1. **Vacancies and Interstitials** These are point defects, consisting of the absence of ions (or presence of extra ions). Such defects are entirely responsible for the observed electrical conductivity of ionic crystals, and can profoundly alter their optical properties (and, in particular, their color). Furthermore, their presence is a normal thermal equilibrium phenomenon, so they can be an intrinsic feature of real crystals.

2. **Dislocations** These are line defects which, though probably absent from the ideal crystal in thermal equilibrium, are almost invariably present in any real specimen. Dislocations are essential in explaining the observed strength (or rather, the lack of shear strength) of real crystals, and the observed rates of crystal growth.

LINE DEFECTS: DISLOCATIONS

One of the most spectacular failures of the model of a solid as a perfect crystal is its inability to account for the order of magnitude of the force necessary to deform a

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[15] For a general reference on excitons, see R. S. Knox, *Excitons*, Academic Press, New York, 1963.
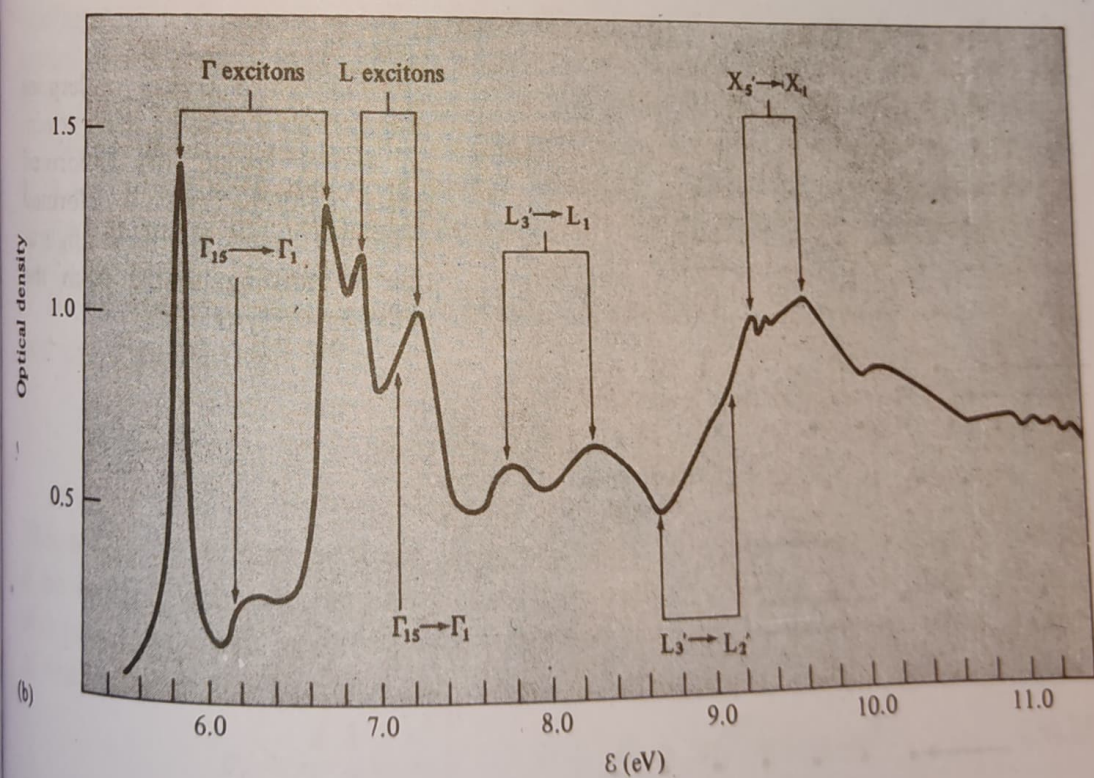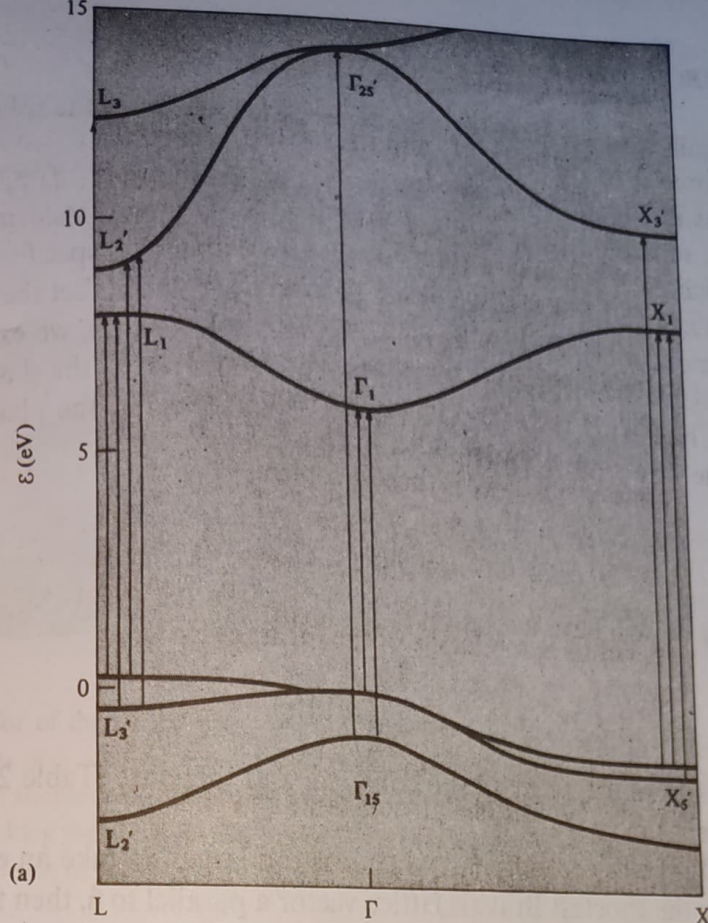
Figure 30.11
(a) The band structure of KI as inferred by J. C. Phillips (*Phys. Rev.* **136**, A1705 (1964)) from its optical absorption spectrum. (b) The exciton spectrum associated with the various valence and conduction band maxima and minima. (After J. E. Eby, K. J. Teegarden, and D. B. Dutton, *Phys. Rev.* **116**, 1099 (1959), as summarized by J. C. Phillips, "Fundamental Optical Spectra of Solids," in *Solid State Physics*, vol. 18, Academic Press, New York, 1966.)

crystal plastically (i.e., permanently and irreversibly). Assuming the solid is a perfect crystal, this force is easily estimated:

Suppose, as in Figure 30.12, that we resolve the crystal into a family of parallel lattice planes, separated by a distance d, and consider a shear deformation of the crystal in which each plane is displaced parallel to itself in a specified direction $\hat{n}$ by an amount x, with respect to the plane immediately below it. Let the extra energy per unit volume associated with the shear be $u(x)$. For small x, we expect u to be quadratic in x ($x = 0$ corresponds to equilibrium) and given by the elasticity theory described in Chapter 22. For example, if the crystal is cubic, the planes are (100) planes, and the direction is [010], then (Problem 4)
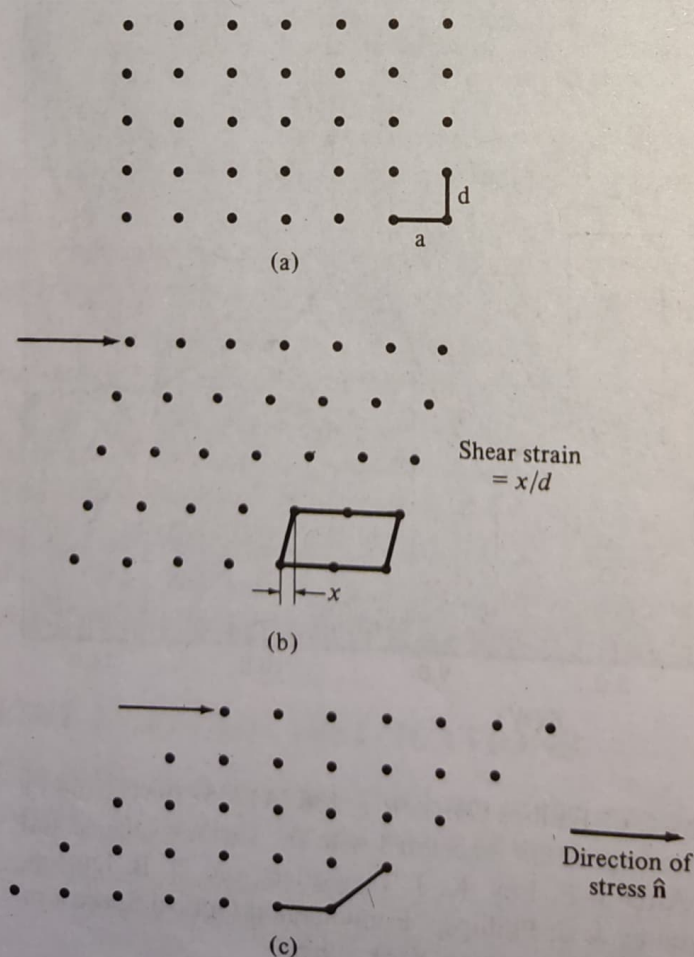
$$u = 2\left(\frac{x}{d}\right)^2 C_{44}.$$ (30.22)

More generally we will have a relation of the form:

$$u = \frac{1}{2}\left(\frac{x}{d}\right)^2 G,$$ (30.23)

where G is the size of a typical elastic constant, and therefore (Table 22.2) of order 10^{11} to 10^{12} dynes/cm^2.

The form (30.23) will certainly fail when x is too large. To take an extreme case, if x is as large as the shortest Bravais lattice vector a parallel to $\hat{n}$, then the displaced

Figure 30.12
An undeformed crystal undergoes progressively increasing shear strain. (a) Perfect crystal. (b) Deformed crystal. In (c) the crystal is deformed so far that the new interior configuration is indistinguishable from the undeformed crystal.
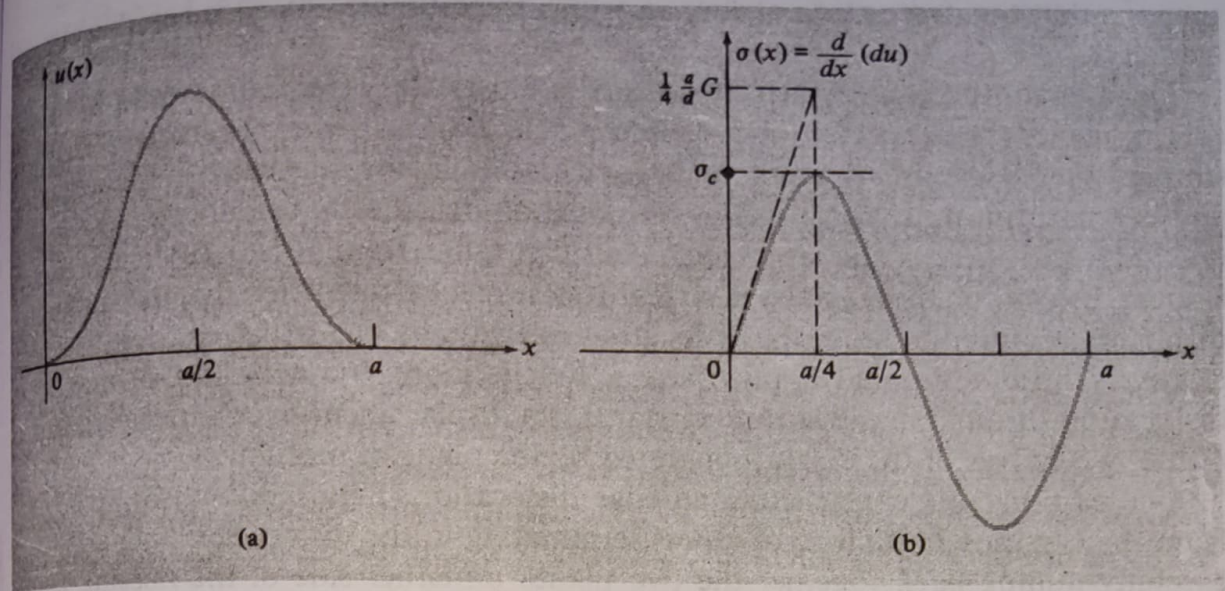
(a) (b)

Figure 30.13
(a) The behavior of the additional energy per unit volume, $u(x)$, due to a shear strain x. Note that $u(x + a) = u(x)$. (b) A plot of the force per unit area per plane necessary to maintain the strain x. In this simple model the order of magnitude of the maximum or critical stress σ_c can be estimated by taking the value of σ at $x = a/4$, or alternatively by extrapolating the linear region of $\sigma(x)$ to this value of x.

configuration (ignoring small surface effects) will be indistinguishable from the undeformed crystal, and $u(a)$ will be 0. Indeed, as a function of x, u will be periodic with period a: $u(x + a) = u(x)$, reducing to the form (30.23) only when $x \ll a$ (Figure 30.13a). As a result, starting from the perfect crystal the force $\sigma(x)$ per unit area of plane (per plane) necessary to maintain the displacement x, known as the shear stress, will not increase indefinitely with x. We estimate its maximum size as follows:

If the crystal is made up of N planes of area A, then the volume is $V = ANd$, and the shear stress is given by

$$\sigma = \frac{1}{NA}\frac{d}{dx}(Vu) = d\left(\frac{du}{dx}\right). \tag{30.24}$$

This will be maximum at some displacement x_0 between 0 and $a/2$ (Figure 30.13b). If we roughly estimate the value at maximum by extrapolating the linear region of $\sigma(x)$ (valid for small x) out to $x = a/4$, then we find that the critical shear stress is of order:

$$\sigma_c \approx \frac{d}{dx}\frac{1}{2}G\frac{x^2}{d}\bigg|_{x=a/4} = \frac{1}{4}\frac{a}{d}G \approx 10^{11} \text{ dynes/cm}^2. \tag{30.25}$$

If a shear greater than σ_c is applied, there is nothing to prevent one plane from sliding over another; i.e., the crystal undergoes slip. It is evident from Figure 30.13b that (30.25) gives only a rough estimate of the critical shear stress. However, the observed critical shear stress in apparently well-prepared "single crystals" can be less than the estimate (30.25) by as much as a factor of 10^4! An error of this magnitude

suggests that the description of slip, on which the estimate (30.25) is based, is simply incorrect.

The actual process by which slip occurs in most cases is far more subtle. A crucial role is played by a special kind of linear defect known as a *dislocation*. The two simplest kinds, *screw dislocations* and *edge dislocations*, are illustrated in Figure 30.14, and described in more detail below. Dislocation densities in actual crystals depend on the preparation of the specimen,[16] but can range from 10^2 to $10^{12}/cm^2$. Along a linear dislocation the crystal is in so high a state of local distortion that the additional distortion required to move the dislocation sideways by one lattice constant requires relatively little additional applied stress. Furthermore, the net effect of moving a dislocation through many lattice constants is a displacement by a lattice constant[17] of the two halves of the crystal separated by the plane of motion.[18]

One can imagine constructing an edge dislocation (Figure 30.14a) by removing from the crystal a half plane of atoms terminating in the dislocation line, and then carefully joining back together the two planes on either side of the missing plane
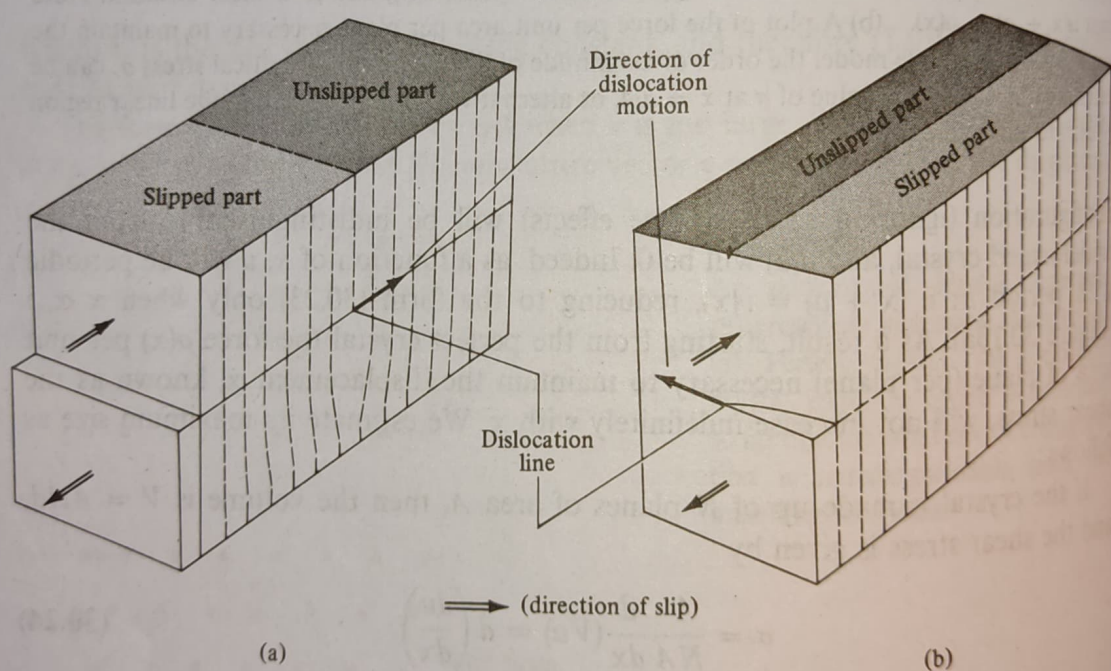
Figure 30.14
(a) Slip in a crystal via the motion of an *edge* dislocation. (b) Slip in a crystal via the motion of a *screw* dislocation.

[16]   As mentioned above linear defects are not a thermodynamic equilibrium phenomenon. There is therefore no intrinsic value to the dislocation density (which can be considerably reduced by annealing).

[17]   There is another kind of slip, mediated by dislocations, in which the slipped portion of the crystal bears a more complex relation to the unslipped part. See the description of "twinning," below.

[18]   The analogy is often made to the passage of a linear ripple across a carpet. The effect is a slight displacement of the carpet, made far more easily than by sliding the entire undeformed carpet the same distance.

in a way that restores the basic order of the perfect crystal everywhere except in the vicinity of the dislocation line.[19]

Similarly, a screw dislocation (Figure 30.14b) can be "constructed" by imagining a plane terminating at the dislocation line, above which the crystal has been displaced by a lattice vector parallel to the line, and then rejoined to the part of the crystal below in a way that preserves the basic crystalline order everywhere except near the line itself.

More generally, dislocations need not be rectilinear. One can describe a general

Figure 30.15
Ambiguities in the "constructive" definition of a dislocation. One plane of a crystal is shown, perpendicular to a single edge dislocation. (The point where the dislocation intersects the plane is most easily perceived by viewing the figure at a low angle along either of the families of parallel lines.) One can describe the dislocation as being produced by the insertion of the extra plane of atoms that intersects the upper half of the figure in the line 6, or, equally well, by the insertion of the extra plane of atoms that intersects the upper half of the figure in the line F. Alternatively, the dislocation can be viewed as produced by the removal of a plane from the lower half of the figure, and that plane can either have been the one that was between 5 and 7 or between E and G. The figure is based on the "bubble raft" photographs of Bragg and Nye. (*Proc. Roy. Soc.*, **A190**, 474 (1947).)

A B C D E F G H I J K   1 2 3 4 5 6 7 8 9 10 11

1 2 3 4 5 7 8 9 10 11   A B C D E G H I J K

---

[19] Only the dislocation line itself has an absolute significance, however. Given an edge dislocation, there are any number of places from which the "removed plane" might have been taken. Indeed, one may also think of the dislocation as having been constructed by the insertion of an extra plane (Figure 30.15). The same is true of screw dislocations.

dislocation as any linear region in the crystal (either a closed curve or a curve that terminates on the surface) with the following properties:

1. Away from the region the crystal is locally only negligibly different from the perfect crystal.
2. In the neighborhood of the region the atomic positions are substantially different from the original crystalline sites.
3. There exists a nonvanishing *Burgers vector*.

The Burgers vector is defined as follows: Consider a closed curve in the perfect crystal passing through a succession of lattice sites, which therefore can be traversed by a series of displacements by Bravais lattice vectors (Figure 30.16, lower curve). Now traverse the same sequence of Bravais lattice displacements in the putatively dislocated crystal (upper curve in Figure 30.16). The test path should be far enough away from the dislocation that the configuration of the crystal in its neighborhood hardly differs from the undistorted crystal, giving an unambiguous meaning to the phrase "same sequence of Bravais lattice displacements." If the series of displacements now fails to bring one back to one's starting point, then the curve has surrounded a dislocation. The Bravais lattice vector **b** by which the endpoint fails to coincide with the starting point is called the Burgers vector of the dislocation.[20]
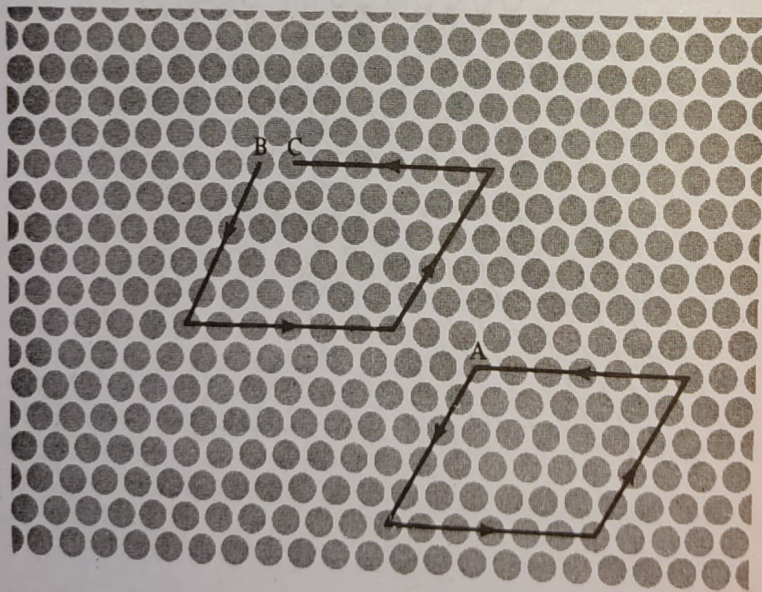
Figure 30.16

Two paths in a lattice plane. The lower path is in a dislocation free region. If one starts at A and moves five steps down, six to the right, five up, and six to the left, one returns to A. The upper path surrounds a dislocation. (The dislocation line is perpendicular to the lattice plane.) If one starts at B and moves through the same sequence of steps (five down, six to the right, five up, and six to the left) one does not return to the starting point B, but to C. The vector from B to C is the Burgers vector **b**. (The dislocation that the second path surrounds is seen most readily by viewing the page at a very low angle.)

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[20]   If **b** = 0, the linear defect is not a dislocation (unless it happens that the path has surrounded two dislocations with Burgers vectors of equal magnitudes and opposite directions). A linear array of vacancies, for example, satisfies criteria 1 and 2, but is not a dislocation. (If an ion in the interior of the lower curve in Figure 30.16 is withdrawn, the path still closes.)

Some thought should convince one that the Burgers vector of a given dislocation does not depend on the path around the dislocation chosen for the test. The Burgers vector is perpendicular to an edge dislocation, and parallel to a screw dislocation. Dislocations more complex than edge or screw dislocations can still be described by a single path-independent Burgers vector, though the relation between the direction of the Burgers vector and the geometry of the dislocated region will not be as simple as it is for edge and screw dislocations.[21]

CRYSTALLINE STRENGTH

The weakness of good crystals was a mystery for many years, in part, no doubt, because the observed data easily led one to the wrong conclusion. Relatively poorly prepared crystals were found to have yield strengths close to the high value we first estimated for the perfect crystal. However, as the crystals were improved (for example, by annealing) the yield strengths were found to drop drastically, falling by several orders of magnitude in very well prepared crystals. It was natural to assume that the yield strength was approaching that of a perfect crystal as specimens were improved, but, in fact, quite the opposite was happening.

Three people independently came up with the explanation in 1934,[22] inventing[23] the dislocation to account for the data. They suggested that almost all real crystals contain dislocations, and that plastic slip occurs through their motion as described above. There are then two ways of making a strong crystal. One is to make an essentially perfect crystal, free of all dislocations. This is extremely difficult to achieve.[24] Another way is to arrange to impede the flow of dislocations, for although dislocations move with relative ease in a perfect crystal, if they encounter interstitials, impurities, or even other dislocations crossing their paths, the work required to move them can increase considerably.

Thus the poorly prepared crystal is hard because it is infested with dislocations and defects, and these interfere so seriously with each other's motion that slip can occur only by the more drastic means described earlier. However, as the crystal is purified and improved, dislocations largely move out of the crystal, vacancies and interstitials are reduced to their (low) thermal equilibrium concentrations, and the unimpeded motion of those dislocations that remain makes it possible for the crystal to deform with ease. At this point the crystal is very soft. If one could continue the process of refinement to the point where all dislocations were removed, the crystal

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[21] If one imagines making a closed dislocation with scalpel and glue, cutting a surface bounding a circuit in the crystal, displacing the surfaces on either side of the cut, and then regluing them together after removing or adding any atoms that are now required to restore perfect order, then the Burgers vector is the amount by which the surfaces have been displaced. The topological definition (which is equivalent) is perhaps more intuitive since it does not require contemplation of these abstruse operations.

[22] G. I. Taylor, E. Orowan, and G. Polyani. (G. I. Taylor, *Proc. Roy. Soc.* A145, 362 (1934); E. Orowan, *Z. Phys.* 89, 614 (1934); G. Polyani, *Z. Phys.* 98, 660 (1934).) Dislocations were introduced into the continuum theory of elasticity, some 30 years earlier, by V. Volterra.

[23] Dislocations were not directly observed for almost another 10 years.

[24] See, however, the description of "whiskers" below.

would again become hard. In certain cases this has actually been observed, as we shall see below.

WORK HARDENING

It is a familiar fact that a bar of soft metal, after repeated bendings back and forth, eventually refuses to be bent, and breaks. This is an example of work hardening. With every bending, more and more dislocations flow into the metal, until there are so many that they impede each other's flow. Then the crystal is incapable of further plastic deformation, and breaks under subsequent stress.

DISLOCATIONS AND CRYSTAL GROWTH

The problem of plastic (i.e., irreversible) flow was unraveled by attributing it to the motion of dislocations. An equally perplexing problem was that of crystal growth, which was solved by invoking the existence of screw dislocations. Suppose we grow a large crystal by exposing a small piece of crystal to a vapor of the same atoms. Atoms from the vapor will condense into lattice positions more readily if neighbors surrounding the site are already in place. Thus an atom is relatively weakly attracted to a perfect crystal plane, more strongly attracted to a step between two planes, and most strongly attracted to a corner (Figure 30.17). If one assumes that grown crystals are perfect, and that growth takes place plane by plane, then whenever a new plane is required, atoms must condense onto the plane below as in Figure 30.17a. Because of the relatively weak binding in this case, such processes (known as "nucleating the next layer") occur far too slowly to account for the observed rate of crystal growth. If, however, the crystal contains a screw dislocation, it is never necessary to nucleate a new plane, for the local planar structure can wind endlessly about the screw dislocation like a spiral ramp (as in Figure 30.17d).

(a)

(b)

(c)

(d)

Figure 30.17
Atoms are relatively weakly attracted to perfect crystal planes (a), are more strongly attracted to a step between two planes (b), and are most strongly attracted to a corner (c). If the crystal contains a screw dislocation, as in (d), then by adding atoms as shown, the local planar structure can spiral endlessly around the dislocation. Crystals can grow much more rapidly in this way, since the nucleation of new planes by the process shown in (a) is never required.
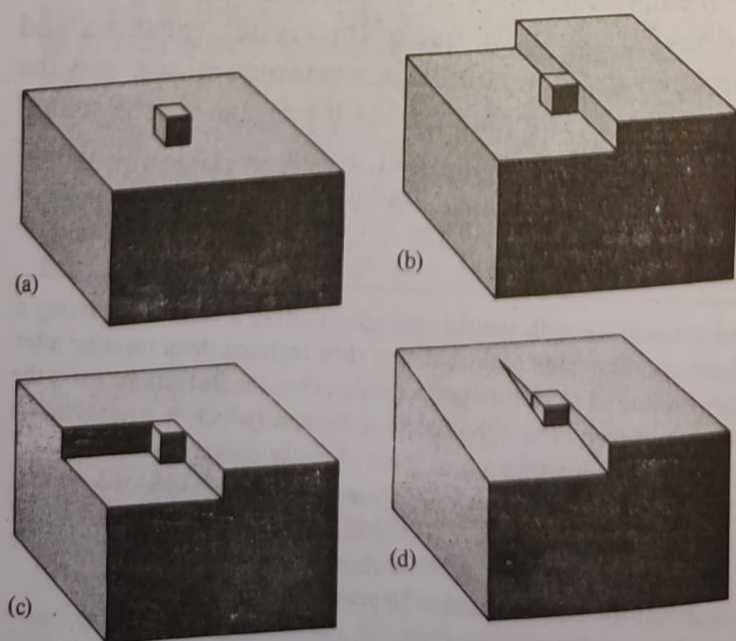
WHISKERS

The type of crystal growth described above can lead to a very long, thin, whisker-shaped crystal winding about and extending a single screw dislocation. Such whiskers may contain only a single dislocation (the nucleating screw dislocation itself) and are observed to have yield strengths comparable to those predicted by the perfect crystal model.

OBSERVATION OF DISLOCATIONS AND OTHER DEFECTS

One of the earliest confirmations that dislocations (and other varieties of defects) can indeed exist in naturally formed crystals was provided by the observations of Bragg and Nye[25] on rafts of identical bubbles floating on the surface of soap solutions. The bubbles are held together by surface tension and a two-dimensional array of them approximate very well a section of crystal. Point defects, dislocations, and grain boundaries were all found to occur in the bubble arrays.

Direct observations in solids have since been made by the technique of transmission electron microscopy. Chemical etching also reveals the intersection of dislocations with solid surfaces. At such points the solid is in a state of considerable strain, and the nearby atoms may be preferentially dislodged by chemical action.

SURFACE IMPERFECTIONS: STACKING FAULTS

There is a more complex kind of slip, mediated by dislocations, in which the applied stress causes the coherent formation of dislocations in successive crystal planes. As each dislocation moves through the crystal it leaves in its wake a lattice plane displaced by a non-Bravais lattice vector, and the result of the passage of the family of dislocations is a region in which the crystalline ordering is the mirror image (in the plane of slip) of the original crystal. Such processes are known as "twinning," and the inverted region is known as a "deformation twin."

For example, in a perfect face-centered cubic, successive (111) planes are arranged in the pattern

$$\ldots ABCABCABCABC \ldots , \qquad (30.26)$$

as in Figure 4.21. After slip giving rise to a deformation twin, the pattern will be

$$\ldots ABCABCABCABCBACBACBACBA \ldots , \qquad (30.27)$$

where the double arrow indicates the boundary of the slipped region. Misplaced planes of atoms such as these are known as "stacking faults." Another example is the arrangement

$$\ldots ABCABCABABCABCABC \ldots , \qquad (30.28)$$

[25] W. L. Bragg and J. F. Nye, *Proc. Roy. Soc.*, **A190**, 474 (1947).

in which a given plane (indicated by the double arrow) is out of step, falling into the hexagonal close-packed sequence rather than that appropriate to face-centered cubic, after which the regular (unmirrored) fcc arrangement is resumed.

LOW-ANGLE GRAIN BOUNDARY

A *grain boundary* is formed by the junction of two single crystals of different orienta-tion along a common planar surface. When the difference in orientations is *small*, the boundary is referred to as a *low-angle* grain boundary. An example known as a *tilt* boundary is shown in Figure 30.18. It is formed from a linear sequence of edge dislocations. There is also a *twist* boundary, which is formed from a sequence of screw dislocations. In general, low-angle grain boundaries are composed of a mixture of both types.
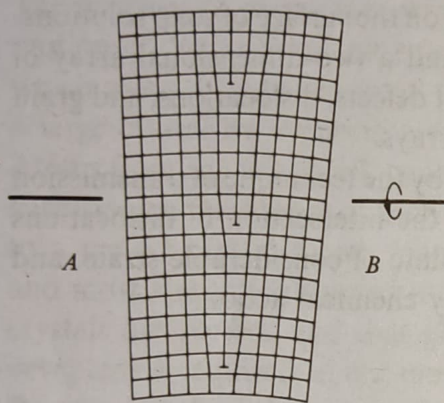

Figure 30.18
A low-angle tilt boundary (a type of low angle grain boundary) can be regarded as formed from a sequence of edge dislocations. If the section B of the crystal is twisted relative to A about the axis shown by a small amount, we may generate (in addition) a twist component in the boundary. A twist boundary, if of small angle, may be viewed as composed of a sequence of screw dislocations.

Unless very carefully prepared, most real crystals consist of many slightly mis-aligned grains, separated by low-angle grain boundaries. The misalignment is little enough for X-ray diffraction to reveal sharp Bragg peaks, but the existence of the grains has an important effect on the intensity of the peaks.

PROBLEMS

1.   Phonon Correction to the Density of Vacancies

A more accurate treatment of the equilibrium number of vacancies in a monatomic Bravais lattice would multiply (30.11) by a phonon correction (see (30.9)):

$$n = Ne^{-\beta\varepsilon_0}e^{-\beta(\partial F^{ph}/\partial n)}. \tag{30.29}$$

Make a simple Einstein theory of the normal modes of the crystal with vacancies, i.e., treat each ion as an independent oscillator, but let the oscillator frequency be either ω_E or $\bar{\omega}_E$, according to whether the ion has or does not have one of its (z) nearest neighboring sites vacant. Show that in this model (30.29) becomes:

$$n = Ne^{-\beta\varepsilon_0}\left[\frac{1 - e^{-\beta\hbar\omega_E}}{1 - e^{-\beta\hbar\bar{\omega}_E}}\right]^{3z} \tag{30.30}$$