



dimensional informations about the structure of matter, that is the lattice parameters of a crystal cell, lattice mismatches (the relative variation in lattice parameters) in layered materials, diffraction phase, and the relative positions of atoms and molecules in crystal unit cell. Therefore multiple diffraction techniques have been widely applied. Efforts of the field include: the determination of lattice parameters, characterization of three-dimensional lattice mismatches between epitaxial layers and substrates, experimental determination of x-ray diffraction phases and their first application, in conjunction with direct method, to crystal structure determination. In addition applications to x-ray optics involve the multi-beam monochromators, a multi-beam interferometer, x-ray standing-wave excitation-fluorescence technique and so on. Chang has given extremely good reviews [10, 11].

Part I introduces the principle, experimental methods of obtaining multiple diffraction pattern. Indexing of pattern and some applications can read part II of this paper.

## I. Principle, Experimental Method

### 1. Basic Principle of Multiple Diffraction

Multiple diffraction depends not only on the structure of matter but also on the radiation employed. In other word, the occurrence of multiple diffraction depends not only on the geometry of crystal itself, but also on the relative arrangement of incident radiation with the crystal. These geometrical factors are the interatomic distances, the space group which the

crystal belongs to, the wavelength of incident xray and experimental arrangement.

### 1.1. Geometry of Multiple Diffraction

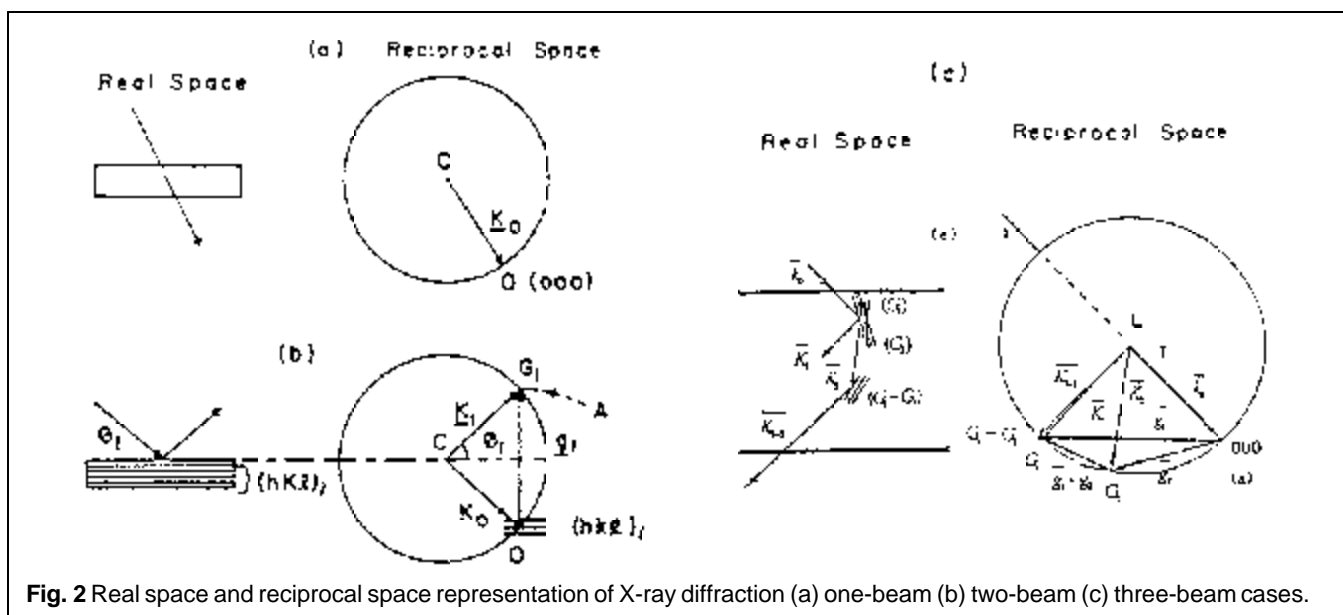
No Bragg reflection occurs when a crystal is arranged so that Bragg's law is not satisfied for any set of atomic planes, this situation can be represented as shown in Fig. 2(a), where only the origin O of the reciprocal lattice [with Miller indices (000)] is set on the surface of Ewald sphere. This case is often referred to as onebeam diffraction, only involving the incident beam. If the crystal is tilted so that an additional reciprocal lattice point A is brought onto the surface of the Ewald sphere at point  $G_1$ , Bragg's law is then satisfied

$$\mathbf{k}_0 + \mathbf{g}_1 = \mathbf{k}_1$$

$$\mathbf{k}_0 \perp \mathbf{g}_1 = -g_1^2/2 \quad (1)$$

where the vectors  $\mathbf{k}_0$  (=CO) and  $\mathbf{k}_1$  (=CG<sub>1</sub>) are the wavevectors of the incident and reflected beams and  $\mathbf{g}_1$  (=OG<sub>1</sub>) is the reciprocal lattice vector of the (hkl)<sub>1</sub> planes. The angle  $\theta_1$  is the Bragg angle of the  $G_1$  reflection. If the two wavevectors  $\mathbf{k}_0$  and  $\mathbf{k}_1$  are symmetric about the crystal surface, this two-beam case is symmetric Bragg reflection, but if the crystal surface is parallel to OG<sub>1</sub>, this is a symmetric Laue reflection, because the diffracted vectors  $\mathbf{k}_0$  and  $\mathbf{k}_1$  are symmetric about crystal surface normal and transmit through the crystal.

If now the crystal is rotated around OG<sub>1</sub> without disturbing  $G_1$  to bring N-2 additional reciprocal



lattice points onto the surface of the Ewald sphere,  $N-1$  sets of planes with reciprocal lattice vectors  $\mathbf{g}_1, \mathbf{g}_2, \dots, \mathbf{g}_{N-1}$  satisfying simultaneously Bragg's conditions, and  $N$ -beam diffraction (including incident beam  $\mathbf{O}$ ) occur. A three-beam case,  $\mathbf{O}, \mathbf{G}_1, \mathbf{G}_2$  is illustrated in Fig. 2(c). For convenience, the reflection  $\mathbf{G}_1$  is called the "primary" reflection and  $\mathbf{G}_2$  is called the "secondary". The vector  $\mathbf{G}_2 - \mathbf{G}_1 (= \mathbf{g}_2 - \mathbf{g}_1)$  indicates the reciprocal lattice vector of coupling reflection  $\mathbf{G}_2 - \mathbf{G}_1$ , i.e.  $h_2 - h_1, k_2 - k_1, l_2 - l_1$ . The geometrical conditions for this  $N$ -beam diffraction are the following:

$$\begin{aligned} \mathbf{k}_0 - \mathbf{g}_i &= -\mathbf{g}_i^2/2 \\ \mathbf{k}_i \cdot (\mathbf{g}_j - \mathbf{g}_i) &= -|\mathbf{g}_j - \mathbf{g}_i|^2/2 \end{aligned} \quad (2)$$

where  $i \neq j$ . For a three-beam case

$$\begin{aligned} \mathbf{k}_0 - \mathbf{g}_1 &= -\mathbf{g}_1^2/2 \\ \mathbf{k}_1 \cdot (\mathbf{g}_2 - \mathbf{g}_1) &= -|\mathbf{g}_2 - \mathbf{g}_1|^2/2 \end{aligned} \quad (3)$$

If all the wavevectors  $\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_{N-1}$  are transmitted through the crystal, one can obtain  $N$ -beams Laue diffraction or an  $N$ -beam Borrmann diffraction. The case when the  $N$ -beam diffraction involves at least one Bragg reflection is called Bragg-type multiple diffraction. When one of the diffracted beams is directed along the crystal surface, the case is called Bragg surface diffraction. When a  $N$ -beam Bragg-type multiple diffraction involves a symmetric Bragg reflection  $\mathbf{G}_i$ , these three Bragg cases can be distinguished by the conditions

$$\mathbf{g}_i \cdot \mathbf{g}_1 \begin{cases} \geq \\ < \end{cases} \mathbf{g}_i^2/2 \quad (4)$$

where the equality ('=') is for the Bragg surface case, the greater than and less than sign are for the Bragg-Bragg and Bragg-Laue cases respectively. For a more general case, the direction cosine ( $\gamma = \mathbf{n} \cdot \mathbf{k} / k$ ) of the diffracted vector  $\mathbf{k}$  is used. For  $\gamma=0$ , the diffraction is a surface case. For  $\gamma < 0$  and  $\gamma > 0$ , the cases are Bragg and Laue, respectively. Here  $\mathbf{n}$  is the inward-pointing crystal surface normal.

### 1.2. Coplanar and Non-coplanar Multiple Diffractions [5]

Most multiple diffractions are usually either lattice-vector coplanar, or wave-vector coplanar. In the former case, all the reciprocal lattice vector (or reciprocal lattice points) lie in a plane which intersect the Ewald sphere. All the reciprocal lattice points are

circumscribed by a circle which is so-called reflection circle, whose radius  $\gamma_0$  is smaller than that of the Ewald sphere. The conditions for this kind of multiple diffraction are

$$\begin{aligned} \gamma_0 &= \mathbf{g}_i \cdot \mathbf{g}_j / (2 |\mathbf{g}_i \times \mathbf{g}_j|) \\ (\mathbf{g}_i \times \mathbf{g}_j) \cdot \mathbf{g}_1 &= 0 \end{aligned} \quad (5)$$

for  $i \neq j \neq 1 \neq i$ . Since the radius is independent of wavelength, this type of diffraction occurs for all wavelength of incident radiation. Therefore it is called persistent or systematic multiple diffraction and depends only on the crystal symmetry. In this case involved all the reflection planes have a common zone axis  $\mathbf{z}$ , i.e. all the  $\mathbf{g}$  vectors are perpendicular to  $\mathbf{z}$ . When  $\gamma_0$  is equal to  $1/\lambda$ , not only the end points of reciprocal lattice vectors, but also those of the wavevectors lie on the great circle of Ewald sphere. This type of diffraction is called coincidental multiple diffraction. Obviously it occurs for only one specific wavelength.

However there is another type of coincidental, the non-coplanar multiple diffraction, for which the reciprocal lattice points involved do not lie in a plane, but lie on the surface of Ewald sphere. On particular occasion, both persistent and coincidental multiple diffractions can occur simultaneously for a given wavelength. For example the eight-beam (000) (022) (022) (004) (311) (311) (313) (313) diffraction of diamond for  $\text{CuK}\alpha_1$  is a case, (022), (022) and (004) have a common zone axis [100] and persistent multiple diffraction occurs, while the rest of the reflections are involved in a non-coplanar coincidental diffraction.

### 1.3. Intrinsic Multiple Diffraction

The number of reciprocal lattice points involved in multiple diffraction determines the number of diffracted beams. In the coplanar case, this number depends on the symmetry of the reciprocal lattice plane containing these reciprocal lattice points and on the relative position of the reflection circle with respect to the lattice points in this two-dimensional plane.

A particular interest case is that one of the reflections involved has its reciprocal lattice vector, with magnitude equal to the diameter of the reflection circle, lying in a horizontal plane which contains the incident beam. Under this condition, whenever this particular reflection is aligned for diffraction in the horizontal plane, the other reflection planes are auto-

matically in positions to diffract an incident beam. In other words, this particular reflection is always accompanied by multiple diffraction. This case is called intrinsic multiple diffraction [12]. Fig. 3 shows example for three-, four-, five-, six- and eight-beam intrinsic diffraction. Since the diameter of the reflection circle must coincide with one of the reciprocal lattice vectors, the position of reflection circle is fixed. The condition for the occurrence of N-beam cases, in relation to the symmetry of reciprocal plane lattice, can therefore be obtained.

This plane lattice can be described in two basic vector,  $v_1, v_2$ . All the reciprocal lattice points in the plane lattice are defined by linear sums of two basic vectors,  $p_1v_1+p_2v_2$ . According to Burbank [12], there are six plane lattice and their existent cases in seven crystal system and the generalized conditions for multiple diffraction are following:

1) **Oblique:**  $v_1 \neq v_2$  and the angle  $\alpha$  between the two vectors is neither  $60^\circ$  nor  $90^\circ$ . All reflection plane normals for triclinic;  $\langle 010 \rangle \langle 0kl \rangle \langle hk0 \rangle$  and  $\langle hkl \rangle$  for monoclinic;  $\langle hkl \rangle$  for orthorhombic, tetragonal and cubic;  $\langle hkil \rangle$  for hexagonal. Two-beam diffraction occurs only.

2) **Primitive rectangular:**  $v_1 \neq v_2, \alpha=90^\circ$ ; monoclinic:  $\langle 100 \rangle \langle 001 \rangle \langle h0l \rangle$ ; orthorhombic:  $\langle 100 \rangle \langle 110 \rangle \langle 001 \rangle \langle 0kl \rangle \langle h0l \rangle \langle hk0 \rangle$ ; tetragonal:  $\langle 100 \rangle \langle 010 \rangle \langle hhl \rangle \langle h0l \rangle \langle 110 \rangle \langle hk0 \rangle$ ; cubic:  $\langle 100 \rangle \langle 110 \rangle \langle hk0 \rangle \langle hhl \rangle$ ; hexagonal:  $\langle 10\bar{1}0 \rangle \langle 1120 \rangle \langle hki0 \rangle \langle h0\bar{h}l \rangle \langle hh2h0 \rangle$ ; four-beam diffraction takes place for non-zero  $p_1$ , and  $p_2$ .

3) **Centered rectangular:** Primitive rectangular lattice with an additional lattice point at  $(v_1+v_2)/2$ , the conditions in seven system are the same 2). The four-

beam diffraction occurs for non-zero integral  $p_1$  and  $p_2$ .

4) **Rhombohedral rectangular:** Primitive rectangular lattice plus two additional lattice points at  $(v_1+v_2)/3, 2(v_1+v_2)/3$ , or at  $-(v_1+v_2)/3, -2(v_1+v_2)/3$ , Cubic:  $\langle hhh \rangle$  and Rhombohedral:  $\langle hhh \rangle$ . One-thirds of the reflection have integral  $p_1$  and  $p_2$ , two-thirds have non-integral  $p$ 's. Four-beam diffraction occurs only for non-zero integral  $p_1$  and  $p_2$ .

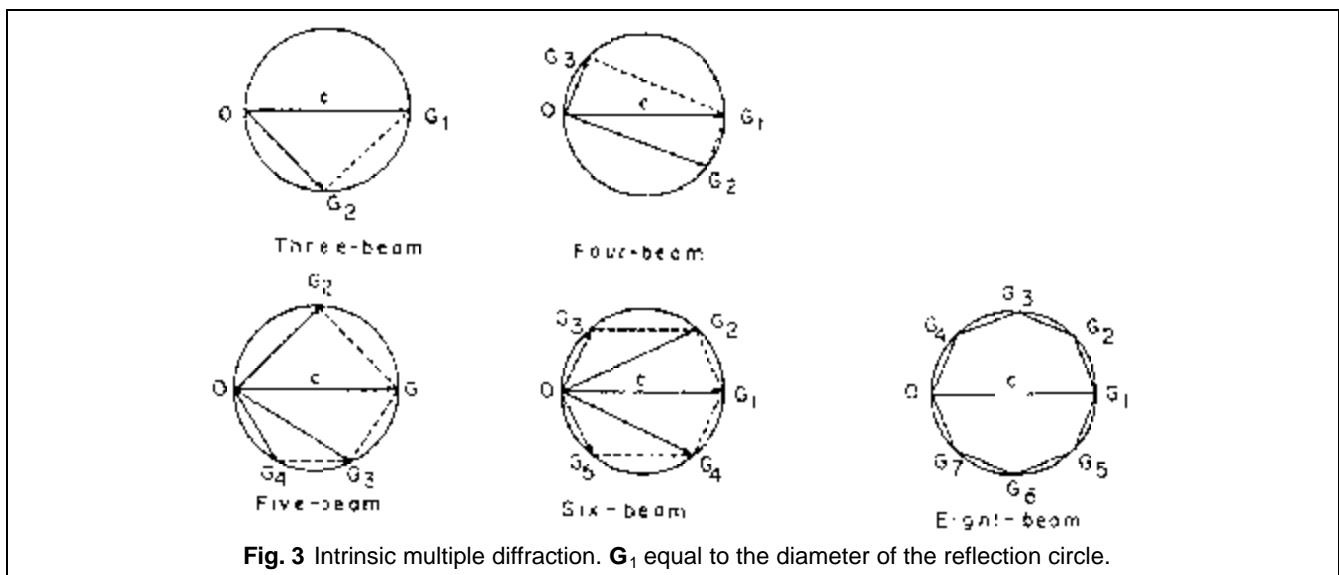
5) **Hexagonal:**  $v_1=v_2, \alpha=60^\circ$ , they present in cubic  $\langle hhh \rangle$  and hexagonal  $\langle 0001 \rangle$ . Four-beam diffraction occurs for odd non-zero  $p_1$  and  $p_2$ , six-beam diffraction occurs for even  $p_1$  or  $p_2=0$  or  $p_1=2$ . Twelve-beam diffraction takes place for even non-zero  $p_1$  and  $p_2$  and  $p_1=p_2$ .

6) **Square:**  $v_1=v_2, \alpha=90^\circ$ . There are these square in cubic  $\langle h00 \rangle \langle 0k0 \rangle \langle 00l \rangle$  and tetragonal  $\langle 00l \rangle$ . The four-, eight-, twelve-, and sixteen-beam cases have been noted [12] for even  $p$ 's, four-, six-, eight-, and twelve-beam cases for odd  $p$ 's.

#### 1.4. Multiple Diffraction Possibilities

The number  $N_{G1}$  of possible multiple diffraction for a given crystal and radiation depends on the crystallographic space group, and on the size of Ewald sphere and the crystal unit cell. According to Prager [13], this number can be estimated from the number of reciprocal lattice points of secondary reflection in the volume  $v^*$  swept out by the surface of the Ewald sphere during a full rotation around the primary reflection vector  $G_1$ . If volume of the reciprocal lattice is  $V^*$  number  $N_{G1}$  is proportional to the ratio  $v^*/V^*$ , i.e.

$$N_{G1} = 2a_{G1}v^*/V^* = 27\pi^2 a_{G1}V\lambda^{-3} \cos \theta_{G1} \quad (6)$$

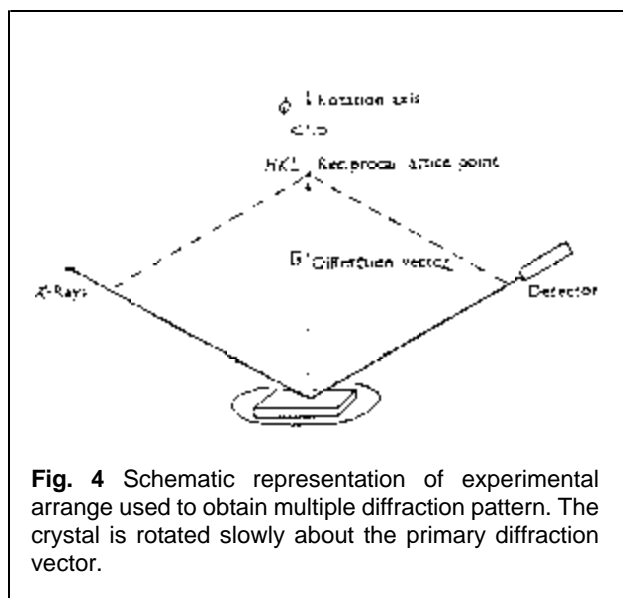


where the volume  $v^*$  is approximately equal to area  $\pi(1/\lambda)^2$  times of the locus of the reflection of the center  $c$ ,  $2\pi(\cos \theta_{G_1}/\lambda)$ .  $\theta_{G_1}$  is Bragg angle of  $G_1$  reflection and  $V$  is the volume of the unit cell. The factor 2 is due to the secondary reciprocal points within the volume  $v^*$  entering and leaving the Ewald sphere. The term  $a_{G_1}$  take care of the systematic extinction of reflection the space group. For example, in the diamond structure, which belongs to the space group  $Fd\bar{3}m$ ,  $(hkl)$  reflections with  $h+k+l=4n\pm 2$  are forbidden reflections. For a given three-beam,  $O$ ,  $G_1$ ,  $G_2$ , diffraction, if two of the three reflection,  $G_1$  (primary),  $G_2$  (secondary) and  $G_2-G_1$  (coupling) are forbidden by space group, no relative intensity variation can be detected. If the primary reflection is a reflection with  $h+k+l=4n\pm 2$ , the secondary reflection is a reflections must involve all odd Miller indices so that the corresponding coupling reflection do not belong to the class  $h+k+l=4n\pm 2$ . In this case  $a_{G_1}$  must be  $1/8$ . Since there is only-half chance of having odd number for each index.

## 2. Experimental Methods of Obtaining Multiple Diffraction Pattern

### 2.1. Collimated-Beam Method

One may know from basic principle of multiple diffraction that the key of experimental method is that sample crystal must slowly be rotated around the diffraction vector, as shown schematically in Fig. 4, Renninger [1] used a collimated X-ray beam and an ionization chamber for intensity detection. Williamson and Fankuchen [14] used a double-crystal



**Fig. 4** Schematic representation of experimental arrange used to obtain multiple diffraction pattern. The crystal is rotated slowly about the primary diffraction vector.

spectrometer to improve the linewidth of multiple diffraction peaks. Cole et al [15] utilized a 2m long evacuated pipe with collimators to confine the beam divergence to 1 to 2 minutes of arc. These methods are called the collimated-beam technique. In these methods, a crystal is first aligned for a simple Bragg (two-beam) reflection, say reflection  $G_1$ . The crystal is then rotated around the reciprocal lattice vector of reflection  $G_1$  without disturbing the setting for this reflection, to bring additional sets of atomic plane in position where they satisfy the Bragg condition. A detector is always placed in the position to monitor the  $G_1$ -relation beam. The concrete methods have ....

### 2.1.1. The Powder Diffractometer to add Rotation Equipment

During using the powder diffractometer to carry out research of crystal wafer, the wafer may be rocked around the diffractometer axis to obtain the optimum orientation of wafer and diffraction intensity maximum. Sometimes the crystal wafer is rotated around the normal of the wafer surface. The latter movement is called the  $\phi$  rotation [16], its rotation speed can be adjusted and rotation range is from  $0^\circ$  to  $360^\circ$ . If the orientation of wafer  $(hkl)$  is very exact, utilizing this  $\phi$  rotation equipment can obtain multiple diffraction patterns. However the wafer orientation generally often exist a deviation, the wafer should be rocked around the axis which is parallel to diffractometer axis, but not directly around diffractometer axis. So that the crystal wafer can be rotated around diffraction vector.

### 2.1.2. Double Crystal Diffractometer and Topographic Methods

For double crystal diffractometer, specially one is controlled by computer, it is easy to realize the rotation about diffraction vector. Therefore one may carry out the multiple diffraction pattern and topographic research of the crystal.

For symmetric Laue case topography, it isn't difficult to realize rotation about diffraction vector. So that one can carry out multiple diffraction topographic research of the near perfect crystal using Lang and Borrmenn methods.

### 2.1.3. Four-Circle Diffractometer

There are  $\phi$ ,  $\chi$ ,  $\omega$  and  $2\theta$  four circles in horizontal-type four-circle diffractometer circle is a rotation circle of crystal holder on which the crystal is installed.  $\chi$  is vertical circle on which crystal holder is rotated about  $\chi$  axis. The action of these two circle,  $\phi$  and  $\chi$ , is that diffraction place is adjusted into vertical

plane position, then this diffraction plane is moved into Bragg's position pass through  $\omega$  axis rotation.  $2\theta$  circle is rotation circle of the detector. The two circles ( $\omega$  and  $2\theta$ ) are set a in horizontal plane and are co-axial.

If one want to use four-circle diffractometer for carrying out multiple diffraction research, it has to add a axis which ought be perpendicular to the  $\omega$  axis and must rotate with  $\omega$  axis rotation to remain this additional axis always is perpendicular to primary diffraction plane. For vertical-type four-circle diffractometer ( $\omega$  and  $2\theta$  axis's are the horizontal position), this additional axis ought are set the vertical position and be perpendicular to  $\omega$  axis and be moved with  $\omega$  axis rotation the rotation is called a  $\psi$ -scan. This diffractometer is called five-circle diffractometer.

Truly,  $\psi$ -scan is a combined movement of three circles ( $\phi, \chi, \omega$ ) of four-circle diffractometer, see part II of this paper.

## 2.2. Divergent-Beam Technique

In collimated-beam method mentioned above, the purpose of crystal rotation is to make the reciprocal lattice of the crystal rotating, but reflection sphere remains static and motionless. Another method utilizing a rotation of the x-ray source can also reach the purpose of obtaining multiple diffraction. The most convenient way of simulating the rotation of the xray source is to use a very divergent incident beam. The divergent beam method is called Kossel technique. When several cones which forms Kossel lines intersect each other, multiple diffraction occur at the intersection points [5].

## II. Indexing of Peaks and Applications

### 3. Indexing of Multiple Diffraction Patterns

#### 3.1. ReferenceVectorMethod[15,10]

During the rotation of a crystal in the generation of multiple diffraction, each secondary reciprocal lattice point enters and leaves the Ewald sphere, or vice versa, see Fig. 5. Fig. 5(b) is the projection of Fig. 5(a) on the plane perpendicular to primary reflection vector OG. The point of enter and exis are denoted as 'IN' and 'OUT'. For simpling, vector  $\mathbf{g}$  and  $\mathbf{p}$  are used as reciprocal lattice vectors of the primary and the secondary reflections. The vectors  $\mathbf{p}_n$  and  $\mathbf{p}_p$  are the components of the vector  $\mathbf{p}$ , perpendicular and parallel to  $\mathbf{g}$ . Vector  $\mathbf{v}$  is a unit vector in a reference direction  $\mathbf{V}$  which is usually chosen to be perpen-

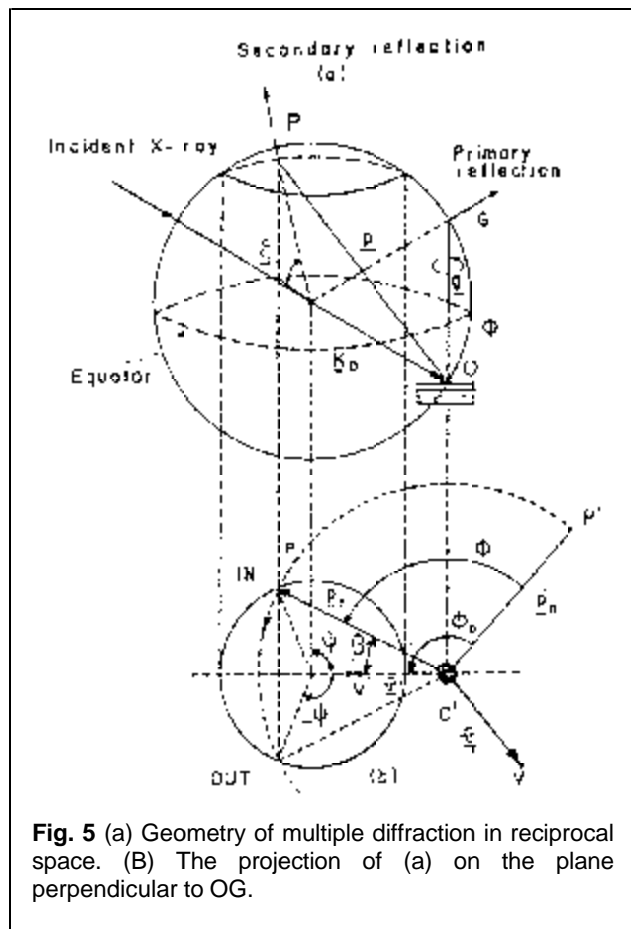


Fig. 5 (a) Geometry of multiple diffraction in reciprocal space. (B) The projection of (a) on the plane perpendicular to OG.

dicular to  $\mathbf{g}$ ;  $\mathbf{u}$  denotes the unit vector of any vector  $\mathbf{U}$ . Suppose that initially the reference unit vector  $\mathbf{v}'$  lies in the plane if incidence of the  $\mathbf{G}$  reflection along the line  $\mathbf{o}\mathbf{v}'$  and that  $\mathbf{p}_n'$  lies along  $\mathbf{O}\mathbf{P}'$  as Fig. 5(b) shows. The angle  $\phi_0$  between  $\mathbf{O}\mathbf{V}'$  and  $\mathbf{O}\mathbf{P}'$  is equal to the angle between  $\mathbf{O}\mathbf{V}$  and  $\mathbf{O}\mathbf{P}$ , because the crystal rotation does not change the angle between any pair of reciprocal lattice vectors. Points V and P are the positions of V' and P' after the crystal has been rotated by an angle so as to give multiple diffraction. The azimuth angle are

$$\phi_1 = \phi_0 - \beta \quad \phi_2 = \phi_0 + \beta \quad (7)$$

for the IN and OUT position respectively, where

$$\beta = \text{Cos}^{-1}(\mathbf{p}_n \mathbf{v}') \quad (8)$$

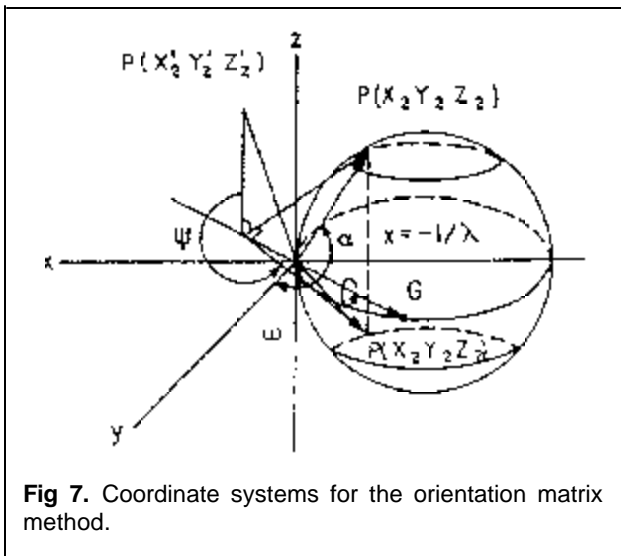
$$\mathbf{V}' = (\mathbf{k}_0 + \mathbf{g}/2) / |\mathbf{k}_0 + \mathbf{g}/2| \quad (9)$$

or

$$\text{Cos}\beta = (p^2 - p_p g)^{1/2} / 2 p_n [(1/\lambda)^2 - (g^2/4)]^{1/2} \quad (10)$$

$$[(1/\lambda)^2 - (g/2)^2]^{1/2} \text{Cos}\beta = (p^2 - p_p g)^{1/2} / 2 p_n = C_{GP} \quad (11)$$





**Fig 7.** Coordinate systems for the orientation matrix method.

Let us consider the Ge (222) multiple diffraction pattern for CuK $\alpha_1$  (Fig. 6). Germanium has a diamond structure and belong to the F3dm space group. The [222] direction has three-fold symmetry. Rotation around [111] axis generates six-fold symmetry. Therefore, multiple diffraction peaks involving equivalent secondary and coupling reflection should appear that every sixty degree in azimuth angle  $\phi$  is a period. Fig. 6 is such an asymmetric portion of the multiple diffraction pattern. The angle  $\phi=0^\circ$  and  $\phi=30^\circ$  correspond to [110] and [121] respectively. The indexing results of Fig. 6 is given in Tab. 1, [110], [011] and [101] are chosen to be reference vectors and correspond to A, B and C respectively. A and C in Tab. 1 are equivalent, but they are different from B, because the [222] axis is three-fold symmetry rather than six-fold symmetry. The ambiguity is often encountered in indexing multiple diffraction pattern, especially for high symmetric crystals. Chang and Catcha-Ellis [17] proposed an experimental way of distinguishing between the two cases. One of cases involves a Bragg-type secondary reflection, say case A or C (Bragg-Bragg), and other a transmission (Laue) reflection, case B (Bragg-Laue). It is easy to distinguishing the BraggBragg case from the Bragg-Laue case by detecting the secondary reflection: if the situation conforms to A or C, the secondary reflection would be measurable on the same side of the crystal as the incident beam, while in case B, the secondary reflection would be detected on the other side of the crystal.

### 3.2. Orientation Matrix Method [18, 10]

Han and Chang [18] replaced the reference vector by an orientation matrix which specifies the initial

position of a crystal on a four-circle xray single-crystal diffractometer. In a four-circle diffractometer, rotation around a primary diffraction vector is called a  $\psi$ -scan which is a combined movement of three circle of the diffractometer, i.e., the rotation angle  $\phi$ ,  $\chi$ , and  $\omega$ . This can be described by the product of three rotation matrix  $M_{\phi}$ ,  $M_{\chi}$ ,  $M_{\omega}$ , about the  $\phi$ ,  $\chi$  and  $\omega$  rotation axes.

$$M_r = M_{r\phi} M_{r\chi} M_{r\omega} =$$

$$\begin{bmatrix} \sin\phi \cos\chi \sin\omega + \cos\omega \cos\phi & & & \\ -\sin\phi \cos\chi \sin\omega + \cos\phi \sin\omega & & & \\ & \sin\phi \sin\chi & & \\ -\cos\phi \cos\chi \sin\omega + \cos\omega \sin\phi & & -\sin\chi \sin\omega & \\ \cos\phi \cos\chi \cos\omega + \sin\phi \sin\omega & & \sin\chi \cos\omega & \\ & -\cos\phi \sin\chi & & \cos\chi \end{bmatrix}$$

(16)

Supposing the initial orientation matrix is  $M_{0r}$ , with  $\phi$ ,  $\chi$  and  $\omega$  equal to zero, the product of  $M_r$  and  $M_{0r}$  yields a new orientation matrix  $M_{0r}'$

$$M_{0r}' = M_r M_{0r} \quad (17)$$

The initial position ( $X_2'Y_2'Z_2'$ ) of the secondary reciprocal lattice point can be determined by using the matrix  $M_{0r}'$  as an operator. Fig. 7 shows the coordinates and the angular relation between  $\phi$ ,  $\chi$  and  $\omega$  when P is brought onto surface of the Ewald sphere. The position ( $X_2Y_2Z_2$ ) of P can be determined from

$$\begin{aligned} X_2'^2 + Y_2'^2 + Z_2'^2 &= \overline{OP}^2 \\ (X_2 + 1/\lambda)^2 + Y_2^2 + Z_2^2 &= 1 \\ (Y_2 - Y_2') / (X_2 - X_2') &= \tan\omega \end{aligned} \quad (18)$$

where

$$\begin{aligned} X_2' &= -p \cos\alpha \sin\omega \\ Y_2' &= -p \cos\alpha \cos\omega \\ Z_2' &= p \end{aligned} \quad (19)$$

The double solutions for equation (19) are

$$\begin{aligned} X_2 &= -\lambda p^2 / 2 \\ Y_2 &= Y_2' + (X_2 - X_2') \tan\omega \\ Z_2 &= \pm [p^2 + X_2^2 - Y_2^2]^{1/2} \end{aligned} \quad (20)$$

for the entering (positive  $Z_2$ ) and leaving (negative  $Z_2$ ) situation. From ( $X_2'Y_2'Z_2'$ ) and ( $X_2Y_2Z_2$ ), the angular distance between the starting position and the multiple diffraction peak is obtained.

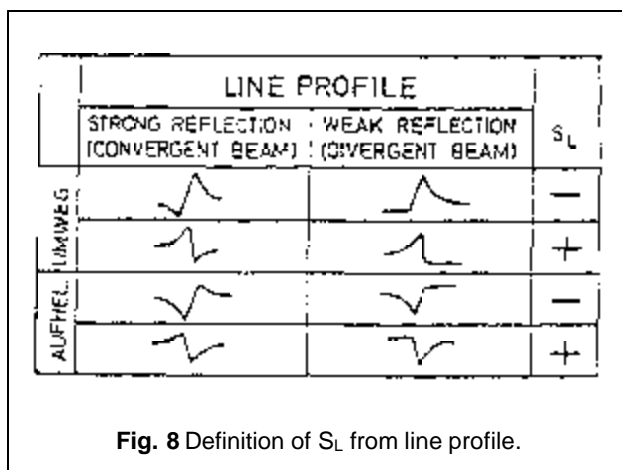
## 4. Some Applications of Multiple Diffraction

### 4.1. Experimental Determination of Diffraction Phase

On the basis of calculation of the triple product of the structure factors, structure invariant quantity,  $F_G F_P F_{G-P}$ , and the asymmetry of the profile bottom of multiple diffraction peak, one can obtain the diffraction phase [19]. Experimental methods of determining phase has:

1. Three-Beam Borrmann Diffraction Method [20, 21]
2. Two Overlapped Three-Beam Umweg Reflections [23]
3. Three-Beam Bragg Reflection

Chang [24] calculated integrated intensity  $I_{222}$  profiles for the three-beam Umweg, (000) (222) (113), and (000) (222) (1 $\bar{1}$ ) cases for incoming and outgoing. These results indicate no matter  $S_{P,T}$  is positive sign or negative, the asymmetry of multiple diffraction profile is reversed just enough for both incoming and outgoing situations. Physically the difference in crystal rotation between the incoming and outgoing situation introduces the phase difference



of 180°. From these profile, the following relation is obtained for phase determination [25]

$$S_{P,E} = S_L S_R \quad (21)$$

where  $S_{P,E}$  is the experimentally determined sign of the phase triplet product.  $S_L$  is the sign defined from the line profiles which are given in Fig. 8 for both Aufhellung and Umweganregung three-beam diffraction.  $S_R$  is determined from the sense of crystal rotation, either incoming or outgoing,  $S_R$  is defined as the sign of the derivative

$$S_R = S \frac{\partial(\gamma\lambda)}{\partial\phi} \quad (22)$$

$S_R$  is therefore positive for incoming and negative for the outgoing situation.

A summary of the experimentally determined results of phases of the some multiple diffraction peaks in Fig. 6 is listed in Tab. 2. Theory calculation SPT agree with experimental determination SPE very well.

The method mentioned above has been used to centrosymmetric crystals [26, 27] and noncentrosymmetric crystals [28]. But it must note that the two side asymmetry of multiple diffraction peaks is obvious after deducting kinematics parts from experimental data of non-centrosymmetric crystal. This method has been used to determine the phase of organic crystal [29-31], biology macromolecule (oxy-hemoglobin) [32] and to study decagonal quasi-crystals [33].

### 4.2. Research of Crystal Symmetry

The symmetry of multiple diffraction pattern has been discussed in 1.2, 1.3 and 3.1 sections and By Parente et al. [34] and author [35]. The crystal symmetry can be obtained from the symmetry of multiple diffraction pattern.

**Table 2.** Determined results of invariance phase in Fig. 2. Ge (222) [19].

Reflection		Rotation		Profile	$S_R$	$S_L$	$S_{P,E}$	$S_{P,T}$
P	G-P							
111	331	-1.79	IN		+	-	-	-
111	133	1.79	OUT		-	+	-	-
311	111	24.57	OUT		-	-	+	+
111	311	35.63	IN		+	+	+	+

### 4.3. Determination of Lattice Parameters of Single Crystals

The possibility of using multiple diffraction for lattice parameter determination was first recognized by Kossel [36] and Renninger. There are two methods of determining lattice parameters using multiple diffraction i.e. the divergent beam [37-39] and the collimated-beam techniques [40-42]. The latter is introduced in this section.

The azimuth position  $\phi$  of multiple diffraction peak is a function of the wavelength of the radiation used and the crystal lattice parameters. For a given known radiation, the lattice parameter of the crystal can be determined from the peak position of multiple diffractions. Since the value of the angle  $\phi$  depends on choice of origin and reference vector, the useful angles for the lattice parameter determination are those independent of the choice of origin. One may know from (7) and (9) equations that  $\phi_1 - \phi_2$  and  $\beta$  satisfy this requirement. The factor  $\cos \beta$  in (11) is only a function of wavelength, the lattice parameters, and the Miller indices of the primary and secondary reflections.

Equation (11) has the following form for cubic crystals

$$a = [\lambda (p^2 - p_p g)] / [2p_n \cos \theta_G \cos \beta] \quad (23)$$

where the angle  $\theta_G$  is the Bragg angle of the primary reflection and  $a$  is the lattice parameter. Differentiating (23) leads to

$$\Delta a/a = (\tan \theta_G) \Delta \theta_G + (\tan \beta) \Delta \beta \quad (24)$$

Since  $\theta_G$  is the same for all multiple diffractions of a given primary reflection, the ratio  $a/a$  is thus affected by the presence of the secondary reflection via the angle  $\beta$ . Multiple diffraction with a small  $\beta$  is therefore suitable for precise measurement of  $a$ .

In Post's experiment [40], multiple diffractions with the secondary reflections {513}, {551} and {117}, and {331} for silicon, germanium, and diamond, respectively, were used for the measurements of the angle  $\beta$ . These angles are about 32.720, 11.330, for Si and Ge, and 15.78 ( $\text{CuK}\alpha_1$ ) and 9.120D ( $\text{CuK}\alpha_2$ ) for diamond. The results are

Multiple Diffraction Method		Optimum results of other method
Si $a = 5.430941 \text{ D}$	$\Delta a/a = 2.0 \times 10^{-6}$	$a = 5.430941 \text{ D}$

Ge $a = 5.657820 \text{ D}$	$\Delta a/a = 1.6 \times 10^{-6}$	$a = 5.65778 \text{ D};$ $a = 5.65786 \text{ D}$
Diamond $a = 3.566986 \text{ D}$	$\Delta a/a = 2.6 \times 10^{-6}$	$a = 3.56687 \text{ DA}$

It can be seen that the preciseness of the Multiple diffraction method is very high [41].

### 4.4. Determination of Lattice Mismatch

Epitaxial layered materials usually possess a tetragonal unit cell, in comparison with the cubic crystals of the substrates, owing to small difference between the lattice mismatch parallel and perpendicular to the interface,  $\Delta a_{||}$  and  $\Delta a_{\perp}$  [42].  $\Delta a_{||}$  and  $\Delta a_{\perp}$  are equal to  $a_{||} - a_s$  and  $a_{\perp} - a_s$ , respectively, where  $a_s$  is the undistorted lattice parameter of the substrate. An indirect observation of  $\Delta a_{||}$  and  $\Delta a_{\perp}$  for  $\text{Ga}_{1-x}\text{Al}_x\text{As}/\text{GaAs}$  has been reported [42] using one symmetric and one include Bragg reflection.

In principle, multiple diffraction can be used to detect simultaneously the lattice mismatches,  $\Delta a_{||}$  and  $\Delta a_{\perp}$ . This research has been carried out for  $\text{GaAlAs}/\text{GaAs}$  [43, 45-47], and  $\text{InGaAsP}/\text{InP}$  [44].

According to (11), the angle  $\beta$  for a tetragonal system can be calculated as

$$\cos \beta = 2 \left\{ \frac{\left[ \frac{(h^2 + k^2)}{a_{||}^2} \right] + \left[ \frac{(l^2 - il)}{a_{\perp}^2} \right] \left[ \frac{(h^2 + k^2)}{a_{\perp}^2} \right]^{1/2}}{\left[ \frac{1}{\lambda^2} \times \frac{L^2}{4a_{\perp}^2} \right]^{1/2}} \right\} \quad (25)$$

if the rotation axis is (00L) the secondary reflection is (hkl). For InP and  $\text{CuK}\alpha_1$  is  $90^\circ$ , since  $a_{||} = a_{\perp} = a_s$ . For the quaternary layer, the deviation from  $90^\circ$  can be determined to be

$$\Delta \beta = \left[ \frac{(h^2 + k^2) \Delta a_{||} + (l^2 - il) \Delta a_{\perp}}{a_s \left[ \frac{(h^2 + k^2)}{a_{\perp}^2} \right]^{1/2} \left[ \frac{1}{\lambda^2} - \frac{L^2}{4a_s^2} \right]^{1/2}} \right] \quad (26)$$

$$\Delta \beta = 0.205 (\Delta a_{||} - \Delta a_{\perp}) \quad (27)$$

where  $\Delta a_{\perp}$  can be determined from

$$\Delta a_{\perp}/a_s = -\cot \theta_G (\Delta \theta) \quad (28)$$

and the angular deviation  $\Delta \theta$  from the Bragg angle  $\theta_G$  of the (006) reflection.  $\Delta \beta$  can be measured from the angular separation between the two four-beam reflection lines.  $a_{||}$  can therefore be determined.

### 4.5. Observation of Crystal Defects [49, 50]

X-ray topography is one of the most frequently used methods in the examination of crystal defects.

Many topographic techniques and their applications have been developed [49]. The topographies taken from at least two non-coplanar reflection are necessary to determine the strain vector, for example, Burgers vector of a dislocation and stacking fault vector etc.

Chang [49] used a fine focus  $\text{CuK}\alpha_1$  radiation and asymmetric 422 reflection from (100) Si as x-ray source and monochromator, respectively. The sample is InGaAsP/InP is first aligned for the symmetric (006) Bragg reflection and then rotated about [006] axis to bring the (111), (115) and (333) atomic planes into position where they simultaneously satisfy Bragg's law. Fourbeam, (000), (006), (111), (115), (333), topograph can be obtained, but their resolution is bad to not observe the images of single defect. Therefore multiple diffraction topography, particular high resolution and multiple beam interference topograph must be further developed.

#### 4.6. Other Applications

Except the some application mentioned above, many applications have been developed or are developing, such as multi-beam x-ray interferometer [51, 52], x-ray collimating by multiple beam diffraction [53, 54, 55], plasma diagnosis [56], determination of mosaic spread of crystals [57] and multiple-beam x-ray standing wave excited fluorescence technique [58] and so on. The applications of multiple diffraction with gain better development in crystal-structure determination [59], characterization of semiconductor materials, one-dimensional superlattice material [60], x-ray optics and surface studies.

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