

Chapter 2

Mechanisms of Crystal Growth from Fluxed Solutions

It was stated in the previous chapter that flux growth can produce high-quality crystals. Although this is an encouraging statement, it probably demands further explanation: What exactly is meant by high-quality crystals, and under what conditions do high-quality crystals grow? These are the questions that can be answered with some understanding of the crystal growth mechanisms, the topic of this chapter.

Although there are various references on the theories of crystal growth, most are written in such a way as to make very heavy going of the subject. This chapter, by contrast, attempts to make the subject approachable for anyone who wishes to obtain basic ideas for growing high-quality crystals. For further details, the following books are especially recommended: *Crystals: Growth, Morphology and Perfection* by Sunagawa [1] and *Crystal Growth from High-Temperature Solutions* by Elwell and Scheel [2]. The figures used in these books were helpful in preparing some of the illustrations presented in this chapter.

2.1 Crystal Morphology

By definition, atoms in a crystal are arranged in an orderly, repetitive array. This internal regularity often shows itself on the outside of the crystal, as flat faces meeting at sharp edges and pointed corners. However, the appearance of a crystal is also affected by the manner in which it was grown—some crystals grow into perfect polyhedra, while others have irregular shapes. For this reason, crystal morphology (crystal shape) is closely related to the study of crystal growth, and this is why we should take a look at this topic before proceeding directly to the growth mechanisms. Crystal morphology is also important for solid-state research, because the shape often limits the usefulness of the crystal as a sample specimen.

Many compounds of interest to solid-state physicists have complex atomic arrangements of crystal structures. However, it is not often necessary to think about every atom in the crystal structure—what we can do instead is to replace the repeating unit by a single point. Therefore, the point may correspond to a single atom in simple structures, or to a group of many atoms in complicated structures. The resulting three-dimensional array made up of these points is called a lattice, from which we can choose a unit cell defined by three axes a , b , and c and three angles α , β , and γ . On the basis of these six parameters, seven crystal systems can be identified: cubic, tetragonal, orthorhombic, hexagonal, rhombohedral, monoclinic, and triclinic. There are 14 different ways of arranging points in space, giving rise to the 14 Bravais lattices (Fig. 2.1). Furthermore, there are 32 independent ways of arranging objects about a point, which make up the 32 point groups, and 230 possible arrangements of objects in space, which are called the 230 space groups.

The 7 crystal systems, 14 Bravais lattices, 32 point groups, and 230 space groups can be used to describe the internal symmetry of crystals. The concepts of symmetry are also useful in understanding the crystal shapes, especially when the shapes are described using the language of crystal form. A crystal form, as defined in crystallography, is a set of identical faces that are related by symmetry. This sounds very abstract, so let us look at real examples.

In the top row of Fig. 2.2, three crystals of different shapes are shown. The left crystal is perovskite $\text{La}_{1-x}\text{Pr}_x\text{AlO}_3$, which has the shape of a cube with six identical square faces. This description of a cube satisfies the definition of a crystal form; therefore, the cube is one type of crystal form. Each face of the cube has a form symbol of $\{100\}$, because it is perpendicular to one of the three cubic crystallographical axes and does not intersect with the other two axes. The middle crystal is spinel MgAl_2O_4 , which has the shape of an octahedron. The octahedron is composed of eight triangular faces, so it is also a type of crystal form. In this case, the faces have a form symbol of $\{111\}$, as each face intersects with three cubic axes at the same distance from their origin at the center of the octahedron. Finally, the crystal on the right side is garnet $\text{Y}_{3-x}\text{Ce}_x\text{Al}_5\text{O}_{12}$, which appears to have twelve rhombic faces to form a dodecahedron. The dodecahedron is yet another example of crystal form, with the rhombic face having the form symbol of $\{110\}$. The cube, octahedron, and dodecahedron are thus three examples of crystal form, each belonging to the cubic system. (In other crystal systems, a crystal form often does not make a complete body on its own. For example, the four side faces of a tetragonal body, called a tetragonal prism, require another form on the top and bottom to make a closed body. Such a form is called an open form, as opposed to the closed forms of the cubic examples. The topic of crystal forms is fully described in mineralogy textbooks.)

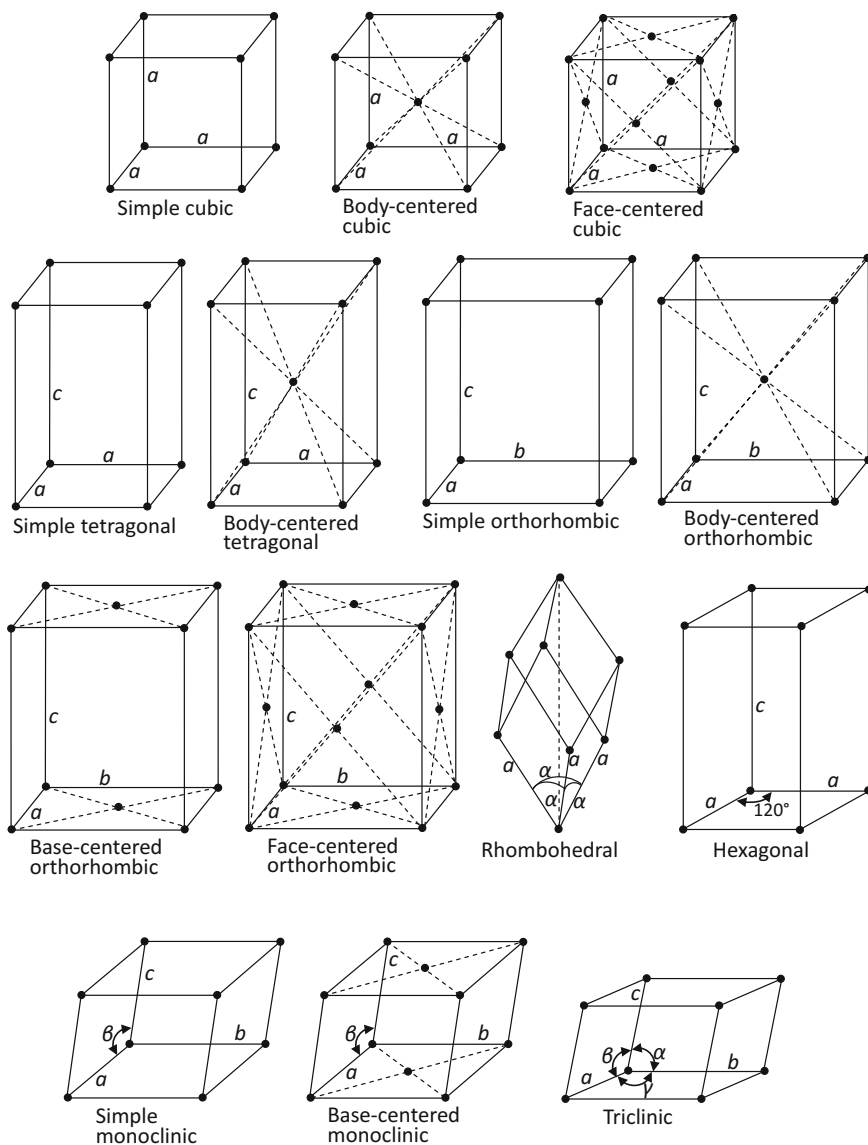


Fig. 2.1 Unit cells of the 14 Bravais lattices, shown with the constraints on the length of edges and angles between edges

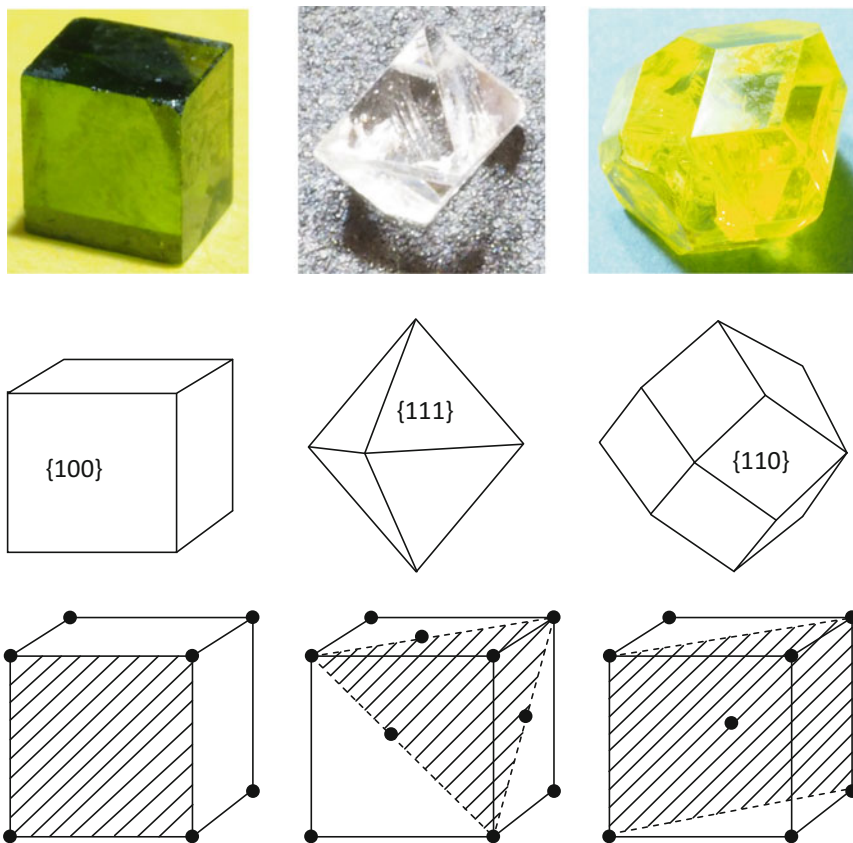


Fig. 2.2 Top: Single crystals of perovskite $\text{La}_{1-x}\text{Pr}_x\text{AlO}_3$ (left), spinel MgAl_2O_4 (middle), and garnet $\text{Y}_{3-x}\text{Ce}_x\text{Al}_5\text{O}_{12}$ (right). Center: Cube, octahedron, and dodecahedron crystal forms. Bottom: Simple cubic, face-centered cubic, and body-centered cubic lattices

In addition to the particular crystals shown in Fig. 2.2, other crystals of perovskites often have the form of a cube, those of spinels have the octahedron form, and those of garnets have the dodecahedron form. Perovskites, spinels, and garnets each refer to a group of compounds with the same basically cubic crystal structure as the mineral of the same name.¹

What, then, determines the form of these crystals? A hint comes from the fact that while these compounds all belong to the cubic system, they have different Bravais lattices: the perovskite structure has a simple (primitive) cubic lattice, the spinel structure has a face-centered cubic lattice, and the garnet structure has a

¹The word “basically” is added because many perovskite compounds, including $\text{La}_{1-x}\text{Pr}_x\text{AlO}_3$, undergo a subtle transition from the cubic perovskite structure on cooling. However, this has no effect on the crystal form.

body-centered cubic lattice. These lattices can be found in Fig. 2.1, and are reproduced at the bottom of Fig. 2.2. Here, we remind ourselves that we are not looking at the actual atomic arrangements, which are much more complex (for example, the unit cell of garnets contains 160 atoms).

According to the Bravais principle, crystal faces are most likely to come from the most densely populated lattice planes. As shown in the bottom images of Fig. 2.2, the simple cubic lattice has a lattice point at each of the eight corners; accordingly, the $\{100\}$ plane has the highest density of lattice points, and this agrees with the cube form of the $\text{La}_{1-x}\text{Pr}_x\text{AlO}_3$ crystal. We can see from Fig. 2.2 that similar arguments apply to the octahedron coming from the face-centered cubic lattice, as well as the dodecahedron from the body-centered cubic lattice. It makes sense that densely populated lattice planes become the crystal faces, as these planes should be thermodynamically and mechanically more stable than sparsely populated lattice planes.

Unfortunately, the simple picture presented in terms of only the Bravais lattice is incomplete. For example, garnets often have $\{210\}$ faces, either by themselves or in combination with the $\{110\}$ faces discussed above. The $\{210\}$ faces come from another type of crystal form, called the trapezohedron, which is a regular polyhedron with 24 sets of four-sided faces.² To explain such observations, it is necessary to use the full symmetry considerations of garnet's space group, rather than just those of the Bravais lattice [3]. In other cases, the direction of chemical bonds becomes important, and this is considered in the periodic bond chain (PBC) model [4].

As the case of garnet has shown, faces of more than one form can appear on a crystal. For example, Fig. 2.3a shows various shapes that are made of the cube, octahedron, and dodecahedron, and Fig. 2.3b shows single crystals of $\text{Pb}_2\text{Ru}_2\text{O}_{6.5}$ with a shape that is intermediate between the cube and octahedron. In crystal morphology, the term “habit” is used for the characteristic shape of a crystal, and we say that each object in Fig. 2.3a has a different habit. It is also possible for different habits to arise from a single form, if the faces develop to different sizes during crystal growth (see Fig. 2.4). In each case, the change in habit modifies the shape of crystal faces, but retains the characteristic angles between corresponding faces. The crystal habit can be affected by changes in various growth conditions, such as growth temperature (Fig. 2.5a) [5], flux composition (Fig. 2.5b) [6], impurities or additives present, and supersaturation. The concept of supersaturation will be discussed in the next section.

Surprisingly enough, it is the fast-growing faces that disappear and the slowest growing ones that determine the final crystal habit—see Fig. 2.6a. This idea can also be understood by picturing an object that is growing from many small simple

²Indeed, small $\{210\}$ faces can be seen on the $\text{Y}_{3-x}\text{Ce}_x\text{Al}_5\text{O}_{12}$ crystal of Fig. 2.2, which is why the crystal does not quite have the shape of a perfect dodecahedron.

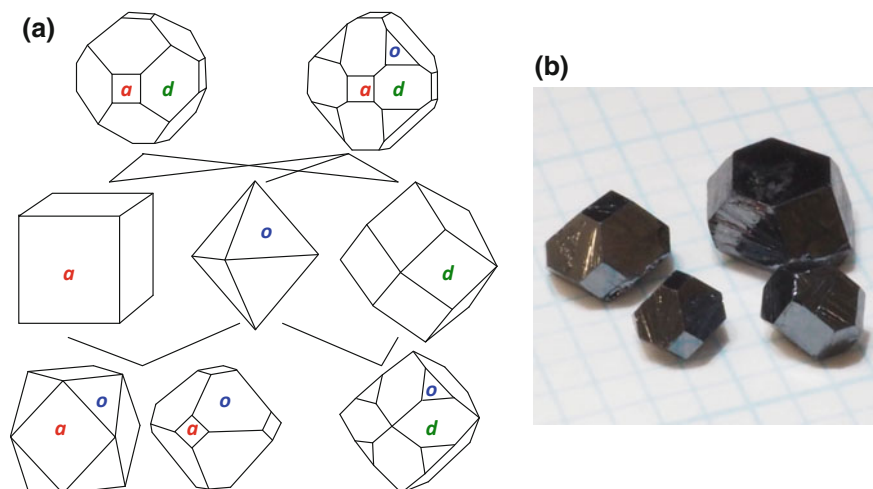


Fig. 2.3 **a** Various habits originating from the cube, octahedron, and dodecahedron crystal forms. The form symbols $a\{100\}$, $o\{111\}$, and $d\{110\}$ are shown, where the letter symbols are frequently used in mineralogical works. **b** Single crystals of $\text{Pb}_2\text{Ru}_2\text{O}_{6.5}$ showing a combination of $\{100\}$ and $\{111\}$ cubic faces

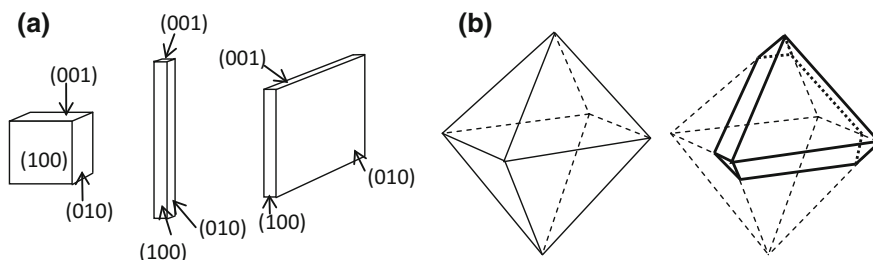


Fig. 2.4 **a** Different habits originating from the cube form. (100), (010), and (001) are the specific faces of the $\{100\}$ form. **b** Tabular crystal originating from the octahedral form

cubes (Fig. 2.6b): At the corner, the diagonal face is always rough, providing many bonding surfaces for the small cubes. Consequently, the growth rate of this rough face is much faster than that of the smooth faces, and soon the entire crystal consists of the six flat faces of a cube.

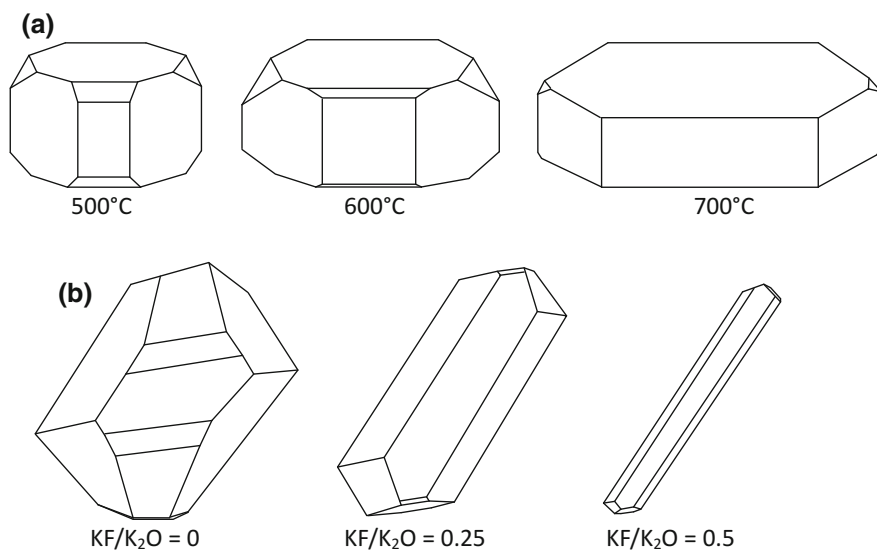


Fig. 2.5 **a** Morphological change of $\text{NdP}_5\text{O}_{14}$ crystals (simple monoclinic structure) owing to a difference in the growth temperature (after [5]). **b** Morphological change of $\text{NdAl}_3(\text{BO}_3)_4$ crystals (base-centered monoclinic structure) owing to a difference in the flux composition (after [6])

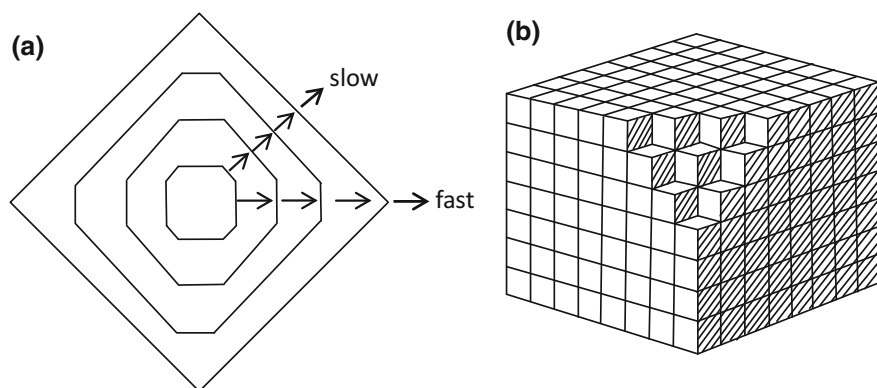


Fig. 2.6 **a** Effect of growth rate on crystal faces. Slow-growing faces survive and rapidly growing faces disappear. **b** A model of a crystal composed of small cubes. The diagonal face is always rough, and incoming growth units of cubes can strongly adhere to this face

2.2 Mechanisms of Flux Crystal Growth

Having looked at the basic ideas of crystal morphology, let us now focus our attention on how crystals grow. In crystal growth from solution, there are three major steps: (1) the attainment of supersaturation, (2) the formation of nuclei of the crystalline phase, and (3) subsequent crystal growth on the nuclei. We look at each of these steps in this section.

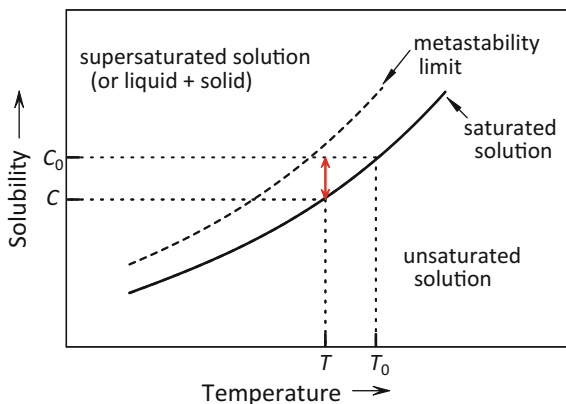
2.2.1 Solubility and Supersaturation

Probably the most important concept in flux growth is supersaturation. Without supersaturation, there is no driving force for crystals to appear in a solution, or to grow larger once they appear in the solution. Being a thermodynamic quantity, supersaturation is related to the decrease in free energy resulting from the growth of crystals. However, there is no need to go into thermodynamics for practical purposes, because supersaturation can be simply defined using a solubility curve.

The solubility curve, as shown in Fig. 2.7, is a plot of the maximum amount of solute that can be dissolved into the solution at each temperature. The region below the solubility curve represents an unsaturated solution; here, the solution can dissolve more solute. On the other hand, the region above the solubility curve indicates a supersaturated solution—the solution contains more than the equilibrium concentration of solute, and it is therefore thermodynamically unstable. It is only at the solubility curve, corresponding to the saturated solution, where a solute crystal in contact with the solution neither dissolves nor grows. The solubility curve in Fig. 2.7 has a positive slope, indicating that more solute can be dissolved at higher temperatures. This is what happens in most solutions.

When a solution is unsaturated, it is thermodynamically stable and no crystal will ever form. However, if the temperature of such a solution is lowered to the

Fig. 2.7 Solubility versus temperature curve



region of supersaturation, there is now more solute in the solution than it can actually handle. Therefore, the excess solute must somehow crystallize out of the solution.

However, crystals do not appear immediately after the solution becomes supersaturated. This is due to the presence of an energy barrier, which we will see in a short while, but here we point out that the solution is now in a metastable region. Such a metastable region is shown in Fig. 2.7 as the area surrounded by the solubility curve and the dashed curve.

We can define supersaturation as follows. If we start with a saturated solution at (T_0, C_0) and lower the temperature to T , the equilibrium concentration of solute decreases to C . This difference in solubility $(C_0 - C)$ is the excess solute in the solution at T , so the supersaturation σ at this temperature can be defined as $\sigma = (C_0 - C)/C$. Evidently, a large σ means that there is a strong driving force for crystallization. It is also evident that the temperature must be lowered during crystal growth to maintain a finite σ , as crystallization removes the excess solute in the solution and lowers the σ . (σ can also be increased by evaporating the flux.)

Although we are looking at supersaturation in the case of crystal growth from solution, it is useful to mention that crystal growth from the vapor occurs when the vapor is supersaturated, and crystal growth from the melt occurs when the melt is supercooled. Supersaturation and supercooling are therefore the driving forces of crystallization in these cases.

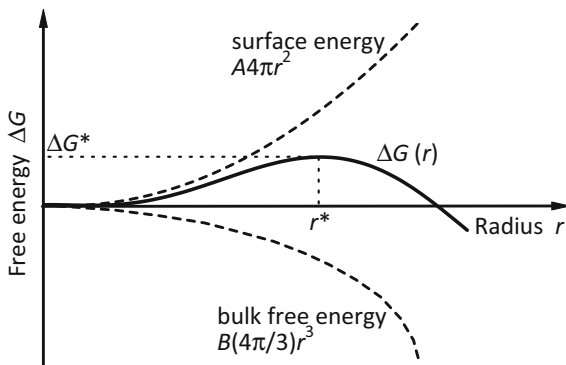
2.2.2 Nucleation

As we have stated earlier, a supersaturated solution is metastable. This means that more stable states can be achieved by forming crystals, which reduces the amount of excess solute dissolved in the solution. However, for crystals to start appearing in the solution, it is first necessary for solute particles to come together and form stable nuclei. This process is called nucleation.

The process of nucleation is similar to the formation of droplets in a supersaturated vapor (see Fig. 2.8). As vapor molecules move about randomly, fluctuations within the supersaturated vapor give rise to small clusters of molecules. The chance that such clusters will grow to form stable droplets depends on their total free energy. On one hand, the bulk free energy of a droplet is always lower than that of vapor under supersaturation. This energy is proportional to the volume of the droplet, or r^3 , where r is the radius of the droplet. On the other hand, a droplet has additional interfacial surface energy, because its outermost molecules are under-bonded and highly strained. This energy is proportional to the surface area of the droplet, or r^2 .

When the radius dependences of both bulk free energy and surface energy are considered, we can find that the total free energy of a droplet goes through a maximum barrier at r^* , which is called the critical radius. This implies that a droplet with a radius smaller than r^* becomes more stable by reducing its size, meaning

Fig. 2.8 Free energy of nucleus as a function of its radius



that it will evaporate and disappear. On the other hand, once a droplet reaches r^* , it is not likely to disappear because it can reduce its free energy by increasing its size. An increase in supersaturation has the effect of reducing of r^* .

A similar situation is found for nucleation in a supersaturated solution. Because solute particles (atoms, ions, or molecules) are in random motion, there is always a chance that some particles will come into contact with each other and form a small cluster. Most of these clusters soon dissipate back into the solution. However, when the supersaturation is high, gathering of more particles is encouraged and some clusters reach r^* , becoming stable nuclei. This process is often referred to as homogeneous nucleation, because no other substances are involved. Various studies have shown that the critical size of the nucleus is of the order of 100 atoms [2].

In real experiments, homogeneous nucleation does not occur frequently. This is because the energy barrier for nucleation is reduced if it occurs on the surface of other substances—on the crucible wall, the surface of the solution, and even some dust particles in the solution. This is called heterogeneous nucleation, and much evidence suggests that this is usually the case in flux growth. (In Fig. 1.6, ruby crystals are grown on the crucible wall.) Furthermore, the energy barrier for nucleation can be completely diminished if a seed crystal of the same material is introduced into the solution. Because crystal growth can start immediately on the seed, it can prevent spurious nucleation from occurring elsewhere in the solution.

In general, nucleation requires much higher supersaturation than the subsequent crystal growth on the nucleus. This is because nucleation is a process of creating initial order from random solute particles, whereas subsequent crystal growth is a process of attaching additional atoms onto an already ordered array. If supersaturation is kept low after the initial nucleation, crystal growth can take place without additional nuclei forming in the solution. This can be done in experiments by slowly cooling the solution. In many cases, the real challenge is to reduce the number of initial nuclei forming in the solution, so that a small number of large crystals, rather than a large number of small crystals, result at the end of crystal growth.

2.2.3 Layer-by-Layer Growth

When a stable nucleus is formed, it is expected to be nearly spherical in shape. It can grow larger through attachment of more solute particles, which reduces the free energy (*see* Fig. 2.8). As this process takes solute particles away from the solution, a thin layer is formed around the growing crystal where the solute is more diluted (less supersaturated) than the bulk of the solution. This concentration difference drives solute particles in the solution to diffuse into the thin layer region and then to attach to the surface of the crystal.

In the past, this simple mechanism was once considered to continue throughout crystal growth. However, it soon became evident that this mechanism will only result in spherical crystals, in contrast to the polyhedral shapes and flat faces found in real crystals. Clearly, there was something missing in the picture. A clue to solving this problem is the presence of various terraced features on crystal faces (Fig. 2.9), which suggests that crystals somehow grow layer upon layer on flat faces.

To explain the flat faces of crystals, the layer-by-layer growth mechanism, on an atomically smooth surface (*see* Fig. 2.10), was introduced in the 1930s [1, 2]. In this mechanism, the solute particles reaching the crystal surface are not immediately incorporated into the crystal, but instead form growth units that are loosely adsorbed on the surface. These units can wander around the surface to find a suitable site for attachment, such as the kinks along the step. Kinks are the preferred site because the growth unit can bond with three or four units of the crystal, compared with just one unit on a flat surface. Some growth units are dissolved back into the solution before reaching a kink. The addition of more units along the kinks and steps causes the layer to spread laterally across the surface.

So far, we have not specified what the solute particles and growth units are made of. They can be atoms, ions, groups of ions, or molecules, depending on the nature of the solute and its interaction with the flux particles. Because a solute particle is bounded by flux particles in the solution, it sheds some of the flux particles upon

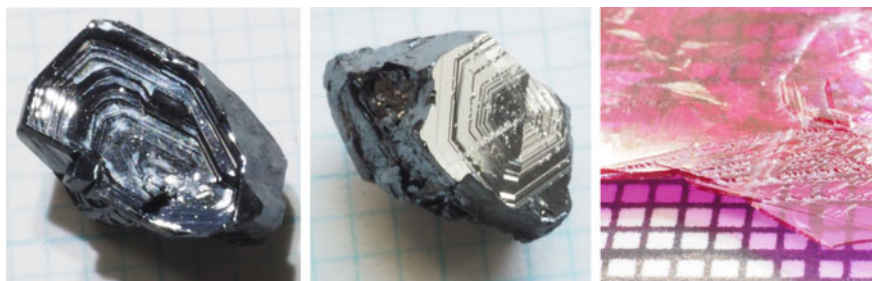
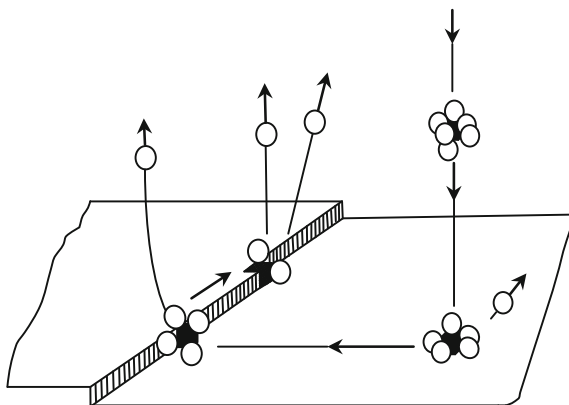


Fig. 2.9 Terraced features on the faces of $\text{Y}_3\text{Fe}_5\text{O}_{12}$ (left), DyMn_2O_5 (middle), and $\text{Al}_{2-x}\text{Cr}_x\text{Cr}_3$ (right) crystals

Fig. 2.10 Schematic of the layer-by-layer growth mechanism due to two-dimensional nucleation. The growth unit is surrounded by flux particles, which are fully desorbed when the growth unit becomes firmly attached at the kinked site along the step. Based on [2]



reaching the crystal surface. This process is called desolvation. As shown in Fig. 2.10, there are additional steps of desolvation until the growth unit is firmly attached to the crystal.

2.2.4 Spiral Growth

The layer-by-layer growth mechanism can explain the flat faces of crystals. However, there is one problem with this mechanism: When the layer is completed, there is no easy place for the new growth unit to attach onto the crystal, and crystal growth cannot continue without starting a new layer. Detailed calculations show that supersaturation of well above 10% must be present for a new layer to nucleate on a completed surface. In reality, however, crystal growth can continue at much lower supersaturation, sometimes well below 1%.

To solve this problem, the spiral growth mechanism was introduced in 1949 [7, 8].³ In this mechanism, a screw dislocation provides a permanent step on the crystal surface. (Screw dislocation, shown in Fig. 2.11a, is a defect that can be visualized by imagining a partial cut into a crystal, followed by a slight twist.) As depicted in Fig. 2.11b, the spiral growth takes place by the rotation of a step around the central point—the layer is never completed. Therefore, this mechanism allows the crystal to grow continuously at low supersaturation, since the nucleation of a new layer is not required.

The theory of spiral growth was soon verified by the observation of spirals on many crystal surfaces; two of the more recent examples are shown in Fig. 2.12 [9, 10]. There are many types of spirals. Both rounded and polygon-shaped spirals are found. The height of the step can be anywhere from one growth unit to hundreds of

³The ideas of layer-by-layer growth and spiral growth were initially introduced for crystal growth from vapors, but they also apply to crystal growth from solutions.

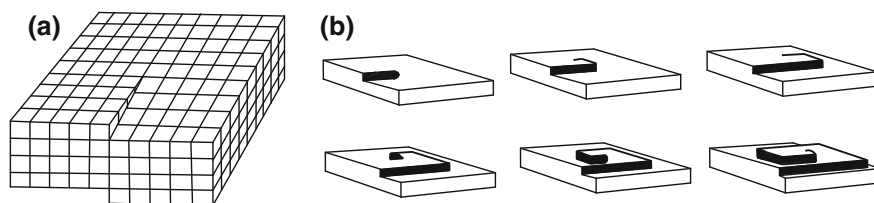


Fig. 2.11 **a** Screw dislocation. **b** Spiral growth around screw dislocation

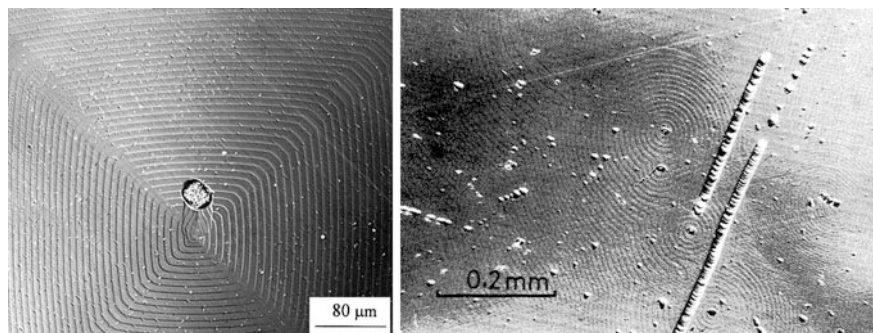


Fig. 2.12 Spiral growth steps on crystal faces of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (left, reprinted with permission from [9]; copyright 2000 Elsevier) and $\text{Sm}_{0.55}\text{Tb}_{0.45}\text{FeO}_3$ (right, reprinted with permission from [10]; copyright 1972 The Japan Society of Applied Physics). Two rows of etch pits, which signal arrays of edge dislocations, can be seen on $\text{Sm}_{0.55}\text{Tb}_{0.45}\text{FeO}_3$

growth units—the latter occurs when the growing layers are bunched together by impurities or other factors. Because each crystal face often contains a number of screw dislocations, several spirals may appear on the same face. It should be emphasized that the spiral growth mechanism does not invalidate the basic idea of the layer-by-layer mechanism, because the process of a layer spreading across the crystal surface is the same. Rather, the spiral growth mechanism provides a source of steps that will not go away.

2.2.5 Hopper Growth and Dendritic Growth

Spiral growth takes place when the supersaturation is not sufficiently high to allow a new layer to nucleate on a flat crystal surface. Conversely, the layer-by-layer mechanism can take place if the supersaturation is sufficiently high to allow surface nucleation, and indeed, this mechanism can achieve higher growth rates than spiral growth under high supersaturation. One point to remember, however, is that because the corners and edges of a crystal overlook a greater volume of solution than the face center, the supersaturation at these regions is higher (this is known as

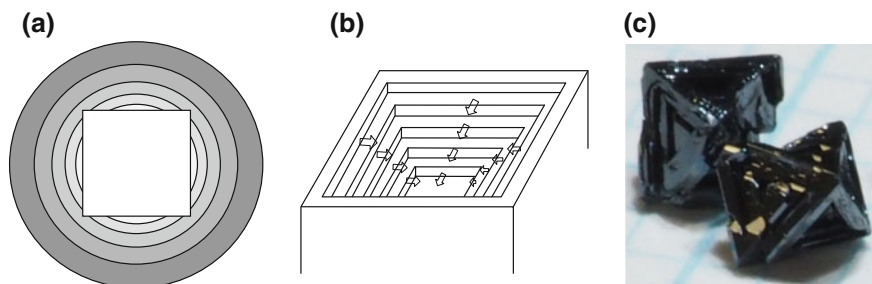


Fig. 2.13 **a** Contours of constant solute concentration (supersaturation) around a growing crystal. The darker/outer region has a higher solute concentration. **b** Hopper morphology on a cube face. **c** Octahedral hopper crystals of $\text{Bi}_2\text{Ru}_2\text{O}_7$

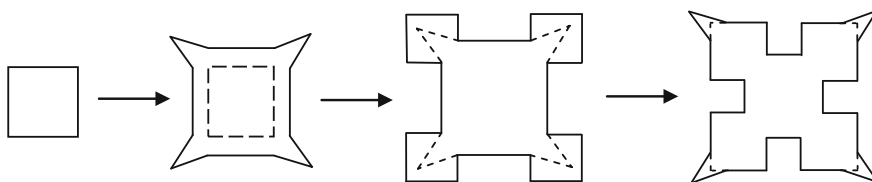


Fig. 2.14 Dendritic growth

the Berg effect; *see* Fig. 2.13a). Therefore, in the layer-by-layer mechanism, a new layer tends to start at the edges and corners of a crystal face, and then spreads toward the center region.

Flat crystal faces are maintained only when layer propagation occurs at a higher rate than layer nucleation. When supersaturation is high, additional layers can be nucleated before the underlying layers are completed. This situation is shown for the square face of a cube in Fig. 2.13b. The resulting crystals are called hopper or skeletal crystals; an example of octahedral hopper crystals is shown in Fig. 2.13c.

If supersaturation is higher still, new layers formed at the edges and corners of a crystal can protrude into the solution, rather than spread across the face (Fig. 2.14). This is called dendritic growth, and the resulting treelike crystals with many branches are called dendrites. Some examples of dendritic crystals are shown in Fig. 2.15.

In flux growth, dendritic growth often occurs at the beginning of crystal growth, when supersaturation is high. As the crystal growth continues and supersaturation drops, the spaces between dendrite arms are filled and flat faces are eventually produced. Spiral growth can then take place on such flat faces.

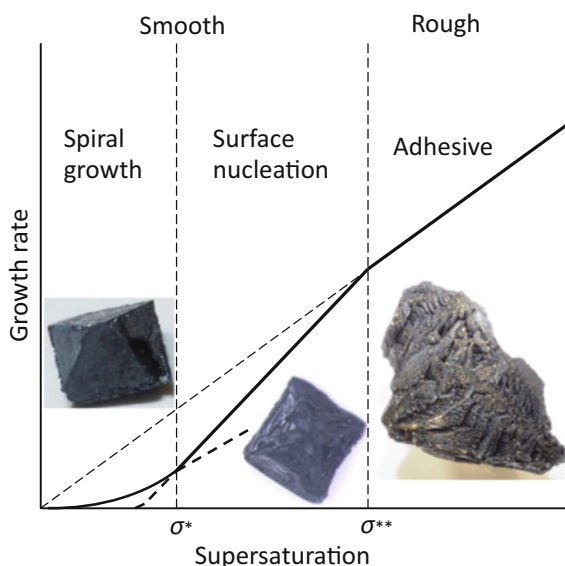


Fig. 2.15 Dendritic crystals of $\text{Tb}_2\text{Ge}_2\text{O}_7$ (left), $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ (middle, three crystals), and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (right)

2.2.6 Summary of Growth Mechanisms

The relationships among spiral growth, hopper growth by the layer-by-layer mechanism, and dendritic growth are summarized [1] in Fig. 2.16. In general, crystals grow faster under higher supersaturation. When supersaturation is very low, surface nucleation is not possible and only spiral growth can take place. However, when supersaturation exceeds σ^* , nucleation of new layers occurs at the edges and corners of the crystal and hopper growth becomes dominant. Both spiral growth and hopper growth are characterized by the spreading of layers at the crystal surface. When supersaturation exceeds σ^{**} , dendritic growth becomes operative. Because dendritic growth occurs on atomically rough surfaces, the growth rate can be very high.

Fig. 2.16 Growth mechanisms as a function of supersaturation. The solid line is the growth rate in each regime of supersaturation. Crystals of Mn_3O_4 grown under each regime are also shown



The above discussion shows that crystals with flat, smooth faces are grown when supersaturation is kept low. Because such growth proceeds slowly, usually at a rate of about 1 mm per day or slower, the accidental formation of various defects can be minimized. The condition of low supersaturation can be achieved by the slow cooling of the solution, but real growth processes often involve interactions of different mechanisms and it is always difficult to predict the exact outcome of a given experiment. Factors such as the viscosity of the solution and temperature instabilities often influence the quality of crystals. Such factors will be discussed in later chapters.

2.3 Imperfections in Crystals

Various types of imperfection are introduced into growing crystals. Crystal imperfections include physical defects, chemical impurities, and various forms of inhomogeneities. In some cases, the most visible imperfection is twinning (Fig. 2.17). A twin is a composite of two or more crystals, each showing a definite crystallographic relationship to the others. In Fig. 2.17b, the twinning plane, where the two parts share atoms along a common plane, is shown as the area surrounded by dashed lines. Most twins originate during the nucleation stage of crystal growth. As the groove at the re-entrant angle between the two parts provides a permanent step during crystal growth, twin crystals may grow into large crystals in this direction (Fig. 2.17c). In some cases, many twins are repeated at a microscopic scale, which can only be detected under a microscope.⁴

Figure 2.18a shows the “butterfly” twins of BaTiO_3 . Here, the faces of plates correspond to the cubic $\{100\}$ faces, whereas the twinning plane is parallel to $\{111\}$. Not to be confused with twin crystals are those of parallel growth, for which two examples are shown in Fig. 2.18b, c. We can see that all faces of the same crystal form are similarly oriented in parallel growth, whereas they are in reverse or mirror-image positions in twin crystals. If multiple crystals are joined with no special orientational relationship, they are neither twins nor those of parallel growth; they are simply called intergrown crystals.

Flux inclusion is another type of imperfection (Fig. 2.19a). It occurs when growth proceeds at a rate much faster than it is possible for flux particles to diffuse away from the surface. Accordingly, this condition is most likely to be met when supersaturation is too high. It occurs particularly when the spaces between the arms of dendrites are being filled, trapping the flux inside. Flux inclusion may be avoided by lowering the cooling rate or by using a less viscous flux.

⁴Crystals that have undergone structural transformation or strong stress can also show microscopic twins. These are called transformation and deformation twins, respectively, and are to be distinguished from the growth twins discussed here.

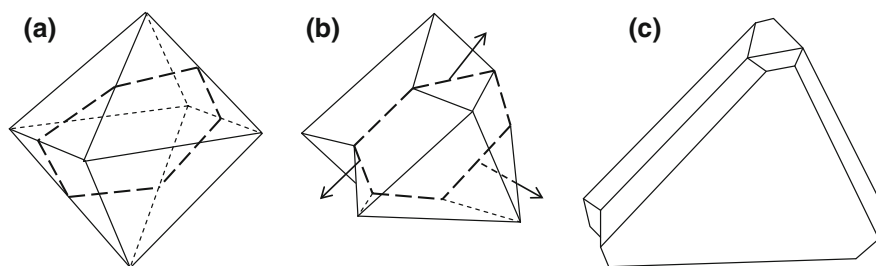


Fig. 2.17 **a** Octahedral crystal. **b** Twinned octahedral crystal, with arrows pointing from the re-entrant angles. **c** Tabular twinned crystal due to favored growth at re-entrant angles

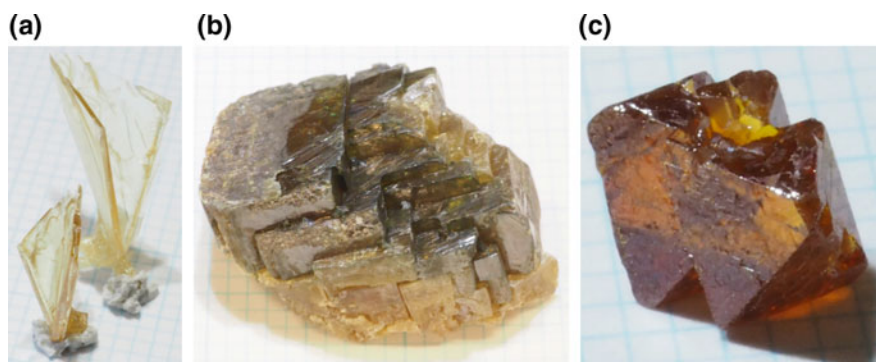


Fig. 2.18 **a** Butterfly twins of BaTiO_3 . **b** Parallel growth of cubic $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3\text{-PbTiO}_3$ crystals. **c** Parallel growth of octahedral $\text{Y}_2\text{Ti}_2\text{O}_7$ crystals

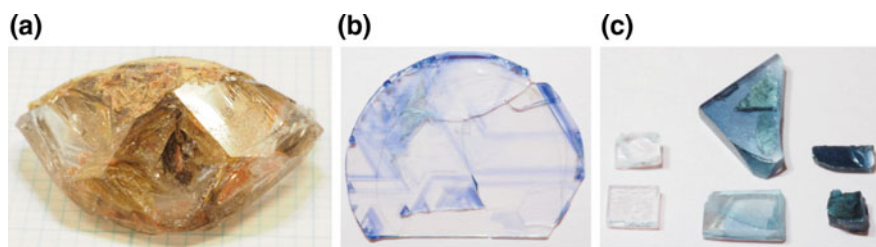


Fig. 2.19 **a** $\text{Y}_3\text{Al}_5\text{O}_{12}$ crystal with massive flux inclusions. **b** Blue-colored growth bands in $\text{Al}_{2-x}(\text{Fe,Ti})_x\text{O}_3$ crystal. The size of this cracked crystal was limited by the crucible. **c** Color centers in KTaO_3 crystals. The blue color, which is caused by oxygen vacancies, increases in intensity from the crystals on the left to those on the right

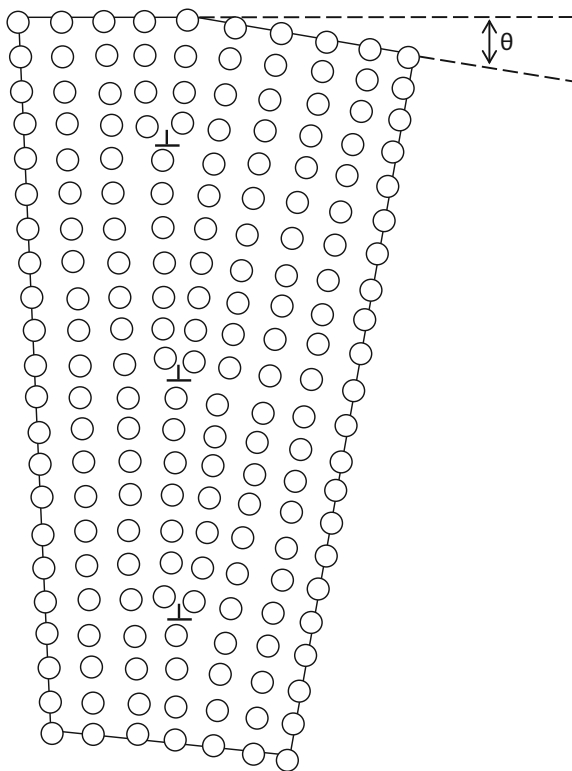
When the supply of solute to the growing surface is interrupted several times during crystal growth, growth bands can form in the crystal. Growth bands are easily recognized when the crystal is transparent, and their shape often reflects the underlying symmetry of the crystal (Fig. 2.19b). As growth bands are spatial

variations in composition or impurities, they can be prevented by minimizing the irregularities in growth conditions, such as temperature fluctuations. When many growth bands appear in a periodic sequence, they are usually referred to as growth striations. Often, growth striations along different crystallographic directions meet at the growth sector boundary; growth sectors are produced when different crystallographic directions grow with a different manner of defect formation.

There are several types of imperfection at the atomic level, which are called point defects. Vacancies, accidental insertion of atoms at interstitial positions, and substitution of impurity atoms are some of the examples. The number of point defects is generally decreased when crystal growth takes place at lower temperatures. When point defects produce color in otherwise colorless crystals, they are often called color centers (Fig. 2.19c).

In addition to screw dislocation, edge dislocation is another type of line defect that can provide active growth centers. An edge dislocation is formed where a plane of atoms extends only part of the way into a crystal lattice; it is shown as an inverted T in Fig. 2.20. In the figure, a series of edge dislocations of similar orientation makes the top half of the crystal slightly wider than the bottom half. This results in angular misorientation between the left half and the right half of the crystal, creating a low-angle grain boundary.

Fig. 2.20 A row of edge dislocations creating a low-angle grain boundary



We have looked at some of the most common types of imperfection found in flux-grown crystals. Some physical properties, such as the resistivity of semiconductors, are very sensitive to many types of imperfection, whereas others are more tolerant. Although imperfections are only viewed as a nuisance for the user of crystals, they can provide important insights on the growth mechanisms, allowing the crystal grower to improve growth conditions.

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