Acta Cryst. (1966). **21**, 293

Multiple Diffraction in the Weissenberg Methods

BY A. SANTORO AND M. ZOCCHI

National Bureau of Standards, Institute for Materials Research, Washington, D.C., U.S.A.

(*Received* 18 *August* 1965)

The conditions for multiple diffraction due to symmetry have been derived for the Weissenberg geometry, for the various crystal systems and for the most commonly used rotation axes.

The orientation of the crystal with respect to the direction of the incident beam and the nature of the rotation axis are the factors responsible for the simultaneous diffraction by symmetry. The values of μ used in the normal-beam, equi-inclination and flat-cone methods determine a symmetrical relation between the reciprocal levels and the reflection sphere. Since in the equal-cone method this symmetrical relation can be avoided by using a proper value of μ, a conclusion of this paper is that the equal-cone method is the most appropriate in intensity measurements.

Introduction

In recent years it has been shown (Hay, 1959; O'Connor & Sosnowski, 1961; Moon & Shull, 1964; Borgonovi & Caglioti, 1962; Willis & Valentine, 1962; Arndt, 1964) that multiple diffraction (Renninger, 1937) plays an important role in measuring intensities in neutron diffraction work.

The occurrence of simultaneous diffraction in the equi-inclination method has been underlined for the first time by Fankuchen & Williamson (1956), and by Yakel & Fankuchen (1962).

Recently, Zachariasen (1965) has shown that: (i) it is not in general permissible to neglect the effect of multiple diffraction in quantitative intensity work; (ii) multiple diffraction is a frequent phenomenon with commonly used X-ray techniques. He has found that for cubic, tetragonal, and orthorhombic crystals rotating about their crystallographic axes, for monoclinic crystals rotating about [010], and for hexagonal crystals rotating about [001], the measurement of the intensities of upper layer reflections is made under conditions of triple diffraction in the equi-inclination method, and of double diffraction in the normal beam method. He also illustrated two cases of zero-level reflections subject to triple and quintuple diffraction.

Burbank (1965) has deduced graphically a set of rules for determining multiple diffraction in the single-crystal orienter and precession techniques for all possible types of reciprocal net.

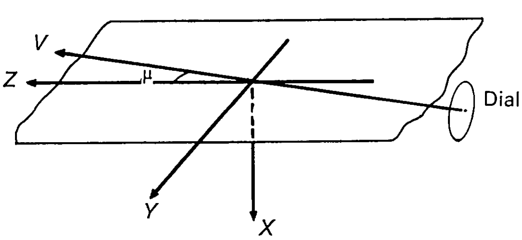

Fig. 1. Relation between the Cartesian coordinate system and the rotation axis of the crystal.

Jeffery & Whitaker (1965) have emphasized the importance of taking equi-inclination photographs for accurate intensity measurements under conditions of single diffraction, and have suggested the deliberate mis-setting of the angle of equi-inclination of *ca* 0·5° so that the axial reciprocal lattice point, if any, is not on the reflection sphere.

It is the purpose of this paper to find a general condition for multiple diffraction in the Weissenberg geometry in order to find a method of avoiding systematic simultaneous diffraction in making intensity measurements.

Diffraction condition

In the Weissenberg methods the crystal is rotated about a zone axis $[ABC] \equiv V$(ω-rotation) at a selected value of the angle μ, where μ is defined in the usual way (Buerger, 1942) and its origin is chosen so that $\mu = 0°$ when V is perpendicular to the primary beam; the origin of ω is arbitrary.

In order to obtain a general condition for reflection, it is convenient to define a Cartesian coordinate system X, Y, Z, in the following way:

(*a*) The Y axis is coincident with the primary beam.

(*b*) The Z axis is perpendicular to Y and lies in the plane formed by the primary beam and the rotation axis of the crystal, which points from the goniometer head to the crystal; the Z axis is coincident with the rotation axis of the crystal in the normal-beam method ($\mu = 0°$).

(*c*) The X axis is perpendicular to the YZ plane and oriented so that right-handed coordinates result (Fig. 1).

The crystal can be conveniently described in terms of three axes **P**, **T**, **V** (and their reciprocals **P***, **T***, **V***) obtained from the conventional crystallographic axes a, b, c by means of the following index transformation:

Old (hkl)	New (ptv)
$(h_1k_1l_1)$	(100)
$(h_2k_2l_2)$	(010)
$(h_3k_3l_3)$	(001)

where $(h_1k_1l_1)$ and $(h_2k_2l_2)$ are two crystal planes belonging to the zone $[ABC]$ and $(h_3k_3l_3)$ is such that $h_3A+k_3B+l_3C\neq 0$.†

Initially, with the camera set at $\mu=\omega=0°$, the crystal is mounted on the goniometer arcs so that $\mathbf{V}$ is coincident with Z, $\mathbf{P}^*$ is coincident with X, and $\mathbf{T}^*$ lies in the XY plane with positive Y component. In this condition, the coordinates x, y, z of a reciprocal point ptv are given by (Santoro & Zocchi, 1964):

$$\begin{aligned} x&=pP^*+tT^*\cos\widehat{P^*T^*}+vV^*\cos\widehat{P^*V^*}\\ y&=tT^*\sin\widehat{P^*T^*}-vV^*\cos\widehat{TV}\sin\widehat{P^*V^*}\\ z&=vV^*\sin\widehat{TV}\sin\widehat{P^*V^*}\,. \end{aligned}\qquad(1)$$

The crystal is then rotated about its V axis at the value of the angle μ, appropriate for the method used; therefore, the initial coordinates x, y, z of the reciprocal points are transformed in the following way:

$$\begin{aligned} x'&=x\cos\omega+y\sin\omega\\ y'&=(-x\sin\omega+y\cos\omega)\cos\mu+z\sin\mu\\ z'&=(x\sin\omega-y\cos\omega)\sin\mu+z\cos\mu\,. \end{aligned}\qquad(2)$$

Reflection takes place when a reciprocal point ptv lies on the reflection sphere. If the center of the sphere has coordinates $x=0$, $y=-1$, $z=0$, the condition for reflection is:

$$x'^2+(y'+1)^2+z'^2=1$$

i.e. $$d^{*2}+2y'=0$$

where $$d^{*2}=x'^2+y'^2+z'^2\,.$$

By substituting from equation (2),

$$2z\sin\mu+2(y\cos\omega-x\sin\omega)\cos\mu+d^{*2}=0\,.\qquad(3)$$

The angle μ is given by:

$$\sin\mu=\sin\nu-v_0s$$

where v_0 is the v index relative to the level under examination, s is the period on the rotation axis and ν is defined in the usual way (Buerger, 1942).

We can write:

$$\sin\nu=ns/2$$

where n is an arbitrary number. Therefore

$$\sin\mu=(ns)/2-v_0s\,.\qquad(4)$$

From this relation we have

$n=2v_0$	$\sin\mu=0$	Normal-beam
$n=v_0$	$\sin\mu=-v_0s/2$	Equi-inclination
$n=0$	$\sin\mu=-v_0s$	Flat-cone
$n=$constant	$\sin\mu=s(n/2)-sv_0$	Equal-cone

† It is assumed that the parametral plane on the new axes corresponds to a plane $(h_0k_0l_0)$ on the old ones, with $h_0=(h_1+h_2+h_3)/m$; $k_0=(k_1+k_2+k_3)/m$; $l_0=(l_1+l_2+l_3)/m$ where m is the highest common factor.

By substituting (4) in (3) we obtain:

$$2zs\left(\frac{n}{2}-v_0\right)+\left[1-s^2\left(\frac{n}{2}-v_0\right)^2\right]^{\frac{1}{2}}(2y\cos\omega-2x\sin\omega)+d^{*2}=0\,.\qquad(5)$$

Equation (5) is the condition for reflection of a reciprocal point valid for a general crystal of any orientation and for any Weissenberg method.

Multiple diffraction and symmetry

From equation (5) it is easily seen that multiple diffraction independent of the wavelength is possible only if the reciprocal points which reflect simultaneously lie on the same vertical net (*i.e.* on a net coinciding with one of the planes formed by the rotation axis and the equatorial reciprocal rows), and, in the normal-beam, equi-inclination, and flat-cone methods, if the vertical net is not oblique. Multiple diffraction occurring on non-oblique vertical nets can be called 'by symmetry'.

One non-oblique vertical net, at least, is present in all the possible orientations, except in triclinic crystals rotated about any zone axis, in monoclinic crystals rotated about $[ABC]$, $[0BC]$, $[AB0]$, $[A0C]$, [100], and [001], and in orthorhombic crystals rotated about $[ABC]$. Simultaneous diffraction by symmetry, then, may take place also in cases in which the rotation axis does not coincide with a symmetry axis of the crystal, or with a row of the reciprocal lattice. For example, for an orthorhombic crystal rotated about [$\bar{1}$10], simultaneous diffraction affects reflections of the class $hk0$; in fact, it can be shown (Fig. 2) that the reflection 020 is in simultaneous diffraction with 220 and 200 in the normal-beam method, the reflection $\bar{1}$20 is in simultaneous diffraction with 020 and $\bar{1}$00 in the equi-inclination method, *etc.*

Equation (5) can be used to obtain the conditions for simultaneous diffraction by symmetry for all the

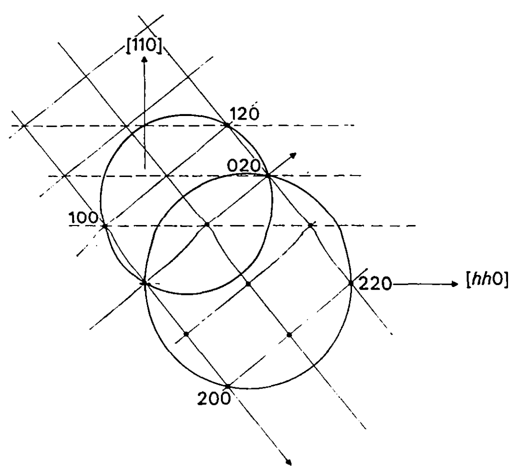

Fig. 2. Net $hk0$ of an orthorhombic crystal rotated about [$\bar{1}$10]; the circles are the intersections of the reflection sphere with the net.

possible rotation axes and for any Weissenberg technique. For all practical purposes, however, only the most commonly used axes need to be considered.

For monoclinic crystals rotating about [010], orthorhombic crystals rotating about [100], [010], and [001], and for tetragonal and hexagonal crystals rotating about [001], all upper layer reflections are measured systematically under conditions of triple and double diffraction in the equi-inclination and normal-beam methods, respectively (Zachariasen, 1965), and of double diffraction in the flat-cone method. If v_0 is the index of the layer under examination and if ptv_0 is in reflecting position, then simultaneous diffraction occurs with $00v_0$ and $pt0$ in the equi-inclination method, with $00(2v_0)$ in the flat-cone method, and with $pt\bar{v}_0$ in the normal-beam method. For hexagonal and tetragonal crystals rotating about [100] and [010] multiple diffraction occurs according to the above general rules, except for the $hk0$ reflections for which particular conditions hold, and, in the case of hexagonal crystals, except for general reflections on odd layer lines which reflect under conditions of single diffraction in the equi-inclination method. Finally, for cubic crystals rotating about any zone axis, simultaneous diffraction always takes place according to particular conditions. Some of these special conditions are given in Table 1 for the most commonly used rotation axes and, in the case of the cubic system, for the most important classes of reflections.

As an example of the application of equation (5) to a particular case, let us consider a primitive tetragonal crystal rotating about [110]. By choosing $(h_1k_1l_1) \equiv (\bar{1}10)$, $(h_2k_2l_2) \equiv (001)$; and $(h_3k_3l_3) \equiv (110)$ we have: $2p=k-h$, $t=l$, $2v=h+k$, and $x=[(k-h)a^*\sqrt{2}]/2$, $y=lc^*$, $z=[(h+k)a^*\sqrt{2}]/2$, and $s=a^*\sqrt{2}$. By substitution in equation (5),

$$a^{*2}(h+k)\left(n-2\frac{H+K}{2}+\frac{h+k}{2}\right) + 2\left[1-2a^{*2}\left(\frac{n}{2}-\frac{H+K}{2}\right)^2\right]^{\frac{1}{2}} \times \left(lc^*\cos\omega-\frac{k-h}{2}a^*\sqrt{2}\sin\omega\right) + \frac{(k-h)^2}{2}a^{*2}+l^2c^{*2}=0\,, \quad (6)$$

where the index HKL is referred to the reflection under examination and the indices hkl to the reflections in simultaneous diffraction. From equation (6), for the $hk0$ reflections we have the following condition:

$$(K-H)\left[2(h+k)\left(n-2\frac{H+K}{2}+\frac{h+k}{2}\right)+(k-h)^2\right] = (k-h)\left[2(H+K)\left(n-\frac{H+K}{2}\right)+(K-H)^2\right]. \quad (7)$$

If, for example, $\bar{2}60$ is the reflection under examination, then from condition (7) it is found that $\bar{3}60$, $\bar{5}50$, $\bar{6}30$, $\bar{6}20$, $\bar{5}00$, $\bar{3}\bar{1}0$, $\bar{2}\bar{1}0$, 120, 130, and 050 diffract simultaneously in the normal-beam method ($n=H+K$), that $\bar{4}40$, $\bar{4}20$, $\bar{2}00$, 220, 240, and 060 diffract simultaneously in the equi-inclination method $\left(n=\frac{H+K}{2}\right)$, and that

Table 1. *Special conditions of simultaneous diffraction*

	Rotation axes	Classes of reflections	Conditions
Cubic	[100], [010] [001]*	$0tv$	$t_0[v(n-2v_0+v)+t^2]=t[v_0(n-v_0)+t_0^2]$†
		$p0v$	$p_0[v(n-2v_0+v)+p^2]=p[v_0(n-v_0)+p_0^2]$‡
		ppv	$p_0[v(n-2v_0+v)+2p^2]=p[v_0(n-v_0)+2p_0^2]$
	[111]	HHL	$(L-H)\left[3(2h+l)(n-2\frac{2H+L}{3}+\frac{2h+l}{3}+2(l-h)^2\right] = (l-h)\left[3(2H+L)\left(n-\frac{2H+L}{3}\right)+2(L-H)^2\right]$
Hexagonal	[100]	$HK0$	$(2K+H)\left[6h\left(n-2\frac{H}{2}+\frac{h}{2}\right)+(2k+h)^2\right] = (2k+h)\left[6H\left(n-\frac{H}{2}\right)+(2K+H)^2\right]$
	[010]	$HK0$	$(2H+K)\left[6k\left(n-2\frac{K}{2}+\frac{k}{2}\right)+(2h+k)^2\right] = (2h+k)\left[6K\left(n-\frac{K}{2}\right)+(2H+K)^2\right]$

* For [100] $p=k$, $t=l$, $v=h$
For [010] $p=l$, $t=h$, $v=k$
For [001] $p=h$, $t=k$, $v=l$

$p_0t_0v_0$, or HKL, are the indices of the reflection under examination, and ptv or hkl the indices of the points in simultaneous diffraction.

† This condition holds also for tetragonal crystals rotated about [010]
‡ This condition holds also for tetragonal crystals rotated about [100]

$\bar{3}40$, $\bar{3}30$, $\bar{2}10$, 100, 310, 430, 440, 360, 170, and 070 diffract simultaneously in the flat-cone method ($n=0$). The geometrical interpretation of these results is given in Fig. 3.

Equation (6) shows also that for other classes of reflections in the normal-beam and flat-cone methods diffraction is double, and in the equi-inclination method is single for odd layer lines and triple for even layer lines.

In the equal-cone method no conditions of simultaneous diffraction occur for general reflections if the parameter n has fractional values and, for special classes of reflections, it is possible to find a value of n for which the number of reflections affected is very small. For example, for a tetragonal or cubic crystal rotating about [010] we have for the $hk0$ reflections,

$$H[k(n-2K+k)+h^2]=h[K(n-K)+H^2]\,. \qquad (8)$$

If 120 is the reflection under examination, for $n=\frac{1}{2}$ $\bar{2}00$ and $\bar{3}20$ are in simultaneous diffraction, while for $n=\frac{1}{3}$ $\bar{3}30$ and $\bar{1}40$ reflect simultaneously; for $n=1/10$, however, no other reflections satisfy equation (8) and the intensity of 120 can be measured in conditions of single diffraction.

For non-primitive Bravais lattices many reflections are exempt (except by accident) from multiple diffraction. In particular, for C-centred monoclinic crystals rotating about [010], orthorhombic C-centered crystals rotating about [100] and [010], orthorhombic body centered and face centered crystals rotating about [100], [010] and [001], and tetragonal body centered crystals rotating about [001], reflections on odd layer lines are unaffected by multiple diffraction in the equi-inclination method. The same is true for tetragonal body centered crystals rotating about [100] and [010], except for the class $hk0$. For rhombohedral crystals rotating about [111], reflections on layer lines which are not a multiple of three are unaffected in the normal-beam, equi-inclination and flat-cone methods. For non-primitive cubic lattices rules of this kind cannot be applied because of the higher specialization of the vertical nets, and the only consideration which can be made in general is that a lower multiplicity of simultaneous diffraction is observed in most cases.

Discussion and conclusions

Multiple diffraction has to be taken into account both in intensity measurements and in the determination of space groups.

From the above discussion it is clear that the normal-beam, equi-inclination, and flat-cone methods should not be used for measuring intensities in all cases in which multiple diffraction may introduce significant errors.

There are cases (Renninger, 1937) in which a reflection forbidden by the space group may appear because of multiple diffraction, and if this is wave-length-independent it is not possible to avoid it by changing the wavelength. As an example, let us consider the case of a cubic crystal of space group $P2_13$ (No. 198 in *International Tables*) rotating about [010]. The extinction conditions for this space group are

hkl	no conditions
$h00$, $0k0$, $00l$	$h, k, l=2n$.

Reflections 500 and 005 should be absent; however, 500 is in simultaneous diffraction with 120, $1\bar{2}0$, 420, $4\bar{2}0$, and 005 is in simultaneous diffraction with 021, $0\bar{2}1$, 024, $0\bar{2}4$. Under these circumstances there is the obvious possibility of observing one or more of these forbidden reflections.

From the conditions given in Table 1 it is possible to derive whether a reflection forbidden by the space group can appear because of simultaneous diffraction. Whenever this happens, experimental conditions in which multiple diffraction does not affect the reflections of interest should be used.

The main difference between the normal-beam, equi-inclination, and flat-cone techniques and the equal-cone method is that in the latter the choice of the parameter n in equation (5) is arbitrary. This fact makes it possible to choose for n fractional values, thus eliminating the symmetric relation between reciprocal lattice and reflection sphere which causes the general conditions for multiple diffraction in the other methods. Therefore, by using the equal-cone method, intensities unaffected by simultaneous diffraction can be measured also if the crystals are rotated about their crystallographic axes.

It is worthwhile to note that with the normal-beam, equi-inclination and flat-cone methods only in a few cases the problem might be circumvented by rotating the crystal about other crystallographic directions (see section on *Multiple diffraction and symmetry*); however, the choice of unusual rotation axes results in a more complicated interpretation of the diffraction patterns and requires tedious reorientations of the crystal.

With the two-circle diffractometer and the diffractometer in which the counter can be set to record the

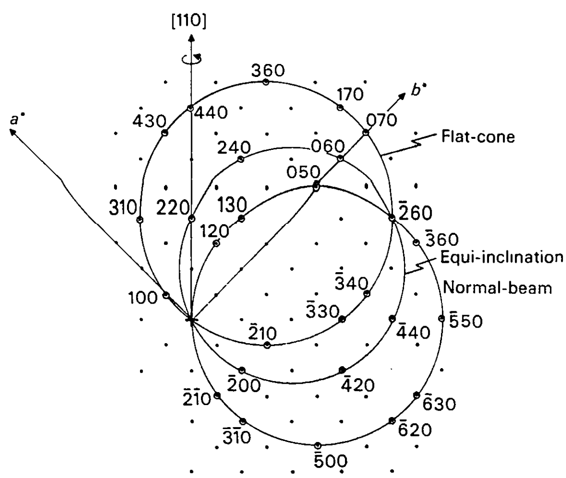

Fig. 3. Net $hk0$ of a tetragonal crystal rotated about [110].

upper layers, the intensities are measured with the normal-beam geometry and therefore the above considerations apply to them as well.

In addition to the discussed λ-independent solutions, equation (5) may have solutions dependent on the wavelength. This type of multiple diffraction may be called 'accidental' and its appearance in a particular case depends on the value of the wavelength used in the experiment. All techniques are affected by this kind of multiple diffraction, whose presence in a particular case can be ascertained by solving equation (5) or by a method like the one discussed by Speakman (1965).

References

ARNDT, U. W. (1964). *Acta Cryst.* **17**, 1183.
BORGONOVI, G. & CAGLIOTI, G. (1962). *Nuovo Cim.* **24**, 1174.
BUERGER, M. J. (1942). *X-ray Crystallography*, p.297. New York: John Wiley.
BURBANK, R. D. (1965). *Acta Cryst.* **19**, 957.
FANKUCHEN, I. & WILLIAMSON, R.S. (1956). Annual Meeting of ACA, French Lick, Indiana.
HAY, H. J. (1959). Atomic Energy Research Establishment, Harwell, AERE-R 2982.
JEFFERY, J. W. & WHITAKER, A. (1965). *Acta Cryst.* **19**, 963.
MOON, R. M. & SHULL, C. G. (1964). *Acta Cryst.* **17**, 805.
O'CONNOR, D. A. & SOSNOWSKI, J. (1961). *Acta Cryst.* **14**, 292.
RENNINGER, M. (1937). *Z. Phys.* **106**, 141.
SANTORO, A. & ZOCCHI, M. (1964). *Acta Cryst.* **17**, 597.
SPEAKMAN, J. C. (1965). *Acta Cryst.* **18**, 570.
WILLIS, B. T. M. & VALENTINE, T. M. (1962). Atomic Energy Research Establishment, Harwell, AERE-R 3959.
YAKEL, H. L. & FANKUCHEN, I. (1962). *Acta Cryst.* **15**, 1188.
ZACHARIASEN, W. H. (1965). *Acta Cryst.* **18**, 705.

Acta Cryst. (1966). **21**, 297

Dynamical Diffuse Scattering from Magnesium Oxide Single Crystals

BY J. GJØNNES* AND D. WATANABE†

School of Physics, University of Melbourne, Parkville, N.2, Victoria, Australia

(*Received* 24 *January* 1966)

Effects of Bragg scattering on the distribution of diffuse scattering from single crystals of magnesium oxide have been studied in transmission electron-diffraction patterns. The crystals were in the form of thin plates with very uniform thickness. The patterns are explained from a theory which includes both Bragg scattering of the diffusely scattered waves (as in ordinary Kikuchi-line theory) and Bragg scattering of the incident wave; only single diffuse scattering has been considered, however.

Fine structure in the Kikuchi-line pattern is shown to depend on the excitation error of the corresponding reflexions, the amplitude of the fine-structure oscillations increasing as the Bragg condition is approached. Also the contribution of the non-oscillating part to the Kikuchi-line contrast was found to change with the reflexion condition of the incident beam. In this case the contrast decreases with decreasing excitation error of the reflexion. When many Bragg reflexions are strongly excited, as when the beam is close to a zone axis, the Kikuchi lines may vanish altogether, leaving a complicated fine structure pattern. Reversal of contrast along a Kikuchi line, from excess to defect, may also result from Bragg scattering of the incident beam. Effects of three- and four-beam interactions were frequently observed, and are discussed for a pattern of weak lines crossing a strong line pair. In addition to bending of the lines near intersections, line fragments which cannot be indexed as Kikuchi lines were found; these occur at a distance equal to a reciprocal lattice vector from an ordinary Kikuchi line, and are related to the Kikuchi envelope. In observation of Kikuchi bands it was found that, when the line pair was symmetrically disposed about the central spot, the individual Kikuchi lines were asymmetric, with the deficient part of the band profile inside the line pair. The contrast of these lines is discussed and is related to the interference form factor, $\langle f(\mathbf{s})f^*(\mathbf{s}+\mathbf{h})\rangle$.

Introduction

The purpose of this paper is to present and discuss some dynamical effects in patterns of diffuse scattering from magnesium oxide single crystals; that is, effects due to dynamical interactions with the Bragg scattering. Some of the patterns can be described as the transmission Kikuchi-line patterns which are explained in terms of a simple geometrical consideration given by Kikuchi; in others the excitation of Bragg reflexions by the incident beam leads to fine structure effects and contrast changes in Kikuchi lines which must be explained from the more complete theory of interactions between Bragg scattering and diffuse scattering.

* Present address: Department of Physics, University of Oslo, Blindern, Norway.
† On leave from The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai, Japan.