DISLOCATION-FREE GROWTH OF REAL CRYSTALS AS A RESULT OF THE LONG-RANGE ACTION OF LOCAL ACTIVE CENTERS

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Abstract

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DISLOCATION-FREE GROWTH OF REAL CRYSTALS AS A RESULT OF THE LONG-RANGE ACTION OF LOCAL ACTIVE CENTERS

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The solution of the problem of crystal formation under conditions of weak supersaturations and finite time intervals, when fluctuation theories of crystallization based on two-dimensional nuclei are inapplicable, was found in the mechanism of spiral growth at the front of a screw dislocation ([1,2]).

The dislocation theory of crystal growth proceeds from the existence of a real defective crystal; however, only one type of defect—screw dislocations—is taken to be responsible for nucleation and growth. Indeed, numerous experimental proofs of the existence of spiral growth have been obtained ([3]), and at present only the concepts of dislocation theory are used to explain the occurrence and growth of nuclei under conditions in which, it would seem, layer growth—requiring either considerable supersaturations or geological intervals of time for its realization—is completely excluded.

In the literature, however, numerous examples are given of layer growth of crystals under conditions of small supersaturations of solutions or slight supercoolings of melts, in the absence of any experimental data on the existence of screw dislocations on the surface of these crystals ([4–8]). In these cases, the observed crystallization patterns are explained by assumptions concerning the possible interaction of pairs of screw dislocations of opposite sign, leading to the extinction of growth spirals. The absence of dislocations is also explained by their migration from the surface of crystals during cleavage, or by admitting the existence of dislocations with small Burgers-vector values, the observation of which is difficult. It is hard, however, to imagine that all dislocation spirals accessible to observation would thus be excluded. In other words, for many cases of layer growth the dislocation mechanism is essentially postulated as the only mechanism capable of explaining crystal growth at small supersaturations or slight supercoolings. A number of works have already pointed out the inadvisability of the universal application of dislocation theory to the growth of real crystals ([8–10]).

Nucleation on the surface of crystals is obviously a particular case of surface processes in general, which include adsorption, catalysis, adhesion, the electrophysical properties of surfaces, etc. All these processes cannot be explained solely by the existence on the surfaces of solids of emergence points of screw dislocations, as is done in the dislocation theory of crystal growth. Surface processes, including crystal growth, can, however, be treated from general points of view if one is guided by the concept of the existence in crystals of local active centers.

The growth of crystals at small supersaturations without the obligatory presence of screw dislocations finds a simple and natural explanation when one takes into account the effect of the long-range action of local active centers on the surfaces of solids, which makes possible elementary acts of crystallization at sufficiently large distances from the centers, as was experimentally established and examined in detail in works by one of the authors ([11]-[13]). Nucleation occurs selectively at active centers—surface defects that are mainly aggregates of vacancies, interstitial and impurity atoms—which possess excess free energy in comparison with neighboring perfect surface regions. It was shown experimentally that, on the surface of single crystals, through fairly thick (500–2000 Å) intermediate amorphous layers, oriented crystallization takes place both at local places on the surface (a spatially separated mosaic single crystal ([13], [14])) and in the form of continuous layers ([15], [16]).

Oriented overgrowth through amorphous intermediate layers is indisputable proof that the microgeometry of the surface (microsteps, places where dislocations emerge) may not play a decisive role in nucleation, since in this case the geometrical factor is completely excluded. The microgeometry of the surface apparently manifests itself in most cases through the action of the local active centers that accompany it. Oriented crystallization at active centers by a long-range mechanism shows that the active centers themselves are built rather regularly and possess a definite symmetry. It follows from the long-range mechanism of crystallization that nucleation at active centers should be regarded not as a purely heterogeneous process but as a heterogeneous–homogeneous volumetric process, solving the problem of the appearance of steps both directly on the growing surface and at finite distances from it. Therefore, the spiral growth of real crystals, for which contact interaction of atoms or molecules with the crystal surface is necessary, is not the only possible and certainly not the obligatory mechanism. Moreover, dislocations are thermodynamically nonequilibrium, whereas point defects and their aggregates (active centers) are thermodynamically equilibrium and are necessarily present in all crystals.

In light of the long-range influence of active centers, the pictures—observed by various methods—of growth steps regularly alternating on the surface of crystals without traces of a spiral structure ([4]-[8]) become entirely understandable. Moreover, these pictures, demonstrating the role of long-range active centers as initiators of nucleation, acquire great cognitive significance and independently lead to very important conclusions previously expressed from other considerations in Ref. ([17]).

Indeed, for the formation of growth pyramids consisting of successive steps of approximately equal width, several conditions must be fulfilled. First, the successively growing steps must arise in separate regions of the surface under the influence in each case of a single active center, which may be located directly on the surface or in some near-surface layer and acts through the entire set of already formed steps. Let us note that the formation of microsteps with widths of tenths of a micron and less is possible only with very high locality of the active centers. Second, the active center must not be inactivated during the elementary act of crystallization. Finally, third, the initial moments of crystallization of successive steps must be separated by equal or nearly equal intervals of time.

The indicated conditions for layered growth by a long-range mechanism, as already mentioned, are convincingly confirmed experimentally. It is precisely the local active centers, revealed by methods of chemical and electrical decoration on the surfaces of many crystals studied (mica, quartz, rock salt, sodalite, silicon, etc.), that are the sites of selective nucleation ([13,18,19]). A high density of active centers should lead to superposition and mutual overlap of growth pyramids, i.e., to complex patterns of layered growth. Active centers—mainly aggregates of point defects—on the surface of crystals (as well as in the volume) are formed by a fluctuation mechanism. During growth, new structural defects arise at various places on the growing surface; these begin to play the role of initiators of nucleation. Inactivation of active centers during crystallization can occur only as a result of exchange electron reactions.

However, in most cases crystallization proceeds without electron exchange between the crystallizing substance and the active centers of the surface and, consequently, without their inactivation, which preserves the long-range influence of the centers. The experimentally established long-range influence of active centers at distances on the order of 1000–2000 Å makes possible the formation of 200–250 layers, 7–10 Å thick, under the action of a single active center.

The observed uniform alternation of growth steps in itself testifies to the rhythmicity of crystallization processes. The frequency of step formation evidently depends, on the one hand, on the activity of the crystallization center and, on the other hand, on the degree of supersaturation of the solution (supercooling of the melt). Naturally, the width of the steps is proportional to the growth rate in the corresponding direction. In ([17,18]), at the electron-microscopic level, a microlayered distribution of defects was experimentally established as an obligatory factor, indicating the rhythmic (possibly self-oscillatory) character of crystallization processes.

In the particular case of crystals with a layered structure, the elementary layers are the growth steps of minimum height. If the growth steps have a height greater than one layer and this is not caused by other factors—for example, polytypism or polymorphism—then, as is evidenced by the fine structure of certain growth pyramids, in the system growing crystal—melt (solution) there exists a set of different types of oscillations, causing alternation both of steps and of elementary layers within the steps. Such alternations are effectively revealed in patterns of gold decoration of the surface of layered crystals observed in the electron microscope ([6,7]). It may be assumed that at low supersaturations of the solution or slight supercooling of the melt, steps of comparatively large width and one-layer height are formed. As the degree of supersaturation (supercooling) increases, the width of the steps decreases. At a high frequency of formation of successive layers, the growth process may become nonuniform because of local changes in supersaturation. This should lead to the formation of packets of layers separated by comparatively large flat areas, which reflects modulation of the principal oscillation by another (or other) oscillation with a lower frequency.

Thus, a new mechanism has been proposed for the dislocation-free growth of real crystals, based on the existence of local active centers—initiators of nucleation—which possess a long-range influence and are not inactivated during the elementary act of crystallization. This mechanism of growth of real crystals explains many phenomena of layered growth from solutions and melts (without the necessity—

of the presence of screw dislocations (or of another geometrical microrelief of the surface), and leads to the conclusion that crystallization processes are rhythmic.

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