Chapter 4: Defects in Crystals

...Perfection's a gift of
> *The gods, few can boast they possess it - and most*
Of you, my dears, don't.
> *- Ovid, The Art of Love*

4.1   INTRODUCTION

A perfect crystal is an idealization; there is no such thing in nature. Atom arrangements in real materials do not follow perfect crystalline patterns. Nonetheless, most of the materials that are useful in engineering are crystalline to a very good approximation. There is fundamental physical reason for this. The preferred structures of solids at low temperature are those that minimize the energy.   The low-energy atomic configurations are almost invariably crystalline since the regular pattern of the crystal lattice repeats whatever local configuration is most favorable for bonding. There is also a fundamental physical reason why the crystal is imperfect. While a perfect crystalline structure may be preferred energetically, at least in the limit of low temperature, atoms are relatively immobile in solids and it is, therefore, difficult to eliminate whatever imperfections are introduced into the crystal during its growth, processing or use.

The fact that real materials are not perfect crystals is critical to materials engineering. If materials were perfect crystals then their properties would be dictated by their composition and crystal structure alone, and would be very restricted in their values and their variety. It is the possibility of making imperfectly crystalline materials that permits materials scientists to tailor material properties into the diverse combinations that modern engineering devices require. As we shall see repeatedly in the body of this course, the most important features of the microstructure of an engineering material are the crystalline defects that are manipulated to control its behavior.

In this Chapter we shall identify and describe the various defects that are found in crystalline solids. We shall hint at their consequences to indicate why they are worth studying, but shall defer a detailed discussion of their behavioral role until we discuss particular classes of engineering properties.

It is useful to classify crystal lattice defects by their dimension. The 0-dimensional defects affect isolated sites in the crystal structure, and are hence called *point defects*. An example is a solute or impurity atom, which alters the crystal pattern at a single point. The 1-dimensional defects are called *dislocations*. They are lines along which the crystal pattern is broken. The 2-dimensional defects are surfaces, such as the external surface and the *grain boundaries* along which distinct crystallites are joined together. The 3-dimensional defects change the crystal pattern over a finite volume. They include *precipitates*, which are small volumes of different crystal structure, and also include large *voids* or *inclusions* of second-phase particles.

4.2   POINT DEFECTS

A point defect disturbs the crystal pattern at an isolated site. It is useful to distinguish *intrinsic defects*, which can appear in a pure material, from *extrinsic defects*, which are caused by solute or impurity atoms.

4.2.1 Intrinsic defects

An intrinsic defect is formed when an atom is missing from a position that ought to be filled in the crystal, creating a *vacancy*, or when an atom occupies an interstitial site where no atom would ordinarily appear, causing an *interstitialcy*. The two types of intrinsic point defects are shown in Fig. 4.1.
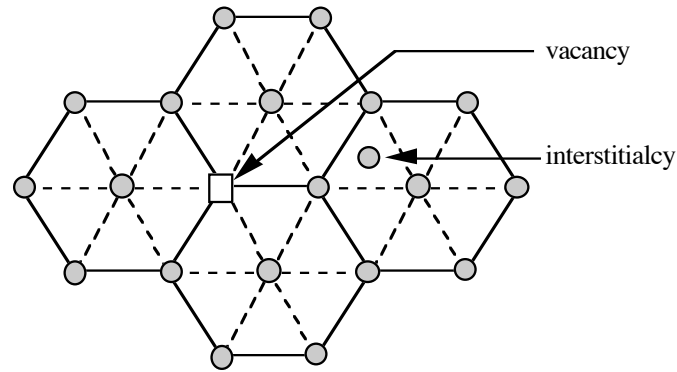
Fig. 4.1:   Illustration of a vacancy and an interstitial in a two-dimensional
            hexagonal lattice.

Because the interstitial sites in most crystalline solids are small (or have an unfavorable bonding configuration, as, for example, in the diamond lattice) interstitialcies are high-energy defects that are relatively uncommon. Vacancies, on the other hand, are present in a significant concentration in all crystalline materials. Their most pronounced effect is to govern the migration of atoms on the crystal lattice (*solid state diffusion*). In order for an atom to move easily from one crystal lattice site to another the target site must be vacant. As we shall see, the rate of diffusion on the crystal lattice is largely governed by the concentration of vacancies.

Ordered compounds can have more complex intrinsic defects. In most compounds the different species are charged to at least some degree. An intrinsic defect destroys the local charge balance, which must be restored in some way. The compound defects that preserve charge are easiest to visualize in binary ionic solids like NaCl. An isolated vacancy in an ionic solid creates an excess charge. The excess charge can be compensated by a paired vacancy on the sublattice of the other specie; for example, the excess charge associated with a Na vacancy is balanced if there is a Cl vacancy nearby. A neutral defect that involves paired vacancies on the cation and anion sublattices is called a *Schottky defect.* Alternatively, the charge imbalance caused by the vacancy can be corrected by adding an interstitial of the same specie; a Na vacancy is compensated by a Na interstitial. A neutral defect that is made up of a paired vacancy and interstitial is called a *Frenkel defect.* In compounds whose atoms are less strongly ionized it is energetically possible for species to exchange sites, so that an A-atom appears on the B-sublattice or vice versa. This type of point defect is called an *anti-site* defect, and is fairly common in semiconducting compounds such as GaAs.

4.2.2 Extrinsic defects

The extrinsic point defects are foreign atoms, which are called *solutes* if they are intentionally added to the material and are called *impurities* if they are not. The foreign atom may occupy a lattice sites, in which case it is called a *substitutional solute* (or impurity) or it may fill an interstitial site, in which case it is called an *interstitial solute.* Since the interstitial sites are relatively small, the type of the solute is largely determined by its

size. Small atoms, such as hydrogen, carbon and nitrogen are often found in interstitial sites. Larger atoms are usually substitutional.

More complex extrinsic defects appear in compounds. If the valence of a substitutional defect in an ionic solid differs from that of the lattice ion then the excess charge is often compensated by a paired vacancy or interstitial. For example, when Mg^{++} ions are substituted for Na^+ in NaCl they tend to be paired with vacancies on the Na sublattice to maintain local charge neutrality. In semiconductors substitutional atoms with the wrong valence acts as electron donors or acceptors, as described below.

Extrinsic point defects affect almost all engineering properties, but they are particularly important in semiconducting crystals, where extrinsic defects are used to control electrical properties, and in structural metals and alloys, where extrinsic defects are added to increase mechanical strength. While these properties will be discussed later in the course, it is perhaps useful to identify the characteristics of the point defects that affect them.

Donors and acceptors in semiconductors

Point defects are intentionally added to semiconductors to control the type and concentration of charge carriers. Consider, for example, boron (valence 3) as a substitutional solute in elemental silicon. The saturated covalent bonds in silicon are shown schematically in Fig. 4.2a, and depend on the availability of four valence electrons per silicon atom. Since the bonds are saturated, silicon has very low conductivity in its pure state; pure silicon can only conduct electricity when electrons are excited into high-energy electron states. If boron is added, as in Fig. 4.2b, a valence electron is missing from the immediate environment of the boron atom, causing a *hole* in the bonding pattern. Electrons can then move from bond to bond by exchanging with the hole. The exchange requires some energy to separate the hole from the boron ion core, but this energy is small compared to that required to excite an electron from a Si-Si bond into a high-energy state. The room-temperature conductivity of Si increases significantly when a small amount of B is added. Electron-deficient solutes like boron that cause holes in the configuration of bonding electrons are called *acceptors.*
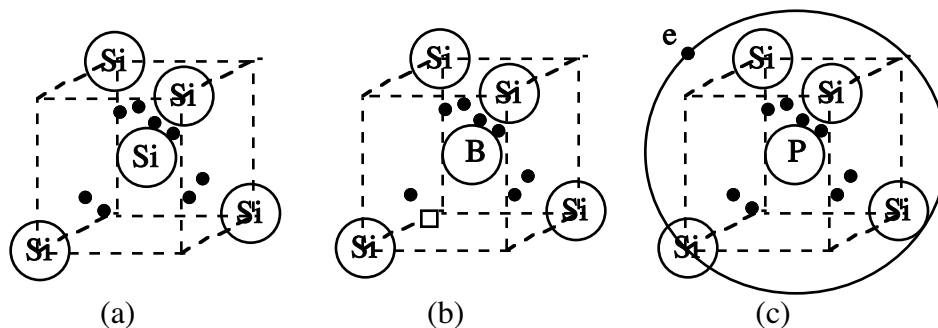

Fig. 4.2: (a) Tetrahedral bonding configuration in Si. (b) Bonding around a B solute, showing a hole (□). (c) Bonding around a P solute, showing an electron (e) in a loose excited orbital.

The conductivity also rises when a solute with an excess of electrons is added to a semiconductor with saturated bonds. For example, let phosphorous (valence 5) be added to Si, as in Fig. 4.2c. The 5 valence electrons of P are sufficient to fill the local covalent bonds with one electron left over. This electron can only go into an excited state, and orbits about the P ion core somewhat as shown in the figure. It requires a relatively small energy increment to free this electron from the P core, in which case it can transport current by moving through the lattice. The conductivity of Si rises dramatically if a small amount of P is added. Electron-excess solutes such as P in Si are called *donors.*

Semiconductors whose electrical properties are controlled by electrically active solutes are called *extrinsic semiconductors.* Almost all of the semiconductors that are used in engineering devices are extrinsic.

Solution hardening in structural materials

The addition of solute atoms almost always increases the mechanical strength of a solid. The phenomenon is called *solution hardening.* It is due to the fact that the solute atom is always a bit too large or a bit too small to fit perfectly into the crystal lattice site it is supposed to occupy, and distorts the crystal lattice in its attempt to fit as well as possible. As we shall see later, this distortion impedes the motion of the linear defects (dislocations) that are responsible for plastic deformation and, consequently, hardens the crystal. The distortion due to a substitutional solute is relatively small, though the associated hardening may be large enough to be useful in the engineering sense. The distortions due to interstitial atoms such as carbon and nitrogen are normally much greater because of the small size of the interstitial void in which they must fit. The hardening effect of interstitial solutes is large and technologically important; for example, high strength structural *steels* are alloys of Fe and C.

There is a simple crystallographic reason why interstitial solutes such as C are particularly effective in strengthening BCC metals such as Fe. The carbon atoms occupy octahedral interstitial sites in the BCC structure Since an atom in an octahedral void in BCC is closer to two of its neighbors that to the other four, it causes an asymmetric distortion of the lattice. As shown in Fig. 4.3, the octahedron is stretched along its short axis, which is the a_3, or z-axis in the case shown in the figure. The asymmetric distortion of the interstitial site increases its interaction with the dislocations that cause plastic deformation and promotes hardening. In FCC alloys the interstitial sites are symmetric, and the lattice distortion is isotropic. Interstitial solutes are effective in hardening FCC alloys, but are less effective than in BCC alloys.
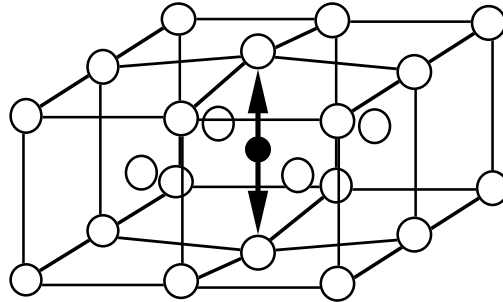
Fig. 4.3:   The local distortion of the BCC lattice by an interstitial atom in
an O_z void.

Random solid solutions

At low concentrations it is usually reasonable to assume that the solutes are randomly distributed over the sites they occupy, in which case the material is called a *random solid solution.* The basic properties of a random substitutional solid solution can often be estimated by treating the material as if it were made up of *pseudo-atoms* that have the average properties of the components of the solution. In keeping with this idea, most of the properties of random substitutional solid solutions are simply proportional to the solute concentration. We shall see many examples in the following. A particular example is *Vegard's Law*, which asserts that when the solute concentration in a cubic solid solution is small its lattice parameter changes linearly with the concentration:

$$\frac{a - a_0}{a_0} = Kx \qquad\qquad 4.1$$

where a_0 is the lattice parameter of the crystal in pure form, x is the atom fraction of solute and K is a constant. The constant, K, is usually much larger for an interstitial solute because the solute atom must be fit into the small interstitial hole.

Tetragonal distortion by octahedral interstitials in BCC

At larger solute concentrations the solute atoms interact and influence one another, and their actual configuration in the crystal becomes important. An important and instructive example occurs in the case of octahedral interstitials in BCC materials, and is responsible for the technologically important fact that steel (Fe-C) that has a carbon content greater than a few tenths of an atom percent has a body-centered tetragonal rather than a BCC structure when it cooled rapidly (quenched) from elevated temperature. The body-centered tetragonal structure (BCT) differs from the BCC in that it is elongated along one of the three crystal axes (assume the a_3, or z-axis), as shown in Fig. 4.4.
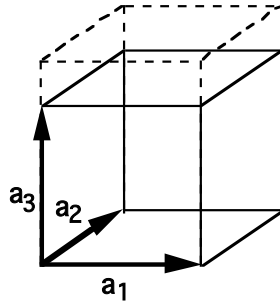
Fig. 4.4: Tetragonal distortion of a cube.   the distortion creates a
tetragonal figure with an increased value of |a_3|.

The source of the BCT structure lies in the asymmetry of the octahedral void that is the preferred site for carbon. Since there are equal numbers of O_x, O_y and O_z octahedra in the BCC lattice, a random distribution of octahedral interstitials causes, on the average, an equal distortion of the three crystal axes and simply expands the BCC lattice. However, because of the asymmetric distortion, octahedral interstitials interact with one another and, if they are present in any significant concentration, preferentially occupy one of the three types of octahedral sites so that their short axes are aligned. When this happens there is a net long-range distortion of the crystal lattice in the direction of the short axis of the interstitial void that changes the structure from BCC to BCT.

When pure Fe is cooled from high temperature its structure changes from FCC to BCC. Carbon is more soluble in the FCC phase. If an FCC Fe-C alloy with a moderate carbon content is cooled very rapidly (quenched) then the carbon is trapped in the BCC product. The carbon interstitials preferentially adopt aligned octahedral sites, with the consequence that the quenched alloy, which is called *martensite*, has a body-centered tetragonal (BCT) structure. It is a very strong material with many important uses.

Decomposition and ordering of solid solutions

Very few species are mutually soluble in all proportions. The solubility range is ordinarily limited by the preferential interaction of the solute atoms, and is limited in one of two ways. If the solute atoms bond preferentially to one another they tend to become associated in the solid solution, or *cluster*. As the concentration of solute increases the tendency to cluster becomes more pronounced, until the solution spontaneously decomposes into a mixture of two solutions, or *phases*, one of which is rich in the solute and one in the solvent. The point at which this decomposition occurs defines the *solubility limit* of the solid solution. On the other hand, if the solute atoms bond preferentially to the solvent then they tend to adopt ordered configurations in which solute and solvent alternate in a regular crystal pattern. When the solute concentration becomes great enough the solution decomposes into a mixture of a solution that is rich in solvent and an *ordered compound* that contains nearly stoichiometric proportions of the two atom types.

Note that the definition of a point defect in an ordered compound of species A and B is different from that in a solid solution of B in A. A point defect in a compound is a deviation from the perfectly ordered state of the *compound* structure. For example, in a solid solution of Au in Cu each Au atom constitutes a point defect, since the pure Cu crystal is the reference. In the intermetallic compound Cu_3Au, on the other hand, an Au atom is a point defect only if it occupies a Cu position in the Cu_3Au structure (in which case it is an anti-site defect), while a Cu atom is a point defect if it occupies an Au site. This re-emphasizes the important point that a "crystal defect" is a deviation from the configuration the crystal would have if it were perfectly ordered, and has no meaning until the reference state, the perfectly ordered crystal, is defined.

4.3 LINE DEFECTS: DISLOCATIONS

Dislocations are linear defects; they are lines through the crystal along which crystallographic registry is lost. Their principle role in the microstructure is to control the yield strength and subsequent plastic deformation of crystalline solids at ordinary temperatures. Dislocations also participate in the growth of crystals and in the structures of interfaces between crystals. They act as electrical defects in optical materials and semiconductors, in which they are almost always undesirable.

The concept of a dislocation in a solid was introduced by Volterra in the nineteenth century. However, it was not until much later that their relevance to the deformation of crystals was recognized; the notion of a dislocation as the carrier of plastic deformation did not appear until 1934. Since the 1950's it has been possible to observe and study dislocations directly using such techniques as transmission electron microscopy and x-ray topography. While dislocations influence many aspects of physical behavior, they are studied almost exclusively in Materials Science. Most of you are encountering the concept of a dislocation for the first time.

4.3.1 The edge dislocation

The simplest way to grasp the idea of a dislocation is to imagine how you might go about creating one. We begin by making an edge dislocation, which is the easiest type of dislocation to visualize in a crystal, and follow the recipe laid down by Volterra.

Consider the solid body that is drawn in Fig. 4.5. For the present purpose it does not matter whether the body is crystalline; it may be easier to imagine that it is rubber.
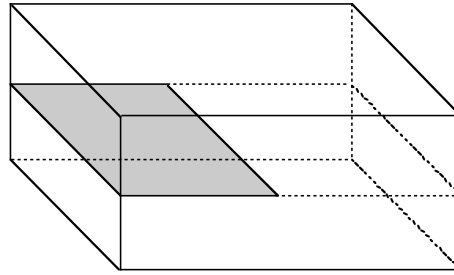
Fig. 4.5:   A block of material with a planar cut indicated by the
              shading.

To create an edge dislocation in this body we first make a planar cut part way through it, as illustrated by the shaded region in the figure. We then fix the part of the body below the cut, and apply a force to the body above the cut that tends to displace it in the direction of the cut, as illustrated in Fig. 4.6. The upper part slides, or *slips* over the lower by the vector distance **b**, which is the relative displacement of the two lips of the cut. The plane of the cut, where slip occurs, is called the *slip plane.* The cut is finite and constrained at its end, so material accumulates there. The end of the cut, or equivalently, the boundary of the planar region of slip, is a linear discontinuity in the material. The situation after the slip is shown in Fig. 4.6.
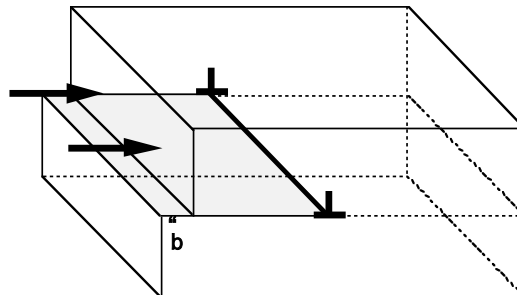

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Fig. 4.6:   The upper part of the body has been slipped by the vector **b**
              over the shaded area. The terminal line is a discontinuity,
              marked by the heavy line.

Now suppose that we have a mechanism for welding the material back together which is so efficient that it is impossible to tell after the fact that the weld was ever made. If we match the material above the shaded plane to that below so that there is no physical discontinuity across the plane and weld the lips together, the shading disappears since it is impossible to tell that the material was ever separated. However, matching the material across the plane of slip requires that excess material be gathered at the line at which slip terminates. This line is, therefore, a linear defect in the material. It is called an *edge dislocation.* It is an isolated defect, as shown in Fig. 4.7 since after the material has been re-welded there is no unique way to determine how the dislocation was created. For example, the dislocation would be exactly the same if the material to the right of it on the slip plane were slipped by the vector **-b** on the same plane. Only the exterior step

indicates the origin of the dislocation, and this may be removed, or may have pre-existed the formation of the dislocation.

However it was created, the edge dislocation in Fig. 4.7 has the property that it defines an element of slip, **b**, where the vector **b** is called the *Burgers vector* of the dislocation. We can always identify the slip plane of a dislocation like that shown in Fig. 4.7. It is the plane that contains both the Burgers vector, **b**, and the line of the dislocation. However the dislocation actually came to its present position, its net effect is that the material above the slip plane to the left of the dislocation (in the direction of **-b**) has been displaced by **b** relative to that below the slip plane. The dislocation is a linear defect whose location is defined by its line and whose nature is characterized by its Burgers vector, **b**. In the case shown in Fig. 4.7 the Burgers vector is perpendicular to the dislocation line. This perpendicularity is characteristic of an edge dislocation.
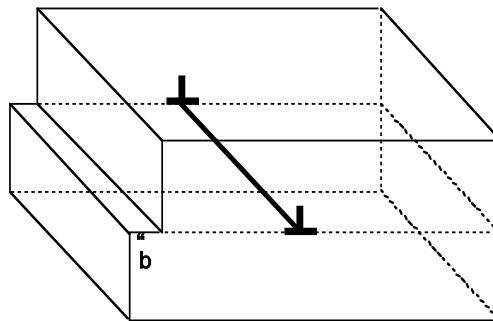
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Fig. 4.7:   Isolated edge dislocation after the cut surface has been rejoined.

If a dislocation moves the area that has been slipped grows or shrinks accordingly. Imagine that the dislocation is initially created at the left edge of the slip plane in Fig. 4.7, and is then gradually moved to the right edge. Applying the construction in Fig. 4.6 to the initial and final positions of the dislocation, it follows that the motion of the dislocation through the body causes the whole volume of material above the slip plane to be displaced by the vector **b** with respect to that below it, as shown in Fig. 4.8.
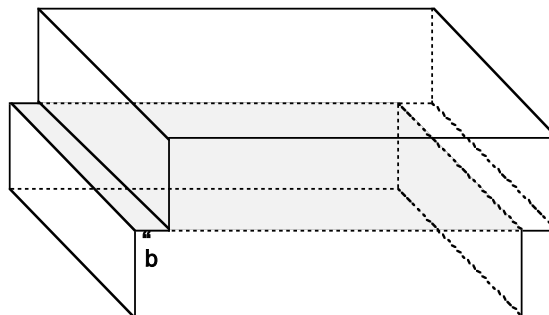

Fig. 4.8:   Final state of the body after an edge dislocation with Burgers' vector **b** has crossed the whole of the slip plane shown.

Fig. 4.8 illustrates the connection between the motion of a dislocation (in this case, an edge dislocation) and the plastic, or permanent deformation of a material. As we shall discuss in more detail when we consider the mechanical properties of materials, plastic deformation changes the shape of a body without changing its volume, since the total number of atoms and the crystal structure remain the same. A change in shape that occurs at constant volume can always be represented geometrically as the sum of elementary deformations of a type known as *simple shear.* A simple shear is the kind of deformation that deforms a cube into a parallelogram; it changes the angles between initially perpendicular directions in the cube. The shear due to the passage of an edge dislocation is illustrated in Fig. 4.9. While the dislocation translates the top of the crystal rigidly over the bottom to create a discrete step, the Burgers' vector has atomic dimensions, so the step is invisible. Macroscopic deformation is the sum of the slip caused by many dislocations.

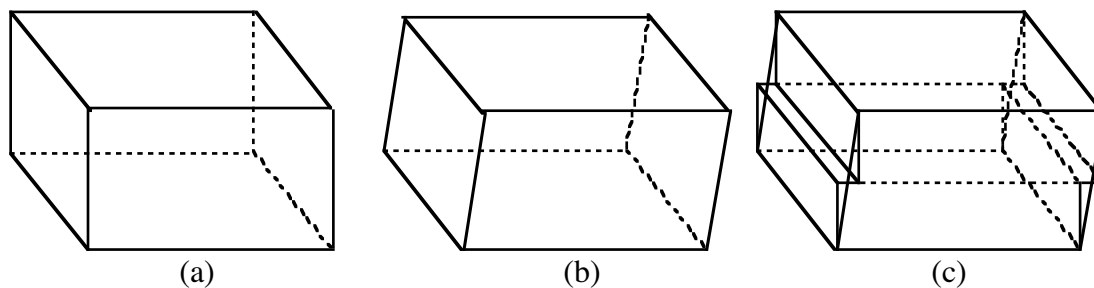(a)   (b)   (c)

Fig. 4.9: Figure (b) is obtained from (a) by a simple shear of the top over the bottom. Figure (c) shows how the same shear can be caused by an edge dislocation.

4.3.2 An edge dislocation in a simple cubic crystal

The procedure that was used to create the edge dislocation that appears in Fig. 4.7 made no reference to the structure of the solid, and can be used to form an edge dislocation in any material. However, when the material is crystalline the ordered pattern of atoms restricts the values that the Burgers vector, **b**, can have. The restriction is introduced by the welding step that is used to change the configuration shown in Fig. 4.6 to that in Fig. 4.7. The welding must be so perfect that it is impossible to tell that the two surfaces were ever separated. If the solid is crystalline this can only be true if the crystal structure is continuous across the slip plane after the weld is made. It follows that the relative displacement across the slip plane must equal a lattice vector so that atoms can re-bond without changing their local atomic configurations. Since the relative displacement is equal to the Burgers vector, **b**, of the dislocation, **b** must be a lattice vector. If the dislocation is an edge dislocation, **b** must also be perpendicular to the dislocation line.

The geometry of an edge dislocation is relatively easy to visualize when the crystal has a simple cubic crystal structure. The atomic configuration around the dislocation line is more complicated in real crystal structures, but it is not necessary to deal with that complexity to understand the behavior of dislocations at the level we shall

need in this course. Whenever we need to consider the crystallography of the dislocation we shall assume that the crystal structure is simple cubic.

An edge dislocation in a simple cubic structure is drawn in Fig. 4.10, which shows both a two-dimensional view and a three-dimensional section along the dislocation line. The dislocation can be created by making a cut in the crystal on the dashed plane that terminates at the dislocation line, displacing the material above the cut plane to the left of the dislocation by one lattice spacing, and allowing the atoms to re-bond across the slip plane. This recipe recreates the simple cubic unit cell everywhere except on the dislocation line itself (ignoring the small elastic distortion of the cells that border the dislocation line). Hence the Burgers vector, **b**, of the dislocation that is drawn in the figure is **b** = **a**[100], where **a** is a vector along the edge of the cubic unit cell.

(a)   (b)
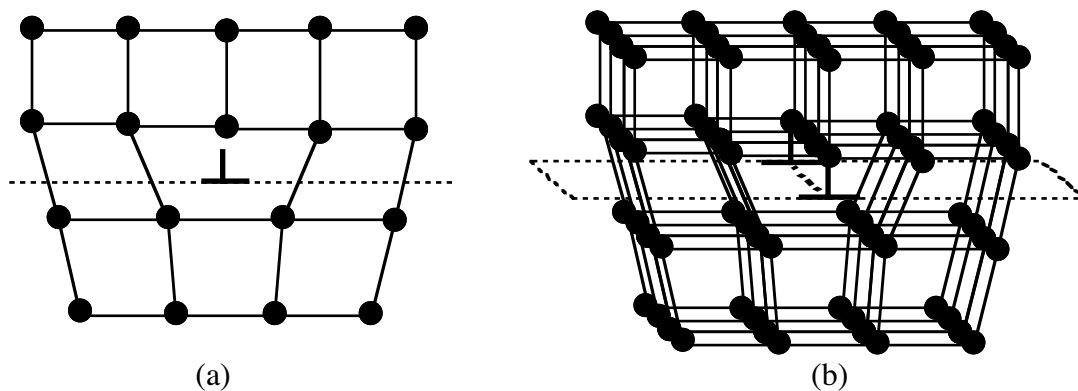
Fig. 4.10:   An edge dislocation in a simple cubic structure. The dotted plane is the slip plane.

The process that creates the edge dislocation shown in Fig. 4.10 leaves one extra vertical half-plane of atoms above the slip plane. This extra half-plane terminates at the dislocation line, and is compressed there, as shown in the figure. The distortion at the dislocation line is local. The simple cubic arrangement of atoms is essentially restored a few atom spacings away from the dislocation line. The influence of the dislocation on the atomic configuration rapidly decays into a small displacement that decreases in magnitude with the inverse cube of the distance from the dislocation line. The local distortion near the dislocation line (or *dislocation core*) is indicated in the figure.

In principle, the Burgers vector of a crystal dislocation can be any lattice vector; for example, it is geometrically possible for an edge dislocation to be the termination of any integral number of lattice planes. In reality, however, the Burgers vector is almost invariably equal to the shortest lattice vector in the crystal. The reason is that the energy per unit length of dislocation line, which is called the *line energy*, or, in a slightly different context, the *line tension* of the dislocation, increases with the square of the magnitude of **b**, $|\mathbf{b}|^2$. (While we shall not prove this, it is obvious from Fig. 4.10 that the local distortion of the crystal would increase dramatically if two or more extra half-planes terminated at the dislocation line.) Let the Burgers vector, **b**, be the vector sum of

smaller lattice vectors, $\mathbf{b} = \mathbf{b_1} + \mathbf{b_2}$. Unless $\mathbf{b_1}$ and $\mathbf{b_2}$ are perpendicular, $|(\mathbf{b_1}+\mathbf{b_2})|^2 >$ $|\mathbf{b_1}|^2 + |\mathbf{b_2}|^2$, and the dislocation can decrease its energy by splitting into two or more dislocations that have smaller Burgers vectors.

4.3.3   The Burgers circuit

While it is always possible to find the Burgers vector, $\mathbf{b}$, of a dislocation by determining the slip that would be required to make it, this is often inconvenient. A simpler method uses a geometric construction known as the Burgers circuit.

To construct the Burgers circuit, choose a direction for the dilocation line and draw a clockwise closed circuit in the perfect crystal by taking unit steps along the lattice vectors. An example is drawn for a {100} plane in a simple cubic crystal in Fig. 4.11. If the same circuit is drawn so that it encloses a dislocation, it fails to close. The vector (from the starting position) that is required to complete the circuit is the Burgers vector, $\mathbf{b}$, of the dislocation, and measures the net displacement experienced by an imaginary observer who completes a circuit around the dislocation that would be closed in a perfect crystal.
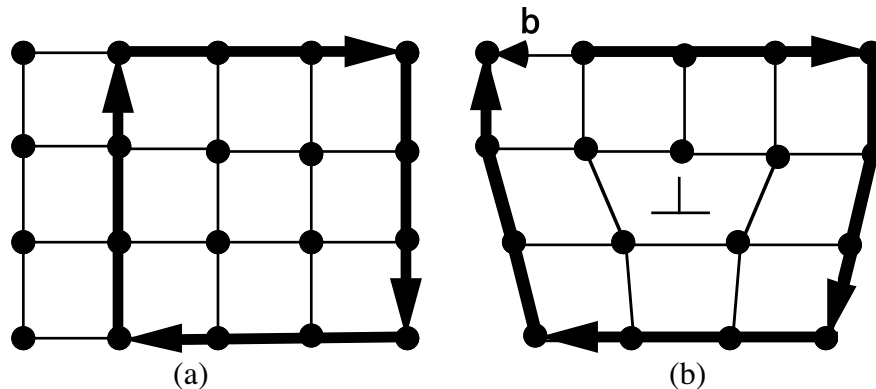

(a)   (b)

Fig. 4.11:   A Burgers circuit closes in a {100} plane of a cubic crystal, but fails to close by the Burgers vector, $\mathbf{b}$, when the same circuit encloses an edge dislocation.

4.3.4   Motion of an edge dislocation: glide and climb

The reason that dislocations control the plastic deformation of crystalline solids is that it is relatively easy to move dislocations to produce shear deformation of the sort that is pictured in Fig. 3.9. It would be enormously difficult to shear a crystal by forcing the glide of rigid planes of atoms over one another; one would have to force the simultaneous reconfiguration of every crystal bond that crossed the slip plane. The same result is more easily achieved by moving dislocations stepwise through the crystal. Stepwise dislocation motion requires a much smaller force since each elementary step can be accomplished by reconfiguring only the bonds that neighbor the dislocation line.

The stepwise motion of an edge dislocation in a simple cubic crystal is illustrated in Fig. 4.12. In order for the dislocation to move one lattice spacing to the right it is only necessary to break the bond indicated by the long dash in 4.12a and establish the bond indicated by the short dash. The new configuration is shown in Fig. 4.12b. Of course one bond must be broken for each plane through which the dislocation threads, so a significant force is still required. But the force is small compared to that required to slip the upper part of the crystal as a rigid body. If the dislocation moves through the crystal in a sequence of individual steps like that shown in Fig. 4.12 it causes a net slip of the material above its plane of motion by the Burgers vector, **b**, and hence causes a rigid displacement of the whole upper part of the crystal.
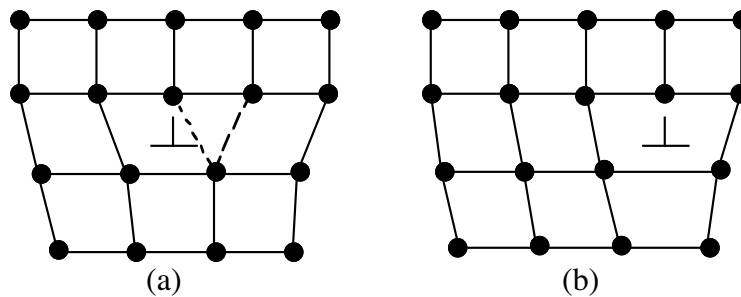

Fig. 4.12:   Glide of an edge dislocation. Only a single bond must be broken per plane for each increment of glide.

The type of motion that is illustrated in Fig. 4.12 is called *dislocation glide*, and is relatively easy to accomplish. However, an edge dislocation cannot glide in an arbitrary direction. It can only glide in a particular plane, the slip plane or *glide plane,* which contains both the Burgers vector and the dislocation line.
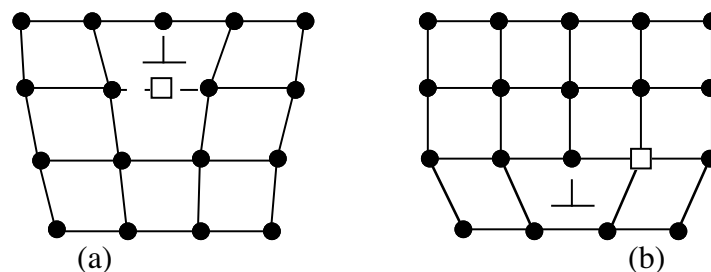

Fig. 4.13:   Climb of an edge dislocation. Movement up out of the plane requires the elimination of atoms by vacancies. Movement down requires the addition of atoms.

When an edge dislocation moves out of its glide plane its motion is called *climb.* The climb of a dislocation is difficult at ordinary temperatures since it requires that atoms be absorbed on or liberated from the extra half-plane of atoms that defines the dislocation line. The climb of an edge dislocation is illustrated in Fig. 4.13. The mechanism is slightly different depending on whether the dislocation moves up, which contracts the extra half-plane, or down, which extends it.

If the dislocation climbs up atoms must be liberated from the edge of the extra half-plane. Since the number of atoms is conserved, this requires the absorption of vacancies from the lattice. One vacancy is needed per plane the dislocation threads. If the dislocation climbs down it must add atoms to the extra half-plane, and can only do this by liberating one vacancy per plane into the matrix, as shown in Fig. 4.13b. Both processes are difficult except at high temperature when, as we shall see, the equilibrium concentration of vacancies is high and the exchange of vacancies and atoms is relatively easy.

Because of the difficulty of climb at ordinary temperatures the plastic deformation of real crystals tends to occur through the motion of dislocations on well-defined planes that are the glide planes of the active dislocations. Under a microscope one can often see discrete *slip steps* on the surface of a crystal that has been deformed. These result from the glide of many dislocations on closely spaced, parallel planes. At high temperature climb becomes possible and the slip planes are less well-defined. When this happens the *strength* of the crystal (its resistance to plastic deformation) decreases dramatically. For this reason most solids are relatively soft at high temperature.

4.3.5   Screw dislocations

Our discussion to this point has dealt only with edge dislocations, that is, dislocations in which the Burgers vector is perpendicular to the dislocation line. Dislocations in real crystals rarely have a pure edge character. Their Burgers vectors lie at various angles to their line directions.   In the extreme case the Burgers vector is parallel to the dislocation line, which is the characteristic of a *screw dislocation.* A screw dislocation is difficult to visualize in a crystal, but can be created by a method suggested by Volterra that closely resembles the way the edge dislocation was formed. A screw dislocation of the general Volterra type is shown in Fig. 4.14.
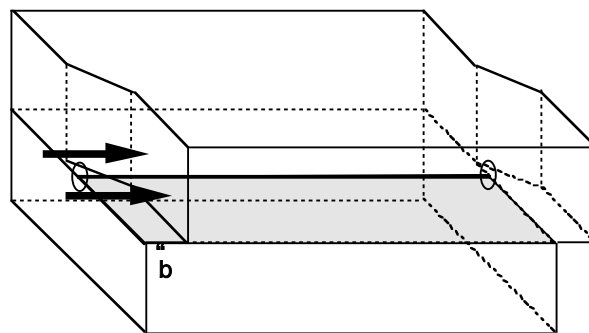

Fig. 4.14:   A method for forming a screw dislocation in a solid.

To introduce a screw dislocation we slice the solid part-way through in the direction of its width, as shown in Fig. 4.14. But instead of displacing the material above the cut toward the dislocation line we displace it by a vector, **b**, that lies parallel to the dislocation line, as shown in the figure. The direction of the force required to do this is

also indicated. The material is then re-welded so that it is continuous across the plane of slip. The residual distortion is concentrated at the dislocation line, which then constitutes an isolated linear defect.

If the body shown in Fig. 4.14 is crystalline then the cut surface shown in the figure is a plane of atoms. In order for the crystal to be continuous across the slip plane after it is rejoined, the displacement, **b**, must be such that this plane of atoms joins continuously onto a crystallographically identical plane. It follows that a closed circuit (Burgers circuit) that encloses a screw dislocation not only fails to close, but produces a net translation by **b** along the dislocation line, where **b** is a lattice vector. A circuit that starts on one plane of atoms finishes on another a distance **b** below. Continuing the circuit causes a displacement by **b** at each revolution, without the circuit ever leaving the atom plane. The effect of a screw dislocation is to join a set of parallel atom planes so that they become a single plane like one that would be created by extending a plane outward from the thread of a screw. Hence the name: screw dislocation.

As in the case of an edge dislocation the line energy of a screw dislocation is proportional to the square of its Burgers vector. Hence the Burgers vector of the screw dislocation is ordinarily the smallest lattice vector that is compatible with the direction of its line.

4.3.6   Screw dislocations and plastic deformation

A screw dislocation differs from an edge not only in its geometry but in the way it accomplishes plastic deformation. The most important qualitative differences concern its direction of motion under an applied force and its relative freedom of movement.

Figure 4.14 suggests the connection between slip and dislocation motion for a screw dislocation. As the screw dislocation is displaced through the width of the body the material above its plane is slipped in the direction of the Burgers vector, hence along the length of the body. It follows that the longitudinal force shown in the figure acts to drive the screw dislocation sideways. If a screw dislocation is passed through the full width of the body it causes the shear shown in Fig. 3.8, which is the same as that caused by the passage of an equivalent edge dislocation through the length.

In contrast to an edge dislocation, a screw dislocation can glide in any plane. Since the Burgers vector lies parallel to the dislocation line both are in any plane that contains the dislocation line, and the screw dislocation can move in any direction perpendicular to its line.

4.3.7   Dislocations in real materials: mixed dislocations

Dislocations in real materials are most commonly neither pure edge nor pure screw in their character, but are *mixed dislocations* whose Burgers vectors lie at an intermediate angle to the local direction of the dislocation line. Because of the way in which they interact with other elements of the microstructure (which we shall discuss at a

later point) dislocation lines are ordinarily curved. Since the dislocation bounds a region that has been slipped by the Burgers vector, **b**, the Burgers vector is the same at every point on the dislocation line. Hence the character of a curved dislocation changes continuously along its length. For this reason it is often most useful to think of a dislocation as the boundary of a surface over which the crystal has slipped rather than as a defect with a particular local atomic configuration.
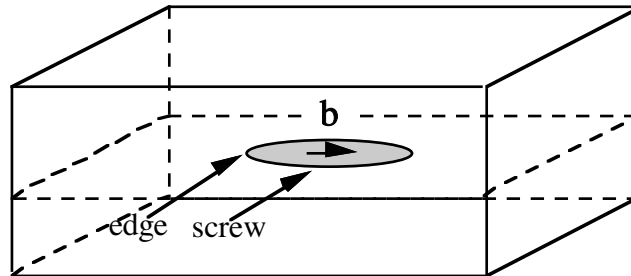

Fig. 4.15:   A dislocation loop in a crystal.

This point is illustrated by the dislocation loop shown in Fig. 4.15. Dislocation loops are relatively common features of the microstructures of structural alloys. The loop shown in the figure is created by a process that is equivalent to a slip of the cylinder of material above the loop by the vector **b**. The dislocation loop is the boundary of the surface on which slip has occurred. The character of the dislocation changes continuously around the loop. The dislocation has pure edge character at the extremities of the loop along the length of the body, and has pure screw character at the extremities along the width.

The qualitative nature of the force on a curved dislocation, such as the loop in Fig. 4.15, can also be understood by regarding it as the boundary of the slipped region. If the force on the body is oriented to shear the body by the vector **b** then the dislocation will tend to move so that it increases the area of slip; the loop will expand. If the force acts to shear the body in the direction -**b**, the dislocation will tend to move so that it shrinks the slipped area; the loop will contract.

Whether edge, screw or mixed in character, all dislocations have three important properties. First, they bound surfaces that divide the crystal so that the part above the surface is slipped by the vector, **b**, with respect to that below. Second, the slip on the surface bounded by the dislocation is constant and equal to a lattice vector. Hence the Burgers vector, **b**, is a lattice vector and has the same value at every point on the dislocation line. Third, since the slip is constant, a dislocation cannot simply end within a material; there is always a boundary between a slipped and an unslipped area. The dislocation can terminate at a free surface, as in Fig. 4.7 and 4.14, it can close on itself, as in Fig. 4.15, or it can end at a junction with other dislocations that bound surfaces over which the magnitude or direction of slip is different.

4.3.8 Partial dislocations

In the original concept of Volterra, the Burgers' vector of a crystal dislocation is a translation vector of the crystal, that is, a vector that connects atom positions so that the crystal can be rejoined perfectly across its glide plane. Such a dislocation is called a *total dislocation*. The element of slip it induces carries an atom in the glide plane from one atom position to another. Only total dislocations can be true two-dimensional defects. If the Burgers' vector were not a translation vector of the crystal the slipped surfaces would not weld perfectly together across the glide plane and a planar, surface defect would be left behind whenever the dislocation moved.

While most crystal dislocations are total dislocations when viewed from sufficiently far away, it is not uncommon to find them dissociated locally into a configuration that can be described as two parallel *partial dislocations* connected by a planar defect that is called a *stacking fault* in the crystal. The prototypic example is found in FCC crystals.
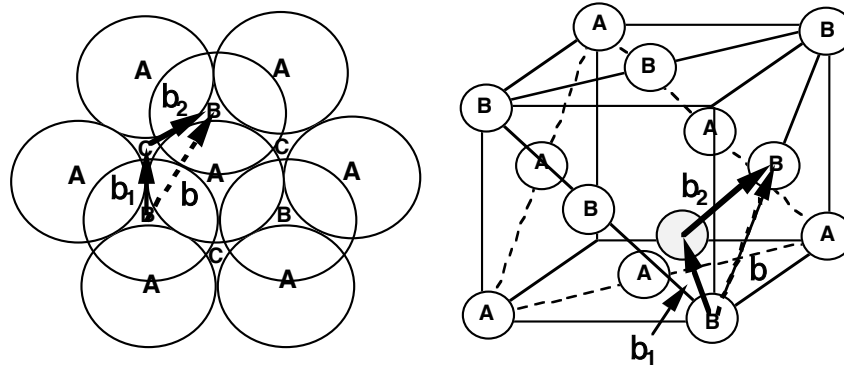
...
Fig. 4.16:   Illustration of the slip of close-packed planes. The dashed arrow shows slip by a total dislocation, $\mathbf{b} = \frac{1}{2}[\bar{1}01]$, which carries B→B. The solid arrows show the competing process of successive slip by two partial dislocations. The shaded atom in the cell is the intermediate, C-site position reached after partial slip.

The common dislocation in the FCC structure is the dislocation that causes close-packed planes to slip over one another. The close-packed planes are {111} planes, and the Burgers' vectors of the dislocations that induce slip on these planes are the $\frac{1}{2}$<110> vectors that connect atoms to their nearest neighbors in the {111} planes. Fig. 4.16 illustrates the path by which an FCC crystal is slipped by one atom spacing in the (111) plane. The slip vector is $\frac{1}{2}[\bar{1}01]$, and is the slip caused by a dislocation with Burgers' vector $\mathbf{b} = \frac{1}{2}[\bar{1}01]$. Assuming that the glide plane of the dislocation lies between (111) planes of A and B-type atom sites, the element of slip carries an atom from one B-site to another, as shown in the figure. For clarity, the figure is drawn twice. The drawing on the left shows the displacement in a stacking of close-packed planes (A,B). The drawing on the right places the A and B planes in an FCC unit cell.

Direct slip from one B position to another is relatively difficult, as one can easily show by trying to slide two close-packed arrays of balls over one another. The atoms (balls) in the B-plane must ride over the A atoms, as illustrated in the figure. It is much easier to accomplish the slip in two sequential steps, as indicated in the figure, that circumvent the A atoms. The B atoms are first slipped into C positions, then moved from C back to B again. The slip can be accomplished by the sequential passage of two dislocations with the Burgers' vectors $\mathbf{b_1}$ and $\mathbf{b_2}$. However, $\mathbf{b_1}$ and $\mathbf{b_2}$ are not lattice vectors; they are examples of *partial dislocations*. Their sum is the *total dislocation*, $\mathbf{b}$.
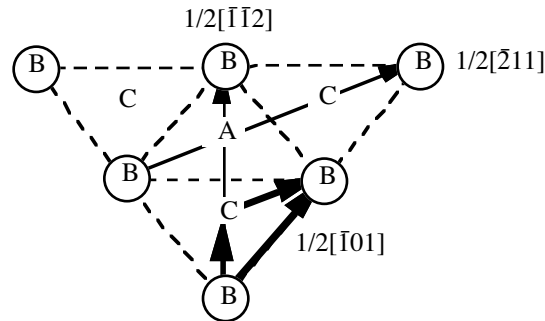

Fig. 4.17:   Configuration of atoms in the (111) plane showing the partial and total slip vectors.

To find the Burgers' vectors of the partial dislocations let the close-packed plane be the (111) plane, as shown in the right-hand figure in 4.16. The atom shift is to the shaded atom position, followed by a shift to the final atom position in the face center. The (111) plane of B-sites in the unit cell in Fig. 4.16 is redrawn in Fig. 4.17. As shown in this figure, the Burgers' vector of the total dislocation is $\mathbf{b} = \frac{1}{2}[\bar{1}01]$. The first partial slip is from the B site at the corner of the unit cell to the nearest C-site in the plane. This slip is 1/3 of the vector connecting B-sites along the height of the triangular configuration of atoms in the plane, which is $\frac{1}{2}[\bar{1}\bar{1}2]$. Hence

$$\mathbf{b_1} = \frac{1}{6}[\bar{1}\bar{1}2] \qquad\qquad 4.2$$

The second partial slip is from the C-site to the final B-site position. As shown in the figure, this vector is parallel to the vector $\frac{1}{2}[\bar{2}11\}$, and is 1/3 of its length. Hence

$$\mathbf{b_2} = \frac{1}{6}[\bar{2}11] \qquad\qquad 4.3$$

The vector sum of the two partial dislocation vectors is

$$\mathbf{b_1} + \mathbf{b_2} = \frac{1}{6}[\bar{1}\bar{1}2] + \frac{1}{6}[\bar{2}11] = \frac{1}{2}[\bar{1}01] = \mathbf{b} \qquad\qquad 4.4$$

Splitting the total dislocation, **b**, into the partials, $\mathbf{b}_1$ and $\mathbf{b}_2$, not only facilitates slip, but also lowers the total energy. The energy per unit length of dislocation line is proportional to $|\mathbf{b}|^2$. Since

$$|\mathbf{b}|^2 > |\mathbf{b}_1|^2 + |\mathbf{b}_2|^2 \qquad\qquad 4.5$$

the energy of a parallel pair of partial dislocations, $\mathbf{b}_1$ and $\mathbf{b}_2$, is less than that of the total dislocation, $\mathbf{b} = \mathbf{b}_1 + \mathbf{b}_2$.
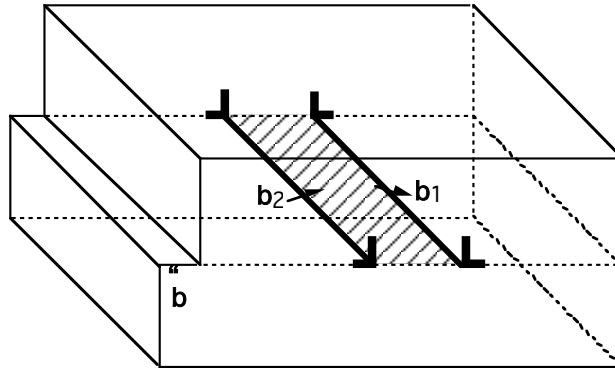

Fig. 4.18:   The total dislocation, **b**, divided into partial dislocations, $\mathbf{b}_1$ and $\mathbf{b}_2$ separated by a stacking fault.

However, to understand the configuration that appears when the dislocation is split we must recognize that eq. 4.5 gives only part of the energy of the pair of partials. Let the total dislocation divide, as illustrated in Fig. 4.18. In the area between the partials, which is shaded in the figure, the region above the slip plane has been slipped by the vector $\mathbf{b}_1$, but has not yet experiences the slip $\mathbf{b}_2$. Let the slip plane lie between A and B-planes, as illustrated in Fig. 4.16. The partial slip $\mathbf{b}_1$ carries the atoms in B-sites into C-sites, and causes corresponding changes C→A and A→B in successively higher planes. The FCC crystal has the stacking ..ABCABC.. But the stacking encountered in a direction perpendicular to the glide plane that passes through the shaded area between the partials is ..ABCA|CABC.., where the slash indicates the glide plane. The partial dislocation perturbs the sequence of close-packed planes; it introduces a planar defect called a *stacking fault* on the glide plane between the two partials.

A stacking fault has a positive energy, σ_s, per unit area. The separation of the two partials, $\mathbf{b}_1$ and $\mathbf{b}_2$, creates a stacking fault whose area increases as the partials move apart. There is, therefore, an equilibrium separation between the partial dislocations. They separate to decrease the energy per length of dislocation, but are attracted by the need to minimize the stacking fault energy. The balance of these two effects determines the equilibrium separation, which is of the order of 5-500Å in typical FCC crystals.

Similar considerations apply to HCP and diamond cubic crystals. Total dislocations in the close-packed planes tend to divide into partials separated by ribbons of stacking fault. In BCC crystals the division of total dislocations into partials is much less

pronounced. Separated partials cannot ordinarily be resolved in BCC, even through high resolution electron microscopy. Their presence is inferred from features of the mechanical behavior that are most easily explained by assuming that total dislocations dissociate slightly.

4.4   TWO-DIMENSIONAL DEFECTS: INTERFACES

The two-dimensional defects that appear in crystals can be usefully divided into three types: *free surfaces*, which are the external surfaces at which the solid terminates at a vapor or liquid, *intercrystalline boundaries*, which separate grains or distinct phases within the solid, and *internal defects* that disrupt the crystalline pattern over a surface within a crystal. All of these defects have two important characteristics. First, since they are surfaces in a crystal they have particular atomic structures that depend on orientation. Second, they have a positive energy. The energy per unit area is ordinarily equal to the *surface tension*, σ, of the interface.
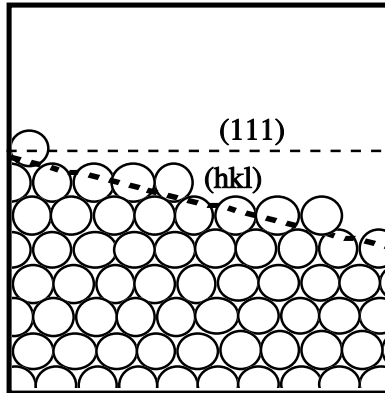
4.4.1   Free surfaces

The interface between a crystalline solid and a vapor or liquid governs the interaction between the two phases, and influences the behavior of the solid in many important ways that we shall discuss later in the course. It also affects the shape of the solid. The shape and properties of the free surface are determined by a combination of its structure and its energy. These two parameters are related to one another.
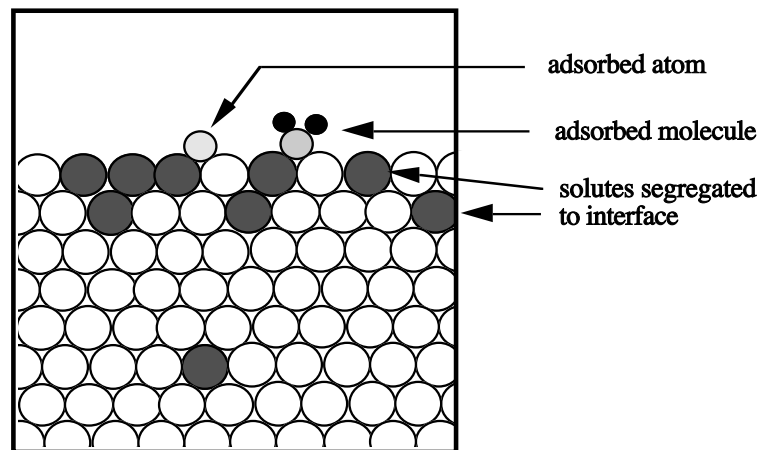
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Fig. 4.19:   Solid surface showing segregated solutes and adsorbates.

The crystal structure of the solid extends up to the free surface. The structure of the surface is derived from the pattern of atomic packing on the crystal plane that lies parallel to the surface, and the behavior of the surface can often be inferred from that pattern. However, the structure of the surface always differs at least a bit from that of a crystal plane that parallels it within the bulk crystal.   Even when the crystal sits in a

perfect vacuum, the atoms in the free surface are bonded on only one side and the spacing and the configuration of the atoms in the first few planes at the interface adjusts to accommodate the asymmetry of the bonding in the bast possible way. The structure of a real interface is further complicated by bonding interactions across the interface and by chemical changes in the interfacial plane. The dangling bonds at the interface provide favorable sites for the adsorption of atoms that do not fit well into the bulk lattice. The interface is often enriched in solute species (*surfactants*). Oxygen, sulfur and phosphorous are common surfactants in engineering solids.

...
Fig. 4.20:   A surface of overall orientation (hkl) made up of close-
               packed segments in steps.

The interfacial tension of the free surface depends on its structure, and is determined, in large part, by the number of bonds that are broken because the crystal is not continued on the far side of the interface. As a consequence the interfacial tension, σ, is a function of the orientation of the surface. In a typical metal, the interfacial tension is a relatively weak function of the orientation. Because metallic bonding is relatively non-directional, the interfacial tension of a typical metal tends to vary with the density of packing in the interface and is minimized for surface orientations that parallel close-packed planes ({111} in FCC, {110} in BCC).   Covalent solids have fewer neighbors, and more directional bonds, and are much more strongly anisotropic in their surface tension.

The external surfaces of metallic and covalent solids tend to parallel the planes of closest atomic packing, as illustrated in Fig. 4.19. This tendency also influences the atomic structures of interfacial planes that have other orientations. An interface that does not parallel a close-packed plane often has a structure in which flat, close-packed segments form ledges of atomic height that give a stepped structure with the proper overall orientation, as illustrated in Fig. 4.20. While the stepped morphology increases the surface area, the overall surface tension is lower because of the relatively low surface tension of the close-packed steps.
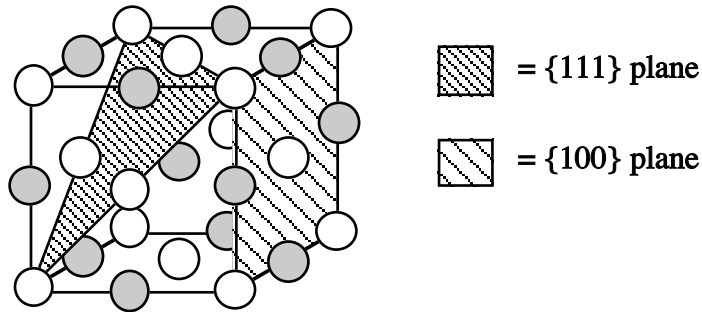
Fig. 4.21:   The NaCl structure, showing the electrical neutrality of the {100} plane and the preferential charge on the {111} plane.

The interfacial tension of a surface in an ionic solid is strongly affected by the distribution of electric charge. In strongly ionic materials (for example, NaCl) the electrically neutral surfaces ({100} in NaCl) have much lower interfacial tensions than the charged surfaces (such as {111} (Fig. 4.21)). The relative interfacial tensions of charged and uncharged surfaces can, of course, be altered by the addition of surfactants, which are often preferentially attracted to the charged surfaces.

The shapes of crystals

The preferred shape of a crystal that is bounded by free surfaces is the one that minimizes its total interfacial energy. The macroscopic surface of the crystal can always be treated as if it were made up of facets, the kth one of which has area, A_k , and interfacial tension, σ_k. The energy is, then,

$$E = \sum_k \sigma_k A_k \qquad\qquad 4.5$$

When the crystal is a simple metal the surface tension is nearly isotropic. The preferred shape is nearly spherical, since a spherical shape minimizes the surface area for given volume. When the crystal is ionic or strongly covalent there are crystal planes whose tensions are, relatively, very low. To minimize the total interfacial energy, ionic and covalent solids tend to assume polygonal shapes with large, flat facets parallel to the low-energy planes.

This is the physical reason that compound solids and minerals often *look* crystalline, while metals usually do not. The natural macroscopic shapes of such compounds are polygonal (*crystalline*) because of the strong anisotropy of the surface tension. You can readily verify, for example, that the grains of common table salt have a cubic shape; this shape reflects the low energy of the neutral {100} surfaces in the NaCl structure. Many common minerals have hexagonal structures in which the *prismatic planes* (the vertical planes in the hexagonal unit cell) are electrically neutral. These materials tend to grow as well-shaped hexagonal prisms. Simple metals, on the other hand, are more

isotropic in their interfacial tensions, and tend to form crystals that are cylindrical or spherical in their macroscopic shapes.

The shapes of crystals can be altered and controlled by adding selective chemical surfactants that modify the surface tensions of particular planes. For example, NaCl can be made to crystallize in an irregular particle with mainly {111} faces by adding a suitable surfactant.

Solid-liquid interfaces

The interface between a crystalline solid and a vapor is usually sharp. The surface is a crystal plane or stepped layer of planes. Interfaces between solids and liquids, on the other hand, are often diffuse. There is a high density of atoms in the liquid near the solid surface, and these may have a local arrangement that does not differ that greatly from the crystalline pattern in the solid. In these cases the tension of the solid-liquid interface is a weak function of surface orientation, and the solid adopts a diffuse interfacial structure like that shown in Fig. 4.22.
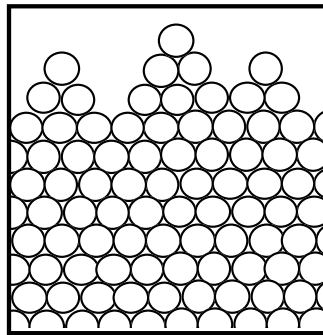

Fig. 4.22:   Possible configuration of a diffuse interface.

The possibility of forming a diffuse interface is important in the solidification of solids from the melt and the growth of crystals from the melt. Atoms of the liquid can be easily incorporated into a diffuse interface, with the consequence that a solid that has such an interface can solidify easily and rapidly.

4.4.2 Interfaces between crystals

The most important internal interfaces in a typical solid are those that separate the individual crystallites it contains. Almost all crystalline solids are polycrystalline. They are composed of many small crystallites (*grains*) of the primary constituent, and may also contain several distinct constituents (*phases*) of different composition and crystal structure. The interfaces that separate grains are called *grain boundaries*. Those that separate phases are called *two-phase interfaces*.

Grain boundaries

The structure of a grain boundary depends on the misorientation of the crystal grains that it separates. When the misorientation is small the boundary, which is then called a *low-angle boundary*, is a reasonably simple planar array of dislocations. When the misorientation is larger the boundary structure is more complicated, and it is often useful to picture the boundary as simply a region of disorder between the two crystal grains.
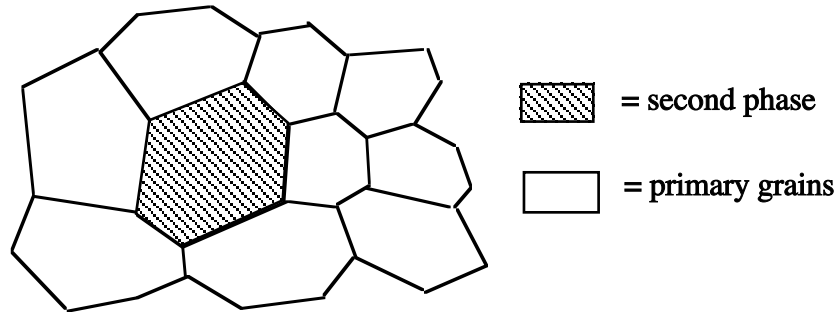
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Fig. 4.23: Schematic drawing of polygranular grain structure showing grain boundaries and two-phase interfaces.

The structure of a *low-angle tilt boundary* is shown in Fig. 4.24. A tilt boundary is a vertical array of parallel edge dislocations. When a tilt boundary is introduced into a single crystal it creates a misorientation by the *tilt angle*, θ, between the volumes of crystal on either side. If the dislocations in the boundary have Burgers' vector, **b**, and are separated by a vertical distance, d, then the tilt angle, θ, is given by

$$\theta = \tan^{-1}\left[\frac{|\mathbf{b}|}{d}\right]$$
4.7
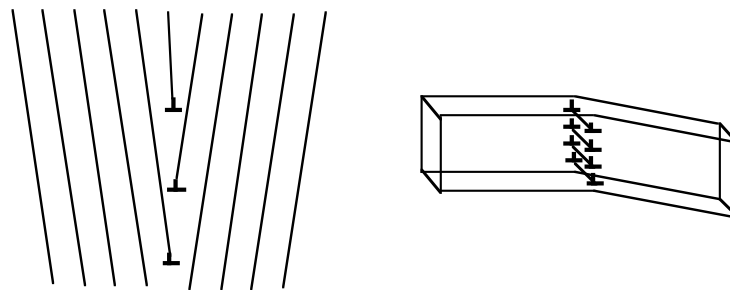
...
Fig. 4.24: A low-angle tilt boundary as a vertical array of parallel edge dislocations.

A second type of low-angle boundary that can also be generated by a simple array of dislocations is a *twist boundary*. If two sets of parallel screw dislocations are arrayed in a perpendicular pattern in a plane the result is a twist in the boundary plane. The crystal on one side of the plane is rotated with respect to that on the other by a *twist angle* about an axis perpendicular to the plane of the boundary. A twist boundary is not simple to draw, and we shall not attempt to do so here.

The structures of *high-angle grain boundaries* can be crudely understood by simply matching two crystals that are misoriented by the angle of the boundary. As illustrated in Fig. 4.25, this process ordinarily leads to a relatively poor match of crystal planes along the boundary. While there are relaxations in the boundary that reduce its disorder somewhat, a typical high-angle boundary is relatively disordered, with a high density empty spaces and open channels. High-angle grain boundaries provide easy paths for atom diffusion in the solid state. They also provide preferential sites for solutes and impurities that do not fit very well in the bulk crystal, and adsorb as *surfactants* on the boundary.
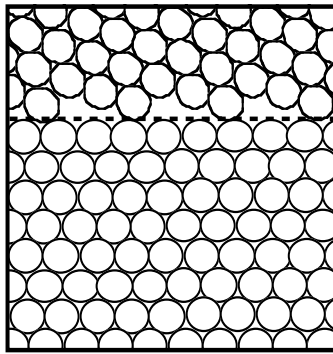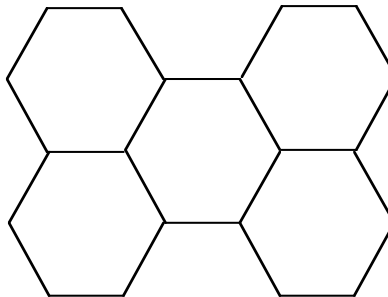

Fig. 4.25:   A possible configuration of a high-angle grain boundary.

There are, however, certain high-angle boundaries whose misorientations provide a relatively good geometric match between the adjacent crystals. These are called *coincidence boundaries.* Their study is beyond the scope of this course.

The equilibrium shape of a grain

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Fig. 4.26:   Ideal hexagonal configuration of a two-dimensional grain structure with constant σ_B.

The interfacial tension of a grain boundary is often a relatively weak function of its orientation; for most purposes we can assume that it has the constant value, σ_B. When this is true a local equilibrium is achieved when grain boundaries meet in three-grain

junctions in a configuration in which the angle between adjacent boundaries is 120°. When the grain structure is two-dimensional, as it is in a thin film one grain thick, then local equilibrium is achieved when the grains are hexagonal platelets, as in Fig. 4.26.

When the grain structure is three-dimensional a microstructure that is very near to local equilibrium can be built up of fourteen-sided polyhedra that are known as *Thomson tetrakaidecahedra.* The tetrakaidecahedron is shown in Fig. 4.27. It looks very complex but, in fact, has a very simple construction. If one takes a body centered cubic array of points and constructs planes that bisect the lines connecting a given point to its first and second nearest neighbors, the inner envelope of these planes is the tetrakaidecahedron. The tetrakaidecahedron is just the *Wigner-Seitz cell* of the BCC structure. It follows that tetrakaidecahedra stack in a body-centered cubic array. The BCC array of tetrakaidecahedra is sometimes useful as a model of a three-dimensional microstructure. However, its accuracy is limited; real polygranular solids are built up of irregularly shaped grains that have a distribution of sizes and an irregular pattern in space (as in Fig. 4.22). The grains in real microstructures are never quite in minimum-energy configurations. A somewhat better model of a real microstructure is a three-dimensional foam of the type that forms on beverages that are familiar to undergraduates.

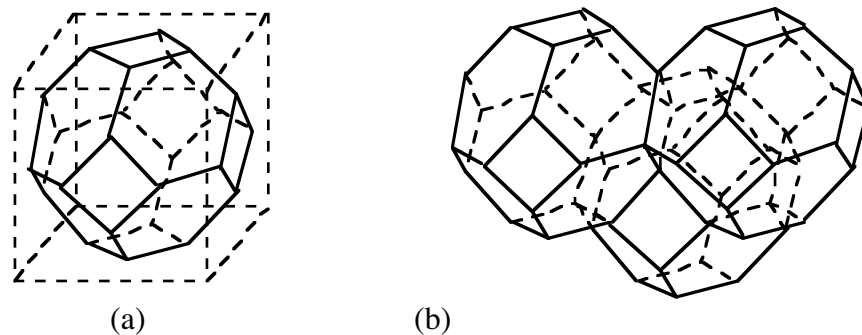(a)   (b)

Fig. 4.27:   (a) Thomson tetrakaidecahedron inscribed in a cube.   (b) Packing of tetrakaidecahedra into a BCC array.

The positive surface tension of the grain boundary has the consequence that the energy of a polygranular material increases in proportion to the total grain boundary area. Large grains have a smaller surface energy per unit volume than small ones. If a polygranular solid is held at high temperature where the atoms are relatively mobile then grains can grow or shrink by adding or losing atoms to adjacent grains. The large grains grow at the expense of the smaller ones to decrease the energy, which causes the mean grain size to increase with time.

The grain structure is usually characterized by its *mean grain size*, which is measured as the mean grain diameter. The mean grain size provides an incomplete characterization of the grain structure; both the distribution of grain sizes and the grain shape are also important. These aspects of the grain structure are more difficult to measure quantitatively. In practice a characterization of the grain structure usually

consists of a value for the mean grain size and a set of photomicrographs that present the geometrical features of the grain structure in visual form.

Two-phase interfaces

Two-phase interfaces have many of the properties of grain boundaries, including a specific structure and interfacial energy. The most important structural characteristic of a two-phase interface is its *coherency*. If it is possible to order the phases on both sides of the interface on the same crystal lattice the interface is said to be *coherent*. A two-dimensional example is given in Fig. 4.28. Coherent interfaces are common in real systems. When small precipitates form in the interior of a solid the precipitate phase that forms first usually involves only a slightly different atomic ordering on the lattice of the parent structure and has a coherent interface with it. In the modern science of thin-film electronics multi-layer structures are often deposited atom layer by atom layer from the vapor phase, to create a *heterostructure* of atom layers of different composition that are coherent with one another.
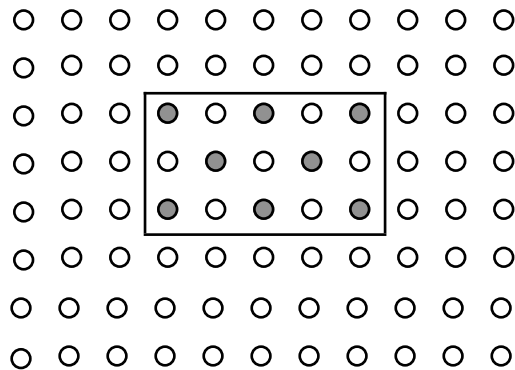
Fig. 4.28:   Coherent, ordered precipitate in a two-dimensional crystal.

On the other hand, since two different crystalline phases almost never fit perfectly together, both are distorted if they are joined by a coherent interface. In the case of a small precipitate particle the lattice distortion that is caused by the coherent interface increases with the particle size, and provides an increasing driving force to destroy continuity at the interface. When a second-phase particle grows to large size it almost always loses coherency with the surrounding matrix. The most common mechanism causing the loss of coherency is the accumulation of dislocations at the interface.

The surface tension of a coherent two-phase interface is highly anisotropic since the two phases only fit well when they have a simple crystallographic relation to one another. The volumetric distortion of the precipitate also depends strongly on its shape and crystallographic fit. As a consequence, coherent second-phase particles such as small precipitates tend to have characteristic shapes and interfaces that lie almost entirely in a particular crystallographic plane of the parent crystal, which is known as the *habit plane* of the precipitate. The well-defined habit is lost when the precipitate is incoherent.

The positive interfacial tension of second-phase particles has the consequence that the energy per unit volume decreases as the particle grows. Given a distribution of precipitate sizes and a temperature high enough to permit atomic rearrangements the larger particles grow at the expense of the smaller ones to decrease the energy, and the second-phase particle distribution *coarsens.*

4.4.3 Interfaces within crystals

The surface defects that commonly appear in the interior of a crystal are of two types: *stacking faults* and *antiphase boundaries.* We have already encountered the stacking fault, which is a defect in the sequence of planes of atom positions in the crystal. An antiphase boundary is a defect in the sequence of atom distributions over the planes. Anti-phase boundaries can only occur in ordered compounds.
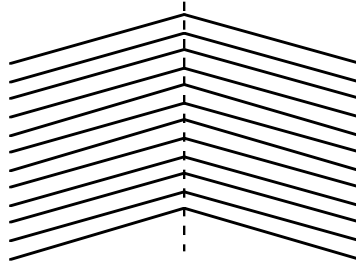
Stacking faults

The simplest examples of stacking faults (and the only ones that we shall study) are found in close-packed structures. Using the notation introduced in the previous chapter, a stacking of close-packed planes in the order ...ABCABC... generates the FCC structure. A stacking fault occurs wherever this pattern is broken. For example, in a crystal with the local stacking sequence ...ABCBABC... the extra B plane in the middle constitutes a stacking fault.

It is sometimes useful to distinguish three kinds of stacking fault. An *extrinsic* stacking fault is one that can be created by inserting an extra plane of atoms into the structure. In the ...ABC|B|ABC... pattern given above the plane marked |B| is an extrinsic stacking fault. Extrinsic stacking faults appear, for example, after an irradiation treatment creates many interstitialcies that subsequently gather together on close-packed planes.

An *intrinsic* stacking fault is one that can be created by removing a plane of atoms. In the sequence ...ABC||BCABC.. the defect marked || corresponds to a missing A-plane, and is hence an intrinsic stacking fault. An intrinsic stacking fault is created by the condensation of vacancies onto a close-packed plane. It is also created by a partial slip of the crystal to the right of the fault that carries A-sites to B-sites, B-sites to C-sites, and C-sites to A-sites. A partial slip of this type is caused by the motion of a partial dislocation of the type discussed at the end of section 4.3.

The third kind of stacking fault is called a *twin boundary*, and is a surface that separates two volumes of crystal that are mirror images of one another, as illustrated in Fig. 4.28. In the sequence ...ABCAB|C|BACBA... the plane marked C is a twin boundary; on either side the crystal has a perfect FCC structure, but the two FCC lattices are mirror images of one another across the twin plane. Twin boundaries are most often introduced during the growth of a crystal. If the crystal grows by adding planes to the right and if an extrinsic fault (B) occurs just to the right of |C|, the energy of the fault is usually minimized if the next plane is added at A, and so on, to maximize the fraction of

proper FCC packing in the crystal. The formation of twin boundaries is also important in the plastic deformation of some materials, as we shall discuss later in the course.

...
Fig. 4.29:   The relation of crystal planes across a twin boundary.

Note that if a stacking fault is repeated with perfect periodicity it does not constitute a fault, but creates a new crystal structure. For example, the sequences ABCAB, ABCABCAB, and ABABABC are regular mixtures of FCC and HCP packing that generate new structures if they are repeated indefinitely. Such mixed structures occur in nature. They are usually found in materials that exhibit both FCC and HCP-type structures, which indicates that the stacking fault energy is relatively small. Mixed structures are particularly common in SiC, ZnS and CdS, all of which have alternate α-ZnS (FCC) and β-ZnS (HCP) structures. The mixed structures are called *polytypes*, and can have very long repeat periods.

Antiphase boundaries

The internal defects known as *antiphase boundaries* only occur in ordered compounds. An example is given in Fig. 4.30, which illustrates a {110} antiphase boundary in a compound with the CsCl structure.

An ordered compound can always be regarded as a stacking of parallel planes, each of which has a particular substitutional pattern of the atomic species. Fig. 4.30a, for example, illustrates how the CsCl structure can be made by stacking {110} planes that alternate in the specific arrangement of the two types of atoms. An antiphase boundary is created when a plane with the wrong pattern appears, and subsequent planes follow it in their patterns. In Fig. 4.29b the third {110} plane has its atom positions shifted by $\frac{1}{2}$ <110> from the expected pattern, and is, hence, an antiphase defect. An antiphase boundary resembles an intrinsic stacking fault in that it can be created either by omitting one plane in the stacking pattern, or by a slip displacement at the antiphase plane. Mechanical slip is an important source of antiphase defects. Note that the antiphase defect in Fig. 4.30b is precisely that which would be created if a dislocation of Burgers vector $\frac{1}{2}$[110] passed through the plane. Since $\frac{1}{2}$[110] is a vector connecting nearest neighbor atoms in the closest-packed planes of the BCC structure, it is a common Burgers vector for dislocations in BCC.
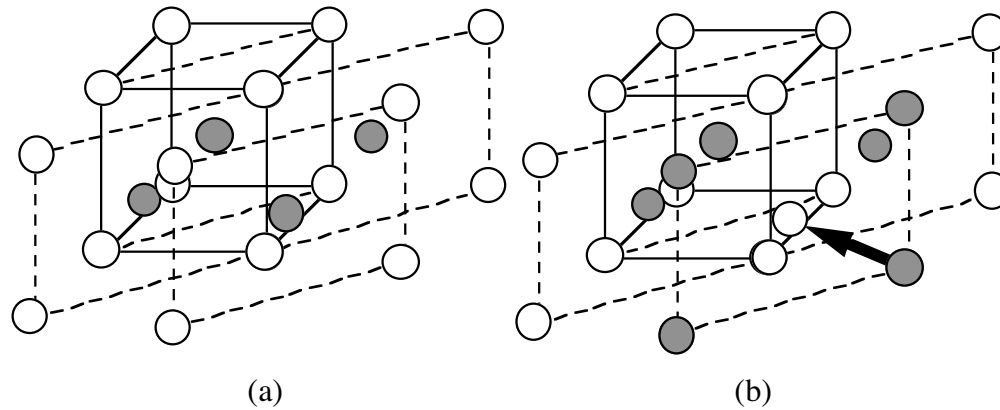
(a)   (b)

Fig. 4.30:   (a) The CsCl structure drawn as a stacking of {110} planes.
(b) An antiphase boundary in the CsCl structure made by a
displacement of the type $\frac{1}{2}$<110> in the third plane.

4.5   VOLUME DEFECTS

Volume defects in crystals are three-dimensional aggregates of atoms or vacancies. It is common to divide them into four classes in an imprecise classification that is based on a combination of the size and effect of the particle. The four categories are: *precipitates*, which are a fraction of a micron in size and decorate the crystal; second-phase particles or *dispersants*, which vary in size from a fraction of a micron to the normal grain size (10-100μm), but are intentionally introduced into the microstructure; *inclusions*, which vary in size from a few microns to macroscopic dimensions, and are relatively large, undesirable particles that entered the system as dirt or formed by precipitation; and *voids*, which are holes in the solid formed by trapped gases or by the accumulation of vacancies.

Precipitates are small particles that are introduced into the matrix by solid state reactions. While precipitates are used for several purposes, their most common purpose is to increase the strength of structural alloys by acting as obstacles to the motion of dislocations. Their efficiency in doing this depends on their size, their internal properties, and their distribution through the lattice. However, their role in the microstructure is to modify the behavior of the matrix rather than to act as separate phases in their own right.

Dispersants are larger particles that behave as a second phase as well as influencing the behavior of the primary phase. They may be large precipitates, grains, or polygranular particles distributed through the microstructure. When a microstructure contains dispersants such properties as mechanical strength and electrical conductivity are some average of the properties of the dispersant phase and the parent.

Inclusions are foreign particles or large precipitate particles. They are usually un-desirable constituents in the microstructure. For example, inclusions have a deleterious effect on the useful strength of structural alloys since they are preferential sites for failure. They are also often harmful in microelectronic devices since they disturb the ge-

ometry of the device by interfering in manufacturing, or alter its electrical properties by introducing undesirable properties of their own.

Voids (or *pores*) are caused by gases that are trapped during solidification or by vacancy condensation in the solid state. They are almost always undesirable defects. Their principal effect is to decrease mechanical strength and promote fracture at small loads.