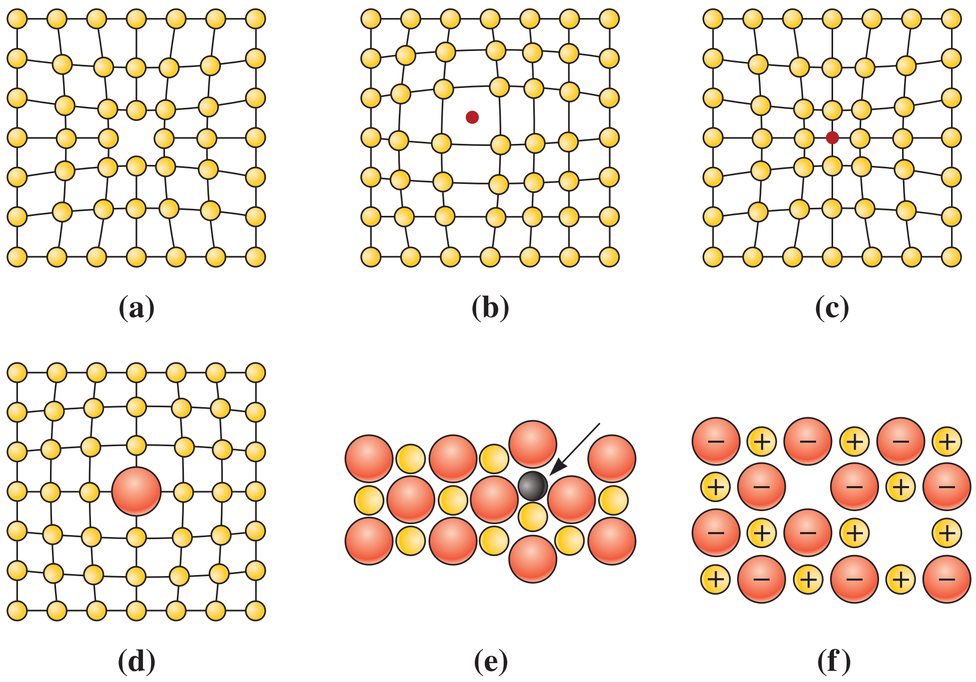
Point Defects

Point defects are localized disruptions in perfect atomic or ionic arrangements in a crystal structure.

Even though we call them point defects, the disruption affects a region involving several atoms or ions.

These imperfections, may be introduced by movement of the atoms or ions when they gain energy by heating, during processing of the material, or by the intentional or unintentional introduction of impurities

Point Defects



Point defects: (a) vacancy, (b) interstitial atom, (c) small substitutional atom, (d) large substitutional atom, (e) Frenkel defect, and (f) Schottky defect.

Vacancies

A **vacancy** is produced when an atom or an ion is missing from its normal site in the crystal structure.

When atoms or ions are missing (i.e., when vacancies are present), the overall randomness or entropy of the material increases, which increases the thermodynamic stability of a crystalline material.

Vacancies are introduced into metals and alloys during solidification, at high temperatures, or as a consequence of radiation damage.

Vacancies

At room temperature (~298 K), the concentration of vacancies is small, but the concentration of vacancies increases exponentially as the temperature increases, as shown by the following Arrhenius behaviour:

$$n_v = n \exp\left(\frac{-Q_v}{RT}\right)$$

n_v is the number of vacancies per cm^3;

n is the number of atoms per cm^3;

Q_v is the energy required to produce one mole of vacancies, in cal/mol or Joules/mol;

R is the gas constant, $1.987 \frac{\text{cal}}{\text{mol} \cdot \text{K}}$ or $8.314 \frac{\text{Joules}}{\text{mol} \cdot \text{K}}$; and

T is the temperature in degrees Kelvin.

Vacancies

Due to the large thermal energy near the melting temperature, there may be as many as one vacancy per 1000 atoms.

Note that this equation provides the equilibrium concentration of vacancies at a given temperature.

It is also possible to retain the concentration of vacancies produced at a high temperature by quenching the material rapidly.

Thus, in many situations, the concentration of vacancies observed at room temperature is not the equilibrium concentration predicted by Equation

Exercise

Calculate the concentration of vacancies in copper at room temperature (25°C). Given the lattice parameter of FCC copper is 0.36151 nm. Assume that 20,000 cal are required to produce a mole of vacancies in copper.

$$n_v = n \exp\left(\frac{-Q_v}{RT}\right)$$

$$n = \frac{4 \text{ atoms/cell}}{(3.6151 \times 10^{-8} \text{ cm})^3} = 8.466 \times 10^{22} \text{ copper atoms/cm}^3$$

At room temperature, $T = 25 + 273 = 298$ K:

$$n_v = n \exp\left(\frac{-Q_v}{RT}\right)$$

$$= \left(8.466 \times 10^{22} \frac{\text{atoms}}{\text{cm}^3}\right) \exp\left[\frac{-20{,}000 \frac{\text{cal}}{\text{mol}}}{\left(1.987 \frac{\text{cal}}{\text{mol} \cdot \text{K}}\right)(298 \text{ K})}\right]$$

$$= 1.814 \times 10^{8} \text{ vacancies/cm}^3$$

Exercise (Continue)

What temperature will be needed to heat treat copper such that the concentration of vacancies produced will be 1000 times more than the equilibrium concentration of vacancies at room temperature?

We wish to find a heat treatment temperature that will lead to a concentration of vacancies that is 1000 times higher than this number, or n_v = 1.814 x 10^{11} vacancies/cm3.

$$n_v = 1.814 \times 10^{11} = n \exp\left(\frac{-Q_v}{RT}\right)$$

$$= (8.466 \times 10^{22}) \exp(-20{,}000)/(1.987T)$$

$$\exp\left(\frac{-20{,}000}{1.987T}\right) = \frac{1.814 \times 10^{11}}{8.466 \times 10^{22}} = 0.214 \times 10^{-11}$$

$$\frac{-20{,}000}{1.987T} = \ln(0.214 \times 10^{-11}) = -26.87$$

$$T = \frac{20{,}000}{(1.987)(26.87)} = 375\,\text{K} = 102°\text{C}$$

Interstitial Defects

An **interstitial defect** is formed when an extra atom or ion is inserted into the crystal structure at a normally unoccupied position

Interstitial atoms or ions, although much smaller than the atoms or ions located at the lattice points, are still larger than the interstitial sites that they occupy

Consequently, the surrounding crystal region is compressed and distorted.

Interstitial atoms such as hydrogen are often present as impurities, whereas carbon atoms are intentionally added to iron to produce steel.

For small concentrations, carbon atoms occupy interstitial sites in the iron crystal structure, introducing a stress in the localized region of the crystal in their vicinity.

Interstitial Defects

the introduction of interstitial atoms is one important way of increasing the strength of metallic materials.

Unlike vacancies, once introduced, the number of interstitial atoms or ions in the structure remains nearly constant, even when the temperature is changed.

Frenkel Defect

vacancy-interstitial pair formed when an ion jumps from a normal lattice point to an interstitial site, leaving behind a vacancy.

Although, this is usually associated with ionic materials, a Frenkel defect can occur in metals and covalently bonded materials.

Schottky Defect

Is unique to ionic materials and is commonly found in many ceramic materials.

When vacancies occur in an ionically bonded material, a stoichiometric number of anions and cations must be missing from regular atomic positions if electrical neutrality is to be preserved.

For example, one Mg^{2+} vacancy and one O^{2-} vacancy in MgO constitute a Schottky pair.

In ZrO_2, for one Zr^{4+} vacancy, there will be two O^{2-} vacancies.

Dislocations

Dislocations are line imperfections typically introduced into a crystal during solidification of the material or when the material is deformed permanently.

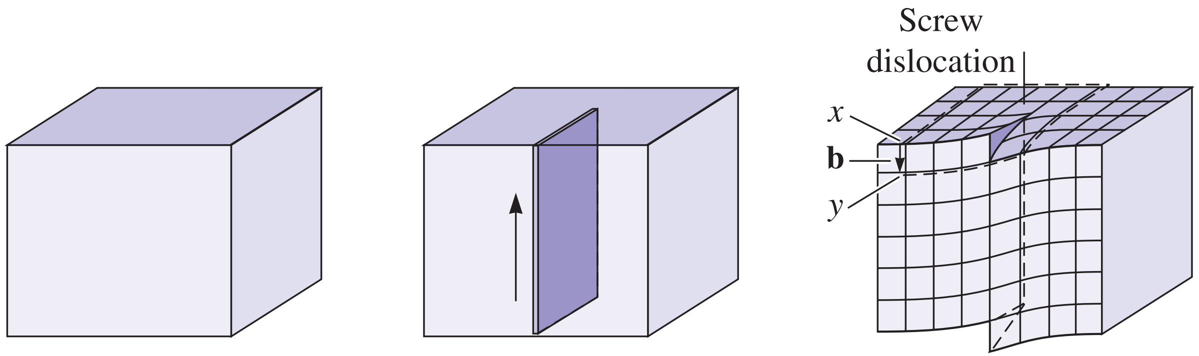
Although dislocations are present in all materials, including ceramics and polymers, *they are particularly useful in explaining deformation and strengthening in metallic materials*.

We can identify three types of dislocations:

1. screw dislocation
2. edge dislocation
3. mixed dislocation

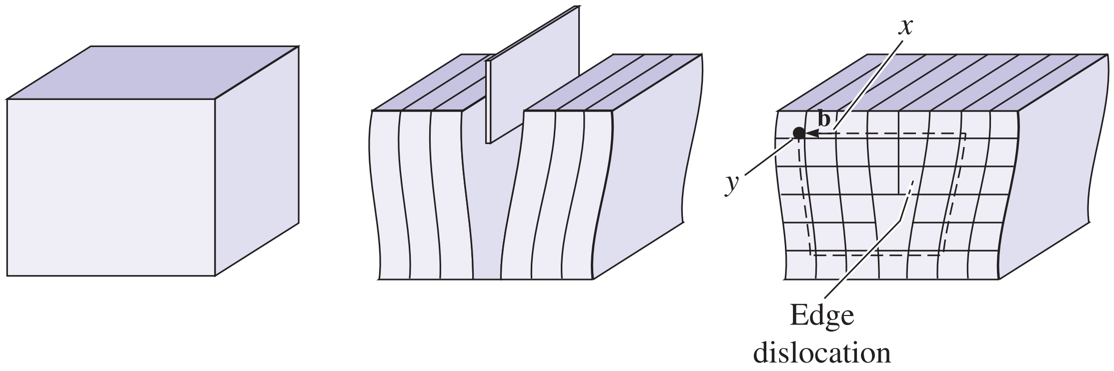
Screw Dislocations

The **screw dislocation** can be illustrated by cutting partway through a perfect crystal and then skewing the crystal by one atom spacing.



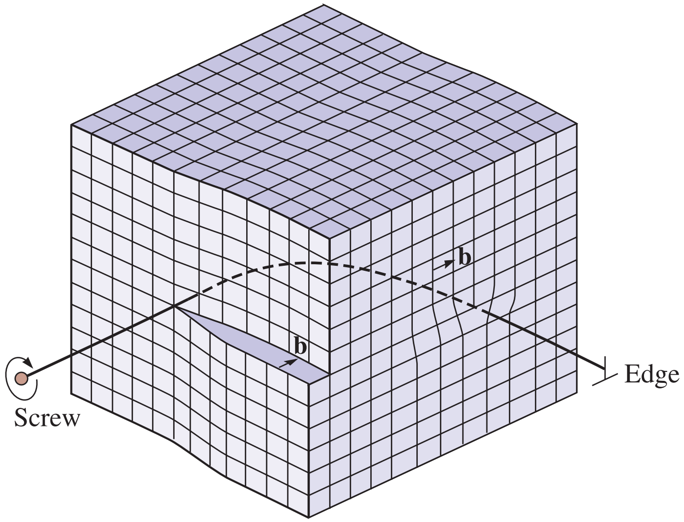
Edge Dislocations

An **edge dislocation** can be illustrated by slicing partway through a perfect crystal, spreading the crystal apart, and partly filling the cut with an extra half plane of atoms.



Mixed Dislocation

Mixed dislocations have both edge and screw components, with a transition region between them.



A mixed dislocation. The screw dislocation at the front face of the crystal gradually changes to an edge dislocation at the side of the crystal.

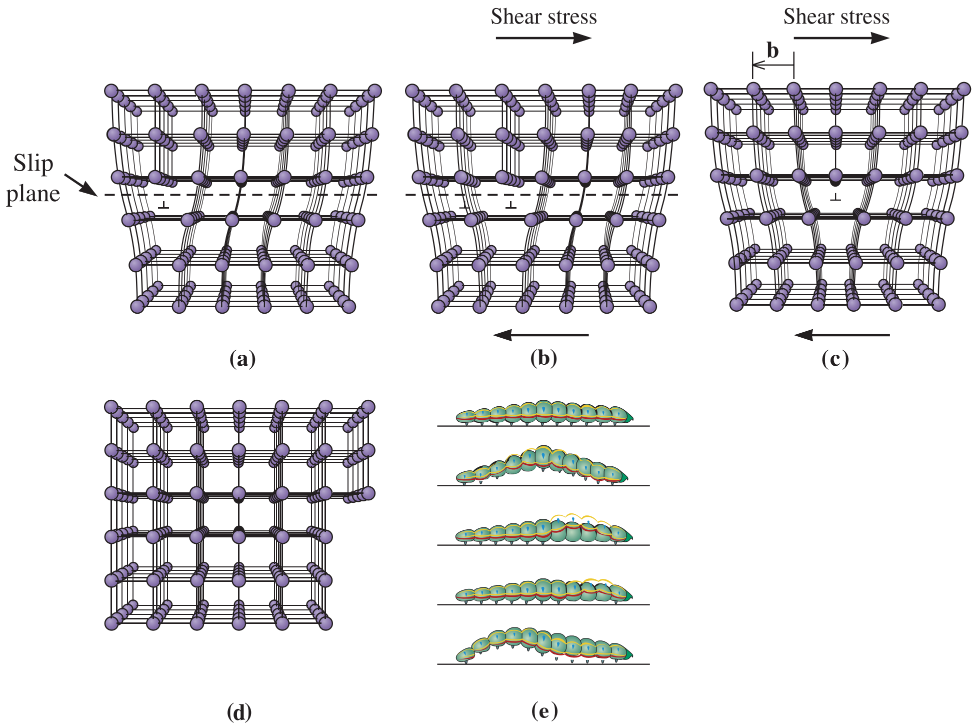
Dislocation Motion

When a sufficiently large shear stress is applied to a crystal containing a dislocation, the dislocation can move through a process known as **slip**.

The bonds across the slip plane between the atoms in the column to the right of the dislocation shown are broken.

The atoms in the column to the right of the dislocation below the slip plane are shifted slightly so that they establish bonds with the atoms of the edge dislocation.

Dislocation Motion



Dislocation Motion

This process of progressively breaking and reforming bonds requires far less energy than the energy that would be required to instantaneously break all of the bonds across the slip plane.

The crystal deforms via the propagation of dislocations because it is an energetically favorable process.

Slip

The dislocation moves in a slip system that requires the least expenditure of energy.

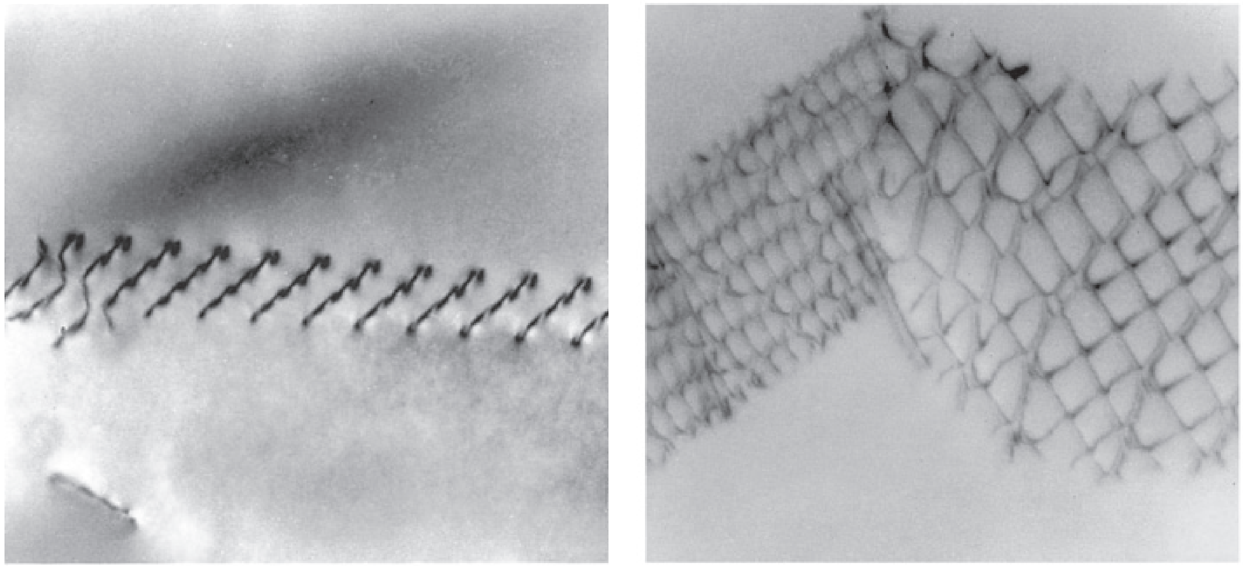
Several important factors determine the most likely slip systems that will be active:

- the slip direction should have a small repeat distance or high linear density. The close-packed directions in metals and alloys satisfy this criterion and are the usual slip directions.
- Slip occurs most easily between planes of atoms that are smooth (so there are smaller "hills and valleys" on the surface) and between planes that are far apart (or have a relatively large interplanar spacing).

Slip

- Dislocations do not move easily in materials such as silicon, which have covalent bonds. Because of the strength and directionality of the bonds, the materials typically fail in a brittle manner before the force becomes high enough to cause appreciable slip. Dislocations also play a relatively minor role in the deformation of polymers.
- Materials with ionic bonding, including many ceramics such as MgO, also are resistant to slip. Movement of a dislocation disrupts the charge balance around the anions and cations, requiring that bonds between anions and cations be broken.

Slip



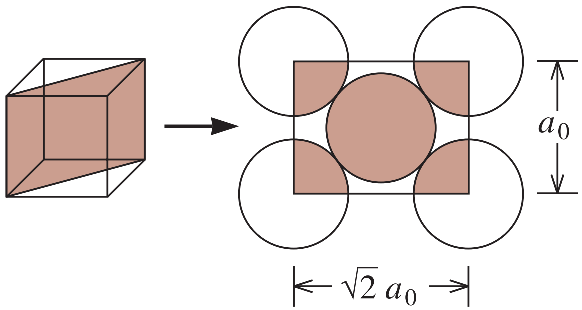
Electron micrographs of dislocations in Ti_3Al: Dislocation pileups (x 36,500).

Exercise-Preferred Slip Planes

The planar density of the (112) plane in BCC iron is 9.94×10^{14} atoms/cm^2.

Calculate the plane density of plane (110). The lattice parameter of BCC iron is 0.2866 nm.

The planar density is



$$\text{Planar density (110)} = \frac{\text{atoms}}{\text{area}} = \frac{2}{(\sqrt{2})(2.866 \times 10^{-8}\text{cm})^2}$$

$$= 1.72 \times 10^{15}\ \text{atoms/cm}^2$$

$$\text{Planar density (112)} = 0.994 \times 10^{15}\ \text{atoms/cm}^2 \text{ (from problem statement)}$$

Exercise-Preferred Slip Planes

Calculate the interplanar spacings for both the (112) and (110) planes.

The interplanar spacings are

$$d_{110} = \frac{2.866 \times 10^{-8}}{\sqrt{1^2 + 1^2 + 0}} = 2.0266 \times 10^{-8}\,\text{cm}$$

$$d_{112} = \frac{2.866 \times 10^{-8}}{\sqrt{1^2 + 1^2 + 2^2}} = 1.17 \times 10^{-8}\,\text{cm}$$

Significance of Dislocation

Dislocations are most significant in metals and alloys since they provide a mechanism for plastic deformation, which is the cumulative effect of slip of numerous dislocations.

Plastic deformation refers to irreversible deformation or change in shape that occurs when the force or stress that caused it is removed.

(Plastic deformation is to be distinguished from **elastic deformation**, which is a temporary change in shape that occurs while a force or stress remains applied to a material.)

Significance of Dislocation

Amorphous materials such as silicate glasses do not have a periodic arrangement of ions and hence do not contain dislocations.

The slip process, therefore, is particularly important in understanding the mechanical behavior of metals.

slip explains why the strength of metals is much lower than the value predicted from the metallic bond.

- If slip occurs, only a tiny fraction of all of the metallic bonds across the interface need to be bro- ken at any one time, and the force required to deform the metal is small.

Significance of Dislocation

slip provides ductility in metals.

- If no dislocations were present, an iron bar would be brittle and the metal could not be shaped by metalworking processes, such as forging, into useful shapes.

we control the mechanical properties of a metal or alloy by interfering with the movement of dislocations.

- An obstacle introduced into the crystal prevents a dis- location from slipping unless we apply higher forces. Thus, the presence of dislocations helps strengthen metallic materials.

Significance of Dislocation

Dislocations also influence electronic and optical properties of materials.

- For example, the resistance of pure copper increases with increasing dislocation density.

Diffusion

Diffusion refers to the net flux of any species, such as ions, atoms, electrons and molecules.

The magnitude of this flux depends upon the concentration gradient and temperature.

Application:

The carburization process can be used to increase surface hard- ness. In carburization, a source of carbon, such as a graphite powder or gaseous phase containing carbon, is diffused into steel components

Self-Diffusion

In materials containing vacancies, atoms move or “jump” from one lattice position to another.

This process, known as **self-diffusion**, can be detected by using radioactive tracers.

As an example, suppose we were to introduce a radioactive isotope of gold (Au198) onto the surface of standard gold (Au197).

After a period of time, the radioactive atoms would move into the standard gold.

Eventually, the radioactive atoms would be uniformly distributed throughout the entire standard gold sample.

Although self- diffusion occurs continually in all materials, its effect on the material’s behavior is generally not significant.

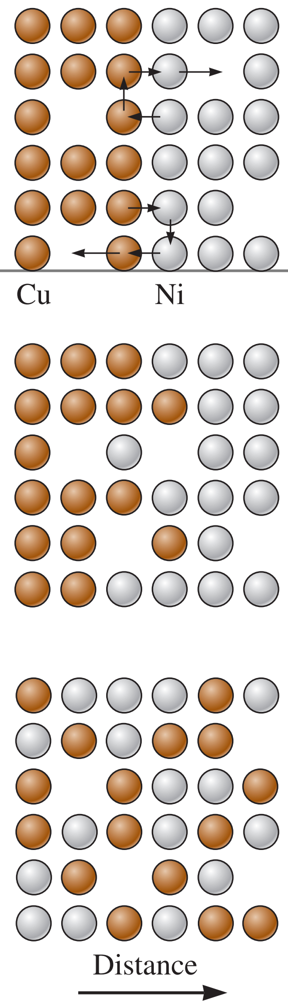
Interdiffusion

Diffusion of unlike atoms in materials also occurs.

Consider a nickel sheet bonded to a copper sheet.

At high temperatures, nickel atoms gradually diffuse into the copper, and copper atoms migrate into the nickel.

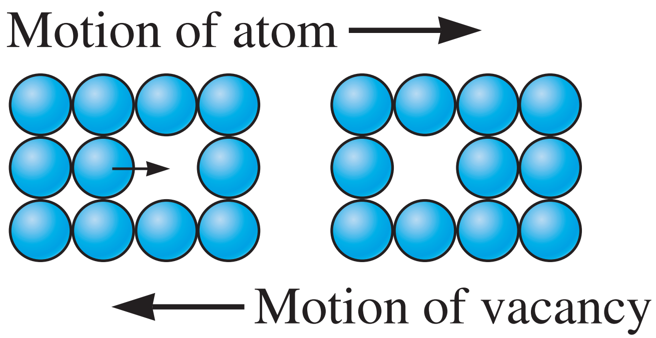
Again, the nickel and copper atoms eventually are uniformly distributed. Diffusion of different atoms in different directions is known as **interdiffusion**.



Vacancy Diffusion

In self-diffusion and diffusion involving substitutional atoms, an atom leaves its lattice site to fill a nearby vacancy (thus creating a new vacancy at the original lattice site).

As diffusion continues, we have counterflows of atoms and vacancies, called **vacancy diffusion**.



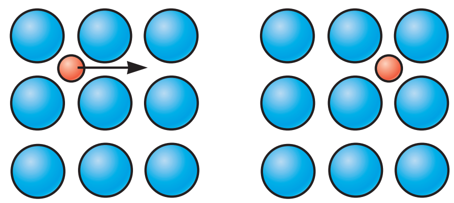
Interstitial Diffusion

When a small interstitial atom or ion is present in the crystal structure, the atom or ion moves from one interstitial site to another.

No vacancies are required for this mechanism.

Partly because there are many more interstitial sites than vacancies, **interstitial diffusion** occurs more easily than vacancy diffusion.

Interstitial atoms that are relatively smaller can diffuse faster.

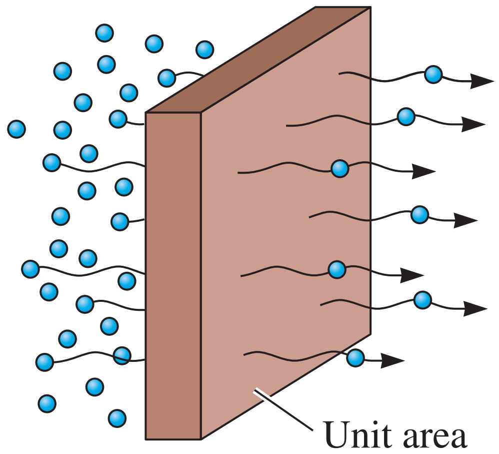


Rate of Diffusion

The rate at which atoms, ions, particles or other species diffuse in a material can be measured by the **flux** *J*.

Here we are mainly concerned with diffusion of ions or atoms.

The flux *J* is defined as the number of atoms passing through a plane of unit area per unit time



Fick's first law explains the net flux of atoms:

$$J = -D \frac{dc}{dx}$$

J is the flux, D is the diffusivity (cm^2/s), *dc/dx* is the concentration gradient ($atom/cm^3.cm$)

The concentration can be expressed as atom percent (at%), weight percent (wt%), mole percent (mol%), atom fraction, or mole fraction. The units of concentration gradient and flux will change accordingly.

Diffusion and Material Processing

Melting and Casting

One of the most widely used methods to process metals, alloys, many plastics, and glasses involves melting and casting of materials into a desired shape.

Diffusion plays a particularly important role in solidification of metals and alloys.

Example: the diffusion of elements during the casting of alloys.

Diffusion and Material Processing

Sintering

Sintering is the high-temperature treatment that causes particles to join, gradually reducing the volume of pore space between them.

A variety of composite materials such as tungsten carbide-cobalt based cutting tools, superalloys, etc., are produced using this technique.

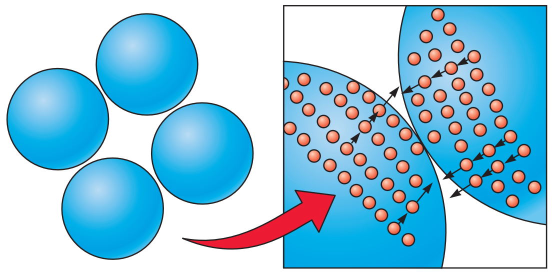
The driving force for solid state sintering of powdered metals and ceramics is the *reduction in the total surface area* of powder particles.

Diffusion and Material Processing

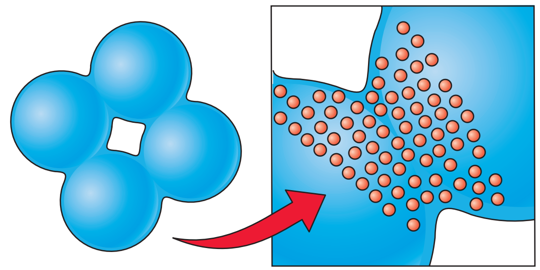
Sintering

Example:

When a powdered material is compacted into a shape, the powder particles are in contact with one another at numerous sites, with a significant amount of pore space between them. In order to reduce the total energy of the material, atoms diffuse to the points of contact, bonding the particles together and eventually causing the pores to shrink.



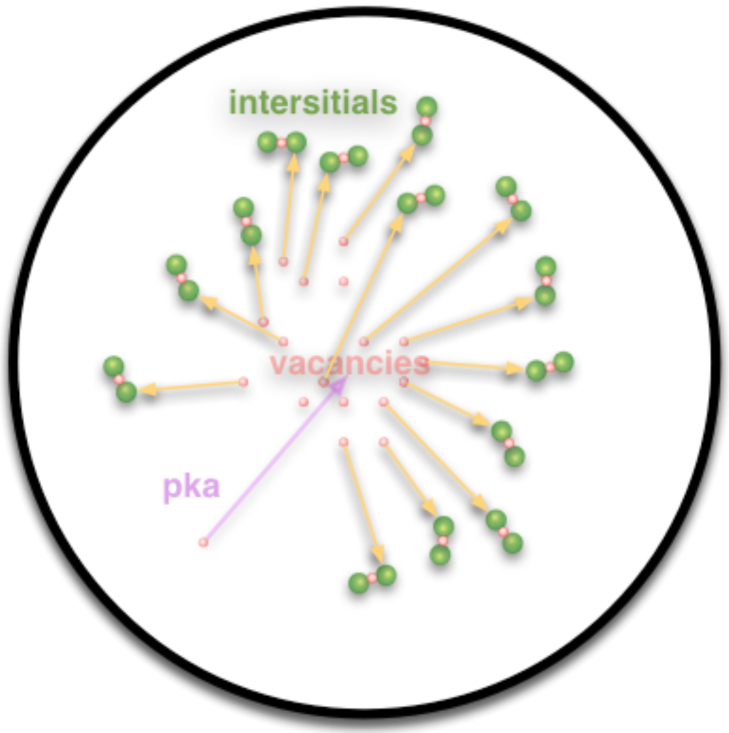
Compacted product

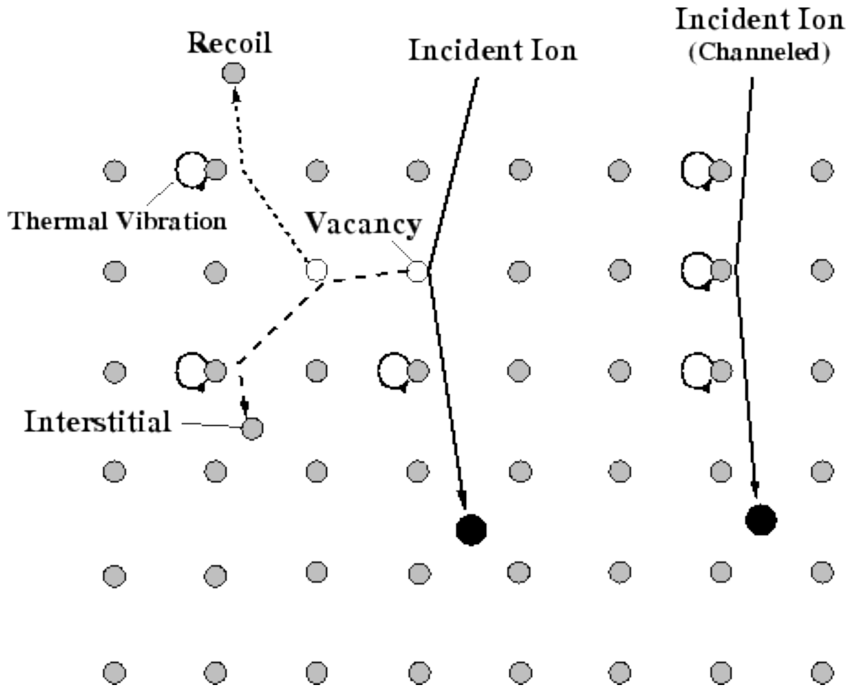


Partly sintered product

Primary Knock-on Atoms (PKA)

1. The first atom that an incident particle encounters in the target.
2. After it is displaced from its initial lattice site, the PKA:
   - can induce the subsequent lattice site displacements of other atoms if it possesses sufficient energy, or
   - come to rest in the lattice at an interstitial site if it does not.
3. A neutron with sufficient energy produces a number of these PKAs which in turn produce knock-ons leading to **displacement/collision cascades** .
4. The atoms displaced by PKAs are known as secondary knock-on atoms.
5. Thus a high energy neutron may produce a number of PKAs which lead to many secondary knock-ons resulting in a large number of atomic displacements.


intersitials
vacancies
pka


Recoil
Incident Ion
Incident Ion
(Channeled)
Thermal Vibration
Vacancy
Interstitial

Collision Models

Upon bombardment, atoms can only be displaced if the energy they receive exceeds a threshold energy E_d.

When a moving atom collides with a stationary atom, both atoms will have energy greater than E_d after the collision only if the original moving atom had an energy exceeding $2E_d$.

Thus, only PKAs with an energy greater than $2E_d$ can continue to displace more atoms and increase the total number of displaced atoms

The majority of displaced atoms leave their lattice sites with energies no more than two or three times Ed.

Such an atom will collide with another atom approximately every mean interatomic distance traveled, losing half of its energy during the average collision.

Assuming that an atom that has slowed down to a kinetic energy of 1 eV becomes trapped in an interstitial site-

- displaced atoms will typically be trapped no more than a few interatomic distances away from the vacancies they leave behind.

There are several possible scenarios for the energy of PKAs, and these lead to different forms of damage.

In the case of electron or gamma ray bombardment, the PKA usually does not have sufficient energy to displace more atoms.

The resulting damage consists of a random distribution of Frenkel defects, usually with a distance no more than four or five interatomic distances between the interstitial and vacancy.

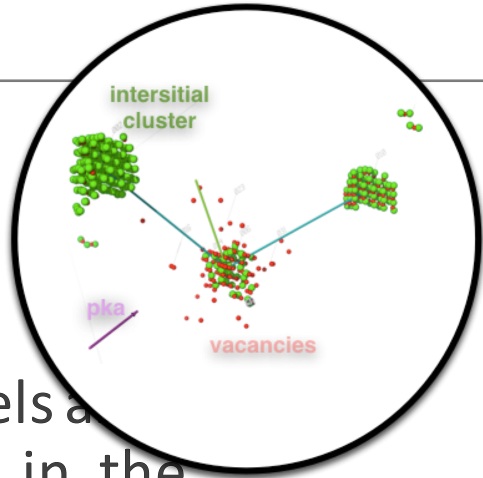
When PKAs receive energy greater than Ed from bombarding electrons, they are able to displace more atoms, and some of the Frenkel defects become groups of interstitial atoms with corresponding vacancies, within a few interatomic distances of each other.

In the case of bombardment by fast-moving atoms or ions, groups of vacancies and interstitial atoms widely separated along the track of the atom or ion are produced.

As the atom slows down, the cross section for producing PKAs increases, resulting in groups of vacancies and interstitials concentrated at the end of the track

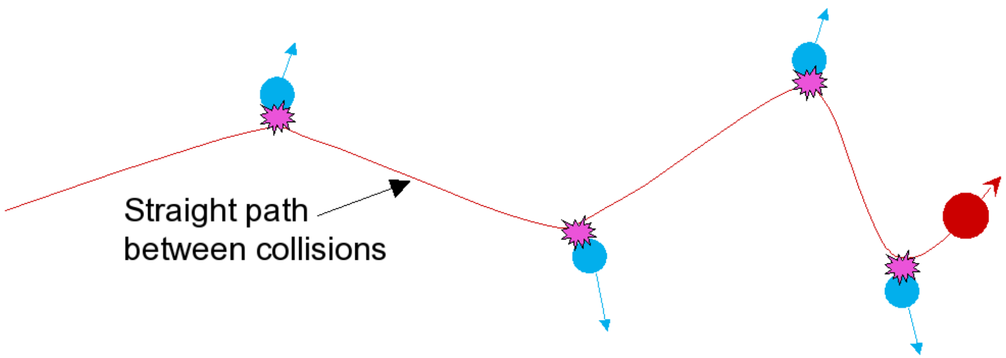
PKA moves through the lattice

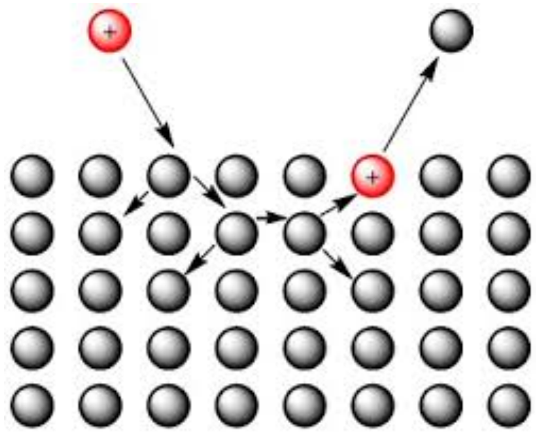
- produces vacancy interstitial pairs (Frenkel Pair)
- PKA slows, reduces mean distance between collisions
- clusters formed



Displacements per atom [dpa] using simple models a evaluated dpa may be related to the changes in the macroscopic properties of the materials.

Collision Cascade

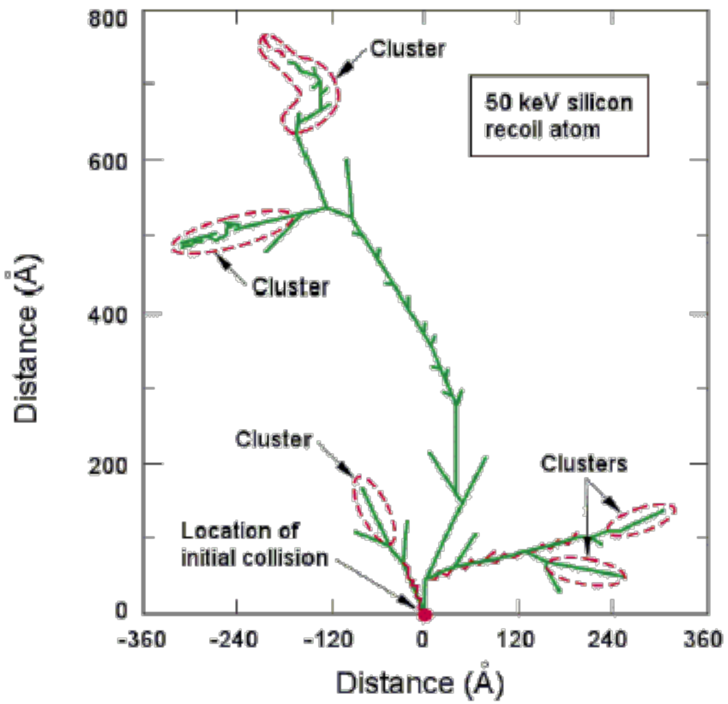




Linear collision cascade theory:

The primary ion collides with an atom on the surface of the target, causing other elastic collisions to occur within the target. Eventually, a target atom or molecule is ejected from the surface.

Collision Cascade in Si



A single incident particle can cause a cascade of collisions to occur to a portion of the affected material (e.g., Si) lattice atoms.

These collisions are produced by both incident "heavy" particles (p, n, ions) and secondary particles.

Defects (vacancies, interstitials, Frenkel pairs, dislocations) are produced along the tracks of the secondary particles and in clusters at the end of these tracks as shown in Figure

1. As the PKA slows to stop, it can collide with all atoms it encounters, impart kinetic energy to other atoms and initiate the ejections of atoms from their localized region
2. The size of the collision cascade is the primary function of the energy of the PKA.
3. The energy of PKA produced in a function of the irradiating species.
4. The nature of residual damage is the function of both PKA energy and the temperature of the material- at high temperature, the frenkel paairs have greater chance of spontaneously recombining to annihilate the damage
5. For metal like Zirconium, the displacement cascade results in the formation of damage zone/depleted zone- characterized by vacancy-rich core surrounded by the interstitial-rich shell

Damage Analysis of PKA

1. The degree to which the lattice is exposed to Frenkel damage is described in term of an accumulated fluence of the irradiating species (neutron).
2. Parameter for damage analysis : number of displacement event which occurred in the atom of the lattice--DISPLACEMENT PER ATOM (dpa)
3. Dpa is affected by the particle fluence, type of irradiating species, energy of the irradiating species.
4. Example:

   Neutron fluence of 1x 10^21 n/cm2 in zirconium in a light water reactor is 1.3 dpa

   Neutron fluence of 1x 10^21 n/cm2 in zirconium in a heavy water reactor is 1 dpa

A fluence of 10^22 n/cm^2 is typical of end-of-life exposure for many zirconium core components

Based on the previous calculation, during the lifetime of the component, every atom is displaced from its laticce site in average ten times.

There must be a process which restore crystallinity to the damaged lattice!

A large fraction of the interstitials and vacancies can recombine with one another to annihilate the vacancy-interstitial pair.

Some vacancies and interstitials diffuse to lattice impefection such as dislocations or grain boundaries where they are absorbed.

All these processes normally occur at very high temperature

Secondary ion mass spectrometer (SIMS)

SIMS is a surface analysis technique used to characterize the surface and sub-surface region of materials.

It effectively employs the ***mass spectrometry*** of ionised particles which are emitted when a solid surface is bombarded by energetic primary particles.

The primary particles may be electrons, ions, neutrals or photons.