

Growth and Morphology of Crystals*

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(Received August 6, 1999; Accepted October 24, 1999)

1. Preface

This issue of “FORMA” presents an English translation of Haeckel’s book “Crystal Souls”, with Alan Mackay’s introduction and detailed annotations. The translation was accomplished by Alan, my respectable old friend since 1950’s. When this book published in 1917, Haeckel tried to attract people to beautifully organized variety of forms exhibited by radiolaria and snow crystals, and the close similarity in forms of inorganic crystals and biological materials. The editor of this journal felt that it would be interesting and informative for the readers, if an article summarizing the development made during this century in understanding the origin of forms of crystals (morphology or morphogenesis) would be printed jointly. He suggested me to translate my article in Japanese on the topic, which appeared in SUURI-KAGAKU (Mathematical Sciences) in 1993 (1).

The article was published as No. 5 of the series of articles entitled “The Course of Physics—from the development achieved in the 20th Century”, which consisted of 30 articles. The series covers whole range of physics, mathematical physics, quantum mechanics, statistical mechanics, solid state physics, elementary particle physics, and cosmic physics, and was later published in a book entitled “Physics of the 20th Century” (2). Among 30 articles, two were directly related to crystalline solids. One by S. Kikuta was on structural crystallography, and the other by myself on growth and forms of crystals.

A couple of new sentences and references were added in this translated version for the sake to help readers in easier reading.

In the introduction of “Crystal Souls”, Haeckel wrote that crystals serve as the image of lifeless, rigid natural bodies. Crystallography which deals with research on “dead” crystals is an “exact science”, which moves on the sure rails of mathematics, and has nothing to do with “life” or “the soul”, the most perfect phenomena of life. Souls, on the other hand, serve generally as indicators of organic life, in contradistinction to the inorganic world of minerals, rocks and crystals. Their main characteristics, sensitivity and movement (“feeling” and “willing”) are tied to the organisation of the “living nature”, to the characteristic assembly of organisms from various organs, and on their regular,

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apparently goal-directed cooperation which life itself is based on.

As Haeckel thought, crystallography is an exact science on “dead body”, when it is aimed to systematize the geometry of forms, to analyze the atomic structure and chemical bonding, and to correlate these with physical properties. However, a crystal can not be formed instantaneously. Initial ordering, i.e. nucleation occurs at first in disordered phase, followed by growth, during which growth conditions and thus growth rates, forms, perfections and homogeneities will be changed abruptly or fluctuated. Each crystal has its own growth history, and the external and internal forms (imperfection and inhomogeneity) of a crystal is the result and record of the growth history. Crystal is no more “dead body”, when we see it from such a standpoint. Even small, a stone has its own growth history and individuality. The science of crystal growth is aimed to understand how and by what mechanism crystals nucleate and grow, and their forms, perfections, homogeneities and textures are determined. Interesting enough, the science of crystal growth has its root in the same 17th Century as structural crystallography started. We shall trace in this article how the science of crystal growth and the understanding on forms of crystals has developed since the 17th Century. For crystal growth and morphology of inorganic matter of simple system, it has now reached to a level that relevant phenomena are understandable in terms of atomistic process. Interests have now expanded to the problem of forms and textures exhibited such as by organic and inorganic crystals formed in living organs through living activities, namely to the problems involved in far more complicated and complex systems. Efforts are now-being paid to build a bridge between living and non-living worlds, through understandings of growth and forms of crystals. Haeckel’s dream is now in the range of our direct interest.

It is the author’s pleasure if the translation of this article is useful and informative enough to readers in extracting something new by correlating Haeckel’s concept and the development in 300 years on growth and forms of crystals summarized in this text.

2. Snow Flakes and Rock-Crystals

It is one of the mysteries in the history of science that the Greek who were talented in geometry and used a word “*κρύσταλλος*” did not pay enough attention to the regular geometric external forms that crystals exhibited. It was only in the 17th Century that adequate attention was paid to geometric forms of crystals. The earliest was the observation and consideration by J. Kepler (3) on the elaborately varied dendritic forms of snow flakes, then followed by treatise of Niccolous Steno (4) on interfacial angles of rock-crystals. The former was appeared in a book “New Year’s Gift” in 1611, and the latter in a treatise published in 1669.

Kepler considered that a crystal was composed of close packing of equi-sized spheres, although it exhibited thousands different dendritic forms. This was the root of the concept of crystal structure. The name of Steno is well known for the discovery of “the law of the constancy of the interfacial angles”, and we often overlook his important contribution to the science of crystal growth. In the treatise, Steno explained (1) that rock-crystals were formed through inorganic action by precipitation of tiny particles formed in high temperature aqueous solution, and not by bacteria action in the soil (in these days and down to the 18th Century, people believed mineral crystals were formed by bacteria action), and (2) that the

reason for that rock-crystals took a variety of polyhedral forms was growth rate anisotropy, i.e. growth rates were different in different crystallographic directions (5). The concept of “growth rate anisotropy” is the most basic concept of the present day’s science of crystal growth.

Two important concepts on the crystal structure and the crystal growth, were unexpectedly formulated in the 17th Century through observations: one on the dendritic snow crystals and the other on the polyhedral rock-crystals bounded by flat faces. How the two concepts have been developed will be discussed in this article.

3. Way to Analyse Crystal Structures

Although Kepler assumed equal sized spheres as building units of a crystal, it was due to a French mineralogist, R. J. Häuy that polyhedrons similar to the present day’s unit cell of a crystal, rather than spheres or ellipsoids were first proposed as building unit of a crystal in the 18th Century (6). A. Bravais (7) derived 14 lattice types, the so-called Bravais’ translation lattice, as possible types of unit cells that may occupy the space without opening. Starting from this, 7 crystal systems, 32 point groups and further 230 space groups were systematized and the geometry of crystals thus developed and almost completed in the 19th Century. However, crystals really consisted of unit cell was proved only in 1912. In this year, M. von Laue and his pupils performed an experiment of X-ray diffraction using a copper sulphate crystal. They demonstrated that the crystal was really consisted of regularly arranged atoms, which can be expressed by translation of unit cell, and that X-ray is an electromagnetic waves with wave length of Ångstrom order (8). X-ray analysis of crystal structures spread all over the world like a rapid spreading of fire set on a dried grass field.

The crystal chemistry was established based on the results of crystal structure analyses and the physical properties of crystals became understandable in relation to chemical bondings and crystal structures. Since the development along this trend has been well explained in other articles in this series, we shall focus our attention on the development of the science of crystal growth started from the treatise of Steno. Particular attention will be paid on morphology or morphogenesis (origin of forms) of crystals, which represent the final results of crystal growth.

4. Polyhedral Crystals Bounded by Flat Faces

Kepler paid main attention on dendritic forms of snow crystals. Steno’s attention was mainly on a variety of forms of polyhedral crystals that a particular crystal species exhibited.

It was Bravais’ law that gave an account for the first time to the relation between forms and unit cell geometry to understand the origin of different polyhedral forms exhibited by different crystal species (7). Bravais derived an empirical rule that crystal faces parallel to the net planes with higher reticular densities (wider interplanar distances) develop larger on actual crystal than those with lower reticular densities. Primitive (P), face-centered (F) and body-centered (I) types of unit cells of cubic system take simple cubic, octahedral and rhombic dodecahedral forms, respectively. Following this rule, J. D. H. Donnay and D.

Harker (9) expanded the Bravais' law based on geometry of 14 lattice types to 230 space groups. Effect of symmetry elements with translation operation (glide plane and screw axes) are taken into consideration in calculating reticular densities. By re-calculating the reticular densities based on 230 space groups, it was demonstrated that most discrepancies noted between observed forms and expected ones on the Bravais' law diminished. According to the Bravais' law, polyhedral crystals of pyrite FeS_2 should be bounded by $\{100\}$, $\{111\}$ and $\{110\}$, but in reality $\{210\}$ develops instead of $\{110\}$. According to the Bravais law, $\langle 0001 \rangle$ face should develop on quartz crystals. The $\langle 0001 \rangle$ face has never been observed on natural rock-crystals, except on unusual samples. These discrepancies can be explained by Donnay-Harker's expansion.

Hartman and Perdok's Periodic Bond Chain (PBC) analysis (10) is on the similar idea. Although attention in treatments by Bravais and Donnay-Harker was paid on the importance of planes, Hartman-Perdok paid attention on zones. They tried to find out strong PBCs in a particular crystal structure, and classified crystal faces into three types, F (flat), S (stepped) and K (kinked) faces, depending on the numbers of PBCs involved in respective faces. An F face contains more than 2 PBCs and develops large, whereas an S face only 1 PBC and a K face does not contain any PBC (Fig. 1). S and K faces will develop small or not appear at all as a flat face on actual crystals. Although Hartman-Perdok's PBC analysis appears to be qualitative and somewhat arbitrary, the method has developed later in a more quantitative manner by calculating attachment energies of PBCs. The PBC analyses have been applied to a wide variety of crystal species, and the results served as criteria for the analyses of growth forms. The analysis became applicable to complicated structures like garnet, by expansion of the concept to connected net model proposed by P. Bennema, and

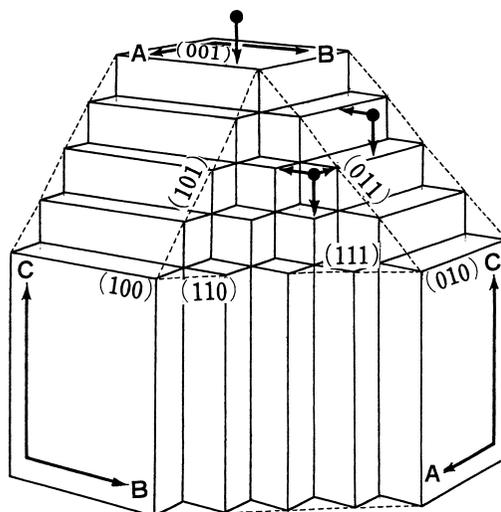


Fig. 1. PBCs and F, S and K faces defined in Hartman-Perdok model. Thick lines with arrows, A, B and C are PBC vectors in a simple cubic crystal (Kossel crystal). F faces: (100) , (010) , (001) , S faces: (110) , (011) , (101) , K face: (111) .

was applied to more complicated crystals including modulated structure and quasi-crystals. Through this expansion, the concept of attachment energy is correlated to the concept of Jackson's α -factor, on which an explanation will be given later. Recent developments along this line are summarized in a book on "Morphology of Crystals" (11).

The methods explained above initiated by Bravais, followed by Donnay-Harker and established by Hartmen-Perdok, are aimed to elucidating an ideally expected form of a crystal assuming that the form of a crystal is determined thoroughly by the internal structure, entirely neglecting the effect of external growth parameters. We may call such a form as "structural form" or "abstract form" which has no relation with thermodynamic parameters such as temperature and pressure or driving force. However, it is perhaps fair to note that the method has now been advanced to predict growth forms (see below) by taking the effect of external factors at interfaces into calculation (12).

Another approach to understand the polyhedral form of a crystal is thermodynamic analysis of the equilibrium form, discussed by J. W. Gibbs (13), P. Curie (14), G. Wulff (15) from the end of the last century to the beginning of this century. Basically, they considered that a crystal is bounded by a combination of crystal faces and the sum of products of whose surface area and surface free energies becomes minimum. The concept of Wulff's plot considers that the equilibrium form can be constructed by inscribing an in-polygon bounded by lines (or planes) of internal tangent at the cusps of a raspberry form obtained by plotting the surface energies of faces. The normal growth rates of faces are proportional to the surface free energies. The equilibrium form is a uniquely determined form for a given crystal at a given thermodynamic condition.

Forms of a real polyhedral crystal are neither determined by structural factors alone nor the one that reached to the equilibrium state. We may call these forms as growth forms. It is to be noted that the structural form and equilibrium form are singular, i.e. there is only one unique form, whereas growth forms are plural. Interests in growth forms of crystals started from the time of Steno, and in the 18th Century, observations were already reported to demonstrate that impurity components gave drastic effect upon the growth morphology of NaCl crystals from aqueous solution. It was reported in the 18th Century (16) that an addition of a small amount of urea to the aqueous solution completely modified the forms of NaCl crystals from simple cube to simple octahedron. Extensive investigations have been made since then on impurity effects, and Buckley (17) summarized the earlier and his own results on this subject.

5. Tracht and Habitus

It is necessary in dealing with growth forms of polyhedral crystals to distinguish between Tracht and Habitus. (There is no equivalent terms in English. The same term "crystal habit" is applied to both.)

Habitus is used to denote characteristic polyhedral form that a particular crystal species generally exhibit, such as isotropic or bulky, prismatic, tabular, bladed, lamellae, etc. This is principally due to anisotropy involved in bonding in the crystal structure. Crystals with unit cell of platy form grown in isotropic environment take prismatic habit elongated perpendicular to the unit cell, and those with unit cell of prismatic form bladed or platy habit elongated perpendicular to the unit cell. It is clear that the difference in

Habitus exhibited by different crystal species is simply due to the growth along the stronger bond directions.

However, NaCl crystals which have isotropic unit cell do not exclusively take ideal isotropic form like cube or octahedron. NaCl crystals formed at the bottom of a beaker may take platy form. If NaCl solution is kept in a leather bag which is kept in shadow, numerous needle-like NaCl crystals will start to grow from the outerskin of the bag. They are whiskers of NaCl. Thin platy NaCl crystals are also known. Both whiskers and platy NaCl crystals are bounded by $\{100\}$ faces. We customally call such variation of forms in terms of Habitus change. The Habitus change appears due to anisotropic development of crystallographically equivalent faces. Such variation in Habitus is inferred to anisotropy involved either in the environmental conditions (e.g. solution flow) or in the anisotropic presence of preferential growth sites.

VLS (vapour-liquid-solid) mechanism for silicon whiskers (18), and a mechanism by capillary transport of solution and immediate crystallization at the exit (for NaCl) are well established growth mechanisms for whiskers. In the former case, eutectic liquid droplet of Au + Si, and in the latter case exits of capillary vessels in the leather skin act as preferential growth sites.

Variation of Tracht appears by combination and relative rate of development of crystal faces. Natural calcite crystals show a wide variety of forms ranging from thin platy, tabular, nailhead, rhombohedral, prismatic, dog-tooth, in spite of that the structural form of calcite is uniquely rhombohedron. Pyrite crystals also exhibit a variety of forms from cube, octahedron and pentagonal dodecahedron as shown in Fig. 2, by combination of $\{100\}$, $\{111\}$ and $\{210\}$ faces. Rock-crystals on which Steno founded the root of the science of

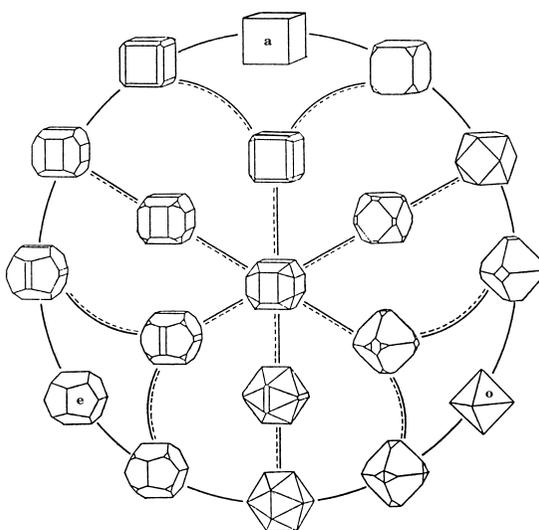


Fig. 2. Tracht variation of pyrite FeS_2 crystals. Forms of polyhedral crystals appearing due to combination of $a\{100\}$, $o\{111\}$ and $e\{210\}$ faces. All forms have been observed in Nature.

crystal growth also show a range of hexagonal prismatic forms, stout, elongated, tapered or flattened, but their variation is far less distinct than the cases of calcite and pyrite. Yet, Steno was able to introduce the concept of growth rate anisotropy 330 years ago. His penetrating eye to extract the truth behind phenomena is really impressive. However, nearly three centuries were necessary to reach the state that the causes of Habitus and Tracht variations could be understood properly based on the atomistic process of crystal growth. The external forms of crystals are the results of crystal growth, and the internal forms (inhomogeneity and imperfections in single crystals) are the record of the growth process. It is necessary to know the atomistic process of crystal growth to understand these problems.

6. Atomistic Process of Crystal Growth

Until 1930's, the main attention in the studies of crystal growth was paid on the relation between bulk environmental phases and characteristics of crystals in bulk. Through the investigations carried out before 1930's and some years after that, various problems were clarified and new concepts emerged such as;

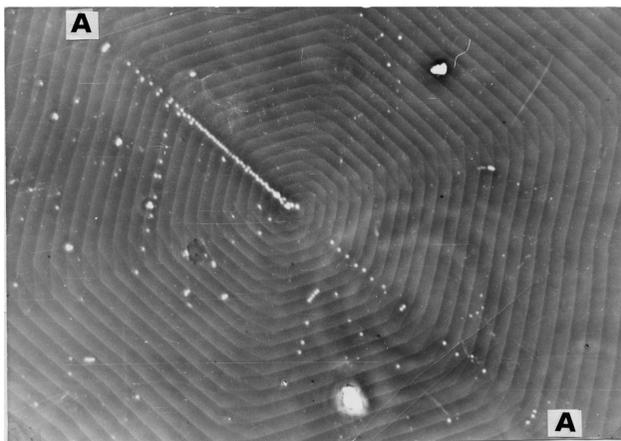
- (1) the presence of diffusion boundary layer around a growing crystal,
- (2) concentration gradient in the diffusion boundary layer which provides the driving force to grow crystals,
- (3) the so-called Berg effect (19), i.e. supersaturation at the center of a face on a growing crystal is much lower than that at the edges and corners,
- (4) experimental verification of various factors that cause Tracht variation.

Before 1930's, the growth process or growth mechanism was not understood at an atomistic level. It was not possible to give a proper explanation for the fact that a crystal can take and maintain polyhedral form bounded by flat faces, in spite of the fact that mass transfer from the bulk solution is isotropic and concentric.

From the end of 1920's to the early 1930's, W. Kossel and I. N. Stranski (20) put forward the two-dimensional layer growth theory which says that a crystal grows by two-dimensional spreading of growth layers parallel to the interface. The theory was the first atomistic model on crystal growth process, and was inspired by an observation of lateral spreading of growth layers on Hg crystals reported by Volmer (21). The theory was based on the analysis of attachment and detachment energies of a unit at various sites on complete (singular, or smooth in the present day's terminology) and incomplete (non-singular, or rough) planes. Based on this model, a reasonable explanation was given at an atomistic level to why a crystal can take and maintain polyhedral forms bounded by flat crystal faces.

Kossel and Stranski classified the interface into two types, complete plane consisting of smooth terrace surface and small number of steps and kinks, and incomplete plane consisting of only kinks. Two-dimensional layer growth takes place only on complete planes, whereas adhesive type growth mechanism is expected for incomplete planes.

When a layer completely sweep the surface, no source for growth steps presents any more on the surface. Kossel and Stranski assumed the formation of island-like two-dimensional nucleus for the source of new growth steps. The growth rate of the interface is thus determined by the rate of two-dimensional nucleation. Namely, below a critical supersaturation, growth will not occur according to this model.

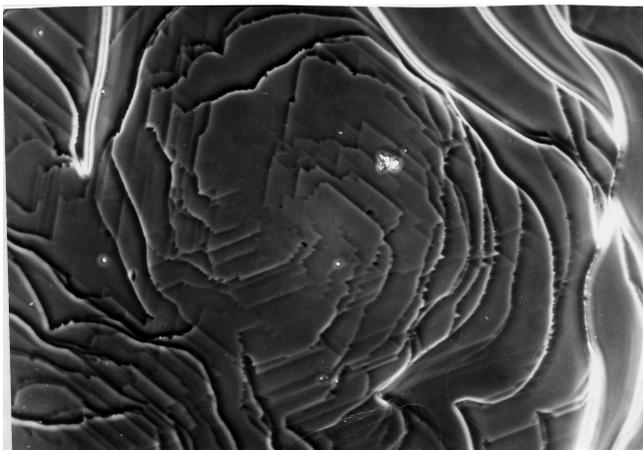


(a)

Fig. 3. Two examples of growth spirals (phase contrast photomicrographs). (a) Silicon carbide, (0001), $\times 1000$. White dots are impurities selectively adsorbed at the outcrops of dislocations. It is observed that edge dislocations moved along A-A and piled up at the outcrop of central screw dislocation due to plastic deformation after growth. The spiral takes an interlacing pattern along six directions, due to zigzag stacking of three elemental layers (6H polytype). (b) Hematite, Fe_2O_3 , (0001), composite spirals originating from a group of dislocations, $\times 250$.

In 1949, the second revolution took place in understanding atomistic process of crystal growth. This was the spiral growth theory put forward by F. C. Frank (22). This is a concept that a crystal can continue to grow even under an extremely small driving force (supersaturation), since steps created by outcrops of screw type dislocations act as self-perpetuating step sources. Frank's spiral growth theory was dramatically testified by the observation of spiral step patterns with step height of nanometer order on faces of various crystals. This was possible because almost concurrently various optical methods to observe and measure the height of steps of nanometer order were just developed, such as phase contrast microscope and multiple-beam interferometry. People were searching for appropriate samples to which these methods could be applied. By means of these optical methods, growth spirals with step height of 2.3\AA , corresponding to molecular height of Fe_2O_3 were successfully observed and the height precisely measured on natural hematite crystals (23). In Fig. 3, two examples of phase contrast photomicrographs of growth spirals are shown.

Dynamic process of spreading and bunching of growth spirals of mono-molecular height is now possible to observe in situ, both under optical microscope and atomic force (AFM) or scanning tunneling (STM) microscopes. Video images are taken to demonstrate how growth layers of mono-molecular height originate from the outcrop of a screw dislocation, and bunch together on the way of spreading to form macro steps, and how the step separation changes in response to a change in supersaturation. Observing these video images gives an impression that a crystal is truly alive, and is breathing.



(b)

Fig. 3. (continued).

7. Solid-Liquid Interface

Spiral growth and layer growth by two-dimensional nucleation is the growth mechanism of crystals expected to operate on atomistically smooth interfaces. Terms like “complete plane”, “singular plane”, and “smooth interface” have been used to denote such an interface. In Table 1, these terms used in the past and present are correlated.

In contrast to a smooth interface, an interface uniquely consisting of kinks is called “rough interface”. Crystallizing particles arriving onto such a rough interface can immediately find sites to incorporate into the crystal. The growth mechanism of such an interface is adhesive type and the interface advances homogeneously, not two-dimensionally.

Depending on the type of interfaces, three types of growth mechanisms, adhesive type, two-dimensional nucleation growth (2DNG) and spiral growth mechanisms are expected. The relation between growth rate versus driving force are different as schematically illustrated in Fig. 4. Therefore, it is understood that the structure of solid-liquid interfaces, rough or smooth, is essentially important in discussing the growth mechanisms and thus forms of crystals. It is natural to expect that theories will develop to analyse or to predict whether a given interface is rough or smooth depending on materials or growth conditions.

Three theoretical treatments on this problem are considered as important contributions; broad classification of materials made by K. A. Jackson using α -factor (24), multiple level model by D. E. Temkin (25), and generalization of Jackson’s α -factor by P. Bennema and G. H. Gilmer (26). In Figs. 5(a) and (b), the results obtained by Jackson and Temkin are illustrated. As can be seen in Fig. 5(a), materials having $\alpha < 2$ values have energy minimum at 0.5 occupancy, whereas those with $\alpha > 2$ values two energy minima at 0 and 1 occupancies. The former corresponds to rough interface, and the latter to smooth interface. $\alpha = \xi L/kT_M$, where L denotes latent heat, k Boltzmann constant and T_M equilibrium

Table 1. Terms used to indicate rough and smooth interfaces.

Kossel, Stranski (20)	Complete plane	Incomplete plane
Burton, Cabrera, Frank (22)	Singular interface	Non-singular interface
Hartman, Perdok (10)	F face	S and K faces
Present	Smooth interface	Rough interface

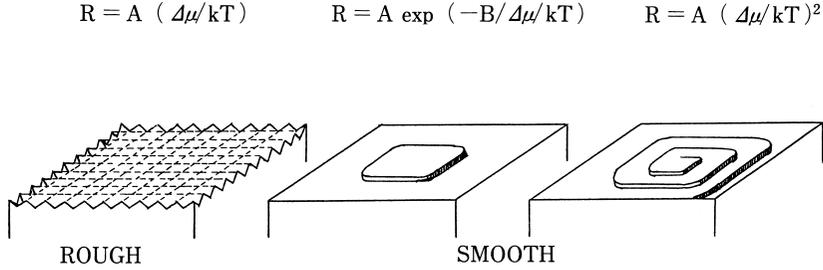


Fig. 4. Interface structures and three types of growth mechanisms. R , growth rate; $\Delta\mu/kT$ driving force (chemical potential difference between solid and liquid phases); A , B , constants.

temperature, and ξ orientation factor.

Metals usually have $\alpha < 2$ values, semiconductors $3 > \alpha > 2$, silicate minerals or polymer crystals having complicated structures $\alpha > 3$. Jackson's classification is useful to broadly classify materials into two groups which are energetically expected to have rough or smooth interfaces, but can be used only as a criterion for crystal growth from solution or vapour phase and actual crystal growth which occurs below T_M . Bennema and Gilmer generalized the expression of α -factor, by taking the solute-solvent interaction energies, growth temperatures instead of equilibrium temperature into account, so that the α -factor concept becomes applicable to real growth systems. Generalized α -factor is expressed as follow, where ϕ_{ss} , ϕ_{sf} , ϕ_{ff} respectively denote solid-solid, solid-fluid, fluid-fluid interaction energies, T_G , growth temperature.

$$\alpha = \xi \frac{\left\{ \phi_{sf} - \frac{1}{2}(\phi_{ss} + \phi_{ff}) \right\}}{kT_G}.$$

Extensive computer simulations have been made using generalized α -factor, which have demonstrated growth rate vs driving force relations for different α -values, and roughening transitions.

As can be seen in Fig. 5(b) showing Temkin's result, the interface roughness is not only controlled by α -factor, but also by β , which corresponds to driving force. It is seen that a smooth interface (in the region A) transforms to a rough interface (in the region B) as β (driving force) increases. Transition from smooth to rough interface is regarded as a kind

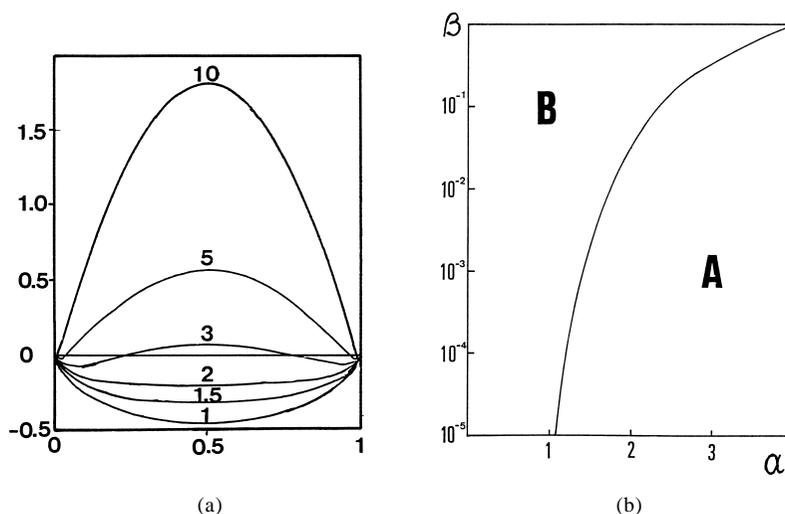


Fig. 5. The results obtained by Jackson (24) (a) and Temkin (25) (b). In (a), vertical axis represents free energy change, horizontal axis site occupancies. In (b), region A corresponds to the area where smooth interface is expected, B to rough interface area. In (b), vertical axis represents driving force β horizontal axis α .

of phase transition, and so a term of “roughening transition” is used. There are “thermodynamic roughening transition” as increasing temperature, and “kinetic roughening transition” as increasing driving force. The roughening transition from smooth to rough interfaces have been shown by computer simulations, and experimentally verified for a crystal growing in solution phase.

8. Morphology of Crystals

As originally pointed out by Steno, growth rate anisotropy determines the forms of polyhedral crystal. The growth rates are determined by the state of interfaces, the growth mechanism and the driving force. We may therefore analyse mutual relations among various forms exhibited by crystals, using Fig. 6 on which the preceding analyses are schematically illustrated (27). In Fig. 6, the vertical axis represents growth rate, and the horizontal axis driving force. Curves *a*, *b* and *c* respectively correspond to the expected growth rate versus driving force relations for spiral growth, 2DNG and adhesive type growth mechanisms.

At points indicated by * and ** in Fig. 6, we see boundaries where two curves cross. Above **, the interface will be rough, and below **, it will be smooth. In the region below *, spiral growth mechanism is expected to be operative, whereas in the region between* and **, 2DNG mechanism is expected to be predominant. Tracht variation is a phenomenon occurring in the region below*, where spiral growth mechanism is predominant.

Figure 6 is a schematic diagram illustrating one section of events. The positions of * and ** are different depending on crystallographic directions, crystal faces, environmental phases (melt, solution and vapour phases), solute-solvent interaction energies in solution

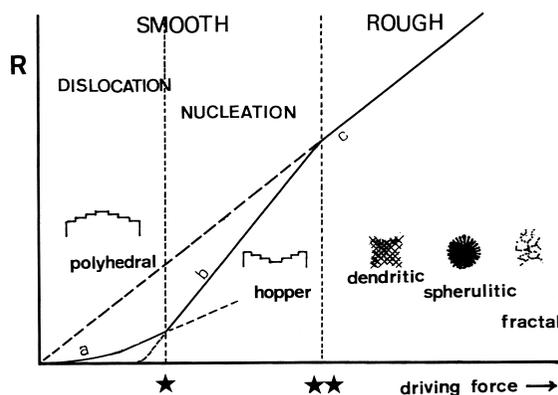


Fig. 6. Schematic illustration of mutual relation among different forms of crystals, in relation to growth rates (vertical axis) versus driving force (horizontal axis) relations in three types of growth mechanisms, smooth and rough interfaces. Curve (a) spiral growth, (b) two-dimensional nucleation growth mechanism, and (c) adhesive type growth mechanism. From Ref. (27)

growth (corresponding to solubility difference), as, well as size of crystals. When a crystal with a small α -value grows in the melt phase, the position of ** is close to the origin, but when it grows in vapour or solution phase, the ** will be situated apart from the origin. This gives an explanation to general tendency that when a crystal grows from the melt phase, dendritic morphology is usually encountered, whereas when the same crystal grows from the vapour or solution phases, polyhedral morphology appears. Changes of * and ** positions depending on crystal size were analysed taking the Berg effect into consideration by T. Kuroda *et al.*, the results is shown in Fig. 7 (28).

In the region below * in Fig. 6, growth is controlled by the spiral growth mechanism. Spiral growth layers advance outward starting from the inner portion of a face, resulting in macroscopically flat crystal faces. Namely, this region is a region where a polyhedral crystal bounded by flat faces is expected. The normal growth rate of a face in this region is determined by the height of spiral growth layers, step separation and the advancing rate of the spiral steps. Since Tracht of a crystal is determined by relative ratio of the normal growth rates of crystal faces, and the faces with higher normal growth rates develop smaller and those with slower normal growth rate develop larger, the factors which cause variation of Tracht are the same factors which affect the step height, step separation and the advancing rate. The step height is determined by lattice spacing, the step separation is related to critical radius of two dimensional nucleation, which is related to the edge free energy and the driving force, and the step advancing rate to the edge free energy and the driving force. Therefore, we may expect that the difference of environmental phases (melt, solution, vapour phases), strength of solute-solvent interaction energies ϕ_{sf} (materials or solubilities), supersaturation, temperature, pressure and impurities are the important factors which cause variation of Tracht (27). Wells (29), in spite of not knowing atomistic models of crystal growth, summarized the observations on Tracht variation of crystals growing from solution, and pointed out the factors that might influence Tracht variation.

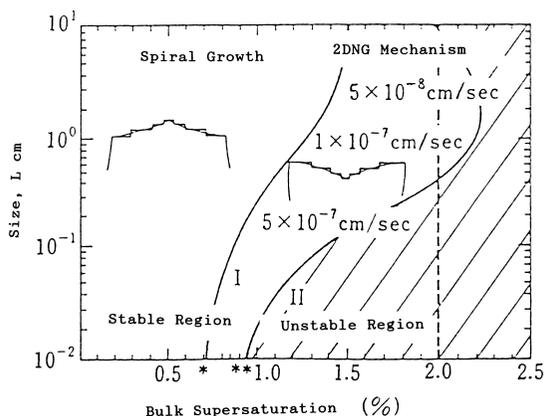


Fig. 7. Changes of * and ** positions depending on the size of crystals (28).

All the factors he pointed out are included in the above article.

The analysis is based on an assumption that the surface of a crystal is naked and in direct contact with the ambient phase, such as vapour or solution. This analysis is acceptable or applicable for the cases where Tracht change is simple, for example when a crystal changes from simple cube, via cubo-octahedron to octahedron as increasing e.g. supersaturation or impurity concentration. However, Tracht changes are not always so simple in real systems. According to the observations on snow crystals by U. Nakaya (30) and his group, polyhedral snow crystals change their Habitus from platy, prismatic and again platy and prismatic as decreasing the temperature. In the famous Nakaya's diagram, this Habitus change is seen under low supersaturation region. Under high supersaturation, hopper or dendritic snow crystals appear. Several different models to account for this repeated Habitus change shown by snow crystals have been put forward. Among these models, Kuroda's model offered a sort of breakthrough to the problem (31). Kuroda assumed the presence of quasi-liquid layer over the surface of a snow crystal whose thicknesses are different between basal and prism faces and decrease and eventually disappear as temperature decreases. Based on this assumption, he gave an appropriate explanation to the observed repeated Habitus change seen on snow crystals, which is schematically shown in Fig. 8. The presence of QLL has been proved later by ellipsometry and near surface X-ray diffraction method.

If the so-called Berg effect (supersaturation over a flat face is low at the center and high near the edges) is taken into consideration, growth layers will preferentially generate near the edges of a face and advance inward in the region between * and ** in Fig. 6. The crystal will be bounded by stepwisely depressed faces, i.e. hopper crystal will appear. Hopper or skeletal morphology commonly encountered on NaCl crystals grown from aqueous solution is a representative form of crystals expected to occur in the region between * and **. The same situation is expected when dislocation outcrops concentrate along the edges, since the advancing rate of spiral layers are high and the step separations are narrower near the edges where higher supersaturation is assumed than at the center of the face.

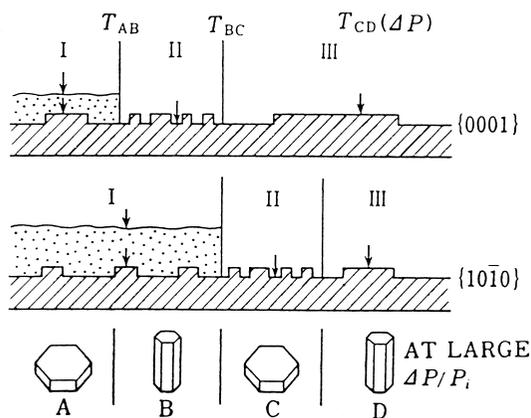


Fig. 8. Kuroda's model to explain repeated Habitus change of snow crystals depending on temperatures (31). Shaded area crystal; dotted area quasi-liquid layer.

It is interesting to note that typical Habitus are different depending on substances growing from similar aqueous solution. NaClO_3 shows polyhedral form, NaCl usually appear as skeletal crystals, whereas NH_4Cl always show dendritic form, when they grow from respective aqueous solution. The difference is due to the difference in the positions of * and **, which are related to the difference in solute-solvent interaction energy or solubility.

9. Morphological Instability

Rough interface is expected above **, in contrast to smooth interface expected in the region below **. In the region above **, the controlling growth mechanism is adhesive type, and the interface is rough and curved. The factors controlling the forms of crystals in this region is very different from those in the region below **. Morphological instability of the interface becomes important, namely whether the interfacial form is stably maintained or not during its advancement.

W. W. Mullins and R. F. Sekerka (32) solved this problem theoretically. The theory is one of the important contributions to the fundamentals of crystal growth made in this century. Interesting enough, Japanese scientists, A. Arakawa and K. Higuchi, both pupils of Nakaya first observed growing process of ice and paid attention to the problem of morphological instability seen on ice crystals. They observed circular platy ice crystals formed on the surface of water, and traced how the circular platy form lost its stability and changed to flower pattern with six pedales, and further to six branched dendritic form, although they did not treat the problem theoretically.

If curved form becomes unstable due to e.g. constitutional supercooling, and protrusions appear along the periphery, the protrusions will be exaggerated by further growth. Starting from smoothly curved parabolic or circular interface, the interface changes to cellular form, and further to dendritic form. Dendritic morphology of snow flakes which attracted

Kepler's interest now became a subject to analyse evolution of forms from the standpoint of crystal growth and morphological instability

A. Papapetrov (33) first paid efforts to observe systematically the morphology of dendritic crystals growing from aqueous solution. He distinguished two types of dendritic crystals in 1935: one showing parabolic tip and the other with a tip bounded by flat crystallographic faces. Among snow dendrites there are cases with rounded parabolic tip and with tip bounded by flat prism faces. The latter appears to be due to later growth under lower driving force condition. Figure 9 shows a snow dendrite taken by the late T. Kobayashi. It indicates parabolic tip at the main stem, but the side branches appearing near the root of the main stem are bounded by prism faces. At the root of main stem, driving force is much lower than at the tip. Transformation of rough interface at the tip to smooth interface at the root can be assumed. Theoretical interest in dendritic crystal was at first focused on understanding how dendritic pattern appears starting from parabolic curved interface. Extensive theoretical analysis, computer simulation and experimental investigation have been made in this respect in recent years. Pattern formation seen in dendritic crystals became a subject of keen interest of theoretical physics.

In the region above **, if much higher driving force is realized, the tip growth becomes so rapid that there is no opportunity that morphological instability occurs near the tip. As a result, individual crystals take strongly anisotropic needle or platy form and rapidly grow radially around a nucleus, resulting in bow-tie or spherulitic crystal aggregates. Morphology of "confits" is basically the same as such spherulites. Under much higher driving force conditions, nucleation repeatedly occur in front of the tips due to concentration fluctuation owing to nucleation, and a connected pattern appears. This corresponds to a fractal pattern, and the pattern such as shown by Mn oxide minerals formed along bedding plane of sedimentary rocks (so-called Shinobu-ishi, hare's foot fern stone) is considered to represent such a growth. The pattern of this type becomes also a subject of theoretical analysis. Patterns shown by Diffusion Limited Aggregate (DLA) is such an example. It is to be noted that dendrite is a form shown by single crystal, whereas spherulite or DLA is a form shown by aggregate of polycrystals.

As explained above, interest and understanding of morphology of crystals which started in the 17th Century, separately one on dendritic form and the other on polyhedral crystal bounded by flat faces have now advanced to the state to be seen from a unique viewpoint through the understanding of atomistic process of crystal growth. It further developed to understand forms exhibited by polycrystalline aggregate, as an extension of understanding on forms of single crystals. It has been reported recently that a series of morphological changes starting from polyhedral to fractal pattern was experimentally observed on $\text{Ba}(\text{NO}_3)_2$ crystals growing in aqueous solution. Also theoretical analysis have been reported to demonstrate changes from polyhedral to dendritic morphology of snow crystals. Both were carried out by young scientists.

Viewing various forms exhibited by crystals in a unified manner, we see another excitingly interesting problem. This is forms exhibited by organic and inorganic crystals formed through living activities.

It is well known that bone and tooth are composed of apatite crystals, and shell, pearl and coral of calcite or aragonite crystals. Magnetite single crystals are another well known inorganic crystals found in algae or cells of pigeon brain. Cocolith is composed of calcite

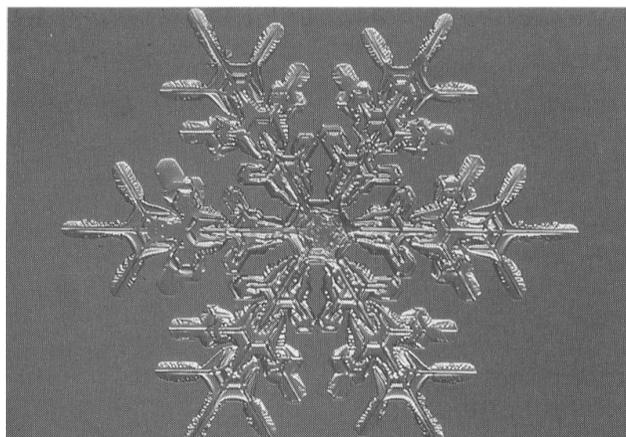


Fig. 9. Dendritic snow crystals. Photograph by the late T. Kobayashi. Note parabolic form at the tip of the main stem, and polygonal tip of side braches at the root of the main stem.

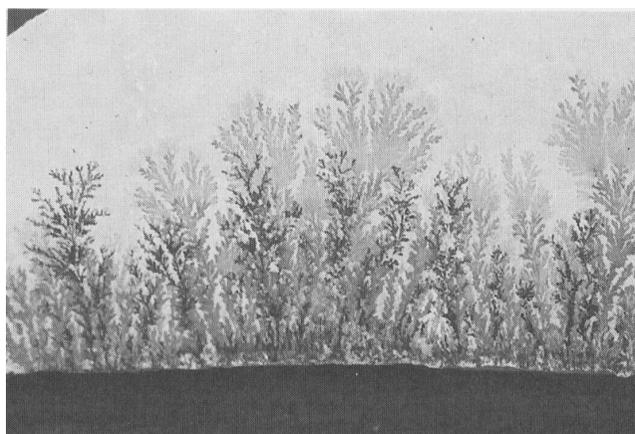


Fig. 10. Fractal pattern observed in Mn oxide polycrystalline aggregates. Shinobu-ishi.

crystals showing unusual, fancy forms, like a plaster's tool. Gall stones, kidney stones and stones formed in various organs are also crystals. Various crystals are formed in the cells of plants, such as dahlia and begonia.

It is said that magnetite crystals in the cells of pigeon brains or dolphine play an essential role in functioning their behavior and movement, so as magnetite crystals in algae. Various inorganic and organic crystals are being produced through living activities, either due to absolute necessity for their living or secretion process of unnecessary compounds for living. Observing morphological characteristics of these crystals, one notices an

interesting difference between the two.

Inorganic crystals which are formed as an activity absolutely necessary for the living of the species usually show uniform forms or regular texture, whereas those formed in organs or plant cells as a result of secretion of unnecessary material usually show spherulitic form. In the former case, crystallization of inorganic compound occurs through co-operation with protein, through which the size and form of inorganic (or organic) crystals are well controlled. In the latter case, there is no such co-operation, and the crystals grow freely, resulting in spherulitic aggregates of polycrystals.

Aragonite crystals in pearls and shells show regular platy form, with equal thickness and size, sandwiched by protein membrane. Inorganic crystallization occurs within a mold of protein membrane. This controls the thickness, size and texture of aragonite crystals. To provide the mold, protein membrane or membranes are at first formed in front of the growing surface, before inorganic crystallization takes place. The numbers of membrane layers are different depending on the species, and positions in the shell, which results in different textures depending on the species, and the portions in the shell. Similar organic and inorganic co-operation is noticed in the formation of apatite crystals in tooth. Based on this view, it is anticipated that magnetite crystals in the brain cell of pigeon and dolphine belong to the former type, since they show well-formed cubo-octahedral habit. It appears that there is no boundary between livings and non-livings from the standpoint of growth and forms of crystals.

10. Concluding Remarks

As compared to rapid progress achieved since 1912 in the analysis of crystal structure, it was only after 1930 that the understanding of crystal growth mechanisms at atomistic level started. However, both have their roots in the curiosity in the 17th Century on a wide variety of forms that crystals exhibited.

Most people will imagine from the word of crystal growth, semiconductor crystals like silicon and gallium arsenide or synthetic gemstones. The success in these industries has been achieved through deep understanding of atomistic process of crystal growth and defect formation. We should however remember that the recent days achievement in obtaining and utilizing highly perfect single crystalline materials to improve the quality of our life has its root in pure curiosity on the origin of various forms of crystals. This curiosity creates another new curiosity in the present days, even after three centuries. Problems relating to forms of crystals are closely related problems to biological activities, formation and changes of solid materials in the Earth and Planets. We may decipher letters sent from the depth of the Earth or from the Space, and also written in the living bodies, by properly understanding the origin of forms and their variations of crystals. No more pages, regrettably, are left to discuss these problems. So I shall conclude this article by citing two phrases by the late Sir Charles Frank.

“If one could understand enough about the morphology of crystals, he understood essential points of fundamentals of crystal growth”.

“Diamonds are letters sent from the depth of the Earth. They are letters conveying more interesting information than snow flakes which are sent from the sky. We can not reach the depth of the Earth”.

11. Postscript (added when the article was published in a book form (2))

Naive questions started in the 17th Century asking why the same crystal species like snow flakes and rock-crystals can take multifarious forms have now been advanced to a state that an answer can be given in terms of atomistic process of crystal growth at least for simple systems, through the advancements achieved in this century in understanding crystal growth mechanisms. It appears to me, however, that recent investigations have been too much focussed on the phenomena occurring at solid liquid interfaces, neglecting the effect of ambient phases. It is an appropriate time to pay more attention on the phenomena involved in ambient phase as well.

Deepening the understandings on atomistic process of crystal growth has contributed much not only to the fundamentals of crystal growth but also to the industries utilizing three or two dimensional crystalline materials. The research activities in the science and technology of crystal growth appear to be a good example that both fundamentals and applications, or theory and experiment co-operate very well, holding a good relation and enjoying mutual benefits, like two wheels of a cart.

In the investigation of crystal growth during the 20th Century, it was not felt absolutely necessary to introduce quantum mechanics. However, there are fields where investigations based on quantum mechanical analyses are required. Epitaxy has now advanced to atomic layer epitaxy or molecular beam epitaxy, enabling to control quality of two dimensional crystals to be used as various electronic devices, including quantum well devices. In these fields, investigations based on quantum mechanics will play important role. There is no doubt that one of the targets of future researches on crystal growth is along this direction. However, there are many problems to be solved or to be answered in complex and complicated systems, based on the knowledge obtained during the 20th Century on simple systems. I believe this is another target of researches of crystal growth in the 21st Century to give effort to solve the problems of forms and textures exhibited not only by single crystals but also by polycrystals in the complex and complicated systems.

Let me give some examples closely related to our daily life. The physical properties of metals, ceramics, or composite materials are determined by their texture, not only by the properties of components alone. Even if a material is composed of soft materials, unexpected toughness appears owing to its texture. Bamboo is a good example, yet we still have not learnt enough the wisdom that bamboo possesses. It is also known that superplasticity appears by controlling the size of particles. There are so many cases to possibly create new functions by controlling the texture. It is clear that the textures in inorganic systems are determined by nucleation and morphology of crystals. These are direct subject of the science of crystal growth. Although mechanism and process of crystal growth in simple systems have become understandable at atomistic level, we are still far behind in evaluating the texture formation properly and understanding their mechanisms, and further freely controlling them in complicated and composite systems. There may be a few engineering trials to create new functions by controlling the textures, it has not been well established to understand the mechanism from the fundamentals. It is due to this that my expectation that another target of researches of crystal growth in the 21st Century is present along this line.

In the living world which is representative of complicated and complex system,

specific function of respective organs is due to respective textures. Is it impossible to see the phenomena in the living world along the extension of understandings achieved in the inorganic simple system? Or, is there absolute discrepancy between the living and non-living worlds? There are a variety of inorganic crystals formed by living activities, such as apatite in tooth and bones, aragonite and calcite in shells, magnetite in algae and pigeon brain. Inorganic crystals absolutely necessary to living activities grow through cooperation with protein, or the texture is controlled by protein membrane. Inversely, there are recent trials to control the texture of inorganic materials by using protein membrane. Also, epitaxial growth of polymer and protein crystals on inorganic substrate have been investigated recently. All these should be a subject of researches in the 21st Century, as an extension of understandings of crystal growth mechanism achieved in the 20th Century. Movement along such a line has already started. Important point is to create atmosphere to see with consistent eyes, independently of the boundaries between living and non-living worlds.

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