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Simultaneous Diffraction with the Three-Circle Diffractometer

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The geometrical conditions of simultaneous diffraction with a three-circle diffractometer have been derived for all the crystal systems and for any crystal orientation. It is shown that λ-independent simultaneous diffraction takes place among reciprocal-lattice points located on the same vertical net, that its multiplicity is generally odd, and that it obeys special conditions in all cases in the cubic system and, for particular orientations and classes of reflection, in the hexagonal and tetragonal systems. Finally, procedures are suggested for avoiding taking intensity measurements under conditions of simultaneous diffraction.

Introduction

In a previous paper (Santoro & Zocchi, 1966) a geometrical discussion of simultaneous diffraction independent of wavelength in the Weissenberg methods has been reported.

The conditions under which simultaneous diffraction occurs for the three-circle diffractometer have been recently indicated by Burbank (1965), and a set of rules has been deduced graphically by him for various possible types of reciprocal net.

It seems useful to derive these conditions in a more general way, taking into account the initial orientation of the crystal and its symmetry, in order to be able to calculate the indices of the reflections in simultaneous diffraction, and to determine the crystal orientations more appropriate in taking intensity measurements.

Simultaneous diffraction independent of wavelength

In order to obtain the condition of simultaneous diffraction, it is convenient to introduce a right-handed Cartesian coordinate system X, Y, Z, attached to the laboratory, as defined in Fig. 1. For $\chi=\theta=0°$, the Φ-, and Θ-circle axes are coincident with Z, and the χ-circle axis is coincident with Y; the positive sense of the rotations is given by the right-hand screw rule.

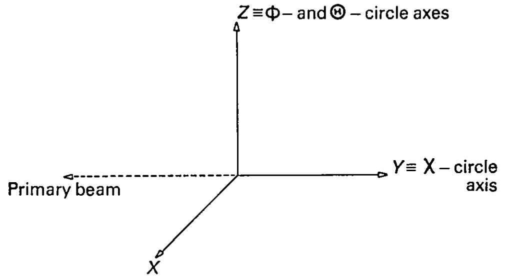

Fig. 1. Reference system and orientation of diffractometer for $\chi=\theta=0°$. The Y axis is antiparallel to the primary beam and the Z axis is perpendicular to the plane of the circle of the detector and points from the diffractometer table up to the crystal.

The crystal is initially oriented on the diffractometer as already described (Santoro & Zocchi, 1964).

In order to bring a reciprocal lattice point of coordinates $x_0y_0z_0$ into reflecting position in the equatorial plane of the diffractometer, the crystal has to be rotated φ_0, χ_0, and θ_0, where:

$$\sin\varphi_0=-(y_0/\xi_0),\ \cos\varphi_0=x_0/\xi_0,\ \sin\chi_0=z_0/d_0^*,$$
$$\cos\chi_0=\xi_0/d_0^*,\ \text{and}\ \sin\theta_0=d_0^*/2$$

where:

$$\xi_0=(x_0^2+y_0^2)^{\frac{1}{2}}\quad\text{and}\quad d_0^*=(x_0^2+y_0^2+z_0^2)^{\frac{1}{2}}\dagger\ .$$

The coordinates $x_iy_iz_i$ of any other reciprocal lattice point are transformed by these rotations into $x_i'y_i'z_i'$. If the center of the reflection sphere is at $x=0$, $y=1$, $z=0$, the point $x_i'y_i'z_i'$ will be in simultaneous diffraction with the 'primary' reflection $x_0y_0z_0$ if:

$$d_i^{*2}-2y_i'=0\ , \tag{1}$$

where $d_i^{*2}=x_i^2+y_i^2+z_i^2$. By expressing equation (1) in terms of the initial coordinates $x_iy_iz_i$ we get:

$$d_i^{*2}-(x_ix_0+y_iy_0+z_iz_0)-\frac{(4-d_0^{*2})^{\frac{1}{2}}}{\xi_0}(y_ix_0-x_iy_0)=0\ . \tag{2}$$

If

$$y_ix_0=x_iy_0 \tag{3}$$

the two points lie on the same vertical net and the condition of simultaneous diffraction reduces to:

$$d_i^{*2}-(x_ix_0+y_iy_0+z_iz_0)=0\ . \tag{4}$$

Condition (4) is independent of the wavelength. In what follows, our attention will be confined to the solutions of equation (4) (λ-independent simultaneous diffraction). However, the more general equation (2) can be used to obtain λ-dependent solutions, if desired.

In his treatment of the single-crystal orienter, Burbank (1965) also has taken into consideration only simultaneous diffraction independent of the wavelength.

From equation (4) it is easily seen that:

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† Here $d^*=\lambda/d$.

(i) For any reciprocal lattice point $x_iy_iz_i$ in simultaneous diffraction with the 'primary' reflection $x_0y_0z_0$, there exists a third reciprocal lattice point $x_0-x_i, y_0-y_i, z_0-z_i$ which also diffracts simultaneously‡. This indicates the fact that the multiplicity of simultaneous diffraction is always odd.

(ii) If $x_0y_0z_0, x_iy_iz_i$, and $x_0-x_i, y_0-y_i, z_0-z_i$ diffract simultaneously the vertical net on which the three points lie is rectangular. In fact, for the second and third point we have:

$$d_i^*d_j^* \cos \varepsilon = x_i(x_0-x_i)+y_i(y_0-y_i) \\ +z_i(z_0-z_i)=0$$

i.e. $\cos \varepsilon = 0$, where $d_j^* = [(x_0-x_i)^2+(y_0-y_i)^2+(z_0-z_i)^2]^{\frac{1}{2}}$ and ε is the angle between the reciprocal vectors $\mathbf{d}_i^*$ and $\mathbf{d}_j^*$.

If the crystal is mounted on the diffractometer so that one of the zone-axes given in Table 1 is coincident with the Φ-circle axis, at least one non-oblique vertical net is present. Therefore, for these orientations, λ-independent simultaneous diffraction takes place. (In Burbank's terminology, for these orientations multiple diffraction is 'intrinsic'; it is worthwhile to note that λ-dependent simultaneous diffraction can also be called 'intrinsic', even if the geometrical situation is different). If the zone-axis is coincident with a reciprocal row (see Table 1), all the reciprocal lattice points are located on vertical nets; under these circumstances, 'systematic' simultaneous diffraction is possible.

Table 1. *Zone-axes lying on at least one non-oblique reciprocal net*

System	Axis
Monoclinic	[010]*
Orthorhombic	$[UV0]$, $[U0W]$, $[0VW]$ [100]*, [010]*, [001]*
Tetragonal and hexagonal	$[UVW]$, $[U0W]$, $[0VW]$ $[UV0]$*, [100]*, [010]*, [001]*
Cubic	Any zone-axis*

* Zone axes coincident with a reciprocal row.

Condition (4) can be written:

$$d_i^* = d_0^* \cos \varepsilon_0 , \tag{5}$$

where ε_0 is the angle between the two vectors $\mathbf{d}_i^*$ and $\mathbf{d}_0^*$.

The relationship between the indices of the two reciprocal lattice points, expressed by equation (3), can be found on the basis of elementary crystallographic considerations for any given initial orientation of the crystal. As an example, for a cubic crystal, if $[UVW]$ is the zone-axis coincident with the Φ-circle axis, and if $h_0k_0l_0$ is the reflection under examination, then the reciprocal lattice points $h_ik_il_i$ located on the same vertical net with $h_0k_0l_0$ are given by:

$$(l_0V-k_0W)h_i+(h_0W-l_0U)k_i+(k_0U-h_0V)l_i=0. \tag{6}$$

There are many initial orientations of a crystal for which a given net is vertical and equation (5), derived for this net, is the same independently of the initial orientation of the crystal. This is a consequence of the particular geometry of a three-circle diffractometer.

Discussion

By applying the above considerations to all possible cases, the results reported in Table 2 are obtained.

Table 2. *Conditions of λ-independent simultaneous diffraction*

Crystal system	Zone axis coincident with the Φ-circle axis	Reflections affected	Exceptions	Reflections affected according to special conditions
Monoclinic	[010]-2nd setting	All	$h00$, $0k0$; $00l$; $h0l$	
Orthorhombic	$[UV0]$	$hk0$	$h00$; $0k0$	
	$[U0W]$	$h0l$	$h00$; $00l$	
	$[0VW]$	$0kl$	$0k0$; $00l$	
	[100]	All	$h00$; $0k0$; $00l$; $0kl$	
	[010]	All	$h00$; $0k0$; $00l$; $h0l$	
	[001]	All	$h00$; $0k0$;$00l$; $hk0$	
Tetragonal	$[UVW]$	$nU, nV, l,$	$00l$; $nU, nV, 0$	
	$[UV0]$	All	$00l$; $h'k'l$ $(h'U+k'V=0)$; $nU, nV, 0$	$hk0$
	$[U0W]$	$h0l$	$h00$; $00l$	
	$[0VW]$	$0kl$	$0k0$; $00l$	
	[100]	All	$h00$; $00l$; $0kl$	$hk0$
	[010]	All	$0k0$; $00l$; $h0l$	$hk0$
	[001]	All	$h00$; $0k0$; $00l$; $hk0$	
Hexagonal	$[UVW]$	$n(2U-V), n(2V-U), l$	$00l$; $n(2U-V), n(2V-U), 0$	
	$[UV0]$	All	$00l$; $h'k'l$ $(h'U+k'V=0)$; $n(2U-V), n(2V-U), 0$	$hk0$
	$[U0W]$	$2h, \bar{h}, l$	$00l$; $2h, \bar{h}, 0$	
	$[0VW]$	$\bar{h}, 2h, l$	$00l$; $\bar{h}, 2h, 0$	
	[100]	All	$00l$; $2h, \bar{h}, 0$; $0kl$	$hk0$
	[010]	All	$00l$; $\bar{h}, 2h, 0$; $h0l$	$hk0$
	[001]	All	$00l$; $h00$; $0k0$; $hk0$	
Cubic	Any	All	nU, nV, nW	All

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‡ Note that $x_0-x_i, y_0-y_i, z_0-z_i$ is the plane which 'indirectly reflects' (James, 1964) in the same direction of x_0, y_0, z_0 part of the intensity reflected by x_i, y_i, z_i, and that x_i, y_i, z_i is the plane which 'indirectly reflects' in the same direction of x_0, y_0, z_0 part of the intensity reflected by $x_0-x_i, y_0-y_i, z_0-z_i$.

The intensity of all the reflections affected (column 3 in Table 2) is systematically measured under conditions of triple diffraction, except for those reflections for which special conditions hold (column 5)†; for reflections with such special conditions, the multiple diffraction is of higher order. These conditions are easily derived from equation (5). For example, in the case of the tetragonal and cubic systems, for the reflections of the vertical net $(001)_0^*$ (*International Tables for X-ray Crystallography*, 1959) the condition is:

$$h_i^2 - h_0 h_i - k_i(k_0 - k_i) = 0 \,. \tag{7}$$

In the case of the hexagonal system, for the vertical net $(001)_0^*$ the condition is:

$$2h_i^2 - h_i(2h_0 + k_0 - 2k_i) + [2k_i^2 - k_i(h_0 + 2k_0)] = 0 \,, \tag{8}$$

where h_0k_00 are the indices of the reflection under examination in both cases. Equations (7) and (8) describe the λ-independent simultaneous diffraction in a square and a hexagonal net, respectively.

In the cubic system all reflections affected obey special conditions. For example, for a cubic crystal with [100] coincident with the Φ-circle axis, equation (7) shows that the primary reflection 860 is in simultaneous diffraction with $4\bar{2}0$, $7\bar{1}0$, $1\bar{1}0$, 800, 930, $\bar{1}30$, 060, 770, 170, and 480; the primary reflection 500 is in simultaneous diffraction with 420, $4\bar{2}0$, 120, and $1\bar{2}0$; *etc.* For the same orientation, the reflection 244 is located on the vertical rectangular net $(0\bar{1}1)_0^*$ for which the following condition holds:

$$h_i^2 - h_0 h_i + 2k_i(k_i - k_0) = 0 \,. \tag{9}$$

From this equation it is found that 200, 422, $\bar{2}22$, and 044 reflect simultaneously with 244.

The above examples show that a great variety of effects is possible for vertical nets for which the diffraction condition is special; under these circumstances no general rules of simultaneous diffraction can be established. This applies also to rectangular nets, as shown by the last example.

When the conditions derived from equation (5) are not special, simultaneous diffraction takes place according to the rules found by Burbank (1965) for rectangular nets; *i.e.* diffraction is single for reciprocal lattice points located on the axes of the net and triple for the others.

For non-primitive Bravais lattices the solutions of the equations derived for the various nets are, in general, but not always, fewer, because some of them are forbidden.

The same considerations hold for space-group extinctions; in this case the possibility of even multiplicity of simultaneous diffraction arises, and for this reason, pure 'Aufhellung' effects (Wagner, 1920) are possible.

Table 2 shows that λ-independent simultaneous diffraction affects a very large fraction of the measurable reflections for the most common orientations.

An obvious way of avoiding λ-independent simultaneous diffraction is to misset the crystal, by using the arcs of the goniometer head, so that there are no vertical nets in the new orientation. The missetting is performed, in general, by rotating the crystal first by a small angle σ about the X axis and then by a small angle ε about the Y axis‡. The angles σ and ε have to be both different from zero for the cubic system; in the other crystal systems, for certain orientations of the crystal, only one of the two rotations is necessary. For example, for a tetragonal crystal with $[10\bar{1}]$ coincident with the Φ axis and d^*_{101} coincident with the Y axis, only a rotation ε is necessary to move the net $(010)_0^*$ from the vertical plane.

In addition, from Table 2 it is clear that in many cases one or two particular orientations of the crystal are sufficient to avoid λ-independent simultaneous diffraction for all the reflections. For example, by setting [101] coincident with the Φ-axis, it is possible to measure all the reflections of tetragonal and orthorhombic crystals, except $h0l$; the reflections $h0l$ can be measured by reorienting the crystal with [011], for instance, coincident with the Φ-circle axis. Similar considerations hold for the other crystal systems, except the cubic system.

Conclusions

From the results of the present investigation and those relative to the Weissenberg (Santoro & Zocchi, 1966) and precession (Burbank, 1965) methods, it appears that only accidental simultaneous diffraction is not easily avoidable in the most used diffraction techniques.

Therefore, in all the cases in which simultaneous diffraction may introduce significant errors in intensity measurements, the problem is to find out what reflections are affected by simultaneous diffraction dependent on the wavelength. However, since this type of simultaneous diffraction is accidental in nature, in general it should not be a serious cause of error, especially if the reciprocal lattice parameters are large.

In those cases in which very accurate intensity measurements are required, and in many neutron diffraction problems (Moon & Shull, 1964; Willis & Valentine, 1962), all the reflections have to be measured under conditions of single diffraction. This can be accomplished by properly using a four-circle diffractometer (Willis, 1961; Santoro & Zocchi, 1964) or, if such an instrument is not available, by measuring the intensities of interest at two different wavelengths, and

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† We define as a 'special condition' an equation, derived from equation (5), in which all the coefficients are rational numbers.

‡ The setting angles φ and χ after the rotations σ and ε are given by:

$$\tan\varphi = \frac{z_0 \sin\sigma - y_0 \cos\sigma}{(y_0 \sin\sigma + z_0 \cos\sigma)\sin\varepsilon + x_0 \cos\varepsilon}$$

$$\tan\chi = \frac{(y_0 \sin\sigma + z_0 \cos\sigma)\cos\varepsilon - x_0 \sin\varepsilon}{\{[(y_0 \sin\sigma + z_0 \cos\sigma)\sin\varepsilon + x_0 \cos\varepsilon]^2 + [y_0 \cos\sigma - z_0 \sin\sigma]^2\}^{\frac{1}{2}}}$$

where $x_0y_0z_0$ are the Cartesian coordinates of the reciprocal lattice point before the rotations σ and ε.

by checking, by means of equation (2), the diffraction conditions in both cases*.

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* It is worthwhile to note that equation (2) is a geometrical condition of simultaneous diffraction and does not take into account the fact that the 'reciprocal-lattice points' are not geometrical points.

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A Theoretical Calculation of X-ray Absorption Cross Sections

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Numerical values of X-ray absorption cross-sections for atoms are given for 10 commonly used X-ray wavelengths. The calculations are based on a multipole expansion of the appropriate matrix elements, using hydrogen-like eigenfunctions, for the *K*, *L*, *M* and *N* electrons. For the given figures, agreement with experiment is in general better than 5%.

Photoelectric absorption cross-sections for X-rays have been calculated by several authors using hydrogen-like eigenfunctions (Bethe & Salpeter, 1957). These calculations have been made for the *K*- and *L*-shells using the dipole approximation. Recently one of us discussed the angular dependence of the Borrmann effect, and it was found that apart from the influence of thermal vibrations within the crystal, this angular dependence is caused by electrical quadrupole transitions (Wagenfeld, 1966).* Here the methods, and to some extent the results of Hönl's (1933) and Eisenlohr & Müller's (1954) calculations of the generalized atomic scattering factor for the region of anomalous dispersion have been used, but the calculations have been extended for the *M*- and *N*-shells as well. A further complication has been the inaccuracy of the screening constants which are needed for the hydrogen-like eigenvalues. Since Bearden (1964) has measured, or given best values for, the X-ray wave length for most elements with high precision, one can determine the screening constants from his data, using Sommerfeld's fine structure formulae for the term values. Since the calculations are based on hydrogen-like eigenfunctions, the eigenvalues for the energies do not agree exactly with the energies of the measured absorption edges. Hence one cannot expect that this calculation will hold for the wavelength region near to and below an absorption edge. In the following tables we therefore publish only the numerical values for the atomic absorption cross-sections which we believe are theoretically justified. For this reason we also do not give cross-sections for the wave length region longer than the *L*-shell absorption edge. However, we compared some of the values with experimental data, and found agreement within 5%. The comparisons showed that these values are significantly better than the theoretical values given in *International Tables for X-ray Crystallography* (1962).

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* Dipole–octupole transitions, which give a smaller contribution than quadrupole transitions, are also included. It can be proved that electrical octupole transitions are very weak. Magnetic transitions do not occur in this case.