PART I FUNDAMENTAL CONCEPTS

In Part I we summarize the fundamental concepts relating to the growth and morphology of crystals, such as atomic processes and mechanisms of crystal growth, and the principles governing the morphology, perfection, and homogeneity of crystals. We base this description on a historical review of the development of the subject. Such fundamental concepts relating to atomic processes and the mechanisms of crystal growth have been acquired throughout the twentieth century through investigations on simple systems and the single phase, and have formed a base for the development of industries, such as semiconductors, in which single crystals are used. Our understanding of the phenomena occurring in complicated and complex systems, such as in the formation of solid earth materials or biomineralization, will be deepened based on the fundamental concepts explained in Part I.

1

Introduction

The crystal, with its regular atomic construction, is the most commonly encountered state of solid materials. The three properties of a crystal, external form, perfection, and homogeneity, are directly related to how the crystal grows. Individual crystals of the same species and atomic construction may have different properties. The mechanism of crystal growth has long been understood at an atomic level, at least for simple systems. Our understanding of the factors determining external form, perfection, and homogeneity provides us with the information necessary for the development of industries which utilize the physical properties of single crystals in forms of bulk and thin film, such as semiconductors. In the twenty-first century, we expect to clarify the relevant phenomena occurring in complex and complicated systems.

1.1 Historical review

On hearing the word “crystal,” most of us call up images of regular, symmetric forms, perhaps the prismatic form of rock-crystal, or the dendritic form of snow crystals. We use the term “crystal clear” to imply something transparent and pure. The ancient Greeks used the term crystal (κρνσταλλο) to imply clear, transparent, and hard ice; rock-crystal was so named as it was thought to be unmeltable ice that existed in fissures of rocks. As in the present day, the regular polyhedral forms were the ones that roused the most interest. Pythagoras, for example, used the word crystal to imply perfection, harmony, and beauty; and Plato listed his famous five polyhedra, related to fire, earth, air, water, and the universe.

Theophrastos (372–287 BC), the author of the oldest book on minerals, *On Stones*, referred briefly to regular polyhedral forms exhibited by mineral crystals [1]. In later books on minerals, polyhedral forms bounded by mirror-flat faces are mentioned.

For example, in the lengthy *Natural History* [2], by the famous Roman natural historian Gaius Plinius Secundus, there are descriptions of polyhedral forms of beryl, rock-crystal, diamond, etc.

It was not until the seventeenth century, however, that special attention was paid to the *forms* of crystals. Kepler was deeply attracted by the highly varied dendritic forms of snow crystals, and he believed that the units constituting snow crystals were equally sized spheres [3]. Kepler described the observed elaborately varied external forms as simply the result of the combination of these spherical units. This marked the beginning of the concept of crystal structure. Starting from Kepler's idea of equally sized spheres as the constituent units, the concept was developed to include equally sized ellipsoidal units by Huygens, and further to polyhedral units by Haüy. These were systematized into seven crystal systems based on the axial lengths and axial angles, and were further subdivided into thirty-two crystal groups (point groups) by the combination of symmetry elements compatible with the seven crystal systems. In the Appendixes we present: the crystal axes; the fourteen Bravais lattices and the seven crystal systems; the indexing of crystal faces and zones; the symmetry elements and their respective symbols; and the stereographic projections of the thirty-two crystal groups. These are mathematical systems, but numerous observations on the real crystals of minerals formed the basis for this ordering. Based on this mathematical structure, the forms exhibited by polyhedral crystals were investigated, and the relationships between these forms and the lattice types were discussed. This type of investigation is called crystal morphology, and was of great interest in the nineteenth and early twentieth centuries. A vast amount of data of descriptive and classification type were accumulated during this period. The results were complied in books such as Goldschmidt's *Atlas der Kristalformen* and Dana's *The System of Mineralogy* (see refs. [1] and [4], Chapter 9).

In 1912, Von Laue demonstrated using X-rays that a crystal is constructed of unit cells, and that it is possible to determine atomic positions by means of diffraction phenomena. Investigations analyzing crystal structure spread quickly, and within a short period the crystal structures of most simple inorganic crystals had been analyzed, deepening the knowledge of chemical bonding and atomic and ionic radius, and leading to the emergence and rapid progress of a new scientific discipline, crystal chemistry. It was during this period that the importance of the 230 space groups, which had been mathematically introduced by Federov, Schoenflies, and Barlow, was pointed out by a Japanese researcher, S. Nishikawa, in analyzing crystal structures. In addition to X-rays, electron and neutron beams are now also used in structural analyses; nowadays, stronger X-ray beams are used, and there have been great developments in the apparatus used for structural analyses, which have now become almost routine, except for crystals of macromolecular proteins.

1.2 The birth of the concept of crystal growth

In the seventeeth century, the Danish anatomist Nicolaus Steno (1638–1687) collected many samples of rock-crystals, and he measured the interfacial angles of hexagonal prisms. He found that the interfacial angles of corresponding faces were constant, irrespective of external form. This was the beginning of the now accepted "law of the constancy of interfacial angles." In the treatise describing his finding, Steno put forward two important concepts. He argued that rock-crystals were not of organic origin formed by the activity of bacteria in the soil, as was widely believed, but that they grew through the agglutination of tiny particles formed through inorganic processes taking place in high-temperature aqueous solution. He explained that the reason why rock-crystals show hexagonal prismatic forms bounded by six triangular faces at the tip and six rectangular faces, and sometimes show tapering prismatic or platy forms, is that the growth rates are different depending on crystallographic direction, i.e. on the different crystal faces [4]. These concepts of crystal growth and growth rate anisotropy provide a basis for the present-day science of crystal growth.

Interest in crystal form continued into the eighteenth century. Hooke noted that alum crystals took regular octahedral forms when they grew on the tip of a string immersed in aqueous solution, whereas their forms changed into platy triangular or hexagonal platy, though bounded by the same faces, when they grew at the bottom of a beaker (see ref. [11], Chapter 4). De l'Isle reported that when NaCl crystals grew in aqueous solution containing a small amount of urea, they took a simple octahedral form, in contrast to the simple cubic form grown in pure solution (see ref. [26], Chapter 4).

In the nineteenth century, when crystal morphology was systematized to fourteen types of unit cells, seven crystal systems and thirty-two crystal groups, the following two macroscopic treatments on the morphology of crystals emerged.

(1) The Bravais empirical rule, which states that there is a close correlation between the polyhedral forms of a crystal and the lattice type.
(2) Theoretical treatments by Gibbs, Curie, and Wulff on equilibrium form showed that the equilibrium form of a crystal having anisotropy should be polyhedral, not spherical, as would be expected for the equilibrium form of an isotropic liquid droplet. (See refs. [6]–[8], Chapter 4.)

It became necessary to understand how crystals grow at the atomic level so as to form a deeper understanding of why crystals can take a variety of forms. This was achieved through the layer growth theory put forward in the 1930s by Volmer, Kossel, and Stranski on the structure and implication of the solid–liquid interface, the spiral growth theory by Frank in 1949, and the theory of morphological

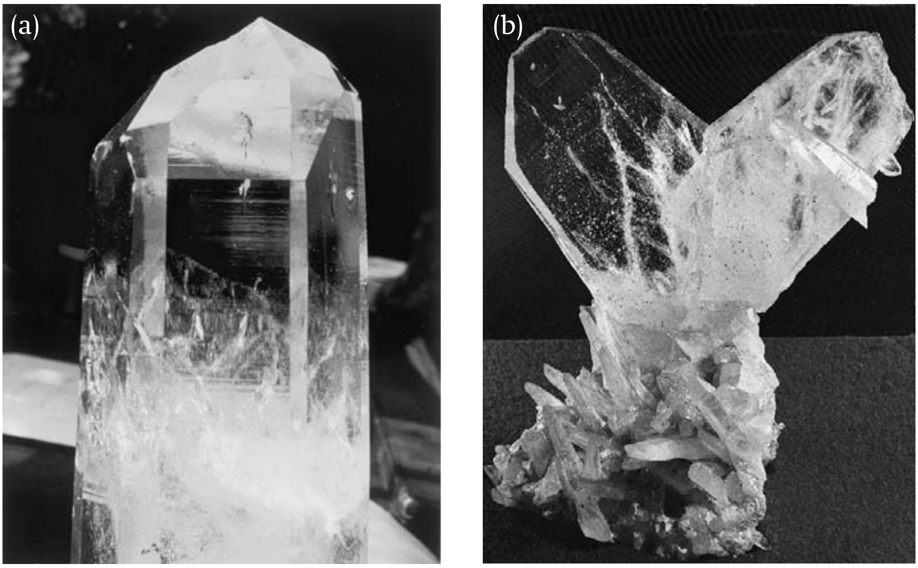

Figure 1.1. (a) This hexagonal prismatic form of rock-crystal appears due to spiral growth on smooth interfaces and growth rate anisotropy. (b) Twinned rock-crystals from the Otome Mine in Japan. According to the Japan Law (see Section 10.6), these are larger and show a more flattened form than the coexisting single crystals.

instability by Mullins and Sekerka in 1963 (see refs. [7]–[11] and [20], Chapter 3). The understanding of the mechanism of crystal growth progressed experimentally in the twentieth century. Before the 1930s, the main work was performed on the relationship between the macroscopic ambient phase and macroscopic crystal forms. Later, advancements in optical microscopy and electron microscopy made it possible to observe and measure growth spirals with step heights of nanometer order. It is now possible to observe the behavior of spiral step advancement of nanometer order in height *in situ*.

1.3 Morphology, perfection, and homogeneity

Since the growth mechanisms of crystals have become understood at the atomic level, at least in single and simple systems, it has become clear how the micromorphology (the morphology of growth spirals and etch pits) and the macromorphology (polyhedral, skeletal, and dendritic forms) of crystals are determined. Since the morphology of crystals is the result of crystal growth, this is related to how lattice defects (point, linear, and planar) are induced and distributed in single crystals, and to how impurity elements participate. This leads to the development of the method of controlling perfection and homogeneity of bulk and thin film single crystals and to the exploration of semiconductor and opto-electronic materials with desirable properties. It is with these developments that today's industries are concerned.

1.4 Complicated and complex systems

Knowledge of the growth mechanism, morphology, perfection, and homogeneity of single crystals creates a base from which we may understand the morphology exhibited by polycrystalline aggregates, or the mechanism of formation of textures and structures that appear in polycrystalline aggregates of multiple phases, such as those shown by ceramics, metals, and rocks.

Many examples are known to exist that show that polycrystalline aggregates exhibit properties different from those of single crystals. For example, on the Mohs scale the hardness of diamond is given as 10, the highest for any known mineral, yet a diamond single crystal is weak to shock due to the cleavage. It is due to the textures formed by polycrystalline aggregation that carbonado and ballas, polycrystalline aggregates of diamonds, have higher toughness and can be used as boring heads, unlike the relatively weak single crystals. Similarly, the toughness of bamboo results from the textures formed by aggregation of soft cells. The outer and inner skins have different textures and different functions.

What determines the physical forms of animals and plants is a subject of much debate within the biological sciences. We know that the basic unit of living bodies is not crystalline; however, should we entirely disregard the units that comprise living organisms as having no link to crystals? Does DNA alone uniquely control all living phenomena?

There are inorganic and organic crystals formed in living bodies as a result of being alive, and these are the link between living phenomena and crystals.

Tooth, bone, shell, and the exoskeleton are formed to maintain life, whereas gallstones, bladder stones, and sodium uric acid (a cause of gout) are the results of excretion processes of excess components. Tooth, bone, and shell are composed of inorganic crystals of apatite, aragonite, calcite, and protein. It is assumed that these crystals grow through the cooperation of both crystals and proteins. Teeth consist of enamel and dentine portions, both constituting aggregates of apatite crystals of different forms and sizes, leading to different textures and functions. In contrast to well controlled forms, sizes, and textures of these polycrystalline aggregates formed by cooperation with protein, crystals constituting calculi in organs, such as gallstones, usually exhibit uncontrolled radial polycrystalline aggregations, suggesting no cooperation between protein and crystals.

It is conjectured that there can be two types of cooperation with proteins for crystals to grow in living bodies: in one, a protein film acts as an envelope; and in the other it acts as a substrate in epitaxial growth (see Section 7.4). When crystals of the same or different species grow in a definite crystallographic relation (orientation) on a crystal face of the substrate, the phenomenon is called *epitaxy*. This phenomenon was originally known to be present in mineral crystals, but it has now been developed as an important technique of crystal growth used to grow thin films of single crystals for semiconductor devices.

Growth mechanisms in epitaxy are now understood at an atomic level in relation to host–guest crystals (interface energy) and driving force. Investigations on host–guest relations have been expanded from those between inorganic and inorganic, to inorganic/van der Waals, inorganic/polymers, and inorganic/protein crystals. The growth of inorganic crystals in living bodies corresponds to the relation between protein crystals as the host and inorganic crystals as the guest. The opportunity may arise for us to unlock a new relationship between inorganic and organic, or inanimate and animate, forms using morphology and textures exhibited by crystals formed through physiological activities.

The aim of this book is to analyze phenomena in complicated and complex systems, such as crystallization in minerals and in the living world, using the morphology of crystals as the key.

Crystal form is the direct result of crystal growth, and we will therefore develop our arguments based on the mechanism of crystal growth. The book consists of two parts: Part I presents the fundamental concepts, and Part II deals with the application of these concepts to complicated and complex systems (by looking at case studies).

In Part I, after systematically summarizing the hitherto used terms in the morphology of crystals, we summarize the developments in the atomic process of crystal growth and morphology achieved in the twentieth century.

In Part II, factual examples concerning minerals and physiology are presented to demonstrate how complicated phenomena may be analyzed based on the understanding explained in Part I.

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More information

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Crystal forms

Crystals are solid materials having regular arrangements of atoms, ions, or molecules. Crystal forms are determined not only by structure but also by the factors involved in growth. The same crystal species may therefore appear in various forms. In this chapter, the external forms of real crystals are systematically classified.

2.1 Morphology of crystals – the problems

The morphology of crystals is the central theme of this book. Our intention is to present systematically the fundamental concepts that allow us to analyze the factors that determine the various forms of crystals. We may then deduce and analyze the phenomena and processes that we cannot observe *in situ*, such as those occurring in the depths of the Earth or in the animate world.

When there is no distortion in the structure or no change in orientation throughout a crystal, we refer to the structure as a single crystal. A solid consisting of many single crystals with different orientations is called a polycrystalline aggregate. There are also polycrystalline aggregates of multiple phases, as in metals, rocks, and ceramics.

Since real crystals may contain various defects of lattice order, we may regard these crystals as nearly perfect single crystals, and we accept the defects as part of the original system. Assuming this to be the case, individual crystals may be classified as single crystals, no matter how big or small they are, and a combination of individual crystals is termed a polycrystalline aggregate. However, when crystalline materials are used in specific industrial purposes, a single crystal of a particular size may be required. Single crystals of silicon of centimeter to meter size are necessary in semiconductor devices, or specific sizes of quartz or ADP (ammonium dihydrogen phosphate, $NH_4H_2PO_4$) may be required for use in piezoelectrics.

Clear, transparent single crystals of centimeter size are used for facet cutting in jewelry making.

This centimeter to meter order of size is generally assumed when we refer to single crystals. Individual crystals of clay minerals, however, are single crystals, although their sizes are of micrometer order. On the other hand, metals and ceramics are generally chosen for the bulk physical properties exhibited by polycrystalline aggregates; single crystalline materials of these solids are in general not required (exceptionally, large single crystals of metals are used). However, to understand the physical properties of metals, it is necessary to grow single crystals of appreciable size and to investigate their properties. Investigations performed on single metal crystals have promoted the rapid development of dislocation theory and physical metallurgy.

The morphology of single crystals is determined by the crystal structure (the internal factors), the crystal growth conditions, and the process of that growth (the external factors). First, it is necessary to understand how the morphology of a single crystal is determined through the interconnection between the external and internal factors. In the case of polycrystalline aggregates of a single phase or multiple phases, the texture and the structure* are determined by the time and density of nucleation of the multiple phases and the morphologies of the respective crystals. Similarly, just as the toughness of bamboo is determined by the texture, which consists of soft cells, characteristic morphologies and properties that are not seen in single crystals may be evident in polycrystalline aggregates. So, we see that understanding the morphology of single crystals assists us in understanding more complicated systems. We shall use this method to extend our discussions to include complex structures.

Crystals having different crystal structures usually take geometrical external forms following the symmetries involved in their respective structures, but they may also take very different external forms if the growth conditions are dissimilar. Snow crystals are a representative example: they exhibit the polyhedral forms of the hexagonal prism and hexagonal plate, but they also may exist in the familiar dendritic form, with branches in six directions, which in Japan is referred to, rather poetically, as the “six petal flower.” It is the purpose of this book to demonstrate why elaborately varied forms of crystals appear, and we are going to base our discussion on the understanding of the atomic process of crystal growth. First, therefore, we will summarize and systematize the problems involved in determining the morphology of crystals.

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* “Texture” and “structure” are not explicitly defined terms. *Structure* is usually applied to macroscopic heterogeneity due to macroscopic movement such as flow structure or foliated structure, whereas *texture* usually refers to microscopic heterogeneity, such as holocrystalline texture, porphyritic texture, and lamellar texture due to exsolution.