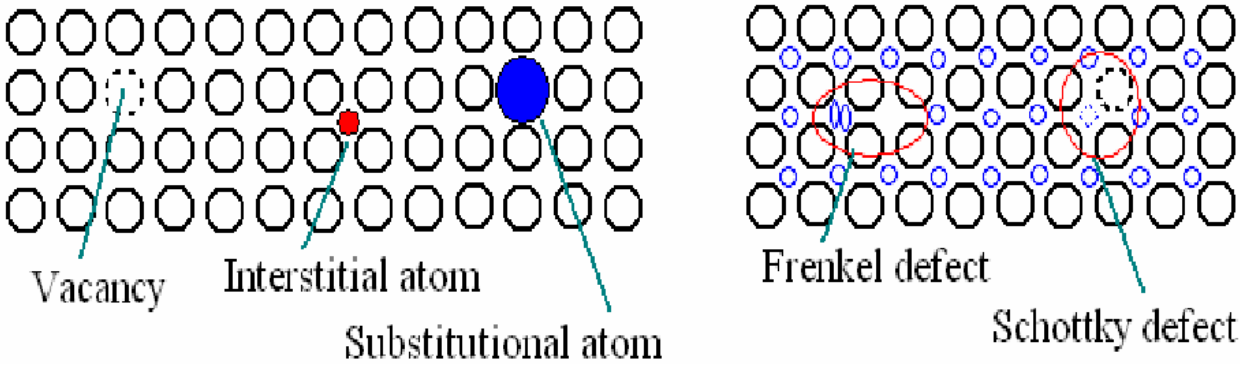
Point Defects

Defects exists any all solid materials. For ease of their characterization, defects are classified on the basis of their geometry, which is realistic as defects are disrupted region in a volume of a solid. Defects are:

a. Point defects (zero-dimensional)
b. Line defects (single dimensional)
c. Surface defects (two dimensional)
d. Volume defects (three dimensional)



Point defects, as the name implies, are imperfect point-like regions in the crystal. Typical size of a point defect is about 1-2 atomic diameters. The simplest examples of lattice disorder are vacant lattice sites, interstitial atoms and substitutional atoms. Different point defects are explained in the following paragraphs:

A ***vacancy*** is a vacant lattice position from where the atom is missing. It is usually created when the solid is formed by cooling the liquid. There are other ways of making a vacancy, but they also occur naturally as a result of thermal excitation, and these are thermodynamically stable at temperatures greater than zero. At equilibrium, the fraction of lattice sites that are vacant at a given temperature (T) are:

$$n/N = e^{-Q/kT}$$

where n is the number of vacant sites in N lattice positions, k is Boltzmann's constant, T is absolute temperature in Kelvins, and Q is the energy required to move an atom from the interior of a crystal to its surface. It is clear from the equation that there is an exponential increase in number of vacancies with temperature. When the density of vacancies becomes relatively large, there is a possibility for them to cluster together and form voids.

An ***interstitial atom*** or ***interstitialcy*** is an atom that occupies a place outside the normal lattice position. It may be the same type of atom as the rest surrounding it (self-interstitial) or a foreign impurity atom. Interstitialcy is most probable if the atomic packing factor is low.

Another way an impurity atom can be fitted into a crystal lattice is by substitution. A ***substitutional atom*** is a foreign atom occupying original lattice position by displacing the parent atom.

In the case of vacancies and foreign atoms (both interstitial and substitutional), there is a change in the coordination of atoms around the defect. This means that the forces are not balanced in the same way as for other atoms in the solid, which results in lattice distortion around the defect.

Vacancies

There are two types of vacancies. In one type the displaced atom migrates in successive steps and eventually settles at the surface: this is a ***Schottky*** defect. A Schottky defect is created in a perfect crystal by transferring an atom from a lattice site in the interior to a lattice site on the surface of the crystal. In the second type, called a ***Frenkel*** defect, in which an atom is transferred from a lattice site to an interstitial position, a position not normally occupied by an atom. So the Frenkel defect includes both atom and vacancy. Because of the additional elastic energy involved in squeezing an atom into an interstitial position, the Frenkel defect requires a large amount of energy and, for this reason, is not usually present in metals except under special circumstances.

Thermal entropy and Configurational entropy

Here, it is necessary to define the terms, 'thermal' (S_{th}) and 'configurational' (S_{cf}) (or mixing) entropies.

The ***thermal entropy*** (S_{th}) is determined by the number of different ways W_{th} in which the total vibrational energy of the crystal may be distributed over the possible vibrational modes. According to Boltzmann relation, $S_{th} = k \log W_{th}$ (1)

For example, in the Einstein model of a solid, W_{th} stands for the number of different ways in which the energy of vibration with total number of vibrational quanta *n* may be distributed over the 3*N* harmonic oscillators representing the solid consisting of *N* atoms. Obviously,

$$W_{th} = \frac{(3N+n)!}{3N!n!} \quad (2)$$

From Eqs. (1) and (2) we get,

$$S_{th} = k \log\left[\frac{(3N+n)!}{3N!n!}\right]$$

$= k\left[(3N+n)\log(3N+n)-(3N+n)-3N\log(3N)+3N-n\log n+n\right]$ using Stirling approximation.

$$\Rightarrow S_{th} = k\left[3N\log\left(\frac{3N+n}{3N}\right)+n\log\left(\frac{3N+n}{n}\right)\right] = k\left[3N\log\left(1+\frac{n}{3N}\right)+n\log\left(1+\frac{3N}{n}\right)\right]$$

For $h\nu \ll kT$, according to Einstein model $3NkT = nh\nu \Rightarrow 3N/n = h\nu/kT \ll 1 \Rightarrow n/3N \gg 1.$

$$\Rightarrow S_{th} = k\left[3N\log\left(\frac{n}{3N}\right)+n\left(\frac{3N}{n}\right)\right] \text{ since } \log\left(1+\frac{3N}{n}\right)\approx\frac{3N}{n} \text{ as } 3N/n \ll 1.$$

$$\therefore S_{th} = 3Nk\left[\log\left(\frac{n}{3N}\right)+1\right] = 3Nk\left[1+\log\left(kT/h\nu\right)\right] \quad (3)$$

This is the expression of thermal entropy.

The ***configurational entropy*** $\left(S_{cf}\right)$ of a crystal has nothing to do with the distribution of energy; it is determined solely by the number of different ways W_{cf} in which the atoms may be arranged over the available number of lattice sites.

Consider for example a lattice containing N_a atoms of type A and N_b atoms of type B -and assume that the lattice sites are all equivalent in the sense that a given lattice site may be occupied by A or B.

$$\therefore W_{cf} = \frac{(N_a+N_b)!}{N_a!N_b!} \quad (4)$$

Here, W_{cf} represents the number of different arrangements of N_a A atoms and N_b B atoms over a total (N_a+N_b) lattice points. The configurational entropy associated with W_{cf} is again given by the Boltzmann relation: $S_{cf} = k\log\left[\frac{(N_a+N_b)!}{N_a!N_b!}\right]$ (5)

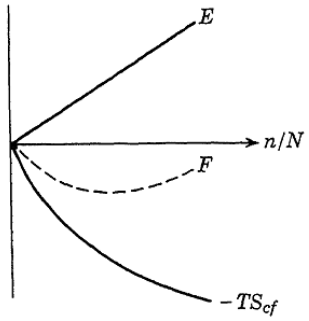
For a perfect crystal containing identical atoms and in the absence of any lattice defects, $W_{cf}=1$ and $S_{cf}=0$ because there is only one possible arrangement of the atoms. The total entropy occurring in the usual thermodynamic formulas is equal to the sum of the thermal and configurational entropies, i.e., $S = S_{th} + S_{cf}$ (6)

Are lattice defects thermodynamically favourable?

In thermal equilibrium a certain number of lattice vacancies are always present in an otherwise perfect crystal, because the entropy is increased by the presence of disorder in the structure.

According to thermodynamics, the equilibrium of a solid (under low external pressure) at a temperature T is determined by the minimum value of the free energy $F = E - TS$. The

defects under consideration are present as a result of the thermodynamic equilibrium conditions. Suppose, in a perfect metallic crystal we produce a certain number of vacant lattice sites by transferring atoms from the interior of the crystal to the surface. This will require a certain amount of energy, i.e., E increases. Consequently F increases and this by itself is thus unfavourable in the thermodynamic sense. On the other hand, the creation of the vacancies increases the disorder in the crystal and thus increases the configurational entropy from zero to a certain value determined by the number of vacancies n produced. In fact, the configurational entropy associated with the possible arrangements of N atoms and n vacancies over a total $(N+n)$ lattice sites is $S_{cf} = k\log\left[\frac{(N+n)!}{N!n!}\right]$. Now, because the entropy enters in the free energy expression in the form-TS, an increase in entropy reduces F and is thus favorable thermo- dynamically. As a result of the above described competition between energy on the one hand and entropy on the other, the stable configuration is one in which a certain fraction of the lattice sites is unoccupied. It has been assumed for simplicity that the thermal entropy is independent of n/N. The equilibrium corresponds to the minimum value of F at the temperature T. Any further increase in the disorder of the lattice would require energy larger than the associated reduction due to the increase in entropy.



Concentration of Schottky defects as a Function of temperature

Let us consider a perfect lattice containing N similar atoms at a temperature T; the free energy of this (unstable) perfect crystal will be denoted by $F_{\text{per}}(\text{T})$. Suppose we create n vacant lattice sites; let the energy required to create one vacancy be φ_v. We shall assume that φ_v is independent of n, which is justified as long as $n << N$; also, we assume that no two vacancies are nearest neighbors of each other. The energy of the imperfect crystal is then increased by $n\varphi_v$ relative to that of the perfect crystal.

The free energy of the imperfect crystal can be written as

$$F(n,T) = F_{per}(T) + n\varphi_v - nT\Delta S_{th} - TS_{cf} \qquad (7)$$

Here, ΔS_{th} is the increase in thermal entropy per vacancy and S_{cf} is the configurational entropy for an imperfect crystal as in Eq. (5). So the Eq. (7) can be rewritten as

$$F(n,T) = F_{per}(T) + n\varphi_v - nT\Delta S_{th} - kT\log\left[\frac{(n+N)!}{n!N!}\right]$$

Using Stirling approximation,

$$\Rightarrow F(n,T) - F_{per}(T) = n\varphi_v - nT\Delta S_{th} - kT\log\left[(n+N)\log(n+N) - N\log N - n\log n\right] \qquad (8)$$

In thermal equilibrium, $\left(\frac{\partial F}{\partial n}\right)_T = 0.$

$$\left(\frac{\partial F}{\partial n}\right)_T = \varphi_v - T\Delta S_{th} - kT\left[\log(n+N) - \log n\right] = 0 \tag{9}$$

$$\Rightarrow \log\left[\frac{(n+N)}{n}\right] = \frac{\varphi_v - T\Delta S_{th}}{kT}$$

$$\Rightarrow \left(\frac{n+N}{n}\right) = e^{\frac{\varphi_v - T\Delta S_{th}}{kT}} \Rightarrow \frac{n}{n+N} = e^{-\frac{\varphi_v}{kT}} e^{\frac{\Delta S_{th}}{k}} \tag{10}$$

Since at equilibrium, the number of vacancies is quite small $(n \ll N)$, we get the equilibrium concentration of Schottky defect in a solid at temperature T: $\frac{n}{N} = e^{-\frac{\varphi_v}{kT}} e^{\frac{\Delta S_{th}}{k}}$ (11)

Physical meaning of thermal entropy change per vacancy

In order to get an insight into the physical meaning of the thermal entropy change ΔS_{th} per vacancy, we shall consider a simple Einstein model of a solid. The thermal entropy of the perfect crystal is then equivalent to the thermal entropy of a system of $3N$ harmonic oscillators with the Einstein frequency ν for $h\nu \ll kT$. In the imperfect crystal, the atoms neighboring a vacancy will have a vibrational frequency ν' ($\nu' < \nu$) because the restoring forces are reduced, particularly along the direction of the line joining the atom and the vacancy. When x is the number of nearest neighbours surrounding a vacancy (x = 6 for sc, =8 for bcc, = 12 for fcc), the Einstein model leads to $3nx$ oscillators of frequency ν' and ($3N - 3nx$) oscillators of frequency ν.

In analogy with Eq. (3), the thermal entropy of the actual (imperfect) crystal is

$$S_{th(ac)} = 3nxk\left[1 + \log\left(kT/h\nu'\right)\right] + \left(3N - 3nx\right)k\left[1 + \log\left(kT/h\nu\right)\right] \tag{12}$$

Subtracting Eq.(12) from Eq. (3), we get

$$S_{th(ac)} - S_{th(per)} = 3nxk\log\left(kT/h\nu'\right) - 3nxk\log\left(kT/h\nu\right)$$

$$\left(S_{th(ac)} - S_{th(per)}\right)/n = 3xk\log\left(\nu/\nu'\right) \Rightarrow \Delta S_{th} = 3xk\log\left(\nu/\nu'\right) \tag{13}$$

So change in thermal entropy per vacancy is a consequence of the change in the frequency spectrum of the lattice vibrations.

From Eq. (11) & (13), we obtain the equilibrium concentration of Schottky defect in a solid at temperature T as

$$\frac{n}{N} = e^{-\frac{\varphi_v}{kT}} e^{\log(\nu/\nu')^{3x}} = \left(\nu/\nu'\right)^{3x} e^{-\frac{\varphi_v}{kT}}. \tag{14}$$

Temperature dependence of φ_v

It is evident that as T increases, the lattice expands, the binding forces are reduced, and thus φ_v decreases with temperature. In first approximation one may write a linear relationship between φ_v and T, i.e., $\varphi_v = \varphi_{v0}(1-\alpha T)$. (15)

where α_0 is a temperature coefficient and φ_{v0} the energy of formation of a vacancy at $T = 0$.

The Eq. (11) becomes, $\frac{n}{N} = e^{-\frac{(\varphi_{v0}(1-\alpha T))}{kT}} e^{\frac{\Delta S_{th}}{k}} = e^{-\frac{\varphi_{v0}}{kT}} e^{\frac{\alpha\varphi_{v0}}{k}} e^{\frac{\Delta S_{th}}{k}}$ (16)

Number of Frenkel defects as a Function of temperature

In case of Frenkel defects we consider n vacant lattice sites; let the energy required to create one vacancy be φ_F. The configurational entropy (S_{cf}) is $S_{cf} = k \log W_{cf}$ where

$W_{cf} = \frac{(n+N)!}{n!N!} \cdot \frac{(n+N_i)!}{n!N_i!}$. N is the number of atoms, N_i is the number of possible interstitial positions.

So the Eq. (7) can be rewritten as in case of Frenkel defects,

$$F(n,T) = F_{per}(T) + n\varphi_F - nT\Delta S_{th} - kT \log\left[\frac{(n+N)!}{n!N!}\frac{(n+N_i)!}{n!N_i!}\right] \quad (17)$$

where, ΔS_{th} is the change in thermal entropy per Frenkel defect.

In thermal equilibrium we can write $\left(\frac{\partial F}{\partial n}\right)_T = 0$.

Using Stirling approximation we finally obtain,

$$\left(\frac{\partial F}{\partial n}\right)_T = \varphi_F - T\Delta S_{th} - kT\left[\log\frac{(n+N)}{n} + \log\frac{(n+N_i)}{n}\right] = 0$$

$$\Rightarrow \varphi_F - T\Delta S_{th} - kT\left[\log\frac{(n+N)(n+N_i)}{n^2}\right] = 0$$

Since at equilibrium, the number of vacancies is quite small $(n \ll N,\ N_i)$,

$$\Rightarrow \varphi_F - T\Delta S_{th} - kT\left[\log\frac{NN_i}{n^2}\right] = 0$$

$$\Rightarrow n^2 = NN_i e^{-\frac{\varphi_F}{kT}} e^{\frac{\Delta S_{th}}{k}}$$

$$\therefore n = \sqrt{NN_i}\, e^{-\frac{\varphi_F}{2kT}} e^{\frac{\Delta S_{th}}{2k}} \quad (18)$$

This is the expression of the equilibrium concentration of Frenkel defect in a solid at temperature T. The factors 2 appear in the exponentials because a Frenkel defect has two components.

Schottky & Frenkel defects in Ionic Crystals

In ionic crystals, existence of point defects is subjected to the condition of charge neutrality. There are two possibilities for point defects in ionic solids.

- when an ion displaced from a regular position to an interstitial position creating a vacancy, the pair of vacancy-interstitial is called ***Frenkel*** defect. Cations are usually smaller and thus displaced easily than anions. Closed packed structures have fewer interstitials and displaced ions than vacancies because additional energy is required to force the atoms into the interstitial positions.

- a pair of one cation and one anion can be missing from an ionic crystal, without violating the condition of charge neutrality when the valency of ions is equal. The pair of vacant sites, thus formed, is called ***Schottky*** defect. This type of point defect is dominant in alkali halides. These ion-pair vacancies, like single vacancies, facilitate atomic diffusion.

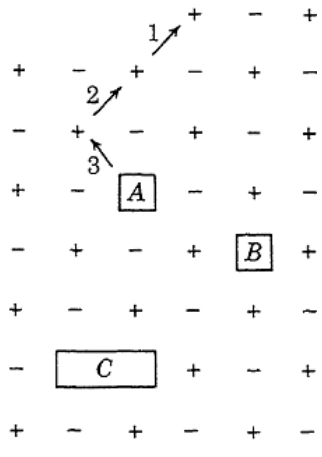


Fig. 7-1. The sequence of jumps 1, 2, 3 may lead to the formation of a positive ion vacancy *A*; *B* represents a negative ion vacancy; *C* an associated pair of vacancies formed as a result of Coulomb attraction.

An ionic crystal should contain equal numbers of positive and negative ion vacancies. Why?

Let us consider an ionic crystal of the composition A^+B^-. Positive ion vacancies may then be produced in a similar way as in metals, viz., by a number of successive jumps of positive ions. The result would be equivalent to taking a positive ion somewhere from the interior of the crystal and placing it at the surface. Suppose now that a number of positive ion vacancies would have been produced in this manner while the negative ion lattice remained perfect. The surface of the crystal would then contain an excess of positive charge, the interior an excess of negative charge. Thus space charges would be set up. It is obvious that such space charges would counteract the formation of more positive ion vacancies. On the other hand, the field set up by the space charges would favor the formation of negative ion vacancies. We thus conclude that as a consequence of the tendency to prevent the build-up of space charges, an ionic crystal should contain nearly equal numbers of positive and negative ion vacancies.

Equilibrium concentration of Schottky defects in Ionic Crystals

Let us consider an ionic crystal made of positive and negative ion vacancies. φ_+ and φ_- are the energy required to produce a single positive and a single negative ion vacancy respectively. It is

obvious from this that their number will be determined only by the sum of the formation energies $\varphi = \varphi_+ + \varphi_-$. (19)

The free energy of the fictitious perfect crystal can be written as $F_{per} = E_{per} - TS_{per}$. (20)

The entropy is thermal entropy only, because for a perfect crystal the configurational entropy vanishes. Let the actual crystal contain n positive and n negative ion vacancies distributed over a total of $(n+N)$. Its configurational entropy is $S_{cf} = k\log\left[\frac{(n+N)!}{n!N!}\right]^2$. (21)

The free energy of the actual crystal may thus be represented by

$F_{ac}(n,T) = F_{per}(T) + n\varphi - T\left(S_{ac} - S_{per}\right) - TS_{cf}$

$\Rightarrow F_{ac}(n,T) = F_{per}(T) + n\varphi - T\left(S_{ac} - S_{per}\right) - 2kT\log\left[\frac{(n+N)!}{n!N!}\right]$ (22)

where S_{ac} is the thermal entropy of the actual crystal. The increase in thermal entropy is $\Delta S_{th} = \left(S_{ac} - S_{per}\right)/n$ for production of a pair of vacancy.

In thermal equilibrium we can write $\left(\frac{\partial F}{\partial n}\right)_T = 0$.

Using Stirling approximation we finally obtain, $n = Ne^{-\frac{\varphi}{2kT}}e^{\frac{\Delta S_{th}}{2k}}$ (23)

In the actual ionic crystal, the Einstein model leads to $6nx$ oscillators of frequency ν' and $(6N - 6nx)$ oscillators of frequency ν, x is the number of nearest neighbours surrounding a vacancy. So the thermal entropies of perfect and actual crystals become respectively as:

$S_{per} = 6Nk\left[1 + \log\left(kT/h\nu\right)\right]$

$S_{ac} = 6nxk\left[1 + \log\left(kT/h\nu'\right)\right] - 6nxk\left[1 + \log\left(kT/h\nu\right)\right] + S_{per}$

$\left(S_{ac} - S_{per}\right)/n = 6xk\log\left(\nu/\nu'\right) \Rightarrow \Delta S_{th}/2 = 3xk\log\left(\nu/\nu'\right)$ (24)

From Eqs. (23) & (24) we can write, $n = NCe^{-\frac{\varphi}{2kT}}$ where $C = \left(\nu/\nu'\right)^{3x}$.

If φ depends on temperature in accordance with a relation,

$\varphi(T) = \varphi_0 + T\left(\frac{d\varphi}{dT}\right) = \varphi_0 - \gamma T$ (25)

the actual expression for the density of vacancies should be

$n = N\left(\nu/\nu'\right)^{3x} e^{\frac{\gamma}{2k}} e^{-\frac{\varphi}{2kT}}$ (26)

Note:

Here, an objection is raised that the temperature variation of the thermal entropy change ΔS_{th} is not taken into account. For zero pressure we have $d\varphi/dT = T\,d\left(\Delta S_{th}\right)/dT$.

Then n/N could be expressed as $n/N = A\exp(-\varepsilon/kT) \Rightarrow \varepsilon = -k\dfrac{d}{d(1/T)}\log(n/N)$

$\Rightarrow \varepsilon = -k\dfrac{d}{d(1/T)}\left[\dfrac{\Delta S_{th}}{2k} - -\dfrac{\varphi}{2kT}\right] \Rightarrow \varepsilon = -\dfrac{1}{2}\left[\dfrac{d(\Delta S_{th})}{d(1/T)} - \dfrac{d(\varphi/T)}{d(1/T)}\right]$

$\Rightarrow \varepsilon = -k\dfrac{d}{d(1/T)} \Rightarrow \varepsilon = -\dfrac{1}{2}\left[\dfrac{1}{T}\dfrac{d(\varphi)}{d(1/T)} - \dfrac{1}{T}\dfrac{d(\varphi)}{d(1/T)} - \varphi\right] \Rightarrow \varepsilon = \varphi/2.$ One can measure φ in this manner.

Note: *It will be evident that a positive and a negative ion vacancy will attract each other as a result of the Coulomb field between them. For large distances, the energy of attraction is equal to* $-e^2/\varepsilon r$, *where* ε *is the dielectric constant of the medium. They may therefore combine to form pairs of vacancies (Fig. 7-1). At a given temperature, there will exist a certain ratio between the number of single vacancies and the number of pairs, the ratio depending on the dissociation energy required to separate a pair into two singlets. There are evidently certain degrees of dissociation depending on whether the distance between the single vacancies is small or large; in a sense one may therefore speak of a thermally excited state of a pair if the distance between the vacancies is only a few atomic diameters.*

The activation energy for the formation of defects in ionic crystals

We derive an expression for the number of vacancies in an ionic crystal in thermal equilibrium at a temperature *T.* This number is essentially determined by the formation energy $\varphi = \varphi_+ + \varphi_-$. Let us consider the energy φ_+ and φ_- involved in the formation of a positive ion vacancy and a negative ion vacancy respectively.

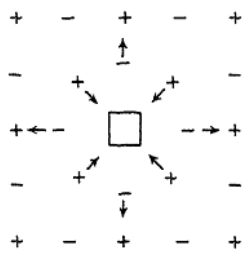


Fig. 7-2. Showing the polarizing effect of a positive ion vacancy on its surroundings. The surrounding negative ions are displaced slightly outward; the positive ions assume positions slightly displaced toward the vacancy. In addition to the ionic displacements, the effective negative charge of the vacancy induces dipoles in the surrounding ions.

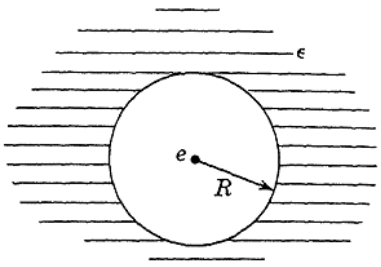


Fig. 7-3. Jost model to calculate the polarization energy resulting from the presence of a vacancy. The vacancy is represented by a spherical cavity of radius R inside a homogeneous dielectric ϵ; the charge e at the center represents the effective charge of the vacancy.

Suppose a positive ion is removed from the interior of the crystal to infinity, while the charge distribution in the crystal is kept the same as it was. The responsible energy is given by

$$\epsilon_L = A\frac{e^2}{a_0}\left(1 - \frac{1}{n}\right) \quad \ldots\ldots (27)$$

where N is the number of ion pairs, A is the Madelung constant, a_0 is the shortest interionic distance, n is the Born repulsion exponent. For NaCl this is equal to about 7.9 eV per ion pair.

Putting the ion from infinity on the surface of the crystal leads to a gain in energy of

$$\frac{1}{2}\in_L = A\frac{e^2}{2a_0}\left(1-\frac{1}{n}\right) \tag{28}$$

We note that from the point of view of the surroundings of a positive ion vacancy, it looks as if an excess of negative charge has been added in the vicinity of the missing positive ion. Consequently the surrounding material will become polarized. This polarization consists first of the formation of dipoles induced in the ions by the Coulomb field of the missing ion, second of a slight ionic displacement as indicated in Fig. 7-2. Because of the long range of Coulomb forces, it is not sufficient to take into account only nearest neighbors; the effect will spread over distances many times the lattice constant. The calculation of this polarization energy may be understood in principle on the basis of a simplified model, first introduced by Jost. If we consider the vacancy as a spherical hole inside a homogeneous dielectric constant ε the hole bearing a charge e at its center, we obtain the situation given in Fig. 7-3. The charge e, due to the missing ion, polarizes the dielectric and thus in turn will create a reaction potential V at the location of the charge. Thus the polarization energy is given by $P_+ = \frac{1}{2}eV = A\frac{e^2}{2R_+}\left(1-\frac{1}{\varepsilon}\right)$ (29)

The Eqs. (27) - (29) gives the value of $\varphi_+ = \in_L -\frac{1}{2}\in_L - P_+ = A\frac{e^2}{2a_0}\left(1-\frac{1}{n}\right) - A\frac{e^2}{2R_+}\left(1-\frac{1}{\varepsilon}\right)$. (30)

For negative ion vacancies $\varphi_- = \in_L -\frac{1}{2}\in_L - P_- = A\frac{e^2}{2a_0}\left(1-\frac{1}{n}\right) - A\frac{e^2}{2R_-}\left(1-\frac{1}{\varepsilon}\right)$ (31)

The energy required to produce a positive and a negative ion vacancy is

$$\varphi = \varphi_+ + \varphi_- = A\frac{e^2}{a_0}\left(1-\frac{1}{n}\right) - A\frac{e^2}{2}\left(\frac{1}{R_+}+\frac{1}{R_-}\right)\left(1-\frac{1}{\varepsilon}\right) = \in_L - P_+ - P_- \tag{32}$$

Self-diffusion in Alkali halide crystals

The self-diffusion of radioactive sodium in NaCl and NaBr is studied in the following manner: A thin layer of radioactive salt containing the isotope Na^{23} was deposited on one face of a cubic crystal. The crystal was then held at a constant temperature for a certain length of dtime. After this diffusion anneal, the distribution of radioactive sodium was determined by means of a sectioning technique, employing a microtome.

Diffusion is the movement of particles in a solid from an area of high concentration to an area of low concentration, resulting in the uniform distribution of the substance. Self-diffusion stands for

that process in same material. Let us consider diffusion of radioactive Na atoms in solid state solution (NaCl / NaBr) in direction x between two parallel atomic planes (separated by Δx).

If there is no change with time in concentration at radioactive atoms at these planes – such diffusion condition is called steady-state diffusion. According to the Fick's First Law of Diffusion, the transfer of radioactive atoms per unit area in a one-dimensional flow can be described by the following equation: $J = -D\frac{\partial n^*(x,t)}{\partial x}$. where J is the number of radioactive atoms crossing unit area in unit time, n^* is the concentration of the radioactive atoms, D is the diffusion coefficient, x is the distance into the substrate, and t is the diffusion time. The negative sign indicates that the diffusing mass flows in the direction of decreasing concentration. From the Conservation of Mass, we also know that: $\frac{\partial n^*(x,t)}{\partial t} + \frac{\partial J}{\partial x} = 0 \Rightarrow \frac{\partial n^*(x,t)}{\partial t} = -\frac{\partial J}{\partial x}$.
If we combine this relationship with the Fick's 1st Law of Diffusion, then we have derived the Fick's 2nd Law of Diffusion, which states: $\frac{\partial n^*(x,t)}{\partial t} = D\frac{\partial^2 n^*(x,t)}{\partial x^2}$.
The solution of this equation for the boundary conditions (at t = 0, n_0^* vanishes everywhere except at x = 0 where it become infinite) is obtained as $n^*(x,t) = \frac{n_0^*}{(\pi Dt)^{1/2}}\exp\left[-\frac{x^2}{4Dt}\right]$.

Here $n^*(x,t)$ is the density of radioactive ions at x after an annealing period t; n_0^* is the initial density at the surface. This solution is based on the assumption that the migration of radioactive sodium is a result of a single diffusion process, because only one diffusion constant D has been introduced.

Derivation of diffusion coefficient in Alkali halide crystals

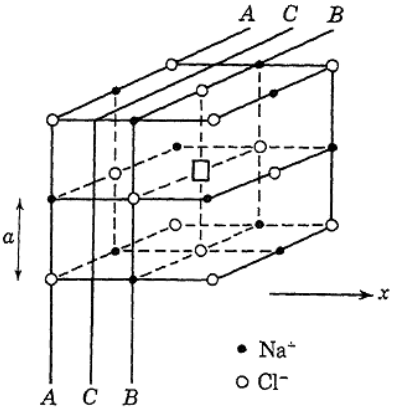
In alkali halide crystals diffusion is therefore possible only by the migration of interstitial ions or by the migration of vacant lattice sites. The positive ions surrounding a positive ion vacancy may jump into the vacancy; consequently, the vacancy moves through the crystal by virtue of positive ions jumping into it and diffusion becomes possible.

Let us consider a sodium chloride structure, assuming for simplicity that the x-axis along which the diffusion of radioactive sodium takes place coincides with one of the cube edges. A particular positive ion vacancy, such as the one in Figure indicated by the square may then in time carry out a jump to any of 12 equivalent positions, assuming the latter are occupied by positive ions. Of these possible jumps, there are 4 in the positive x-direction, 4 in the negative x-direction, and the remaining 4 leave the vacancy in the original plane. Thus if p is the probability per second for the vacancy to make any jump, $p/3$ is the probability per second for a displacement $+a$, $-a$, and 0, respectively, if a is the shortest interionic distance. Let us represent the number of

radioactive positive ions crossing 1 cm^2 of the plane C in Figure per second, going from plane A to B, by $N^*_{\rightarrow}$. Similarly, let $N^*_{\leftarrow}$ represents the same number crossing plane C by going from plane B to A. Then if N is the density of positive ions per cm^3, n is the density of vacancies, and n^* is the density of radioactive positive ions,

$$N^*_{\rightarrow} = \frac{1}{2a^2}\cdot\frac{n}{N}\cdot\frac{p}{3}\cdot\frac{n^*}{N}$$

$$N^*_{\leftarrow} = \frac{1}{2a^2}\cdot\frac{n}{N}\cdot\frac{p}{3}\cdot\frac{1}{N}\left(n^* + \frac{\partial n^*}{\partial x}a\right)$$

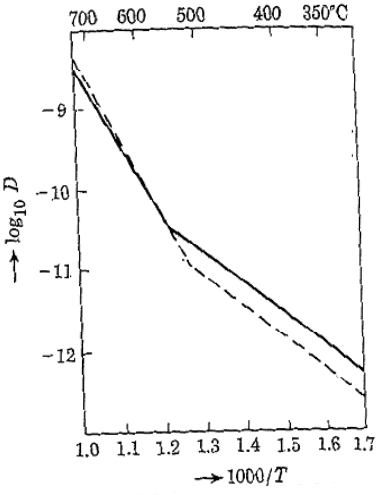


Here $\frac{1}{2a^2}$ represents the total number of positive lattice sites per cm^2 on plane A or B [In area a^2 total number of positive ions = 2 X (1/4) = 1/2]; n/N represents the probability that such a site is vacant, and n^*/N represents the probability that a positive ion in plane A is radioactive. Consequently the net number of radioactive positive ions passing 1 cm^2 of plane C per second from left to right is

$$J = N^*_{\rightarrow} - N^*_{\leftarrow} = -\frac{1}{6a}\cdot\frac{np}{N^2}\cdot\frac{dn^*}{dx} \qquad (33)$$

Comparing (33) with the relation $J = -D\frac{dn^*}{dx}$ and remembering that $N = \frac{1}{2a^3}$ [In volume a^3 total number of positive ions = 4 X (1/8) = 1/2] one obtains for the diffusion constant associated with the migration of single positive ion vacancies

$$D = \frac{a^2}{3}\cdot\frac{n}{N}\cdot p \qquad (34)$$



As expected, the self-diffusion coefficient is proportional to the number of vacancies per unit volume n and to the jump probability of a vacancy per second p. which may be written in the form $p = \nu\exp\left[-\varepsilon_j/kT\right]$; (35)

where ν is a frequency and ε_j is the activation energy associated with a jump. Finally then, the coefficient of self-diffusion based on the assumption of the *migration of single positive ion vacancies* may be obtained as

$$D = \frac{1}{3}\cdot C\nu a^2\cdot\exp\left[-\varphi/2kT\right]\exp\left[-\varepsilon_j/kT\right] \qquad (36)$$

The constant C arises from the thermal entropy change associated with the production of vacancies.

We note that in a plot of log$D$ versus $1/kT$, the slope of the line according to the above interpretation is determined by the sum $\left(\varepsilon_j + \varphi/2\right)$, i.e., by the energy required for the

formation of vacancies plus the activation energy for jumping. Thus, from the diffusion measurements of Na in NaCl, represented in Figure, it follows from the slope in the high-temperature region that $\varepsilon_j + \varphi/2$ = 1.80 eV.

Explanation of the break in the logD versus 1/kT curve in the low-temperature region

The break in the log*D* versus 1/*kT* curve leading to a smaller slope in the low-temperature region may in principle be a result of either or both of the following two causes:

(1) ***The presence of divalent positive impurities***: *Suppose that a salt like NaCl contains in solid solution a small amount of $SrCl_2$ or of the chloride of another divalent metal, the divalent positive ions occupying sites which are normally occupied by the singly charged Na^+ ions. The condition of electric neutrality then requires that for each divalent positive ion present, there must be a positive ion vacancy. Such crystals then may contain at lower temperatures more positive ion vacancies than would be expected on the basis of thermal equilibrium alone. In fact, below a critical temperature, the number of vacancies per unit volume would then remain constant, the critical temperature being higher the larger the density of divalent impurities.*

At high temperatures, however, the number of thermally produced vacancies would predominate over the number required by the presence of the divalent ions and the crystal would behave in a normal fashion. Now, if the number of vacancies per unit volume is independent of temperature, the temperature dependence of the diffusion coefficient is according to Eqs. (34) and (35) determined by the factor $-\varepsilon_j / kT$ in the low-temperature region. In the log D versus 1/T curve, the activation energy for jumping may be obtained separately from the slope of the curve in the low-temperature region. If the presence of divalent metallic ions is accepted as the cause of the break in the log D versus 1/T curve, $\left(\varepsilon_j + \varphi/2\right)$ is known from the high-temperature slope, both ε_j and φ may be obtained.

(2) ***The freezing-in of positive ion vacancies***: The latter hypothesis is based on the following reasoning: Suppose a crystal contains a certain number of lattice defects in thermal equilibrium at a high temperature. If the temperature is suddenly lowered, it will take a certain amount of time for the new equilibrium to be established because this requires a migration of vacancies. At lower temperatures such time intervals may be very long and consequently, the crystals may contain many more defects than would be permitted by the equilibrium conditions.

For the diffusion of positive ion vacancies in NaCl, it follows from the slope in the low-temperature region of Figure that ε_j = 0.77 eV. Hence, it fits with the slope in the high-temperature region $\left(\varepsilon_j + \varphi/2\right)$ = 1.80 eV leading to the experimental value of φ = 2.06 eV.

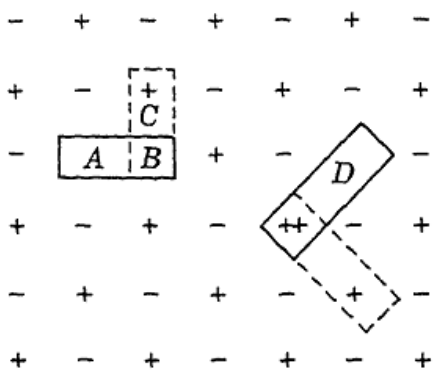


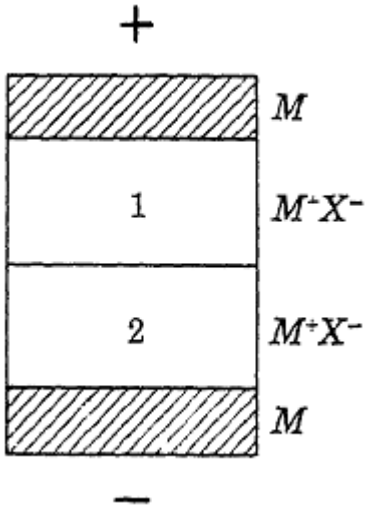
Fig. 7-7. The pair *AB* may diffuse by the positive ion *C* jumping into the vacancy *A*, or by a negative ion jumping into *B*. The associated complex divalent positive ion-positive ion vacancy may migrate as a result of interchange between the divalent ion and the vacancy *D*, combined with singly charged positive ions jumping into the vacancy.

Note: *Diffusion of positive ions does not necessarily take place as a result of migration of single positive ion vacancies only. In fact, at least two other possible diffusion mechanisms must be considered in the alkali halides: (i)* ***Diffusion resulting from migration of pairs****. (ii)* ***Diffusion resulting from migration of divalent positive impurities together with associated vacancies.***

The influence of the presence of divalent positive ions on the diffusion may be understood as follows: For each divalent positive ion, there must be a positive ion vacancy to satisfy the neutrality condition. A certain fraction of these vacancies are free and contribute to the diffusion as discussed above. However, not all these vacancies are free, because they are attracted by the divalent positive ions as a result of Coulomb interaction. Thus there will be a certain number of associated complexes, consisting of a divalent positive ion and a neighboring vacant positive ion site. This unit may migrate through the crystal as a result of other positive ions jumping into the vacancy and as a result of possible jumps of the divalent ion into the vacancy.

Ionic conductivity in "pure" alkali halides

When a potential difference is applied between two opposite faces of an ionic crystal, the currents is mainly a result of the migration of ions under influence of the electric field, similar to the electrolytic conduction of aqueous solutions of salts.



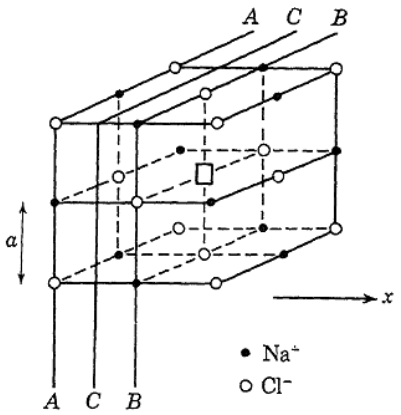
Two slabs of a salt M^+X^- are pressed together between two electrodes of the metal M. For the polarity as indicated, the two following extreme possibilities exist:

- *(i) Only positive ions move; in that case the cathode will grow at the expense of the anode, the thickness of the two salt slabs remaining the same.*
- *(ii) Only the negative ions move; the X^- ions are then neutralized at the anode and form new layers of salt. Hence the anode decreases in thickness, the cathode increases. Furthermore, slab 1 will grow at the expense of slab 2.*

If both types of ions contribute to the current, the result will be intermediate between (i) and (ii).

The ionic conductivity of an isotropic crystal is defined by the scalar equation, $I = \alpha E$; where I is the current density, E is the field strength, and α is the conductivity. If the conductivity of the positive ions alone is α_+, the transport number of these ions is defined by $t_+ = \alpha_+ / \alpha$. Similarly, $t_- = \alpha_- / \alpha$ leading to $t_+ + t_- = 1$.

In the alkali halides the experiments show that the positive ions are much more mobile than the negative ones. However, that the presence of small amounts of divalent positive ions has a marked influence on the measured transport numbers. We have seen above that in the alkali halides the ionic current is carried for the greater part by the positive ions. This is not always the case, however. In the halides of barium and lead, for example, the negative ions are mainly responsible for the ionic conductivity.



In the alkali halides ionic conductivity, like diffusion, is explained in terms of the motion of vacant lattice sites. As the mobility of the positive ion vacancies is appreciably larger than that of the negative ones and it will therefore be assumed that the conductivity is entirely due to the motion of the former. For simplicity we shall use the geometry of Figure, assuming an electric field along the x-axis. Let us denote the number of positive ion sites per cm^3 by *N*, the number of positive ion vacancies per cm^3 by *n*. If the electric field in Figure is directed to the right, a positive ion vacancy will jump with a higher probability to the left than to the right, because it is negatively charged. The potential energy along the line of motion may therefore be represented by the full curve in Fig. 7-9 which is the resultant of the dashed field-free curve and the linear potential due to the external potential difference. Clearly then, the probabilities per second for a jump to the left and to the right are, respectively,

$$p_{\leftarrow} = \frac{1}{3}\cdot\nu\cdot\exp\left[-\left(\varepsilon_j - \frac{1}{2}aeE\right)\Big/kT\right]$$

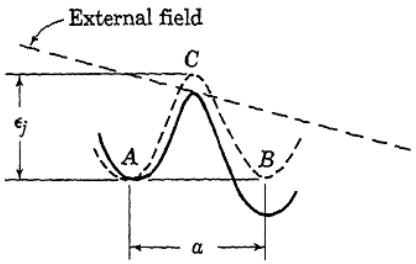


Fig. 7-9. The fully drawn curve represents the resultant of the field-free potential curve (dashed) and the linear potential (dashed) resulting from the external field *E*. *A*, *B*, and *C* may be associated with positions of a positive ion in the planes *A*, *B*, *C* of Fig. 7-6.

$$\text{and } p_{\rightarrow} = \frac{1}{3}\cdot\nu\cdot\exp\left[-\left(\varepsilon_j + \frac{1}{2}aeE\right)\Big/kT\right] \qquad (37)$$

where ν is a frequency and ε_j is the activation energy associated with a jump, *E* represents the field strength. The current density, i.e., the net flux of charge passing per second through 1 cm^2, is then equal to

$$I = \frac{1}{2a^2}\cdot\frac{n}{N}\left(p_{\leftarrow} - p_{\rightarrow}\right)e \qquad (38)$$

because $1/2a^2$ is the number of positive ion sites in a plane perpendicular to the x-axis of an area of 1 cm^2 and *n/N* is the probability for such a site to be vacant. From Eq. (38), we have

$$I = \frac{1}{2a^2}\cdot\frac{n}{N}e\frac{1}{3}\cdot\nu\cdot\left\{\exp\left[-\left(\varepsilon_j - \frac{1}{2}aeE\right)\Big/kT\right] - \exp\left[-\left(\varepsilon_j + \frac{1}{2}aeE\right)\Big/kT\right]\right\}$$

$$\Rightarrow I = \frac{1}{2a^2}\cdot\frac{n}{N}e\frac{1}{3}\cdot\nu\cdot\exp[-\varepsilon_j/kT]\cdot\left\{\exp\left[\frac{1}{2}aeE\Big/kT\right] - \exp\left[-\frac{1}{2}aeE\Big/kT\right]\right\}$$

Now, for nearly all practical cases, $aeE<<kT$, so that in first approximation

$$\Rightarrow I = \frac{1}{2a^2}\cdot\frac{n}{N}e\frac{1}{3}\cdot\nu\cdot\exp[-\varepsilon_j/kT]\cdot\{1+aeE/2kT-1+aeE/2kT\}$$

$$\Rightarrow I = \frac{1}{2a^2}\cdot\frac{n}{N}e\frac{1}{3}\cdot\nu\cdot\exp[-\varepsilon_j/kT]\cdot aeE/kT$$

$$\Rightarrow I = \frac{1}{6a^2kT}\cdot\left(\frac{n}{N}\right)e^2\nu\cdot\exp[-\varepsilon_j/kT]\cdot E = \sigma E \qquad (39)$$

Now putting the number of vacancies n in Eq. (39), the conductivity is equal to

$$\sigma = \frac{Ce^2\nu}{6akT}\cdot\exp[-(\varepsilon_j+\varphi/2)/kT] \qquad (40)$$

where $C = \exp[-\Delta S_{th}/2k]$. We note that the current density is proportional to E only as long as $aeE<<kT$, i.e., Ohms law is valid only under this particular condition. For very high electric fields such that aeE is not small compared with kT, the current increases exponentially with the field strength. According to Eq. (40), the conductivity associated with the positive ion vacancies depends on the two activation energies ε_j; and φ, as does the coefficient of self-diffusion. From Eqs. (36) and (40) it follows that

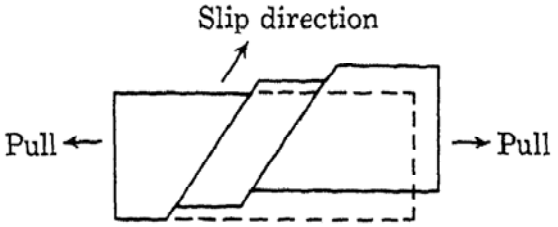
$$\sigma/D = \frac{Ne^2}{kT}. \qquad (41)$$

It must be emphasized that the Einstein relation is valid only if the conductivity and self-diffusion are due to the same mechanism; in the present case the assumption implicit in the derivation of Eq. (41) is that both phenomena are a result of the migration of single positive ion vacancies. First of all, in the high-temperature region the slope of the diffusion coefficient curve as calculated from Eq. (41) appears to be slightly larger than the directly measured one. This may be explained as a result of the fact that a small fraction of the ionic current is carried by the negative ion vacancies; these, of course, do not contribute to the self-diffusion of Na. In the low-temperature region, the calculated diffusion coefficient is somewhat smaller than the directly measured one. This implies that besides the diffusion of positive ion vacancies, there is some diffusion associated with the migration of neutral carriers. For example, pairs of vacancies and positive divalent ions associated with vacancies may contribute to the diffusion but will not contribute to the ionic conductivity.

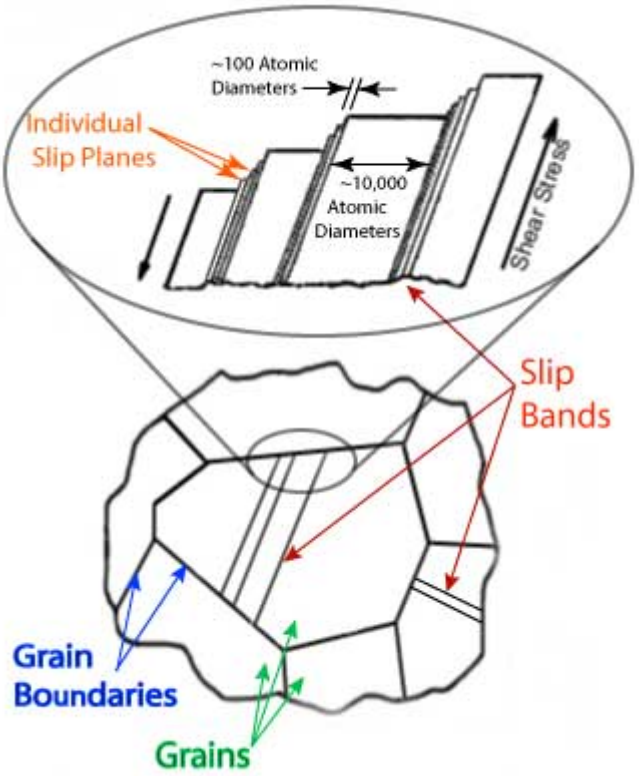
Plastic deformation

When a crystal is deformed elastically under influence of applied stresses, it returns to its original state upon removal of the stresses. However, if the applied stresses are sufficiently large, a certain amount of deformation remains after removal of the stresses: the crystal has been plastically deformed. We shall see below that the atomic interpretation of plastic flow of crystals requires the introduction of a new type of lattice defects, viz., dislocations.

In many crystals plastic flow results from the sliding of one part of a crystal relative to another. In Figure we have illustrated schematically how such a process may lead to an increase in the length of a crystal under influence of tension. The sliding process is referred to as slip; the plane and direction in which the slip occurs define, respectively, the slip plane and the slip direction. This type of mechanism evidently deforms the outer surface of the crystal and leads to so-called slip bands. The amount of slip associated with a slip band may be several thousand Angstroms.

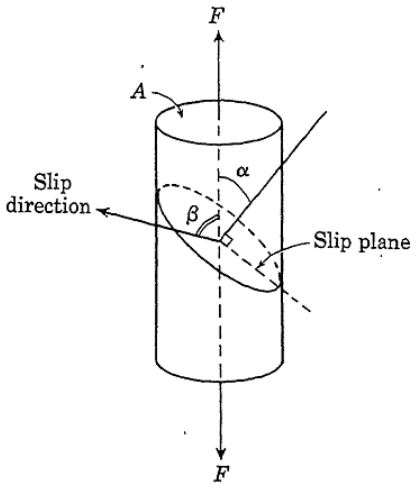


Plastic deformation is inhomogeneous in the sense that only a relatively small number of atoms actually take part in the slip process, viz., only those atoms which form layers on either side of a slip plane. Elastic deformation, on the other hand, affects all atoms in a crystal. This difference between plastic and elastic deformation indicates that the atomic interpretation of plastic flow must be based on an entirely different model than that of elastic deformation. In fact, the elastic properties of solids can be understood quite well in terms of interatomic forces acting in a perfect lattice; plastic deformation, however, cannot be discussed properly on the basis of a perfect lattice, i.e., it cannot be discussed by simply extending the theory of elasticity to the case of large stresses and strains. It will be shown below that if plastic flow were to occur in a perfectly periodic lattice, much larger shear stresses would be required than those for which plastic flow is observed.



Besides being characterized by inhomogeneity, plastic flow is also anisotropic. Since the energy required to move is lowest along the densest planes of atoms, dislocations have a preferred direction of travel within a grain of the material. Slip usually takes place preferentially in planes of high atomic density, e.g. along {111} planes in a f.c.c. lattice. Also, the direction of slip commonly coincides with a direction along which the number of atoms per unit length is high. This results in slip that occurs along parallel planes within the grain. These parallel slip planes group together to form slip bands, which can be seen with an optical microscope. A slip band appears as a single line under the microscope, but it is in fact made up of closely spaced parallel slip planes as shown in the image.

Critical shear stress



Let us consider a cylindrical crystal of cross section A under influence of a force F. Let the normal to the active slip plane make an angle α with F. Let the angle between the slip direction and F be β. The resolved shear stress, i.e., the force acting per unit area of the slip plane in the slip direction, is then given by $\tau = (F/A)\cos\alpha\cos\beta$, (41)

since the area of the slip plane is $(A/\cos\alpha)$. Similarly, the tensile stress per unit area normal to the slip plane is $\tau = (F/A)\cos^2\alpha$. (42)

Suppose now that for given values of α and β, the force F is gradually increased from zero. Even for relatively small stresses a certain amount of plastic flow occurs, but the rate of flow is small. It turns out, however, that the rate of flow increases very rapidly whenever the resolved shear stress τ reaches a critical value τ_c. At the same time, the results indicate that the tensile stress normal to the slip plane is of little or no influence on the mechanism of slip. For pure crystals, the critical shear stress lies in the range between 10^6-10^7 dynes per cm^2.

Prove that, the theoretical critical shear stress based on a perfect lattice is much larger than the observed values for pure crystals.

For this purpose, we resort to a simplified model suggested by Frenkel. With reference to Figure, consider a cross section through two neighboring atomic planes separated by a distance d. Without external forces, let the fully drawn circles represent the equilibrium positions of the atoms. Suppose now that a shear stress τ is applied, and that as a result, all atoms in the upper plane are displaced by an amount x relative to their original position.

Changing the role of dependent and independent variables, we may say that for a displacement x, a shear stress $\tau(x)$ is required. Suppose that we want to plot τ as a function of x. First we note that as a result 1e periodic nature of the system, τ will vanish for x = 0, a/2, a, etc., where a is the distance between neighboring atoms within the planes. Oversimplifying the problem, we shall assume that this periodic function is given by $\tau(x) = \tau_c \sin(2\pi x/a)$ (43)

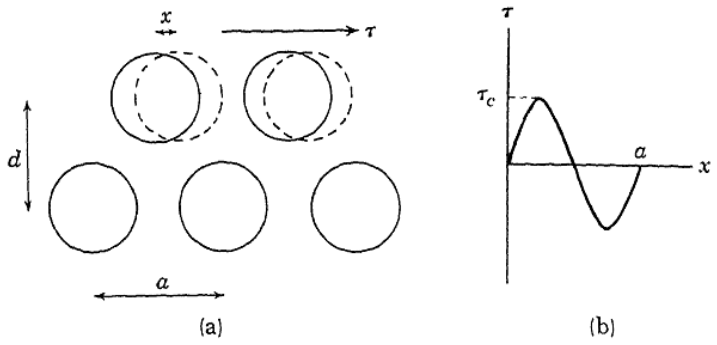


Fig. 3-14. Under influence of the shear stress τ the upper plane of atoms in (a) is displaced over a distance x (dashed circles). The periodic behaviour of τ, according to Frenkel, is indicated in (b).

τ_c is evidently the critical shear stress in this model. We can apply the usual theory of elasticity for $x \ll a$, then $\tau(x) \simeq \tau_c(2\pi x/a)$ (44)

On the other hand, for small elastic strain, applying Hooke's law, $\gamma = \tau/G = x/d$, (45)
where G is the shear modulus.

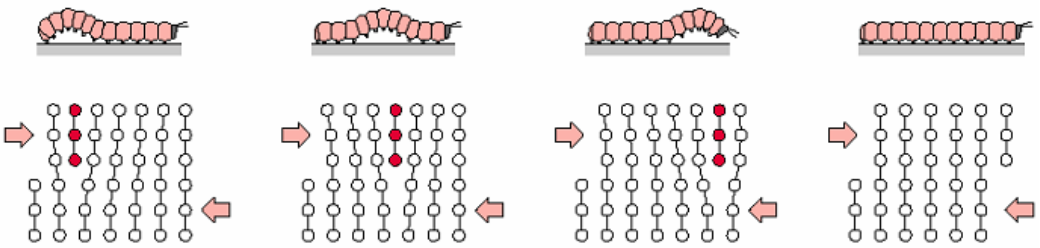
From the last two equations $\tau_c = \tau(a/2\pi x) = \tau(a/2\pi)(G/\tau d) = (G/2\pi)(a/d) \simeq G/2\pi$. where the last approximation is justified because $a \simeq d$. Since $G = 10^{11}$ dynes per cm^2, one obtains in this model a theoretical shear stress $\tau_c = 10^{10}$ dynes per cm^2, which is several orders of magnitude larger than the observed ones.

Objection against Frenkel's Model

Frenkel's model assumes that the atomic planes glide past each other in the manner assumed above. It was assumed that the atoms of the upper atomic plane move simultaneously relative to the lower plane; this assumption is tied up with the assumption of a perfect lattice and here we are at the root of the difficulty.

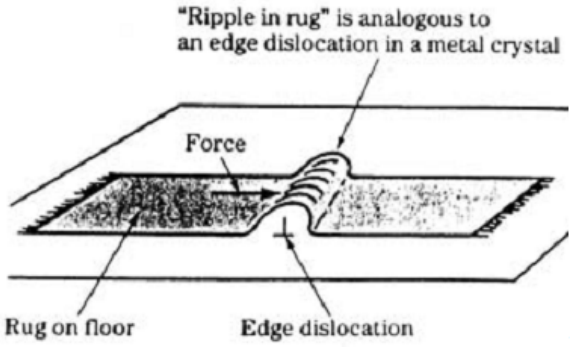
Realisation of Slip motion and dislocation

In an attempt to remove the said difficulty, let us assume that the slip process is governed, not by the simultaneous motion of the atoms of one plane relative to another, but by the consecutive motion of these atoms. Slip motion based on the dislocation model is analogous to movement of a caterpillar (worm). Caterpiller moves forward by displacing its segments one after the other rather than by a simultaneous displacement of all the segments. Understanding the movement of a dislocation is the key in understanding why dislocations allow deformation to occur at much lower stress than in a perfect crystal.



Caterpillar analogy

Carpet analogy



The dislocation model for slip may be introduced with reference to the crystal of Figure a; let the plane PQR be a slip plane. This plane has been redrawn in Figure (b). In the slip plane consider an arbitrary closed curve ABC; the region inside this curve is hatched in Figure (b). Let us suppose that (in some way or other) the material located over the hatched area in the upper half of the crystal is displaced by an amount *b* relative to the lower half of the crystal; at the same time, the material in the upper half lying over the area outside ABC is left undisplaced. In this manner we have obtained a situation in which only a fraction of the upper half of the crystal has slipped relative to the lower half.

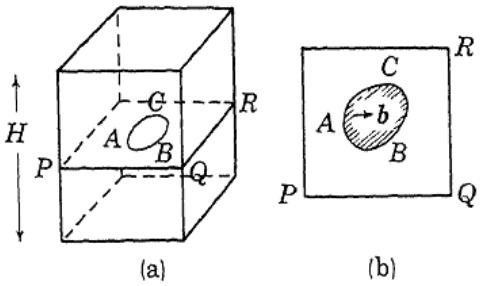


Fig. 3-15. Schematic representation of a ring dislocation *ABC* in a slip plane *PQR*. Slip has occurred only across the hatched area.

The line ABC introduced above marks the boundary in the slip plane between slipped and unslipped material; this line is called a ***dislocation line***. The vector *b* which defines the magnitude and direction of the slip is called the ***Burgers vector***. Since the atoms always seek positions of minimum energy, it will be evident that *b* must connect two atomic equilibrium positions, i.e., the possible vectors *b* are determined by the crystal structure. In a bcc crystal, $b=\frac{a}{2}[111]\Rightarrow b^2=a^2\left[\frac{1}{4}+\frac{1}{4}+\frac{1}{4}\right]\Rightarrow b=a\sqrt{3}/2$. In case of fcc, $b=\frac{a}{2}[110]\Rightarrow b=a/\sqrt{2}$.

The ratio *f* of the area ABC and the total area of the slip plane will be referred to as the fraction of slip that has occurred in this plane. Thus, if in some way or other the area ABC could be made to grow, *f* would increase and for $f = 1$ the whole upper half of the crystal would be displaced by an amount *b* relative to the lower half. For $f < 1$, the average displacement of the upper half relative to the lower half is *fb*.

Depending on the magnitude of the Berger vector *b*, dislocation can be classified as:

i) ***Perfect Dislocation***: The Berger vector (*b*) is equal to an exact inter-atomic distance in case of ***perfect dislocation***. If *b* is a non-integral multiple of the inter-atomic distance, then it is known as ***imperfect dislocation***. If *b* is smaller than the inter-atomic distance, we call it ***partial dislocation***.

ii) ***Super Dislocation***: If the magnitude of b associated with dislocation is several times the inter-atomic distance, the dislocation is called ***super dislocation***.

Density of dislocations

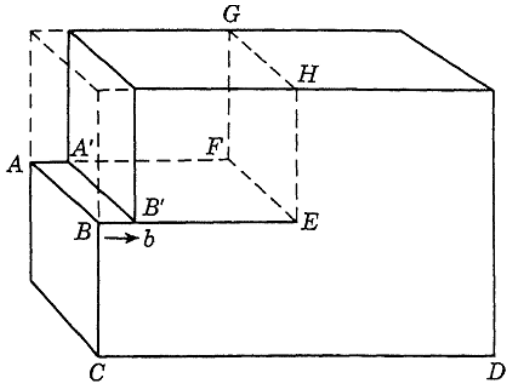
We see, a single dislocation line sweeping across a slip plane gives rise to a displacement of the order of a few Angstroms. Thus any appreciable plastic deformation must be the result of a large number of dislocations sweeping across many slip planes. The rate of plastic is expected to be proportional to the total length of all active dislocation lines and the average velocity with which the elements of these lines move. So the concept of "dislocation density", is introduced as $\rho = S/V$, where *S* is the total length of the dislocation lines and *V* is the volume of the crystal. Let us consider a line element *dS* of a dislocation line such as ABC in Figure 3-15. Let *v* be the velocity of the element along the direction of the normal to *dS* in the slip plane. When *H* is the height of the crystal and *A* is the area of the slip plane, the increase in strain per second due to the motion of the element *dS* is equal to $d\gamma/dt = v\,dS\,b/AH$, γ being the strain.

Considering the rate of flow resulting from all dislocations in planes parallel to the plane PQR in Figure 3-15, we have to sum the above expression in a suitable fashion, i.e., we must replace *dS* by the total length *S* of all these dislocations and *v* by some average velocity $\langle v \rangle$. Hence, $d\gamma/dt = \langle v \rangle S\,b/AH = \rho b \langle v \rangle$, where ρ is the dislocation density.

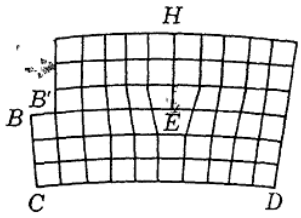
Edge and Screw Dislocations

The dislocation is called a line defect because the locus of defective points produced in the lattice by the dislocation lie along a line. A pure ***edge or Taylor-Orowan dislocation*** is defined as a dislocation for which the Burgers vector *b* is everywhere perpendicular to the dislocation line. A ***screw or Burgers dislocation*** is defined as a dislocation for which the Burgers vector *b* is everywhere parallel to the dislocation line. Thus in Fig. 3-l5b the vertical elements are of the edge type, the horizontal elements are of the screw type; the remainder is mixed edge and screw.

Edge dislocations: The simplest edge dislocation is one for which the dislocation line is straight. Suppose the block of material is cut across the area ABEF so that across this area the upper and lower parts are disconnected.



(a)

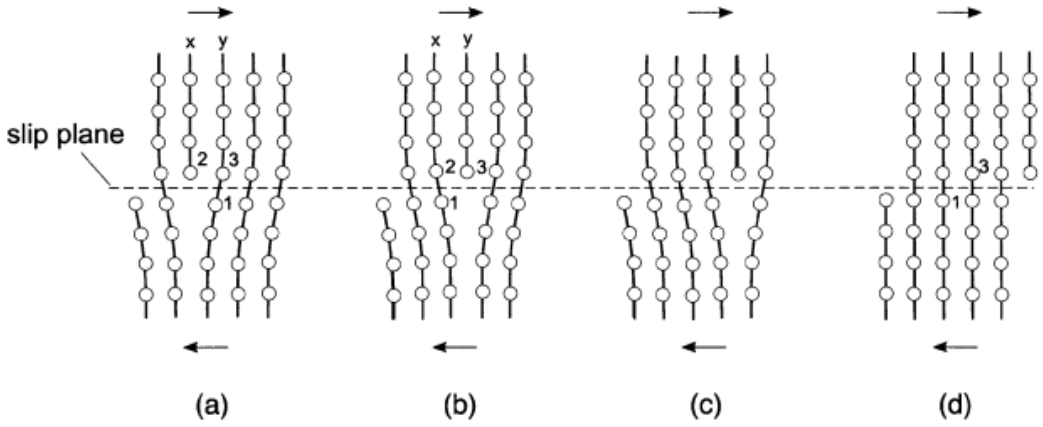


(b)

The upper half is then pushed sideways such that the line A' B' which initially coincided with AB is shifted by an amount *b* as indicated. If in this position the two halves were glued together, we would have produced an edge dislocation. The upper half of the block will clearly be under compression, the lower half under tension. A square network of lines drawn on the front face BCD before and after the operation would look as indicated in Figure b. This strain pattern suggests the existence of an extra half plane (EF) in case of the edge dislocation. Note that if the extra half plane HE were displaced to the right, slip would progress, and when HE has finally reached the right-hand side of the block, the upper half of the block has completed slip by an amount *b*. So the edge dislocation moves parallel to the direction of stress. Edge dislocations for which the extra half plane lies above the slip plane are called positive. If the extra half plane lies below the slip plane, one speaks of a negative edge dislocation.

The presence of an extra half plane of atoms in an edge dislocation restricts the motion of an edge dislocation mainly to the slip plane. The reason is that any motion perpendicular to the slip plane requires either a growth or a reduction of the half plane. Thus the easy direction of motion of an edge dislocation is in the slip plane since the number of atoms in the extra half plane is conserved in this case. Any motion of an edge dislocation perpendicular to the slip plane is termed nonconservative because it involves either rejecting or accepting "extra" atoms.

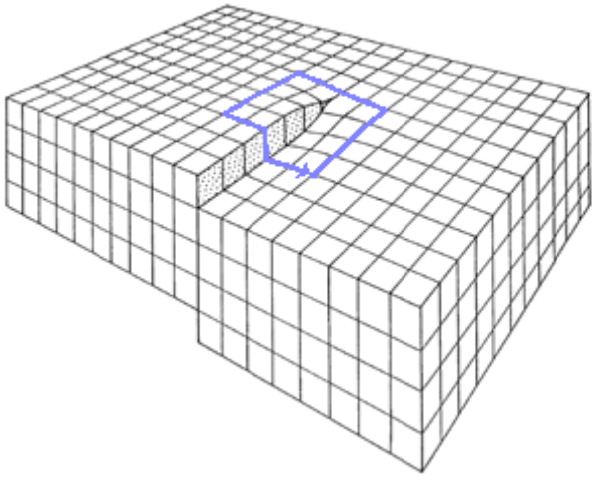
For better perception:

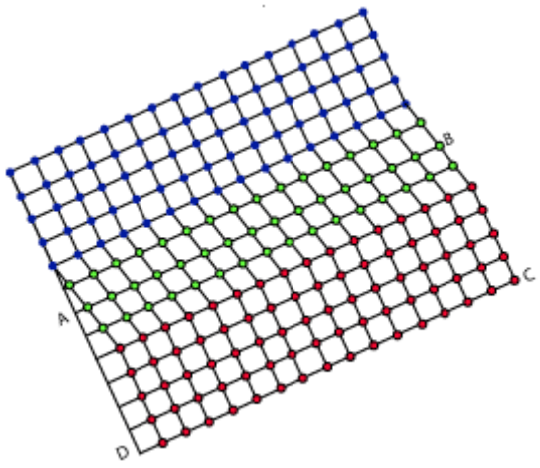


As shown in the set of images above, the dislocation moves similarly moves a small amount at a time. The dislocation in the top half of the crystal is slipping one plane at a time as it moves to the right from its position in image (a) to its position image (d) finally. In the process of slipping one 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.

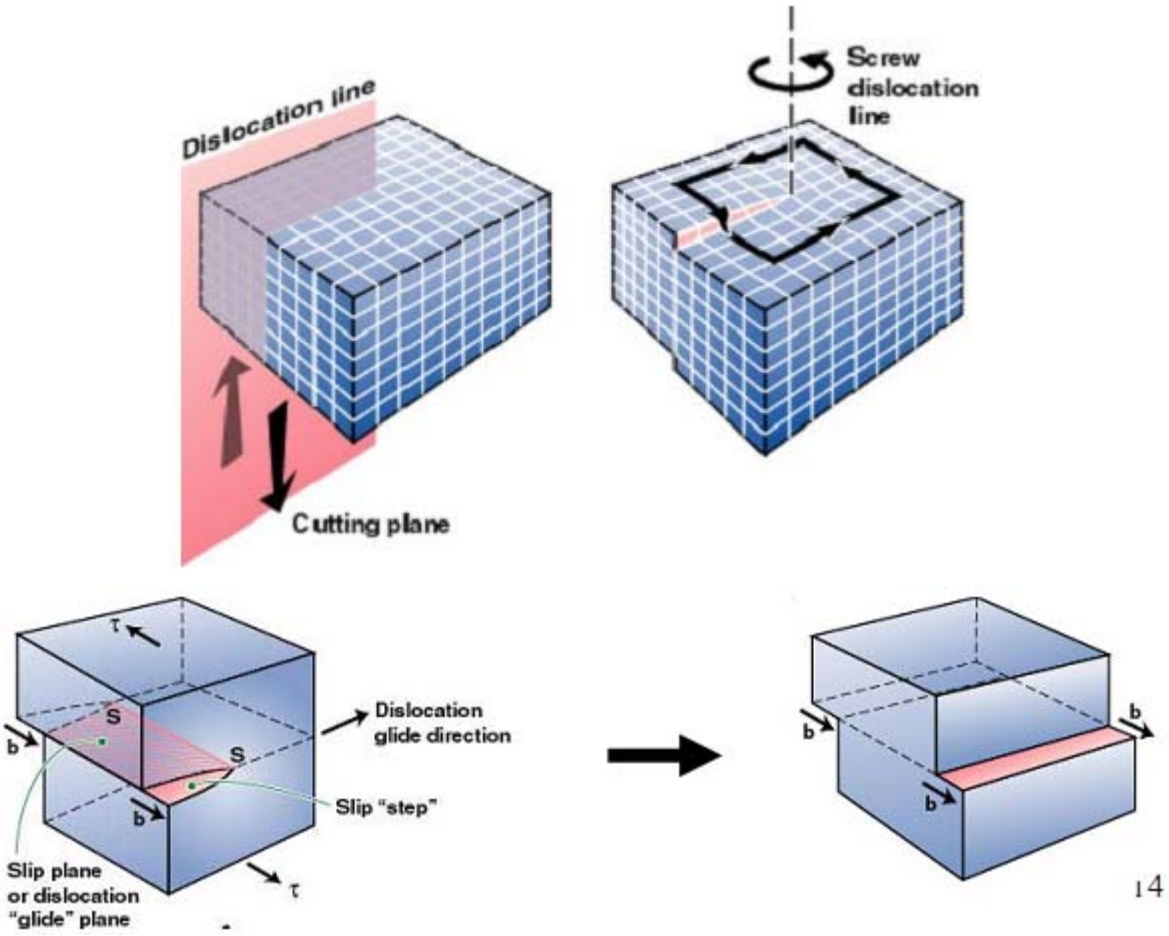
Screw dislocation: A ***screw or Burgers dislocation*** is defined as a dislocation for which the Burgers vector *b* is everywhere parallel to the dislocation line. The motion of a screw dislocation is also a result of shear stress. To visualize a screw dislocation, let us imagine a block of metal with a shear stress applied across one end so that the metal begins to rip (left figure). The screw dislocation will move upward (right figure), which is perpendicular to direction of the stress. Since no extra half plane is involved in a screw dislocation, one cannot speak in this case of nonconservative motion. Thus the motion of a screw dislocation is less restricted than that for an edge.

The right figure 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 reestablished 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. If the shear force is increased, the atoms will continue to slip to the right. A row of the green atoms will find their 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).

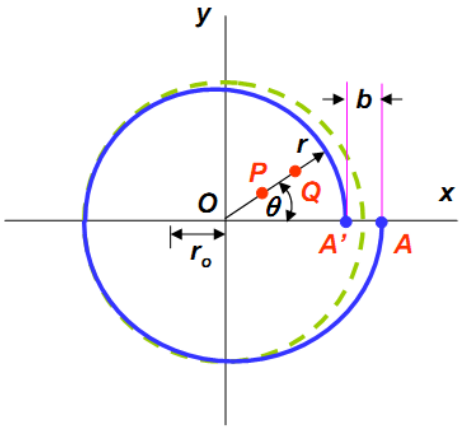




Additional figures for perception:



Strain energies of dislocations

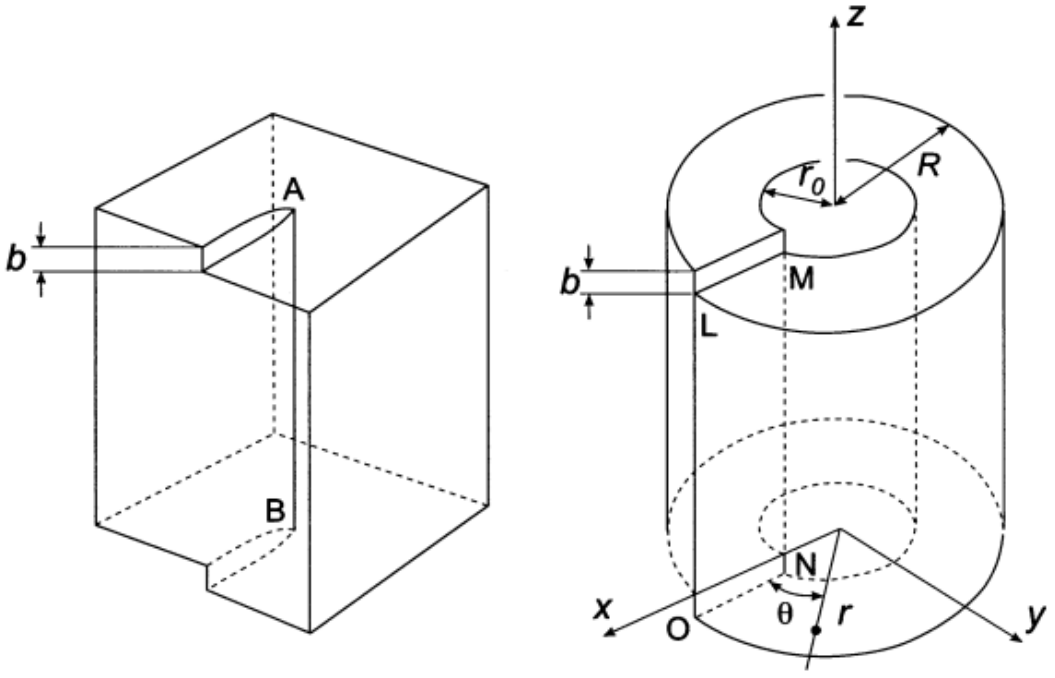


The ***strain energy*** involved in the formation of an ***edge dislocation*** can be estimated from the work involved in displacement the cut OA a distance *b* along the slip plane.

Let us consider the cross section of a cylindrical piece of material; the axis of the cylinder will be taken as the z-axis of a Cartesian coordinate system. Suppose we produce a cut in the plane y = 0, which extends between the axis and the outer surface as indicated. We now let the material above the cut slip to the left by an amount *b*. We now let the material above the cut slip to the left by an amount b, leading to the configuration indicated by the dotted line. We have then produced a positive edge dislocation along the z-axis with a Burgers vector along the

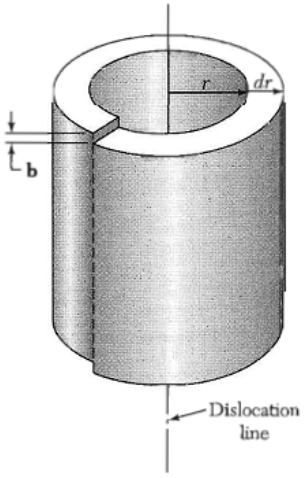
x-axis; the plane y = 0 is the slip plane. Then the strain energy can be calculated as $U = \frac{Gb^2}{4\pi(1-\nu)} \ln \frac{r_1}{r_0}$, G and ν being the shear modulus and Poisson ratio.

Strain energy of a screw dislocation



(a) (b)

The elastic distortion around an infinite-long, straight dislocation can be represented in terms of a cylinder of elastic material. Let us consider the screw dislocation AB shown in Fig. (a). A radial shift LMNO was cut in the cylinder parallel to the z-axis and the free surfaces displaced rigidly with respect to each other by the distance b, the magnitude of the Burgers vector of the screw dislocation, in the z-direction.



We consider the shell of radius *r* and thickness *dr*. The shell is assumed to be stressed by an amount b in a circumferential length $2\pi r$.

The shear strain = $\frac{b}{2\pi r}$

The shear stress = G X shear strain = G X $\frac{b}{2\pi r}$

Hence, the elastic energy *dE* of the shell of volume *dV* due to presence of dislocation = (1/2) X stress X strain

$= \frac{1}{2} \cdot \frac{Gb}{2\pi r} \cdot \frac{b}{2\pi r} \cdot 2\pi r l dr$, where $dV = 2\pi r l dr$, l being the length of the cylinder.

$\therefore dE = \frac{Gb^2}{4\pi} \cdot \frac{dr}{r} \cdot l$

The elastic energy per unit length of the cylinder, $E = \frac{Gb^2}{4\pi} \int_{r_0}^{r_1} \frac{dr}{r} \Rightarrow E = \frac{Gb^2}{4\pi} \ln\left(\frac{r_1}{r_0}\right)$; r_0 and r_1 are the approximate upper and lower limits for the variable *r*.

Possible values of r_0 ***and*** r_1

Distribution of the dislocation is random. The potential field of a certain dislocation exists up to a certain limit due to the presence of other neighbouring dislocations. Experimental observation shows that the limiting distance in crystal is approximately 10^4a (atomic spacing), which is the measure of the upper limit (r_1). The lower limit (r_0) cannot be zero since elastic energy would be infinite at $r_0 = 0$. It is noted that Hooke's law does not holds good near the dislocation line due to highly stressed region. It is reasonable to consider r_0 equal to Berger vector *b*. For perfect dislocation, $r_0 = b = a$.

So the elastic energy per unit length of the cylinder, $E = \frac{Gb^2}{4\pi} \ln\left(\frac{r_1}{r_0}\right) = \frac{Gb^2}{4\pi} \ln\left(\frac{10^4 a}{a}\right)$

$\therefore E = \frac{Gb^2}{4\pi} \ln\left(10^4\right)$

If we take $\ln\left(\frac{r_1}{r_0}\right) \simeq 4\pi$, the total elastic energy per unit length of the cylinder becomes $E = Gb^2$.

So, elastic energy is found directly proportional to b^2. It becomes minimum for dislocation is obtained in stable equilibrium. Hence we find dislocations in the most densely packed planes.

Planar Defects

Stacking Faults and Twin Boundaries

A disruption of the long-range stacking sequence can produce two other common types of crystal defects: 1) a stacking fault and 2) a twin region. A change in the stacking sequence over a few atomic spacings produces a stacking fault whereas a change over many atomic spacings produces a twin region.

A stacking fault is a one or two layer interruption in the stacking sequence of atom planes. Stacking faults occur in a number of crystal structures, but it is easiest to see how they occur in

close packed structures. It is known that face centered cubic (fcc) structures differ from hexagonal close packed (hcp) structures only in their stacking order. For hcp and fcc structures, the first two layers arrange themselves identically, and are said to have an AB arrangement. If the third layer is placed so that its atoms are directly above those of the first (A) layer, the stacking will be ABA. This is the hcp structure, and it continues ABABABAB. However it is possible for the third layer atoms to arrange themselves so that they are in line with the first layer to produce an ABC arrangement which is that of the fcc structure. So, if the hcp structure is going along as ABABAB and suddenly switches to ABABABCABAB, there is a stacking fault present.

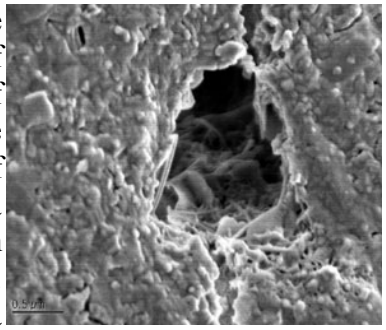
Alternately, in the fcc arrangement the pattern is ABCABCABC. A stacking fault in an fcc structure would appear as one of the C planes missing. In other words the pattern would become ABCABCAB_ABCABC.

If a stacking fault does not corrects itself immediately but continues over some number of atomic spacings, it will produce a second stacking fault that is the twin of the first one. That means the deformed part of the crystal is a mirror image of the undeformed part after twinning. For example if the stacking pattern is ABABABAB but switches to ABCABCABC for a period of time before switching back to ABABABAB, a pair of twin stacking faults is produced. The red region in the stacking sequence that goes ABCABCACBACBABCABC is the twin plane and the twin boundaries are the A planes on each end of the highlighted region.

Grain Boundaries in Polycrystals

Another type of planer defect is the grain boundary. Up to this point, the discussion has focused on defects of single crystals. However, solids generally consist of a number of crystallites or grains. Grains can range in size from nanometers to millimeters across and their orientations are usually rotated with respect to neighboring grains. Where one grain stops and another begins is know as a grain boundary. Grain boundaries limit the lengths and motions of dislocations. Therefore, having smaller grains (more grain boundary surface area) strengthens a material. The size of the grains can be controlled by the cooling rate when the material cast or heat treated. Generally, rapid cooling produces smaller grains whereas slow cooling result in larger grains. For more information, refer to the discussion on solidification.

Bulk Defects



Bulk defects occur on a much bigger scale than the rest of the crystal defects discussed in this section. However, for the sake of completeness and since they do affect the movement of dislocations, a few of the more common bulk defects will be mentioned. Voids are regions where there are a large number of atoms missing from the lattice. The image to the right is a void in a piece of metal The image was acquired using a Scanning Electron Microscope (SEM). Voids can occur for a number of reasons. When voids occur due to air bubbles becoming trapped when a

material solidifies, it is commonly called porosity. When a void occurs due to the shrinkage of a material as it solidifies, it is called cavitation.

Another type of bulk defect occurs when impurity atoms cluster together to form small regions of a different phase. The term 'phase' refers to that region of space occupied by a physically homogeneous material. These regions are often called precipitates.