.

4.3. *Accuracy of the phase or sign determined by the WMD method*

What is measured in the WMD technique is the intensity gradient of Bragg reflections; the procedures involved are simpler than those of other methods of phase determination in which integrated intensity is measured for several wavelengths. The procedures are particularly simple for centrosymmetric crystals and, as (12*a*) suggests, the sign of $A(hkl)$ is determined by inspecting whether the intensity profile of the reflections in a WMD pattern has a positive or a negative slope. $\partial f'_H/\partial\lambda$ is included in (12*a*) but it is only necessary to know its sign at λ where the gradient is measured. Errors in the estimation of the wavelength dependence of the primary-beam intensity and the sample absorption do not affect the results unless they upset the sign of the intensity gradient. There may be reflections for which the gradient is very small, even though their $|A(hkl)|$ are large. For such reflections, the accuracy of the sign determination may be low.

For noncentrosymmetric crystals, not only the signs of $A(hkl)$ and $B(hkl)$ but also their magnitudes are required and the accuracy of the phase determination is not the same as in the case of centrosymmetric crystals. The accuracy depends primarily on how accurately the intensity gradient is measured. In the first way described in §2, in which the measurements are extended to the short-wavelength side of the absorption edge, estimation of the correction for the wavelength dependence of the sample absorption may be the largest source of error. In the second way (§2), in which the Bijvoet pair of reflections are used, the measurements are made solely on the long-wavelength side and the estimation can be made fairly accurately. Care should be taken to ensure that the geometrical and physical factors affecting the intensity are the same for each reflection of the pair. The choice of the way to measure the intensity gradient depends on the chemical contents of the sample and on the unit-cell size.

Reliability of the $\partial f'/\partial\lambda$ and $\partial f''/\partial\lambda$ values has an influence on the accuracy of the phase determination for noncentrosymmetric crystals. The table of Sasaki (1989) is based on the results of quantum-mechanical calculations of f' and f'' by Cromer & Liberman (1970), which are not necessarily accurate enough for the wavelength very close to the absorption edge. One way to obtain reliable values is to determine f'' from absorption measurements on a sample and to derive f' by making use of the Kramers–Kronig transformation (Hendrickson, 1991). It is also necessary to check the actual location of the absorption edge, since the effect of chemical shift may be present.

Practical application of WMD is in progress at the Synchrotron Radiation Center at Ritsumeikan University and a full report of the results will be published in due course.

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