Acta Cryst. (1969). A25, 471

X-ray Diffraction from Double Hexagonal Close-Packed Crystals with Deformation Stacking Faults

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(*Received* 23 *September* 1968)

The diffraction pattern for a double hexagonal close-packed crystal containing deformation stacking faults is derived under the assumption that the crystal is infinite in size with faults covering entire basal planes and distributed at random. It is found that such faulting broadens only reflexions with $H-K\neq 0$ mod. 3, $L=0$ mod. 4, 1 mod. 4, 2 mod. 4, and 3 mod. 4. The broadening is equal and symmetrical without any shift in the position of the peaks.

Introduction

A double hexagonal close-packed (d.h.c.p.) crystal can be considered as a layer structure produced by the regular stacking of its basal planes in the $ABAC\ldots$ sequence according to the A,B,C notation applied to face-centred cubic (f.c.c.) and hexagonal close-packed (h.c.p.) crystals. The stacking patterns for the normal, as well as for the faulted, d.h.c.p. crystals are shown in Fig. 1. The deformation fault has been introduced respectively at the layers numbered 0 mod. 4, 1 mod. 4, 2 mod. 4, and 3 mod. 4 in Fig. 1(*b*), (*c*), (*d*) and (*e*).

We present in this paper the X-ray diffraction effects for a d.h.c.p. crystal with deformation faults. Our approach is similar to that used in the diffraction theories developed recently for deformation and extrinsic faulting in f.c.c. (Johnson, 1963) and in h.c.p. (Lele, Anantharaman & Johnson, 1967) crystals. This approach is different from the one used by Paterson (1952) and Christian (1954) for deformation faulting in f.c.c. and h.c.p. crystals respectively. The derivation of the diffraction pattern is subject to the following assumptions:

(1) only deformation faults are present;
(2) the crystal is infinite in size and free of distortions;
(3) the scattering power is the same for all the close-packed planes;
(4) there is no change in the lattice spacing at the faults;
(5) the faults are distributed at random;
(6) the faults extend over entire basal planes.

General calculation of the diffracted intensity

In terms of hexagonal basis vectors $\mathbf{A}_1,\mathbf{A}_2,\mathbf{A}_3$, the atoms of a (possibly faulted) d.h.c.p. crystal lie at positions:

$$\mathbf{R}_m=m_1\mathbf{A}_1+m_2\mathbf{A}_2+\tfrac{1}{4}m_3\mathbf{A}_3+\mathbf{f}\,.\,q_m\,, \qquad (1)$$

where $\mathbf{R}_m$ is the position vector of the m_1,m_2 atom in the m_3 layer. The inter-layer spacing is $\frac{1}{4}|\mathbf{A}_3|$ and the offset vector $\mathbf{f}$ is given by:

$$\mathbf{f}=\tfrac{1}{3}(\mathbf{A}_1-\mathbf{A}_2)\,. \qquad (2)$$

Expressing vectors in reciprocal space in terms of the vectors $\mathbf{B}_1,\mathbf{B}_2,\mathbf{B}_3$ and continuous variables h_1,h_2,h_3, the diffracted intensity becomes (Warren, 1959):

$$\begin{aligned} I(h_3)&=\psi^2\sum_{m=-\infty}^{\infty}\langle\exp[2\pi i(H\mathbf{B}_1+K\mathbf{B}_2+h_3\mathbf{B}_3)\,.\,\mathbf{f}(q_{m_3}\\ &\quad -q_{m_3}')]\rangle\exp[2\pi imh_3/4]\\ &=\psi^2\sum_{m=-\infty}^{\infty}\langle\exp[i\Phi_m]\rangle\exp[2\pi imh_3/4]\,, \qquad (3)\end{aligned}$$

where ψ^2 is a function of h_1 and h_2, which vanishes except when $h_1=H$ and $h_2=K$ and the phase difference is given by:

$$\Phi_m=\frac{2\pi}{3}(H-K)(q_{m_3}-q_{m_3}')=\frac{2\pi}{3}(H-K)q_m\,. \qquad (4)$$

From equations (3) and (4), it is clear that only reflexions with $H-K=1$ mod. 3 or 2 mod. 3 are affected

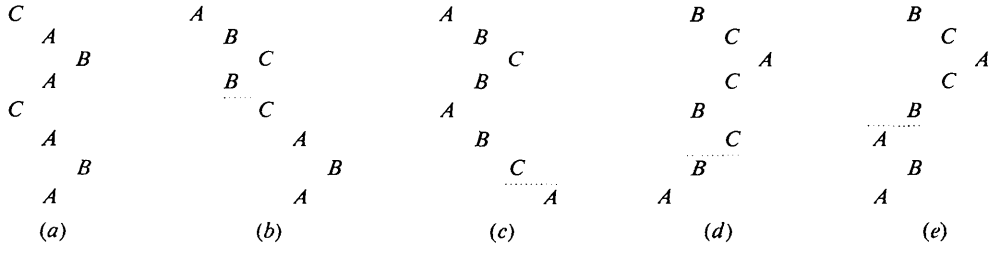

Fig. 1. Stacking sequences for (*a*) perfect d.h.c.p. crystal, (*b*) fault after 0 mod. 4 layer, (*c*) fault after 1 mod. 4 layer, (*d*) fault after 2 mod. 4 layer, and (*e*) fault after 3 mod. 4 layer.

by faulting, while reflexions with $H-K=0$ mod. 3 remain unaffected.

The algebraic signs of phase changes of magnitude $\varphi_0=(2\pi/3)$ across successive planes for perfect as well as faulted crystals are given in Table 1. It may be noted that

$$\left.\begin{aligned}\Phi_0&=0\\ \Phi_{-m}&=-\Phi_m\,.\end{aligned}\right\} \tag{5}$$

Diffraction from a crystal with deformation faults

We shall consider the case $H-K=1$ mod. 3 only, since the case $H-K=2$ mod. 3 is equivalent to it. In the d.h.c.p. crystal, a pair of alternate layers occupies the same position while the other pair of alternate layers occupy different positions. We call layers of the first pair A_1 and A_2 type layers and layers of the second pair B and C type layers. A layer is of A_1 or C type if, in the absence of a fault, the phase difference between it and the succeeding plane is $+\varphi_0$, while it is of A_2 or B type if the phase shift is $-\varphi_0$. Let the phase differences in an m plane sequence starting with planes of the type A_1, B, A_2 and C respectively be $\Phi_m^{A_1}$, Φ_m^B, $\Phi_m^{A_2}$, and Φ_m^C. To determine these phase differences, let the planes be numbered from 0 to m and let k_0, k_1, k_2 and k_3 respectively be the number of faults occurring on planes with numbers of the type 0 mod. 4, 1 mod. 4, 2 mod. 4, and 3 mod. 4. Reference to Table 1 now enables us to write the following expressions for the phase differences:

$$\Phi^{A_1}_{m,k_0,k_1,k_2,k_3}=+\varphi_0\left[\frac{1-(-1)^m}{2}\cdot(-1)^{(m-1)/2}+(k_0+k_1-k_2-k_3)\right],\quad m\geq 0\,; \tag{6a}$$

$$\Phi^{B}_{m,k_0,k_1,k_2,k_3}=+\varphi_0\left[\frac{-1+3(-1)^m-(-1)^{m/2}[1+(-1)^m]}{4}+(k_0-k_1-k_2+k_3)\right],\quad m\geq 0\,; \tag{6b}$$

$$\Phi^{A_2}_{m,k_0,k_1,k_2,k_3}=-\varphi_0\left[\frac{1-(-1)^m}{2}\cdot(-1)^{(m-1)/2}+(k_0+k_1-k_2-k_3)\right],\quad m\geq 0\,; \tag{6c}$$

$$\Phi^{C}_{m,k_0,k_1,k_2,k_3}=-\varphi_0\left[\frac{-1+3(-1)^m-(-1)^{m/2}[1+(-1)^m]}{4}+(k_0-k_1-k_2+k_3)\right],\quad m\geq 0\,. \tag{6d}$$

The probability of getting a phase difference equal to that given by any one of the equations (6*a*) to (6*d*) is just the probability, $P(m,k_0,k_1,k_2,k_3)$, of obtaining k_0,k_1,k_2,k_3 faults on planes of the type 0 mod. 4, 1 mod. 4, 2 mod. 4, 3 mod. 4 respectively in an m plane sequence. Since the probability $P(n_i,k_i)$ of having k_i faults on n_i planes of the type i mod. 4 is independent of the probability $P(n_j,k_j)$ of having j faults on n_j planes of the type j mod. 4 ($i\neq j$), we may write:

$$P(m,k_0,k_1,k_2,k_3)=P(n_0,k_0)\,.\,P(n_1,k_1)\,.\,P(n_2,k_2)\,.\,P(n_3,k_3)\,, \tag{7}$$

where

$$\left.\begin{aligned}&n_0=n_1=n_2=n_3=\frac{m}{4}\ \text{for } m=0 \text{ mod. } 4\,,\\ &n_0=n_2=n_3=\frac{m-1}{4}\,,\ n_1=\frac{m+3}{4}\\ &\qquad\text{for } m=1 \text{ mod. } 4,\\ &n_0=n_3=\frac{m-2}{4}\,,\ n_1=n_2=\frac{m+2}{4}\\ &\qquad\text{for } m=2 \text{ mod. } 4,\\ &n_0=\frac{m-3}{4}\,,\ n_1=n_2=n_3=\frac{m+1}{4}\\ &\qquad\text{for } m=3 \text{ mod. } 4.\end{aligned}\right\} \tag{8}$$

If α is the probability for the occurrence of a deformation fault in the crystal, then

$$P(n_i,k_i)=\binom{n_i}{k_i}\alpha^{k_i}\,.\,(1-\alpha)^{n_i-k_i}\ (i=0 \text{ to } 3)\,, \tag{9}$$

and hence from equation (7), we obtain:

$$P(m,k_0,k_1,k_2,k_3)=\prod_{i=0}^{3}\binom{n_i}{k_i}\alpha^{k_i}\,.\,(1-\alpha)^{n_i-k_i}\,. \tag{10}$$

The expectation value $\langle\exp[i\Phi_m]\rangle$ can now be written down as follows:

Table 1. *Phase changes for perfect and faulted d.h.c.p. crystals (with origin at A_1)*

	$H-K=1$ mod. 3	$H-K=0$ mod. 3
Normal crystal	$\cdots+--++--++\cdots$	...00000...
Fault at 0 mod. 4	$\cdots+---+--++\cdots$	...00000...
Fault at 1 mod. 4	$\cdots---+--++\cdots$	...00000...
Fault at 2 mod. 4	$\cdots++-++--++\cdots$	...00000...
Fault at 3 mod. 4	$\cdots+-+++--++\cdots$	...00000...

$$\langle \exp[i\Phi_m]\rangle = \sum_{k_0=0}^{n_0}\sum_{k_1=0}^{n_1}\sum_{k_2=0}^{n_2}\sum_{k_3=0}^{n_3} \tfrac{1}{4}P(m,k_0,k_1,k_2,k_3) \times \{\exp[i\Phi^{A_1}_{m,k_0,k_1,k_2,k_3}] + \exp[i\Phi^{B}_{m,k_0,k_1,k_2,k_3}] + \exp[i\Phi^{A_2}_{m,k_0,k_1,k_2,k_3}] + \exp[i\Phi^{C}_{m,k_0,k_1,k_2,k_3}]\}, \quad (11)$$

since the probabilities of the occurrence of any one of the four types of layers A_1, B, A_2 and C being at the origin are equal and work out to $\frac{1}{4}$. Substituting from equations (6), (8) and (9) in equation (11) and simplifying, we obtain

$$\langle \exp[i\Phi_m]\rangle = \varrho^m \qquad m=0 \text{ mod. } 4 \;\&\; \geq 0, \quad (12a)$$

$$\langle \exp[i\Phi_m]\rangle = -\frac{1}{2\varrho}\cdot\varrho^m \qquad m=1 \text{ mod. } 4 \;\&\; \geq 1, \quad (12b)$$

$$\langle \exp[i\Phi_m]\rangle = \frac{1}{4\varrho^2}\cdot\varrho^m \qquad m=2 \text{ mod. } 4 \;\&\; \geq 2, \quad (12c)$$

$$\langle \exp[i\Phi_m]\rangle = -\frac{1}{2\varrho}\cdot\varrho^m \qquad m=3 \text{ mod. } 4 \;\&\; \geq 3, \quad (12d)$$

where

$$\varrho = |\alpha \exp[\pm i\varphi_0] + (1-\alpha)| = (1-3\alpha+3\alpha^2)^{1/2}. \quad (13)$$

Combining the equations (12*a*) to (12*d*), we have

$$\langle \exp[i\Phi_m]\rangle = \tfrac{1}{4}\varrho^m\left[\left(1-\frac{1}{\varrho}+\frac{1}{4\varrho^2}\right)+(-1)^{m/2} \times\left(1-\frac{1}{4\varrho^2}\right)+(-1)^m\left(1+\frac{1}{\varrho}+\frac{1}{4\varrho^2}\right) +(-1)^{3m/2}\left(1-\frac{1}{4\varrho^2}\right)\right], \quad m\geq 0. \quad (14)$$

From equations (5) and (14), we have

$$\langle \exp[i\Phi_{-m}]\rangle = \langle \exp[-i\Phi_m]\rangle = \langle \exp[i\Phi_m]\rangle^* = \langle \exp[i\Phi_m]\rangle. \quad (15)$$

Substituting from equations (14) and (15) in equation (3), we obtain for the diffracted intensity

$$I(h_3) = \psi^2\left[1+\sum_{m=1}^{\infty}\frac{\varrho^m}{4}\left\{\left(1-\frac{1}{\varrho}+\frac{1}{4\varrho^2}\right)+(-1)^{m/2} \times\left(1-\frac{1}{4\varrho^2}\right)+(-1)^m\cdot\left(1+\frac{1}{\varrho}+\frac{1}{4\varrho^2}\right) +(-1)^{3m/2}\cdot\left(1-\frac{1}{4\varrho^2}\right)\right\}\right]\{\exp[2\pi i m h_3/4] + \exp[-2\pi i m h_3/4]\}. \quad (16)$$

Carrying out the summations, we get

$$I(h_3) = \frac{\psi^2}{4}\left[\left(1-\frac{1}{\varrho}+\frac{1}{4\varrho^2}\right) \times\left(\frac{1-\varrho^2}{1-2\varrho\cos(\pi h_3/2)+\varrho^2}\right) +\left(1-\frac{1}{4\varrho^2}\right)\frac{1-\varrho^2}{1-2\varrho\cos[\pi(h_3-1)/2]+\varrho^2} +\left(1+\frac{1}{\varrho}+\frac{1}{4\varrho^2}\right)\cdot\frac{1-\varrho^2}{1-2\varrho\cos[\pi(h_3-2)/2]+\varrho^2} +\left(1-\frac{1}{4\varrho^2}\right)\frac{1-\varrho^2}{1-2\varrho\cos[\pi(h_3-3)/2]+\varrho^2}\right]. \quad (17)$$

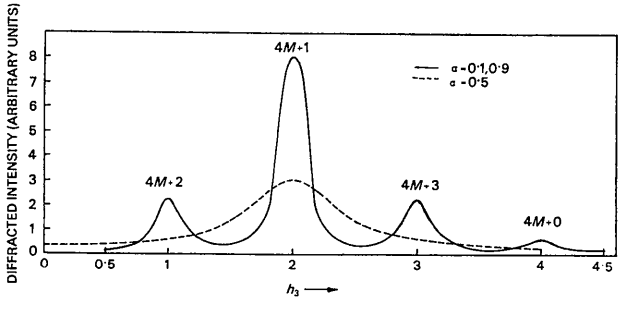

Fig. 2. Diffracted intensity as a function of h_3 for two degrees of faulting.

Description of diffraction effects

The diffraction pattern of a d.h.c.p. crystal containing deformation faults thus consists of sharp peaks corresponding to $H-K=0$ mod. 3 and symmetrically broadened peaks corresponding to $H-K\neq 0$ mod. 3 centred about $L=0$, 1, 2, and 3 mod. 4. There is no shift of peak position for any value of the faulting probability.

The integrated intensities T_0, T_1, T_2 and T_3 for reflexions with $H-K\neq 0$ mod. 3 and $L=0$ mod. 4, 1 mod. 4, 2 mod. 4, and 3 mod. 4 respectively can be readily found by taking the relevant term in equation (17) and integrating it with respect to h_3 within appropriate limits. The final results are:

$$T_0 = \psi^2\left(1-\frac{1}{\varrho}+\frac{1}{4\varrho^2}\right), \quad (18a)$$

$$T_1 = \psi^2\left(1-\frac{1}{4\varrho^2}\right), \quad (18b)$$

$$T_2 = \psi^2\left(1+\frac{1}{\varrho}+\frac{1}{4\varrho^2}\right), \quad (18c)$$

$$T_3 = \psi^2\left(1-\frac{1}{4\varrho^2}\right). \quad (18d)$$

For $\alpha=0$ or 1 (*i.e.* $\varrho=1$), T_0, T_1, T_2 and T_3 have the values $\psi^2/4$, $3\psi^2/4$, $9\psi^2/4$ and $3\psi^2/4$ respectively, which are characteristic of a perfect d.h.c.p. crystal. As α increases from 0, intensity is transferred from the other three reflexions to the peaks centred at $L=2$ mod. 4. At $\alpha=0{\cdot}5$, only the peaks centred at $L=2$ mod. 4

remain, while those at $L=0$, 1, and 3 mod. 4 vanish. As α increases further, there is reversal of the process until at $\alpha=1{\cdot}0$, the crystal becomes a perfect d.h.c.p. crystal again. The per cent values of T_0, T_1, T_2 and T_3, and T_2/T_1 have been given in Table 2 for a few selected values of α.

Table 2. *X-ray diffraction effects of deformation faults in d.h.c.p. crystals*

α	β	T_0	T_1	T_2	T_3	T_2/T_1
0·00	0·00	6	19	56	19	3·00
0·05	0·16	5	18	59	18	3·35
0·10	0·32	4	16	64	16	4·00
0·15	0·48	3	15	67	15	4·50
0·20	0·64	2	13	72	13	5·52
0·30	0·98	1	8	83	8	10·35
0·40	1·24	1	7	85	7	12·00
0·50	1·33	0	0	100	0	∞

The integral breadths of all the broadened reflexions are equal and given by

$$\beta=4\cdot\frac{1-\varrho}{1+\varrho}\ (\simeq 3\alpha\ ,\ \alpha\ll 1)\ . \tag{19}$$

Some values of β are given in Table 2.

The Fourier series expansion of the broadened component of the intensity about $h_3=L$ is obtained by writing equation (3) in the form

$$I(h_3)=\psi^2\sum_{m=-\infty}^{\infty}A_m\exp\left[2\pi im(h_3-L)/4\right] \tag{20}$$

with

$$A_m=\exp\left[2\pi imL/4\right]\langle\exp\left[i\Phi_m\right]\rangle\ . \tag{21}$$

Discussion of results

The present work has shown that the X-ray diffraction effects of random deformation faults in a d.h.c.p. structure are very similar to those in an h.c.p. structure. For both structures, the broadening of all the reflexions with $H-K\neq 0$ mod. 3 is symmetrical and equal to 3α for small values of α without any shifts in the positions of the peaks. Also, in both cases, there is a transfer of intensity to reflexions centred at $L=2$ mod. 4 from the remaining reflexions (Fig. 2). For f.c.c. structures also, deformation faults give rise to symmetric broadening of reflexions, the integral breadths being again equal to 3α. However, there is no transfer of intensity in this case and positions of the peaks are shifted, unlike the cases of the h.c.p. and d.h.c.p. crystals.

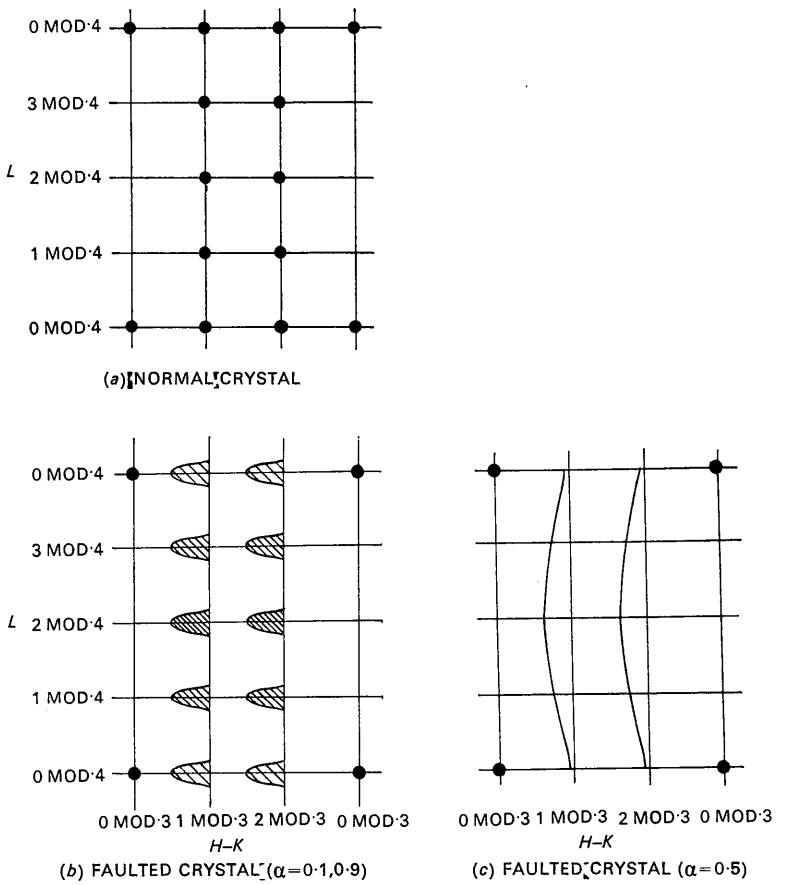

Fig. 3. Reciprocal space intensity maps for normal and faulted crystals.

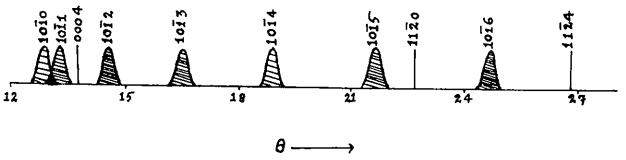

Fig. 4. Schematic powder pattern for faulted crystals ($\alpha = 0{\cdot}1$, $0{\cdot}9$).

The reciprocal lattice and the powder pattern (schematic) for deformation-faulted d.h.c.p. crystals are illustrated in Figs. 3 and 4. The nature of the powder pattern suggests a possible method of determining α in practice. Consider the pair of reflexions 0004 and $10\bar{1}2$, the first of which is unaffected by faulting, while the second is affected. If we assume that the broadening of the two reflexions by all factors other than faulting is equal, then the broadening resulting from these other factors can be removed from the total broadening of the $10\bar{1}2$ reflexion by the method due to Stokes (1948), yielding the fault broadening and thus α. Alternatively, α can be evaluated, although not so accurately, from a comparison of the ratios of the integrated intensities of reflexions with different values of L (Table 2).

The rare earth metals lanthanum, cerium (below -10 °C), praseodymium, neodymium and americium are known to exhibit the d.h.c.p. structure (Barrett & Massalski, 1966) besides many intermetallic compounds. Interesting results may be expected from X-ray diffraction studies of these metals and alloys after deformation.

Two of the authors (S.L. and B.P.) wish to thank the University Grants Commission, New Delhi, for the award of Research Fellowships.

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Acta Cryst. (1969). A**25**, 475

The Effects of *n*-Beam Dynamical Diffraction on Electron Diffraction Intensities from Polycrystalline Materials

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(*Received* 29 *October* 1968)

Calculations based on *n*-beam dynamical diffraction theory have shown that the intensities of rings and arcs in diffraction patterns from polycrystalline materials are strongly dependent on the experimental conditions. For arc patterns from BiOCl, calculations confirm a revised formula for the intensities from very thin crystals and indicate dependences on the distributions of orientation, thickness and bending of the crystals which are sufficient to account for the wide deviations of recent experimental results from the predictions of the primary extinction formula, based on the two-beam approximation. Inferences regarding the possible errors in electron diffraction analysis of crystal structures, especially for materials containing heavy atoms, are drawn from calculations relating to the intensities of arc patterns from $AgTlSe_2$. It is suggested that *n*-beam calculations should be made in order to avoid serious error in the refinement stages of a structure analysis.

Introduction

The presence of dynamical diffraction effects in the intensities of electron diffraction ring patterns from polycrystalline materials has been recognized for many years through the success of the primary extinction formula of Blackman (1939); see, *e.g.*, Kuwabara (1957). However, the use of accurate electronic recording equipment and of filters to remove inelastically scattered electrons has revealed significant discrepancies between experimental results and the theoretical values based on the assumption of two-beam dynamical conditions. Thus Horstmann & Meyer (1962) found that the 400 and 222 intensities in ring patterns from polycrystalline aluminum did not lie on the primary extinction curve, and Wedel (1963) reported similar, but larger discrepancies in the case of silver. Recently Kuwabara, Turner & Cowley (1966) and Kuwabara (1967) have shown that intensities in arc patterns from

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