On the Terminology of the Phenomena of Mutual Crystal Orientation

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A system for designation of various types of mutual orientation of crystals and the processes during which they are formed is proposed. The neutral terms *oriented overgrowth, oriented intergrowth* and *oriented inclusions*, and in special cases *polycrystal* and *single-crystal films*, are considered to be sufficient for describing the fact of regular joint growth. As interpretative and genetic, four basic terms are submitted: *epitaxy* – for oriented growth of a phase on the crystal surface of another phase; *syntaxy* – for simultaneous growth of the mutually oriented crystals of two or more phases; *topotaxy* – for oriented transformation in an open system with a partial alteration in chemical composition of the primary crystal; and *endotaxy* – for oriented transformation in a closed system, without exchange of components between the system (primary crystal) and its environment. For a later oriented overgrowth of crystals of one and the same phase (in parallel or twin position) it is possible to use the term *autoepitaxy*.

The phenomena of regular mutual orientation of crystals of various substances have a wide-spread occurrence and have drawn considerable attention recently. However, the terminology of these phenomena is still rather vague and the terms used by various authors have no strict conventional meaning. In the present paper an attempt is made to compile and substantiate a system of terms to serve for the designation of the various processes of formation of mutually oriented crystals. It is made on the basis of terms which have already been suggested and more or less widely used. The phenomena covered by each of these terms are also specified.

The mutual regular crystallographic orientation of crystals of two (sometimes more) phases sharing a common surface arises in the process of their simultaneous or successive crystallization. This gives reasons for calling such a process *oriented crystallization* or *oriented crystal growth*. The orientation can be formed either during the crystallization, from gas or liquid (solution or melt), or during crystal growth taking place in a solid single-crystal medium as a result of chemical reactions and transformations.

The mutual orientation of the crystals of the various phases is strictly fixed in space and has no degrees of freedom. The regular orientation is assumed to be conditioned and controlled by the structural analogy between the crystalline phases and, consequently, is crystallochemically determined.

Cases in which the orientation has one degree of freedom are also known. Such are, for example, the axial textures (with one vector in parallel position in each of the intergrowing crystals), which are regarded by Bliznakov (1965) as an epitaxy of the first type to be distinguished from the classical epitaxy called by him epitaxy of the second type. Axial textures are formed through crystallization on structureless substrates or under the influence of various fields of forces (for example, gravitational, magnetic) *etc.* These textures,

however, display only a partial orientation, usually between crystallites of one and the same phase, and are not a result of any crystallochemical interaction, because of which they will be not discussed in greater detail.

As pointed out by Bernal & Mackay (1965), two kinds of terms are needed for designating the various types of mutual orientation of crystals and the processes during which they are formed.

1. *Observational* terms. These are employed to designate the mere fact of the regular orientation without any reference to its genesis. The neutral terms *oriented overgrowth, oriented intergrowth* and *oriented inclusions* are fully adequate for the purpose. In special cases, the term *polycrystal* (Donnay & Donnay, 1953) is suitable for designation of an edifice composed of two or more structurally distinct species in regular intergrowth and simulating a single crystal. The term *oriented single-crystal films* has also been widely used recently, but its use in the cases where the deposit consists of spatially separated crystallites is not justified. All these terms describe the spatial arrangement of the phases and the character of the composition surface.

2. *Interpretative* terms – employed for the explanation of the joint growth. Moreover, they should also reflect the temporal relationship between the different species and the manner of formation of the orientation, *i.e.* they should also be *genetic* terms. Accordingly, four basic genetic terms may be suggested: *epitaxy, syntaxy, topotaxy* and *endotaxy*. They may be defined in such a way as to cover the whole variety of spatial, temporal and quantitative relationships in the phenomena of this kind of crystallization.

Epitaxy

This term, in the sense introduced by Royer (1928), is most widely used. In *epitaxy* the crystals of one phase (guest crystals) grow on the surface of a crystal of another phase (host crystal) in one or more strictly de-

fined crystallographic orientations. The two species crystallize one after the other.

The particular case of oriented overgrowth of a phase on the surface of a crystal of the same phase (in parallel or twin position) is designated as *autoepitaxy*.

The use of the term epitaxy in a wide sense for designating regular joint growth and oriented inclusions regardless of their genesis and structure cannot be considered suitable.

The reticular control of epitaxic orientation in most cases is characterized by a two-dimensional structural analogy between the two species in the plane of junction ('dipériodique épitaxie' of French authors). However, cases of one-dimensional control are also known (Seifert, 1940; 'monopériodique épitaxie' according to Royer, 1954, and Monier, 1954). In these cases various crystal faces belonging to the zone of the row of atoms along which there is a structural correspondence, can serve as substrates. There is another, intermediate, case in which a certain structural correspondence exists in one direction while in yet another the analogy is vague ('1- bis 2-dimensionale Gitteranalogie', 'partielle Netzebenenanalogie' of Neuhaus, 1952; 'hypodipériodique épitaxie' of Monier, 1954). Of particular importance are the cases of three-dimensional lattice analogy ('tripériodique épitaxie') between the two species (for example, Si and Ge, sphalerite and chalcopyrite) in which an epitaxic overgrowth with mutually parallel axes is possible on every face of the host crystal.

Syntaxy

Ungemach (1935a) has introduced the term *syntaxy* in order to describe the complex oriented intergrowth of coquimbite and paracoquimbite crystals. This term 'désignera une épitaxie spéciale, épitaxie de deux corps chimiquement identiques et cristallisés simultanément avec alternances et faciles passages de l'un à l'autre de deux réseaux différents'. Ungemach (1935a, b) has pointed out that these two polymorph modifications grown jointly with mutually parallel axes have strictly rational ratios of cell edges. Other similar cases of syntaxic growth discussed by Ungemach are observed in the polytypes of SiC, *etc*. Disregarding the restriction of chemical identity, Donnay & Donnay (1953) widen this term, using it also for constituent substances that are chemically different and have corresponding cell edges. The syntaxic intergrowths of the rare-earth carbonates, bastnaesite, parisite, roentgenite and synchysite studied by them are of this kind. Other authors, Rimsky (1960) for example, use this term in a similar sense.

In the cases of syntaxic intergrowths studied so far, there is a three-dimensional structural analogy between the two phases. As in the case of epitaxic overgrowth with mutually parallel axes, the presence of such an analogy makes intergrowth along every pair of corresponding planes possible. However, the morphology of intergrowths shows that in fact the lattice control of the mutual orientation is effected by definite closely packed crystal planes and is of two-dimensional character. In coquimbite–paracoquimbite intergrowths for instance the controlling role is played by the (0001) planes which in most cases bound the alternating lamellae of the two mutually oriented species. The (0001) planes play the same role in bastnaesite–parisite–synchysite intergrowths. In a number of cases the contact surface of the two species has a complex configuration. Taking into account layer-by-layer growth of the crystals, it may be assumed that the greater part of this uneven composition surface has not played any active orienting role during the crystallization. Hence, it can be assumed that a three-dimensional analogy between the jointly growing phases is not necessary; a two-dimensional analogy, for instance, may suffice.

All the above considerations justify the use of the term *syntaxy* in a purely genetic sense – for the designation of the simultaneous growth of mutually oriented crystals of two or more phases ('syngenetic epitaxy'). The crystallochemical correspondence between the two species sharing a common surface determines the mutual orientation of their crystals. (The cases of oriented transformations in single-crystal media which control the orientation are not included in syntaxic processes.) This concept is close to the initial definition of Ungemach who several times emphasized the simultaneous formation of syntaxic intergrowing species. In the genetic sense here accepted the term syntaxy acquires an extended meaning, including however all previously described cases mentioned above. In a similar way the term is also employed by Grigor'ev (1965). Obviously, such an interpretation of the term rules out its utilization as a neutral, descriptive one, as proposed by Bernal & Mackay (1965).

The relative quantities and the arrangement of the intergrowing phases may be different. When one of the phases (guest) is considerably smaller in amount, it forms oriented inclusions in the crystals of the other phase (host). The inclusions can be deposited continuously or periodically depending on the physicochemical conditions (degree of supersaturation). The inclusions are syngenetic with respect to the host crystal and, their designation as syntaxic (not epitaxic) is most suitable.

A variety of oriented intergrowths can be formed when the two phases are present in more or less equal amounts. Eutectic syncrystallization is often (but not always) of this kind (Kerr, 1969).

An interesting example is presented by the crystals which have zonal structure (some 'bravoites' for instance) built up of parallel alternating zones of two or more phases which have different chemical compositions but similar structures. These present a three-dimensional analogy. The individual zones with sharp boundaries between them are deposited one after the other. This repeated epitaxy may be considered as syntaxy with regard to the formation of the whole polycrystal edifice as pointed out by Ungemach earlier for similar

cases. In such a way epitaxic growth may became syntaxic.

The formation of primary twins during the joint growth of several mutually oriented crystals of one and the same phase may be treated as a special case of syntaxy.

Topotaxy

An important case of formation of mutually oriented crystals is presented by the oriented transformations taking place in the bulk of the crystalline substance as a result of solid state reactions and characterized by a regular crystallographic orientation of the products obtained with respect to the initial crystal. To designate these phenomena, the term *topotaxy*, introduced by Lotgering (1959), is used widely. The transformation may take place in a closed physicochemical system, without any exchange of components with the surrounding medium, or in an open system, when an exchange of components does take place. Although most authors do not distinguish between these two cases (Bernal, 1960; Dent Glasser, Glasser & Taylor, 1962; Kleber, 1962; Shannon & Rossi, 1964, and others) it is necessary to draw a line between them since they take place under considerably different conditions.

It seems appropriate to use the term *topotaxy* for the oriented transformation of a crystalline substance taking place in an open system with a partial alteration of its chemical composition as a result of topotaxic (Lotgering, 1959) topochemical reactions. As early as 1956, Kostov (1956) defined these phenomena as epitaxic replacement. The term *endotaxy* is suitable for the cases of oriented transformation in a solid medium where there is no exchange of substance between the system and its environment.

Bernal (1960) considered the retention of all or part of the crystallographic symmetry axes of the initial crystal in the final product as the main specific feature of topotaxy. In accordance with this formulation, Shannon & Rossi (1964) and Shannon & Pask (1964) introduced the idea of high degree topotaxy (with preservation of all or at least one of the symmetry axes) and low degree topotaxy (without preservation of the symmetry axes). They proposed that the experimentally established degree of orientation be used for classifying the topotaxic transformations. Actually, the orientation during the replacement is determined by the concrete structural–dimensional relationships and can be perfect even when the crystallographic axes are not preserved. Such a case is the johannsenite–bustamite transformation where $[012]_j//[11\bar{1}]_b$ are the only parallel directions (Morimoto, Koto & Shinohara, 1966) as well as the anatas–rutile transition (Shannon & Pask, 1964). On the other hand, the degree (*i.e.* the perfection) of the orientation and even the law of orientation obtained during one and the same reaction can be different depending on the concrete physicochemical conditions (presence of water, supersaturation, *etc.*)

Consequently, as pointed out by one of the referees

'Bernal's (1960) ideas on preservation of symmetry axes are sterile; they give the wrong emphasis to symmetry control (instead of the well established lattice control) of the mutual crystal orientation. Shannon's distinction of 'degrees' in topotaxy is misleading: it would probably be better applied to the mutual orientation than to the topotaxy, whose specific feature is the intervention of a solid state reaction'.

The presence of a three-dimensional correspondence between the initial crystal and the product of its transformation is an important specific feature of many of the cases of topotaxy and endotaxy but in principle it is not an obligatory condition since the transformation can also take place if only a two-dimensional or even a one-dimensional correspondence exists (Guenter & Oswald, 1969, 1970).

In a number of cases the replacement begins from the surface (surface topotaxy according to Bernal & Mackay, 1965) and proceeds inward into the bulk of the crystal, which distinguishes sufficiently clearly this process from epitaxy where the growth proceeds from the surface outward. Atoms from the substrate can diffuse into the transitional epitaxic layer, being included in the composition and, in some cases, ensure a coherent transition between the two structures ('hemoepitaxy' according to Čistjakov, Schneider & Weinhold, 1969).

Topotaxy in the more restricted sense accepted here includes almost all cases to which it has been applied so far (exsolution, for example, has almost never been described as a topotaxic process) and for that reason an introduction of a new term to compensate for this restriction is not necessary.

Endotaxy

The term *endotaxy* was introduced by Palatnik & Papirov (1964) to designate the processes of oriented segregation taking place in the bulk of a given crystal but it does not allow for the clear distinction between these processes and the topotaxic ones. In this sense the term is used by Čistjakov *et al.* (1969) who, however, designate the formation of mutually oriented crystals by chemical reactions as ' hemoendotaxy'.

The phenomena of endotaxy, in the sense accepted here, take place under conditions where an energy (but not substance) exchange can only exist between the system (the primary crystal) and its environment, expressed in changes of temperature and pressure.

The phenomenon of endotaxy includes the following:

(1) Exsolution during disintegration of solid solutions and alloys where the inclusions of the new phase are oriented regularly with respect to the matrix.

(2) Decay of unstable phases with a formation of oriented eutectoid intergrowths.

(3) Oriented polymorphic, allotropic and polytypic transitions which can be either transformations of one structural type into another (for example, the α–β quartz inversion, the martensitic transformations, the

SiC 2*H* and 3*C*–6*H* transitions *etc*.) or order–disorder transitions.

Some oriented transitions are connected with minor changes in the composition (for example, hexagonal–monoclinic pyrrhotite, probably marcasite–pyrite) and probably they should not be considered as endotaxic but as topotaxic. *Sensu stricto*, if the substances do not have identical composition they cannot be considered as polymorphs either.

The first two cases of endotaxy are usually connected with diffusion processes leading to a redistribution of the substance in the bulk of the initial crystal and to formation of new phases which are stable (or metastable) under the given conditions. The last type of transformation normally takes place without diffusion, through negligible displacement of the atoms, and has cooperative character, the composition of the separate parts of the primary crystal being preserved while the structure is modified.

The formation of secondary twins through deformation can be considered a special case of a diffusionless endotaxic alteration which, however, is not connected with any phase transformation.

Genetic terms and lattice control

As has already been pointed out, the mutual orientation of crystals is normally crystallochemically determined, *i.e.* it is related to a certain correspondence between rows, nets or lattices. Accordingly it is said that there is one, two or three-dimensional reticular control on the orientation. The descriptive designation of the lattice control (for example, one-dimensional epitaxy) is sufficient and the use of other special terms for this purpose is hardly necessary. All other characteristics may also be given in a descriptive way. In this sense it seems unsuitable to use the terms epitaxy and syntax not as genetic terms but only for the designation of the type of the lattice control, two- or three-dimensional respectively, as suggested by Donnay (1971). Such an interpretation of the term epitaxy does not correspond to its general use for designation of the process of oriented overgrowth on a crystalline substrate. On the other hand, this is not quite correct either, since epitaxy is not necessarily related to a two-dimensional control alone. Similar considerations hold true for the term syntax which if restricted to three-dimensional control only, should, strictly speaking, not be applied to the greater part of the intergrowths for the description of which it was introduced.

Thus, it seems reasonable to use the cognate terms, epitaxy, syntax, as well as topotaxy and endotaxy as genetic terms without specifying the type of lattice control but without dismissing it either. This makes it possible to designate briefly and definitely the various processes of formation of the mutually oriented crystals. Thus, for example, the oriented inclusions and intergrowths of chalcopyrite in sphalerite and *vice versa* could be the result of topotaxy, endotaxy or syntax, and it is by no means unimportant to specify their actual genesis.

The individual genetic terms are not subordinate to each other since they describe different phenomena.

Other terms

A number of similar terms are found in literature which, however, have not gained wide currency at the present. They are synonyms of the terms discussed above or have a broader and not always definite meaning because of which they are to be avoided. Such are, for example, the terms metataxy (=topotaxy) (Bernal, 1960); heteroepitaxy (=epitaxy), hemoendotaxy (=topotaxy) and others (Čistjakov *et al.*, 1969); entaxy – any regular oriented intergrowth of two species (Friedlaender, 1970); homoepitaxy (=autoepitaxy); heterotaxy and homeotaxy – crystal growth with oriented heterogeneous or homogeneous nucleation respectively (Kleber, 1962, 1964).

The terms *anomalous mixed crystals, partial-isomorphic mixed systems* (Spangenberg & Neuhaus, 1930; Seifert, 1935, 1936, 1937) and *adsorption mixed crystals* (Kleber, 1959) are also closely connected with the question discussed. It has recently been accepted (Kleber, 1959; Kern, 1968) that these crystals include adsorption two-dimensional compounds (layers) of some admixture substances which are formed under the conditions of very low concentration (subsaturation) insufficient for the formation of an individual phase and selectively deposited on certain crystal surfaces as a result of a definite crystallochemical similarity. In many cases, however, it is established by optical or electron microscopy, X-ray diffraction and other methods that these are in fact heterogeneous two-phase systems containing separated three-dimensional oriented inclusions of an additional phase. Therefore their incorporation in the group of the anomalous mixed crystals is not justified. In such a case, the syngenetic oriented inclusions should be considered a result of syntax ('primary anomalous mixed crystals' of Seifert) and the epigenetic ones – a result of endotaxy ('secondary anomalous mixed crystals' of Seifert) or topotaxy. This concept does not exclude the existence of adsorption mixed crystals in the sense accepted by Kleber and Kern.

In the processes of epitaxy, syntax, topotaxy and endotaxy several symmetrically equivalent orientations of the growing or replacing phases are often possible, because of which the individual crystals of the phases may happen to be in a twinned position with respect to each other, too. Since this secondary twinning is not a special case of crystal growth but is only the result of some of the types of oriented crystallization discussed above, it is not necessary to designate it by special terms.

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On the Interpretation of Anisotropic Temperature Factors

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A lattice-dynamical formulation of the anisotropic vibration tensors of the atoms in a crystal is presented which may contribute to a better understanding of how the interatomic thermal coupling is expressed in the anisotropic temperature factors.

Introduction

In many instances the atoms in a crystal are linked by strong forces so that one may expect the thermal motions of the individual atoms to be coupled. An obvious example is given by the rigid-body motions of largely rigid molecules. The Debye–Waller factor, however, only refers to one particular atom and there are no cross terms in the expressions for the structure factor and the Bragg intensity which would explicitly account for the coupling of the thermal motions of different atoms in the unit cell. On the other hand, the good results obtained with many molecular structures, which have been refined with thermal rigid-body parameters, show that the Debye–Waller factor is appropriate in its present form. This means that the coupling of the thermal motions of different atoms in the crystal is correctly accounted for by the structure factor and thus by the Debye–Waller factors of the individual atoms. How does this take place?

In the historical context our problem may be pictured as follows. In 1913 Debye derived the temperature factors by assuming that the motions of the different atoms in the crystal are not coupled. After becoming acquainted with Born & von Karman's (1913) paper on the dynamics of crystal lattices, in which the interatomic forces were taken into account, Debye (1914) derived the temperature factor anew. The surprising result was that the temperature factor for the Bragg intensities did not change its form [cf. James (1948), the derivations in Chapters I, 3b and V,1]. On the other hand, Faxen (1918) was able to show that the expression for the thermal diffuse scattering changed pronouncedly by introducing the interatomic forces