Crystal imperfections

Classification of defects & Point defects

Perfect crystals do not exist. Defects in crystal which result in departure from periodicity. Some defects are the result of crystal growth and handling (dislocations, grain boundaries), others are intrinsic properties of the crystalline state at non-zero (Kelvin) temperature (vacancies or intersticials). Various defects affect various type of physical or chemical properties of crystalline solids. It is thus extremely important to understand the origin and nature of defects in crystals. In this chapter we will discuss the three basic classes of defects in crystals.

i. Point defects – 0 dimensional defect (atoms missing or in irregular places in the lattice (lattice vacancies, substitutional and interstitial impurities, self-interstitials)

ii. Line defects – 1 dimensional defect (groups of atoms in irregular positions (e.g. screw and edge dislocations)

iii. Planar defects – 2 dimensional defect (the interfaces between homogeneous regions of the material (grain boundaries, stacking faults, external surfaces).

iv. Volume defects – 3 dimensional defect

Point Defects:

– Vacancies: Diffusion, Color Center

– Interstitials: Mechanical Properties, Diffusion

– Impurity Atoms: Electrical Properties

Line Defects:

– Dislocations: Mechanical Properties

Planar Defects:

– Grain Boundaries: Fabrication, Corrosion

– Stacking Faults: Mechanical Properties

Volume Defects:

– Voids: Porosity, Precipitation

– Second Phase: Mechanical and Magnetic Properties

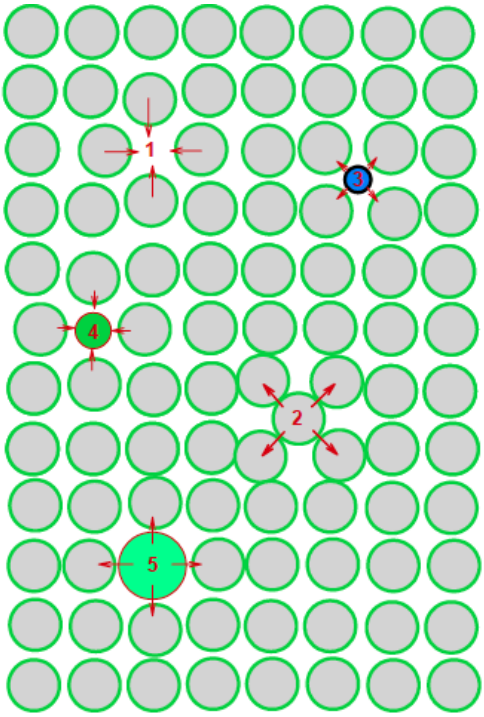
Point Defects:

A perfect crystal with regular arrangement of atoms cannot exist. There are always defects, and the most common defects are point defects. This is especially true at high temperatures when atoms frequently and randomly change their positions leaving behind empty lattice sites, called vacancies. Point defects include (a) vacancies (b) self-interstitial atoms (c) interstitial impurity atoms (d) substitutional atoms (e) Frenkel defect (f) Schottky defect.

Intrinsic point defects: Interstitials – atoms that are squeezed in between regular lattice sites. If the interstitial atom is of the same species as the lattice atoms, it is called self-interstitial. Creation of a self-interstitial causes a substantial distortion in the surrounding lattice and costs more energy as compared to the energy for creation of a vacancy ($E_i > E_V$), under equilibrium conditions, self-interstitials are present in lower concentrations than vacancies. Foreign, usually smaller atoms (carbon, nitrogen, hydrogen, oxygen) are called interstitial impurities. They introduce less distortion to the lattice and are more common in real materials and more mobile. As shown in the schematic drawing, all point defects introduce local distortions to the lattice, and due to these distortions they can feel each other (interact) and feel external stresses. The external stresses or stresses from a larger defects can give a directionality to an otherwise random jumps of atoms.

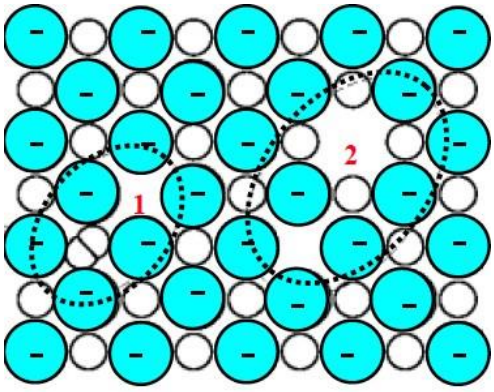
In ionic crystals (e.g. table salt – Na^+Cl^-) the bonding is provided by coulombic forces between positively and negatively charged ions. Point defects in ionic crystals are charged as well. The Columbic forces are very large and any charge imbalance has a very strong tendency to balance itself. To maintain charge neutrality several point defects can be created. A Frenkel defect is a pair of cation (positive ion) vacancy and a cation interstitial. Or it may also be an anion (negative ion) vacancy and anion interstitial. However anions are much larger than cations and it is not easy for an anion interstitial to form. A Schottky defect is a pair of anion and cation vacancies. In both Frenkel and Schottky defects, the pair of point defects stay near each other because of strong columbic attraction of their opposite charges.

Extrinsic point defects: If the foreign atom replaces or substitutes for a matrix atom, it is called a substitutional impurity. The extrinsic point defects are foreign atoms, which are called solutes if they are intentionally added to the material and are called impurities. The foreign atom may occupy a lattice site, 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.



Schematic representation of different point defects in a crystal. (1) vacancy; (2) self-interstitial; (3) interstitial impurity; (4), (5) substitutional impurities. The arrows show the local stresses introduced by the point defects.

Fig 1: Point defect and their types.



Schematic representation of (1) Frenkel defect (vacancy-interstitial pair) and (2) Schottky defect (a pair of cation and anion vacancies) in an ionic crystal.

Fig 2: Frenkel and Schottky defect

Effect of Temperature:

The higher is the temperature, more often atoms jump from one equilibrium position to another and larger number of vacancies can be found in a crystal. Actually, the number of vacancies, N_v, increases exponentially with the absolute temperature, T, and can be estimated using the equation (Boltzmann Distribution):

$$N_v = N_s \exp\left(-E_v / k_B T\right)$$

where, N_s is the number of regular lattice sites, k is the Boltzmann constant, and E_v is the energy needed to form a vacant lattice site in a perfect crystal. Using this simple equation we

can estimate that at room temperature in copper there is one vacancy per 10^{15} lattice atoms.

Line defects: Dislocations, Edge and Screw 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. 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.

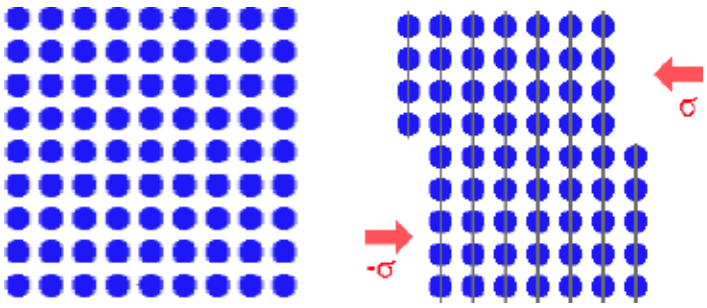


Fig3: Edge dislocation: the force to break all the bonds is much higher than the force needed to cause deformation in a plane.

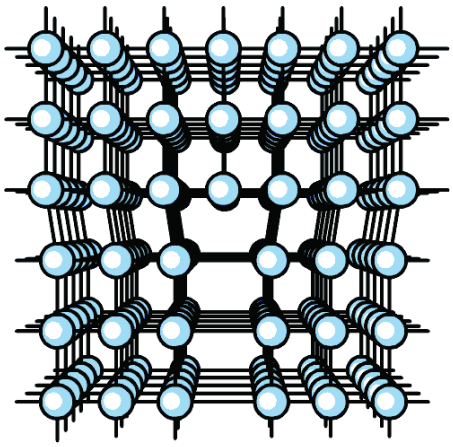


Fig 4: This picture shows the inserted half plane dislocation going through the center

Edge dislocation:

The edge defect can be easily visualized as an extra half-plane of atoms in a lattice. The dislocation is called a line defect because the locus of defective points produced in the lattice by the dislocation lie along a line. This line runs along the top of the extra half-plane. The inter-atomic bonds are significantly distorted only in the immediate vicinity of the dislocation line.

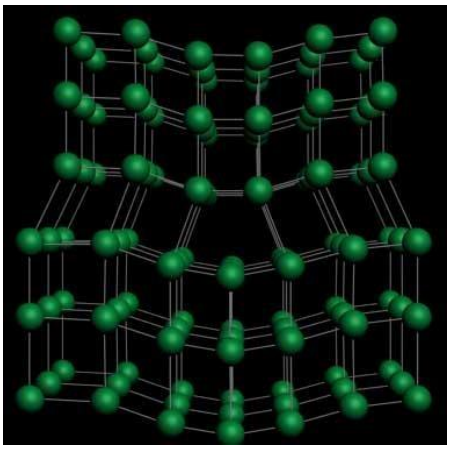


Fig 5. Edge dislocations

Understanding the movement of a dislocation is key to understanding why dislocations allow deformation to occur at much lower stress than in a perfect crystal. Dislocation motion is analogous to movement of a caterpillar. The caterpillar would have to exert a large force to move its entire body at once. Instead it moves the rear portion of its body forward a small amount and creates a hump. The hump then moves forward and

eventual moves all of the body forward by a small amount.

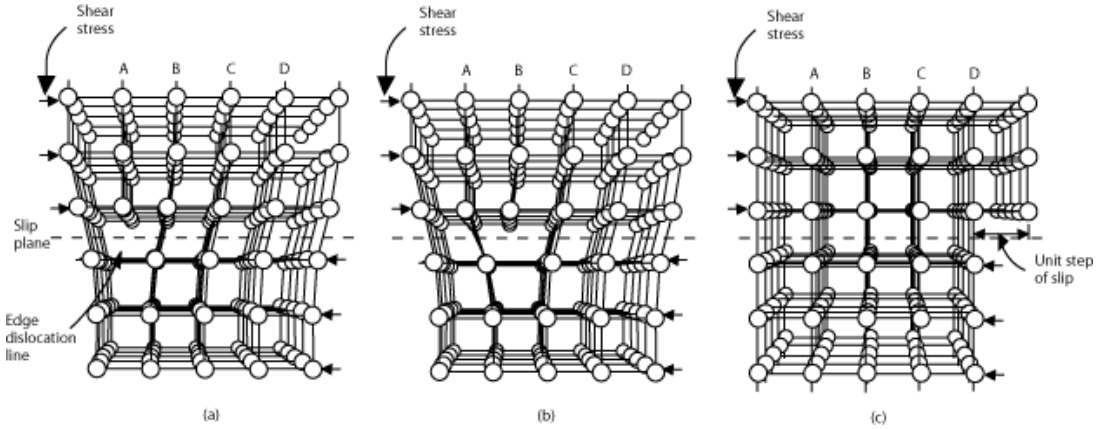


Fig 6. Burger vectors – Edge dislocations

As shown in the set of images above, the dislocation moves similarly moves a small amount at a time. The dislocation in the top half of the crystal is slipping one plane at a time as it moves to the right from its position in image (a) to its position in image (b) and finally image (c). In the process of slipping one plane at a time the dislocation propagates across the crystal. The movement of the dislocation across the plane eventually causes the top half of the crystal to move with respect to the bottom half. However, only a small fraction of the bonds are broken at any given time. Movement in this manner requires a much smaller force than breaking all the bonds across the middle plane simultaneously.

Screw dislocation:

There is a second basic type of dislocation, called screw dislocation. The screw dislocation is slightly more difficult to visualize. The motion of a screw dislocation is also a result of shear stress, but the defect line movement is perpendicular to direction of the stress and the atom displacement, rather than parallel. To visualize a screw dislocation, imagine a block of metal with a shear stress applied across one end so that the metal begins to rip. This is shown in the upper right image. The lower right image shows the plane of atoms just above the rip. The atoms represented by the blue circles have not yet moved from their original position. The atoms represented by the red circles have moved to their new position in the lattice and have re-established metallic bonds. The atoms represented by the green circles are in the process of moving. It can be seen that only a portion of the bonds are broke at any given time. As was the case with the edge dislocation, movement in this manner requires a

much smaller force than breaking all the bonds across the middle plane simultaneously.

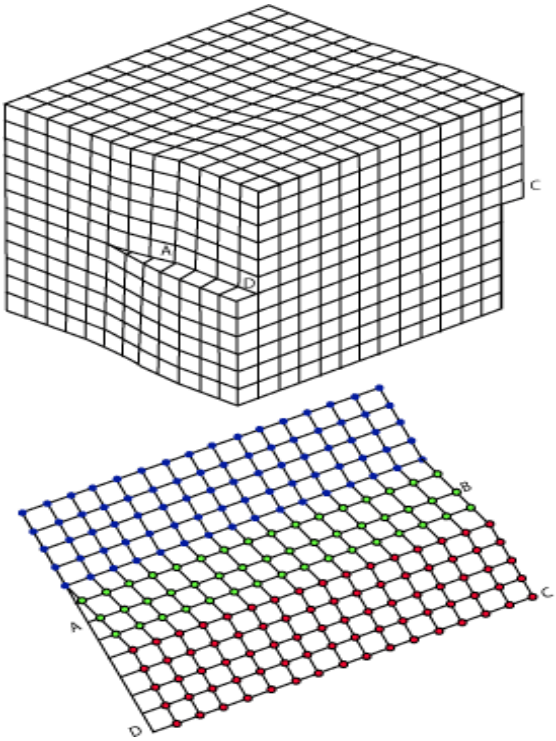


Fig 7. Screw dislocation

If the shear force is increased, the atoms will continue to slip to the right. A row of the green atoms will find there way back into a proper spot in the lattice (and become red) and a row of the blue atoms will slip out of position (and become green). In this way, the screw dislocation will move upward in the image, which is perpendicular to direction of the stress. Recall that the edge dislocation moves parallel to the direction of stress. As shown in the image below, the net plastic deformation of both edge and screw dislocations is the same, however.

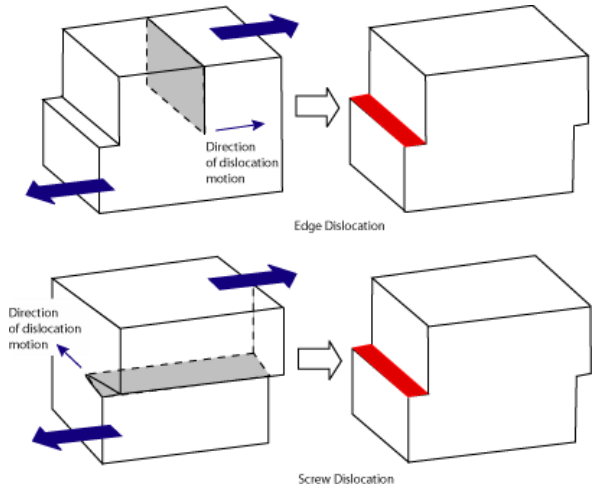


Fig 8: to show edge and screw dislocations

The dislocations move along the densest planes of atoms in a material, because the stress needed to move the dislocation increases with the spacing between the planes. The screw dislocation is parallel to the direction in which the crystal is being displaced (Burgers vector is parallel to the dislocation line).

Burgers Vector: To describe the size and the direction of the main lattice distortion caused by a dislocation we should introduce so called Burgers vector, **b**.

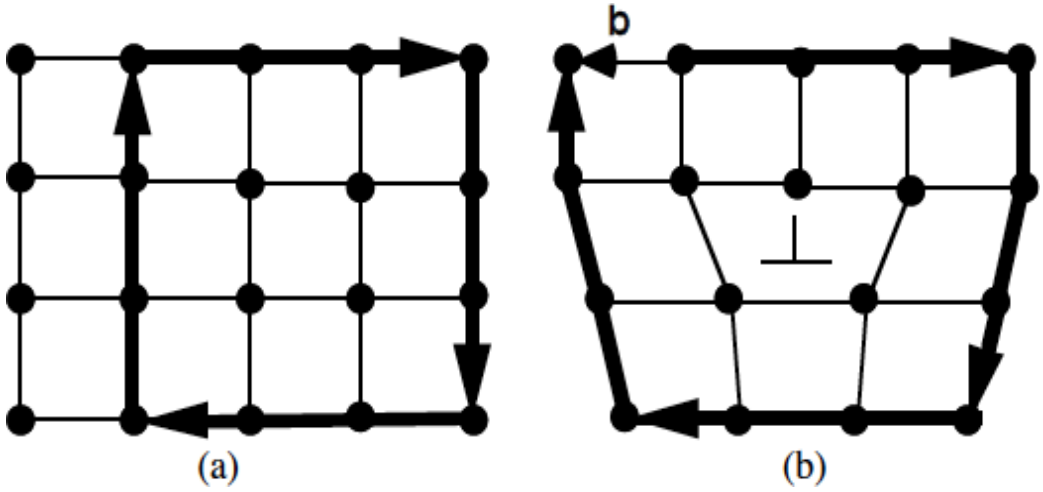


Fig 9. Burger Vector: A Burgers circuit closes in a {100} plane of a cubic crystal, but fails to close by the Burgers vector, b, when the same circuit encloses an edge dislocation.

To find the Burgers vector, we should make a circuit from atom to atom counting the same number of atomic distances in all directions. If the circuit encloses a dislocation it will not close. The vector that closes the loop is the Burgers vector **b.** Dislocations that have been considered until now have Burgers vector directed perpendicular to the dislocation line. These dislocations are called edge dislocations. There is a second basic type of dislocation, called screw dislocation. The screw dislocation is parallel to the direction in which the crystal is being displaced (Burgers vector is parallel to the dislocation line). The exact structure of dislocations in real crystals is usually more complicated than the ones shown in this pages. Edge and screw dislocations are just extreme forms of the possible dislocation structures and even they usually would be split in "partial" dislocations. Partial dislocations have their cores

spread out over a larger area and look much more complicated.