



Chapter 3

DEFECTS IN CRYSTALS AND DIFFUSE X-RAY REFLECTIONS

Defects in Crystals

Imperfections or defects are used to denote any chemical impurity or structural imperfection which makes the solid deviate from a chemically pure, structurally perfect crystal. The simplest classification is based on the dimensionality of the defect.

Zero-dimensional or point defects

Zero-dimensional or point defects are the simplest structural imperfections only affecting a very small region within a crystal. There are three types of point defect as shown in Fig. 3.1

a. Vacancy

A vacancy exists when a single atom or molecule is absent from the position it should occupy so a hole is left in the structure.

b. Interstitial defect

An interstitial defect occurs when an extra atom either of the same kind as those already present, or of a completely different kind, is present in a position not normally occupied in that structure. Small atoms or ions can occupy interstitial positions more than can large ones.

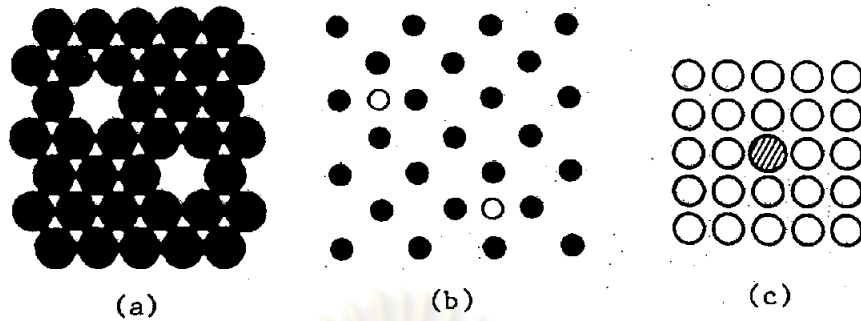


Fig. 3.1 (a) Vacancies, (b) Interstitials and (c) A substitutional atom

c. Substitutional defect

A substitutional defect occurs when an atom or molecule of one kind occupies a position normally occupied by one of another kind.

In an ionic crystal there are two types of point defect as shown in Fig. 3.2. The combination of an anion and cation vacancy is a Schottky defect and the combination of a vacancy and an interstice is a Frenkel defect. A Schottky defect has an equal number of cation and anion vacancies. Such defect can be regarded as displacement of cations and anions from a number of random lattice positions, to the crystal surface. A Frenkel defect is formed by the transference of an ion from a normal lattice position to an interstitial position in different regions of the crystal. It is usually the cation which is transferred in this way since this is often smaller ion and thus more easily accommodated at the inter-lattice point.

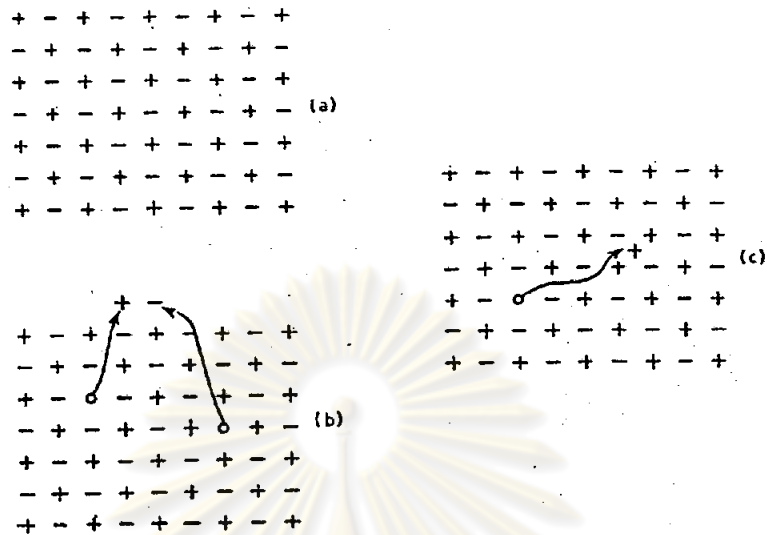


Fig. 3.2 Schottky and Frenkel defects

- (a) Region of perfect lattice
- (b) Schottky defect formation
- (c) Frenkel defect formation

One - dimensional defects

If the structure is composed of identical, parallel planes of atoms which are displaced parallel to one another in a regular or irregular manner from the ideal positions of a perfect lattice then the irregularity is one-dimensional. One dimensional defects (line defects or dislocations) are the boundaries between the slipped and unslipped regions. They can be distinguished into two basic types.

(a) Edge dislocation

An edge dislocation as shown in Fig. 3.3 arises when one of layers of atoms placed one on top of another is just a half layer,

uses the stacking of the layers to be disturbed for a few
on either side of the extra half layer.

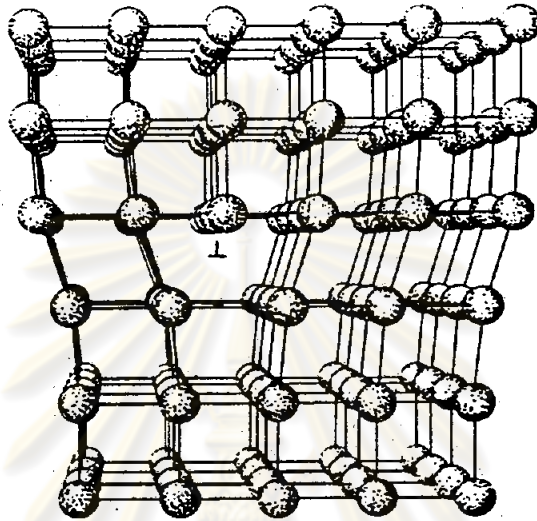


Fig. 3.3 Positive edge dislocation

the slipped region ABEF in which the atoms
more than half a lattice constant and the
th displacement less than half a lattice
tion extends indefinitely in the slip
o the slip direction.

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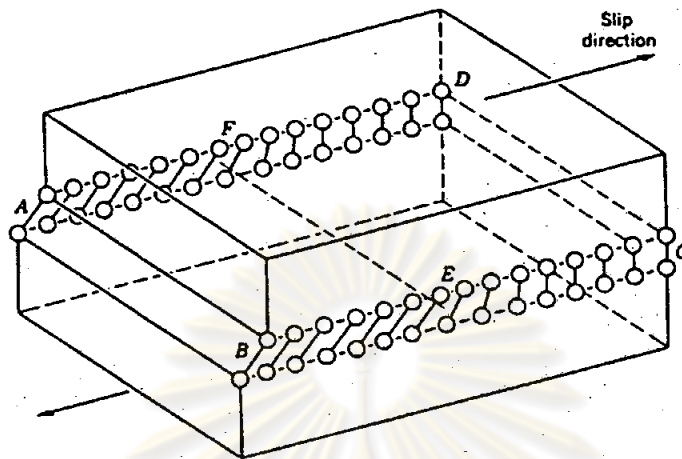


Fig. 3.4 An edge dislocation EF in the plane ABCD.

For a simple cubic crystal as illustrated in Fig. 3.5 (a), the atoms are held together by a binding mechanism which is represented by the flexible springs. All the atomic bonds intersected by plane ABCD are broken, the lattice would separate along this line if pulled in tension. The arrangement of atoms around an edge dislocation can be found by inserting an extra plane of atoms in the slot as sketched in Fig. 3.5 (b). The line DC is a positive edge represented by symbol \perp . There is a severe distortion around the dislocation and a small bending of the lattice planes. A negative edge dislocation obtained by inserting the extra plane of atoms below plane ABCD is represented by symbol Υ .

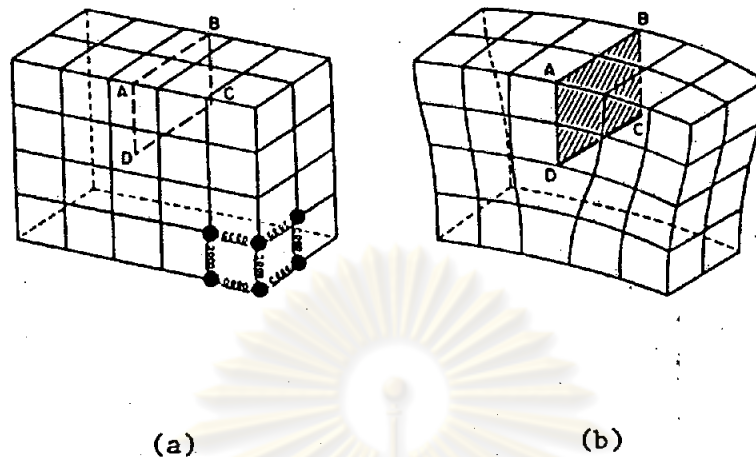


Fig. 3.5 (a) Model of a simple cubic lattice; the atoms are represented by hard spheres, and the bonds between atoms by springs, only a few of which are shown, (b) positive edge dislocation DC formed by inserting an extra half plane of atoms in ABCD.

(b) Screw dislocation

A screw dislocation or Burgers dislocation consists of a line of atoms each of which has the correct number of atoms coordinating it; however, the coordination polyhedron is distorted. The genesis of a screw dislocation is most clearly seen in a three-dimensional view of the crystal. Fig. 3.6 shows what happens when one part of the crystal is displaced relative to the rest of the crystal and the displacement terminates within the crystal. The row of atoms marking the termination of the displacement is the screw dislocation. In the region surrounding the dislocation the atoms are in their correct array, for example, on any of the vertical faces in Fig. 3.6. Along the dislocation line, however, the coordination polyhedra of the atoms have become distorted by the displacement.

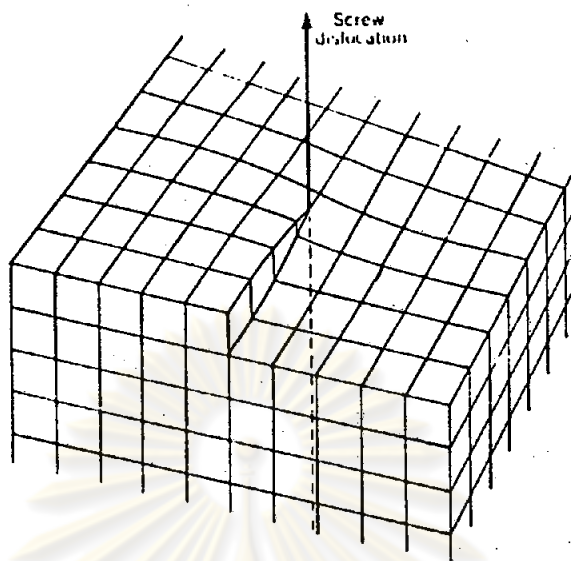


Fig. 3.6 Screw dislocation

The nature of the distortion can be seen in Fig. 3.7 which shows a side view of the dislocation and the two sets of atom rows lying in the planes just above and below the plane along which the displacement occurred. The atoms in the upper layer are represented by slightly smaller solid circles in Fig. 3.7 while the atoms in the lower layer are represented by open circles. To the left and the right of the dislocation line each atom is coordinated by four atoms in the same plane (joined by solid lines) and by two atoms, respectively, lying in the planes directly above and below (shown by the dotted vertical line), forming a regular octahedron. In the disturbed region, however, the octahedron is no longer regular, as can be seen by noting the shape of the bottom half of the distorted octahedron. On the other hand, the atoms, in the next layer above, are arranged according to the array of solid circles so that the amount of distortion gradually disappears with increasing distance from the dislocation line.

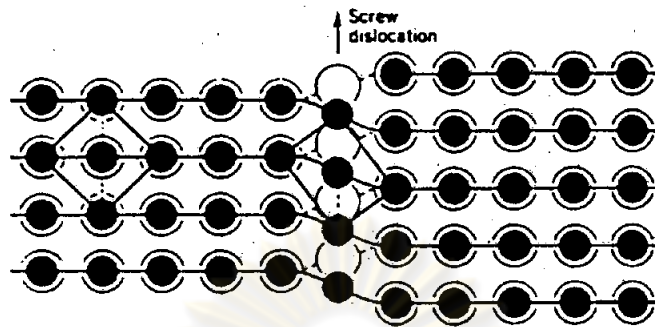


Fig. 3.7 A side view of the screw dislocation in Fig. 3.6

A dislocation can be described alternatively by means of a closed loop surrounding the dislocation line. This loop, or Burgers circuit, is formed by proceeding through the undisturbed region surrounding a dislocation in steps which are integral multiples of a lattice translation. The loop is completed by going an equal number of translations in a positive sense and negative sense in a plane normal to the dislocation line. Such a loop must either close upon itself (if it does not enclose a dislocation) or fail to do so by an amount called a Burgers vector

$$S = n_a a + n_b b + n_c c$$

where n_a , n_b , n_c are equal to integers or zero and a, b, c are the three primitive lattice translations. The Burgers circuit for a screw dislocation is shown in Fig. 3.8. Starting at some lattice point at the front of the crystal, the loop fails to close on itself by one unit translation parallel to the dislocation line. This is Burgers vector "S" which always points in a direction parallel to the

screw dislocation. It is noted that if the loop is continued, it will describe a spiral path around the Burgers dislocation similar to the thread of a screw.

A Burgers circuit surrounding an edge dislocation is shown in Fig. 3.9. In this case the Burgers vector is perpendicular to the edge dislocation. It is thus possible to distinguish the two kinds of dislocations according to the direction of their respective Burgers vectors. Fig. 3.9 shows that the atoms in the upper half of the crystal, that is above the plane containing the edge dislocation, are in a state of compression which is largest at the edge dislocation itself. Conversely, directly below the dislocation, the atoms have larger than normal separation. In general, a dislocation may be a curved line. Such a dislocation can always be analyzed in terms of how much edge character and screw character it has by drawing a Burgers circuit around it.

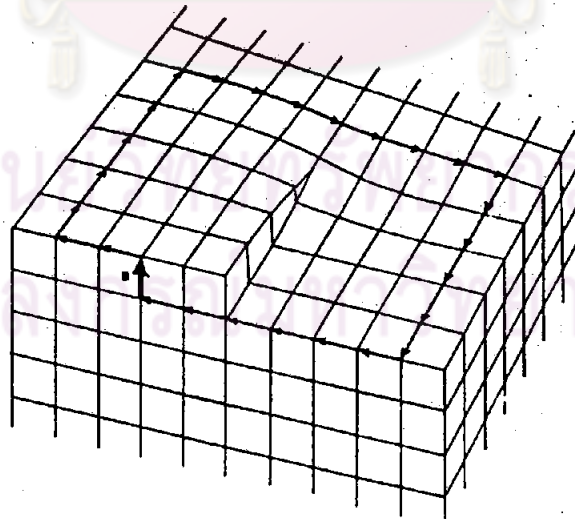


Fig. 3.8 Burgers circuit surrounding a screw dislocation

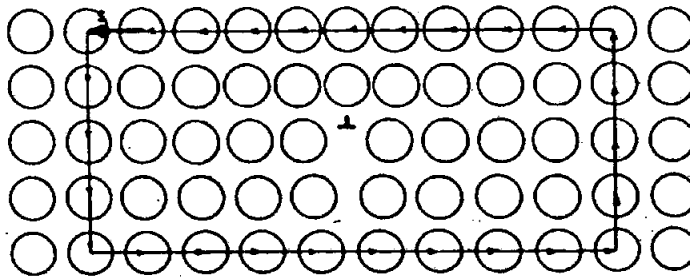


Fig. 3.9 Burgers circuit for an edge dislocation

Two-dimensional defects

Many structural defects in solid encompass planes of atoms or surface. There are two types of two-dimensional defects.

a. Grain boundaries

Crystalline solids usually consist of a large number of randomly oriented grains separated by grain boundaries. Each grain is a single crystal and contains the defects.

1. Wide-angle grain boundaries

The angles between the crystallite orientations of nearby grains are large and the structure of the grain boundary is a complex one that conforms to the details of shape and orientation of the adjacent crystals. This is shown in Fig. 3.10

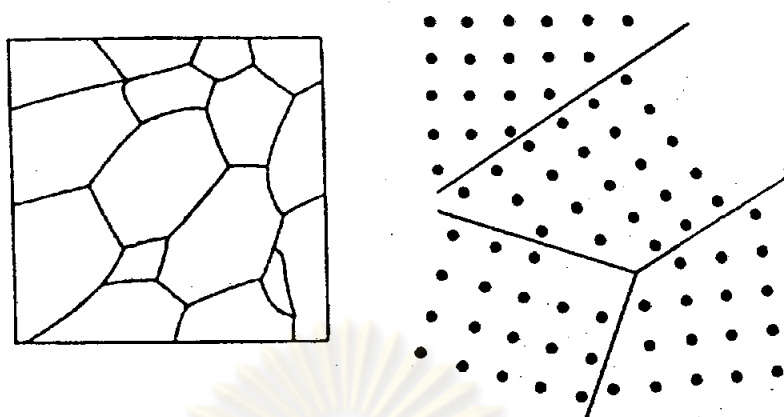


Fig. 3.10 Wide-angle grain boundaries

2. Small-angle grain boundaries

The grain boundaries are not large-angle and show misorientations of no more than a few degrees. Fig. 3.11 shows a small-angle tilt boundary which consists of a series of edge dislocations.

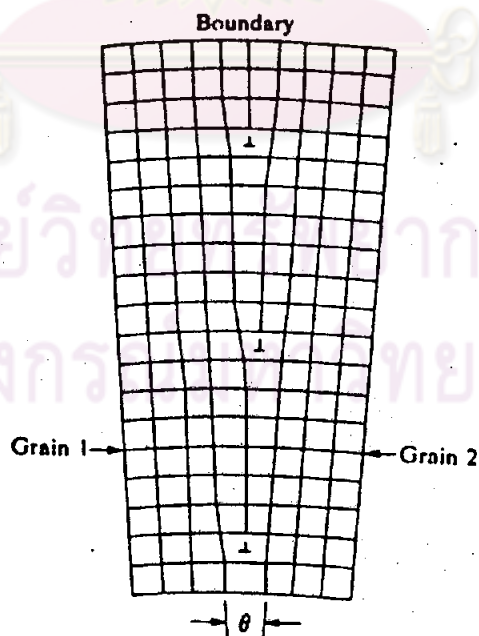


Fig. 3.11 Small-angle boundary

3. Twin boundaries

When adjacent parts of a crystal are regularly arranged such that one part is a mirror image of the other, the two parts are said to be twin related. The mirror plane is called the composition plane and is illustrated in Fig. 3.12. The open circles represent the positions of the atoms before twinning and the black circles the positions after twinning. The atoms above x-y are mirror images of the atoms below it and therefore x-y represents the trace of the twin composition plane in the plane of paper. Twinning can be represented as a homogeneous shear of the lattice parallel to the composition plane. Twins are formed during the growth of a crystal and by mechanically deforming a crystal, for example, by shear. The transformation between high-temperature and low-temperature modifications of a crystal may occur via twinning.

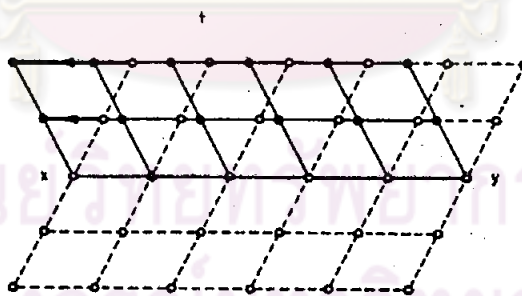


Fig. 3.12 Arrangement of atoms in a twin structure

4. Twist boundaries

The two parts of the crystal are rotated through a small angle, about an axis which is perpendicular to the grain boundary, the result is a twist boundary as illustrated in Fig. 3.13. Just as the low-angle tilt boundary results from a series of edge dislocations, so the twist boundary results from sets of screw dislocations.

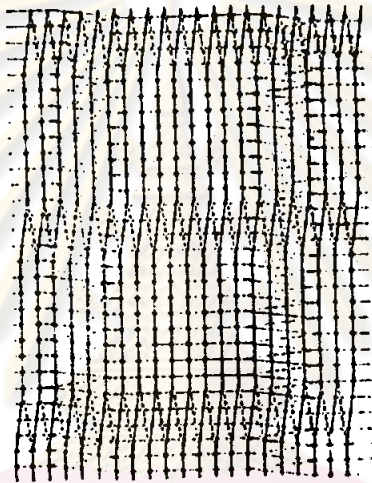


Fig. 3.13 A twist boundary

A pure twist boundary parallel to the plane of the Fig. 3.13. The two grains have a small relative rotation about their cube axis, which is normal to the boundary.

Stacking faults

As its name implies, it is a local region in the crystal where the regular sequence has been interrupted. Stacking faults are not expected in planes with ABABAB. Sequences in body-centred or face-centred cubic lattices because there is no alternative site for an "A" layer resting on a "B" layer. However, for ABCABC..... stacking of the

close-packed lattices, there are two possible positions of one layer resting on another. A closed-packed layer of atoms resting on an A layer can rest equally well in either a "B" or a "C" position and geometrically there is no reason for the selection of a particular position. In a face-centred cubic lattice two types of stacking fault are possible, referred to as intrinsic and extrinsic. These are best described by considering the change in sequence resulting from the removal or introduction of an extra layer. In Fig. 3.14 (a) part of a "C" layer has been removed which results in a break in the stacking sequence. This is an intrinsic fault and it can be seen that the lattice patterns above and below the fault plane are continuous right up to the fault plane. In Fig. 3.14 (b) an extra "A" layer has been introduced between a "B" and a "C" layer. There are two breaks in the stacking sequence and it is referred to as extrinsic fault. The extra layer does not belong to the continuing patterns of either the lattice above or below the fault.

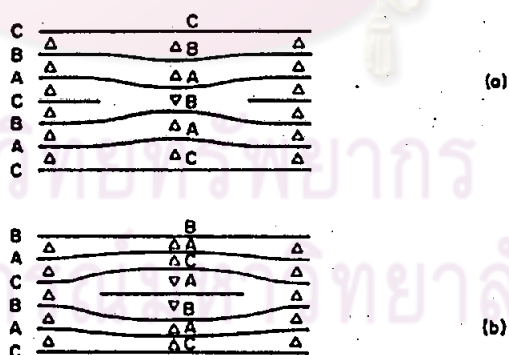


Fig. 3.14 Stacking faults in face-centred cubic lattice.

The normal stacking sequence of (111) planes is denoted by ABCA... Planes in normal relation to one another are separated by Δ ; those with stacking error by ∇ , (a) intrinsic stacking fault, (b)

Three-dimensional Defects or Volume Defects

The tendency of imperfections to interact with each other leads to a formation of clusters of various defect types. For example, there is some evidence that diffusion may proceed in certain crystals via vacancy pairs rather than isolated vacancies. Larger agglomeration of vacancies can lead to the formation of dislocations in crystals, a process is described as a "collapse" of vacancy clusters. Similarly, interstitial or substitutional atoms tend to cluster under certain conditions sometimes leading to the formation of regular nuclei which may then proceed to grow. This process leads to phase segregation and is more likely to occur at elevated temperatures at which diffusion proceeds more easily. Since such defect clusters can attain sizeable proportions, the term volume defect is proposed to describe them.

The clustering of vacancies, sometimes combined with interacting dislocations, can lead to the formation of cracks inside a crystal. Substitutional or interstitial atoms may form volume defects of various shapes or they may collect along certain crystallographic planes that offer a more favourable environment.

Superlattices

The structure is said to be ordered when all the atoms occupy their correct sites, and it is said to be disordered when some of the atoms occupy incorrect sites. The array of open and shaded circles in Fig. 3.15 a. is considered as a simple example of an ordered structure of a binary compound. When this structure is disordered (Fig. 3.15 b) the two kinds of atoms may occupy the two kinds of sites

completely at random so that the sites become statistically equivalent. Since their occupation by either atom is equally likely, the scattering factor for such a statistically averaged atom is a weighted average of the scattering factors of each of the two atoms. A comparison of the two drawings shows that the point-group symmetry of the two structures is the same, $4mm$, but the plane-group symmetry has changed from $P4mm$ for the ordered array to $C4mm$ for the disordered one. It is noted that the primitive cell in Fig. 3.15 b is, of course, smaller than the centered one. Thus it appears as if the ordered crystal structure has a superlattice compared with the disordered one.

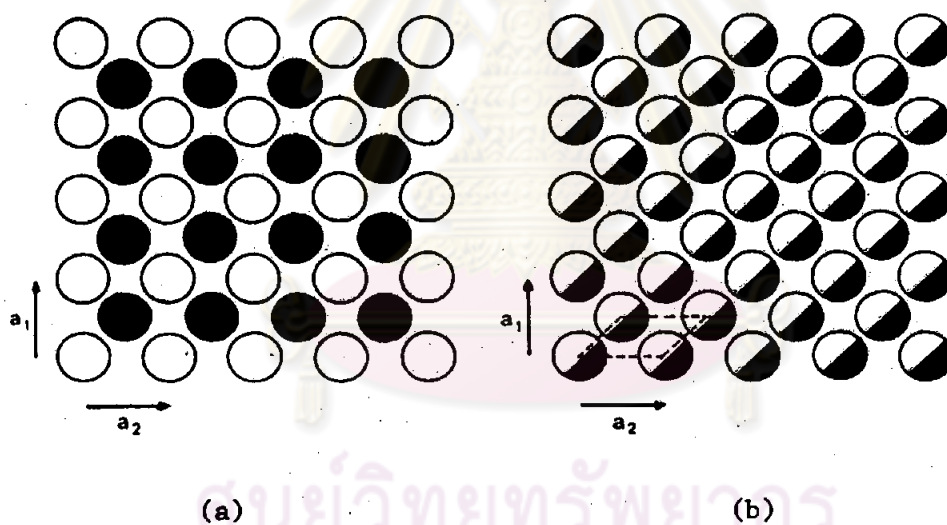


Fig. 3.15 (a) Ordered structure. (b) Disordered structure.

When the diffraction of X-rays by two such structures is considered, it is clear that reflections from the ordered structure, having a primitive lattice, can have all possible hkl values, while those from the disordered structure can have only those indices that are allowed by the extinction rules for the appropriate centered

lattice. This means that both structures will have certain hkl reflections in common, called fundamental reflections. The ordered structure, however, give rise to an additional set of reflections, called superlattice reflections.

Diffuse X-ray Reflections Due to Static Defects

A perfect lattice consisting of stationary atoms in a regular array would give Bragg reflections. Real crystals possessing disorder of many kinds cause diffuse regions.

The X-ray diffuse scatterings arise from dynamic effects and static displacements. The dynamic effects are due to the thermal vibrations of atoms in a crystal. These thermal vibrations give rise to diffuse reflections which in some crystals are confined to directions fairly close to the normal Bragg reflections. In more complicated crystals they may be spread over a very much greater angular region. Static displacements which are used to describe any departure from the ideal regularity of a perfect lattice obtaining Bragg reflections, give diffuse reflections as diffuse clouds or streaks. It is a fundamental difficulty to uniquely separate thermal scattering from disorder diffuse scattering. Some attempts in the past neglect the influence of the distorted crystal on the lattice vibrations. It is common for the two types of diffuse X-ray reflection to occur at the same time. For instance, vanadium gives a thermal diffuse scattering and it also gives the spikes in the neighbourhood of certain reciprocal lattice points. The thermal diffuse scattering lies beyond the scope of this thesis. Only the disorder diffuse scattering is discussed in the fundamental level.

Diffuse scattering caused by lattice imperfections may be divided into three principally different diffraction effects.

1. Distortions have a direct influence on the shape of the X-ray reflections.

2. Distortions may only be detected in the diffuse background without any change of the form of sharp reflections.

3. Crystal distortions are large enough to destroy all sharp reflections in reciprocal space.

Obviously distortions of all three types by disorder diffuse scattering are connected by a continuous series of degrees of disorder.

The study of diffuse reflections by Laue photographs. The essential matter to be considered is the shape of the diffuse reflections. By shape is meant the distribution of points around reciprocal lattice points that give rise to diffuse reflections. To find such shapes it is necessary to take a series of Laue photographs, the setting of the crystal being changed by a few degrees between one photograph and the next. There are two types of spots from a Laue photograph of a defective crystal

1. Bragg spots

The Laue method requires a polychromatic X-ray beam and stationary crystal during the entire experiment. However we must recall that the characteristic radiation of the target is by far the most intense in the spectrum. This component has important consequences in Laue photographs, producing a few strong easily recognizable diffraction spots. These are the Bragg spots of the Laue photograph.

Two features help in the recognition of Bragg spots : first, the Bragg spots have high intensity compared with the average Laue spots; second, the Bragg spots in Laue photographs of oriented crystals appear along layer lines, similar to those observed in oscillation photographs.

2. Diffuse-scattering spots

Bragg spots are not the only consequence of the effect of the characteristic radiation. Possessing disorder of many kinds of real crystals causes diffuse regions of appreciable intensity that are not concentrated only at the nodes of the reciprocal lattice. In such circumstances it is quite likely that the Ewald sphere may intersect one or more such scattering regions, and that the consequent scattering will be recorded on the Laue photographs. The presence of this diffuse scattering is easily recognized in Laue photographs : the diffuse-scattering spots may be associated with strong Bragg spots or they may cover wide regions of the Laue photograph in a cloudlike manner.

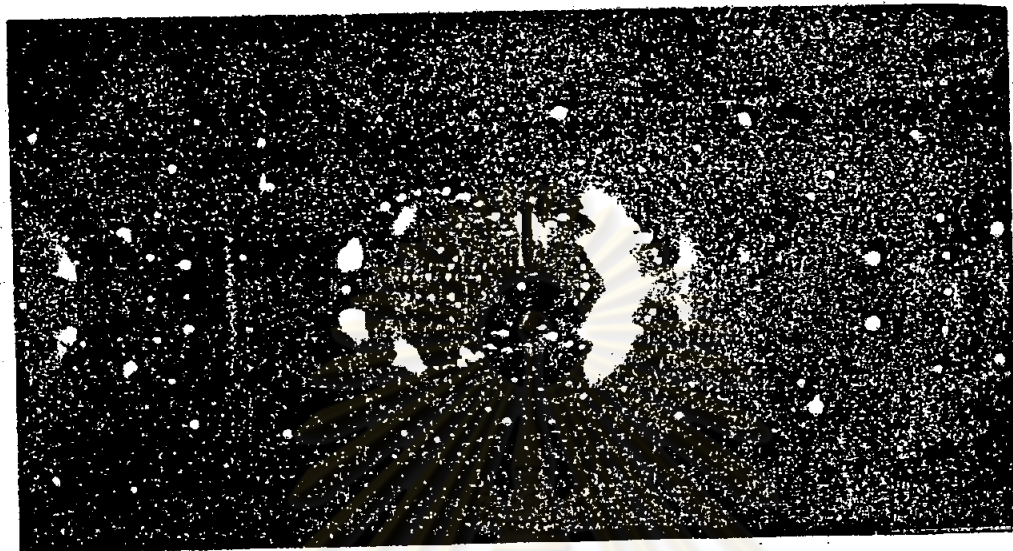
The X-ray diffuse scattering arising from thermal or statistical disorder in the crystal structure is much weaker than the intensity of the Laue or Bragg reflections. The diffraction of any wavelength of the polychromatic radiation used in the Laue method gives rise to some diffuse scattering. But the main consequence of the sum of the diffuse scattering due to the wavelengths of the continuous spectrum is to increase the general background of the photograph. The characteristic radiation has high intensity and, consequently, the diffuse scattering that is observed in Laue photographs, superimposed on the general background of uniform intensity,

is due only to the contribution of this characteristic radiation. This allows one to study diffuse scattering with the aid of Laue photographs.

Since the X-ray diffuse scattering is produced by the characteristic radiation, it is sufficient to filter the X-ray beam to obtain a monochromatic background due to the K_{α} radiation. Therefore, the interpretation of the diffuse scattering appearing in a Laue photograph is fairly simple : the diffuse scattering is simply the projection on the film of the diffraction space cut by the K_{α} Ewald sphere. Because diffuse scattering is very weak, the exposure time of the Laue photograph must be long enough to allow it to be recorded. It is obvious that if the crystal remains stationary, as in the Laue method, the exposure time necessary to register diffuse scattering will be much less than if moving-film methods are used. The method that takes advantage of this situation has been called the monochromatic Laue method although a better name is the characteristic Laue method.

The first basic question about the diffuse scattering observed in a Laue photograph concerns its monochromatic nature. A qualitative proof can be obtained by comparing a Laue photograph with a photograph taken by oscillating the crystal a few degrees. Figure 3.16 a reproduces a cylindrical Laue photograph of succinic acid $[(\text{CH}_2\text{CO}_2\text{H})_2]$ a monoclinic crystal, taken with the X-ray beam at 20° from $[100]$. Diffuse scattering regions are clearly shown. A photograph taken in the same orientation but with an oscillation of $7\frac{1}{2}^\circ$ about the cylinder axis is reproduced in Fig. 3.16 b. The Laue spots have disappeared and only Bragg reflections occur. In both photographs, however, the diffuse scattering appears in the same positions. Since the diffraction recorded in the oscillation photograph is due only to the characteristic radiation

(except the radial streaks), it follows that the diffuse scattering observed in the Laue photograph is also due only to the characteristic radiation and, therefore, is monochromatic in nature.



(a)



(b)

Fig. 3.16 X-ray photographs taken with a cylindrical camera of a succinic acid crystal with $[010]$ parallel to the cylinder axis. (a) Laue photograph. (b) Oscillation photograph.

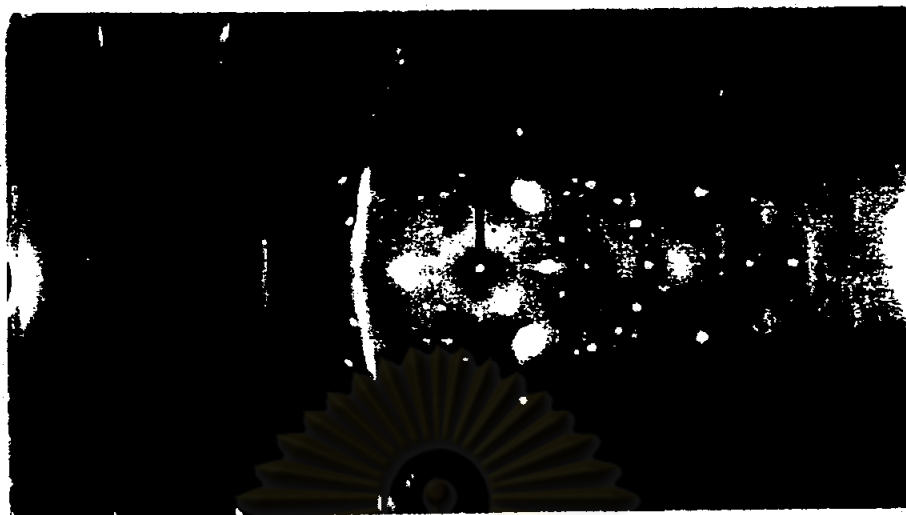
A more powerful proof of the monochromatic origin of diffuse scattering is given by comparing a Laue photograph with a photograph taken of the same crystal in the same orientation but using an X-ray beam rendered monochromatic by crystal reflection. This technique was used by Lonsdale and Smith. (22) The diffuse scattering observed in the Laue photograph was identical to that recorded by using a strictly monochromatic X-ray beam.

A disordering of the structure units of the crystal causes the appearance of diffuse scattering. Its appearance can be shown in the transition from ferroelectric to paraelectric phases. For instance, Fig. 3.17 shows a Laue photograph of NaNO_2 , an orthorhombic ferroelectric crystal at room temperature.

Thermal diffuse scattering can be seen in the Laue photograph. By raising the temperature, the crystal undergoes a phase transition into a paraelectric phase in which the NO_2 groups are statistically oriented along the c axis. A Laue photograph taken above the transition point (Fig. 3.17 b) shows diffuse streaks, in addition to the normal thermal-diffuse scattering. These streaks are due to the disorder of the NO_2 groups in the structure.



(a)



(b)

Fig. 3.17 NaNO_2 . Laue photographs taken with a cylindrical camera. (a) Ferroelectric, ordered structure at 20°C
 (b) Paraelectric, ordered structure at 180°C

A full record of diffraction space that can be made by taking Laue photographs of a crystal in a systematic manner is called the systematic Laue method. In this method the crystal is mounted for rotation about a known crystal direction, and a Laue photograph is then made with sufficient exposure time to bring out the detail in the diffuse scattering. The crystal is then rotated through a small angle to a new orientation in which another Laue photograph of the same exposure time is made. The procedure is repeated as many times as is necessary to complete the survey of all diffraction space. The character of extension of diffuse scattering is dramatically shown in Fig. 3.18, which consists of a series of Laue photographs of NH_4NO_3 at room temperature taken at successive orientations of the crystal. The orientation of the crystal was changed for each photograph, that is,

the crystal was rotated 6° about the vertical axis [100] from one photograph to the next. The angles referred to in the figure are based upon assigning 0° as the orientation of the crystal that fulfills the Bragg condition for 020. It can be observed that the Laue spot [010] migrates from the left to the right of the Bragg reflection 020, indicating the variation of the orientation of the crystal in the different Laue photographs. The diffuse scattering associated to 020, in the contrary, does not change its position but does change its intensity and shape, the highest intensity coinciding with the setting at 0° . The diffuse scattering associated with 020 is so extended in depth that it can even be observed at orientations of the crystal $\pm 30^\circ$ from the position for the reflection 020. The whole diffuse domain has the shape of a biconvex lens centered on the 020 reciprocal-lattice point with maximum intensity at the lattice point. In a similar way, other domains of diffuse scattering can be observed in this crystal.

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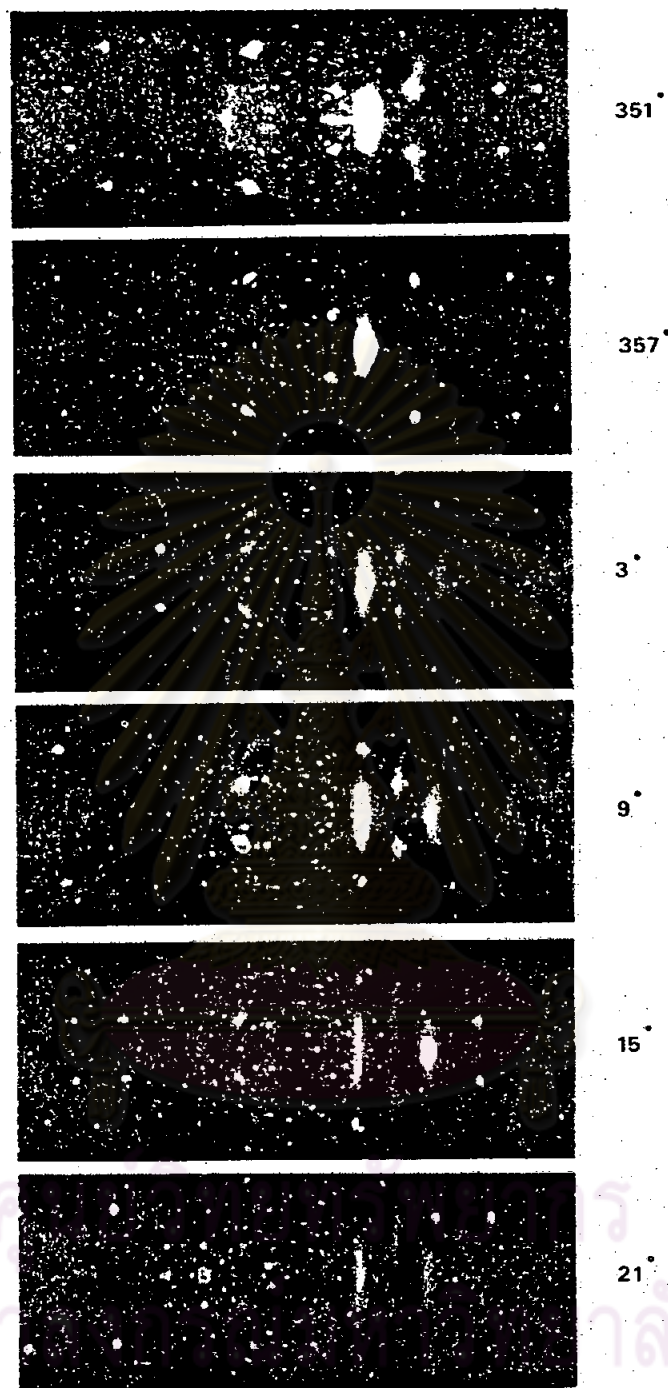


Fig. 3.18 A series of Laue photographs of NH_4NO_3

Diffuse reflections of Wollastonite

The study of particular type of lattice defect is described by an example of sheet-like of mineral wollastonite, CaSiO_3 (Jeffrey, 1953).⁽²³⁾ On a Weissenberg photograph (Fig. 3.19) by Jeffrey of this crystal, oscillating about the b-axis, the even-order layer line photographs had sharp spots whereas the spots on the odd-order layer line photographs were diffuse and drawn out into streaks along curves corresponding to a^* .



Fig. 3.19 (a) Superimposed zero- and 2nd-layer equi-inclination Weissenberg photographs about "b".
 (b) 1st-layer equi-inclination Weissenberg photograph about "b".

Wollastonite with a monoclinic structure has the perfect distribution of atoms within any one (100) plane of atoms and neighbouring (100) planes translated in a random manner relative to one another by a distance $b/2$. The displacement of the individual (100) planes means that diffuse spikes perpendicular to the (100) planes

and parallel to a^* will be observed. Further, since the random displacement is $b/2$ the distribution lattice will have a unit cell of dimensions a , $b/2$, c . The reciprocal cell equivalent to this will have sides a^* , $2b^*$, c^* . Thus hkl reflections for which k is even will correspond to the cooperation of all the atoms, since these will be the reflections from atoms on the distribution lattice. When k is odd diffuse reflections arise with an elongation parallel to a^* . Willis (1958) used an optical diffractometer to investigate this type of structure. To concentrate on the essentials he chose a simple cubic lattice rather than the monoclinic lattice of Wollastonite. The type of displacement of the horizontal rows of atoms is shown in Fig. 3.20. The optical masks carried many thousands of holes and Fig. 3.20 a. shows only a small portion of such a mask. The dotted lines show where a displacement of half a cell side has occurred. Fig. 3.20 b gives the corresponding diffraction pattern produced by such a mask. It will be seen that some spots are sharp while others are diffuse and the latter are drawn out in a direction normal to the dotted lines of Fig. 3.20.

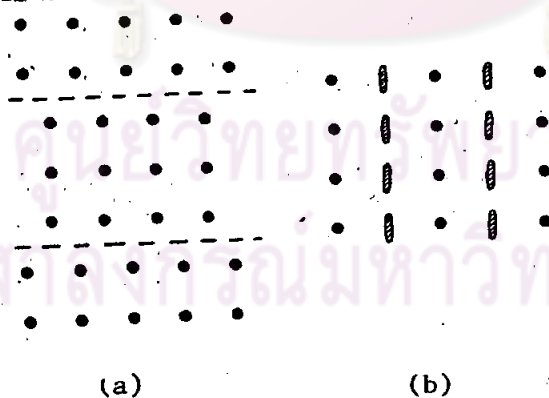


Fig. 3.20 a. Diagram representing an idealized Wollastonite-type of lattice faulting.

Fig. 3.20 b. Diagram of the optical diffraction pattern corresponding to the mask of which Fig. 3.20 a is a small part.