

Adsorption Mechanisms of the Nonequilibrium Incorporation of Admixtures in a Growing Crystal

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Received June 13, 2006

Abstract—The nonequilibrium partition of components between a crystal and solution is mainly controlled by impurity adsorption on the surface of the growing crystal. The specificity of adsorption on the faces of various simple forms leads to the sectorial zoning of crystals. This effect was studied experimentally for several crystallizing systems with different impurities, including isomorphous, 2d-isomorphous, and nonisomorphous, readily adsorbed impurities. In all systems, the sectorial selectivity of impurity incorporation into host crystals has been detected with partition coefficients many times higher than in the case of equilibrium partition. Specific capture of impurities by certain faces is accompanied by inhibition of their growth and modification of habit. The decrease in nonequilibrium partition coefficients with degree of oversaturation provides entrapment of impurities in the growing crystals. Thereby, the adsorption mechanism works in much the same mode for impurities of quite different nature. The behavior of partition coefficient differs drastically from impurity capturing by diffusion mechanism.

DOI: 10.1134/S1075701507080156

INTRODUCTION

The partition of the components between a growing real crystal and a solution is always a nonequilibrium process. The actual (effective) partition coefficient K_{ef} can differ from the equilibrium coefficient K_0 by as much as several orders of magnitude. Moreover, the former coefficient may be different for the growth sectors of various simple crystal forms, which results in a sectorial inner structure of the crystal, a phenomenon that is extremely widely occurring among mineral crystals. The behavior of K_{ef} is controlled by the extent of the deviation from equilibrium or oversaturation $\Delta\mu$. However, the relationships between K_{ef} and $\Delta\mu$ are ambiguous and are largely controlled by two processes: the diffusion of admixtures in the medium around the crystal and their adsorption on the crystal surface. The role of the diffusion processes in the segregation of the component during the growth of crystals is known well enough (*Modern...*, 1980): these processes determine the tendency of K_{ef} toward unity at an increasing oversaturation (growth rate of the crystal). Therefore, the actual growth rates of the faces of different simple forms in natural and synthetic crystals may merely account for insignificant differences in the K_{ef} of these crystal faces (see, for example, Reeder and Grams, 1987; Punin et al., 1999b). Because of this, the diffusion effects do not play a very significant role during the nonequilibrium incorporation of admixtures by a crystal and the development of its sectorial zoning. The main reasons for the nonequilibrium composition and sectorial heterogeneity of crystals are adsorption effects (Lemlein, 1973, pp. 26–47; Shearer and Larsen, 1994). However, the adsorption-controlled

crystallization of the components is still understood very poorly (Watson, 1996) and is equally poorly examined experimentally. It is unclear as to which values can be assumed by the effective partition coefficients and how they can differ for admixtures of different types. The problem of the influence of the crystallization conditions on the adsorption incorporation of admixtures is very intricate and largely obscure. First and foremost, this pertains to such an important factor as the oversaturation of the crystallization medium. There is still no consensus concerning the possible dependence of the intensity and sectorial selectivity of admixture incorporation on the oversaturation (or growth rate): some researchers (Hollister and Gancarz, 1971; Watson, 1996; Tauson, 2005) believe that both phenomena are intensified with a greater deviation from equilibrium, others (Khaimov-Mal'kov et al., 1962; Grigor'ev and Zhabin, 1975; Downes, 1974) maintain that they, conversely, weaken, and there is the opinion (Reeder and Grams, 1987; Shearer and Larsen, 1984) that there is no correlation at all between them and the growth rate. None of these opinions has, however, received convincing argumentation, and all of them are underlain mostly by results obtained on natural crystals.

This publication summarizes the results of our experimental studies and still scarce available literature data on the adsorption incorporation of admixtures by growing crystals. Because most of the data discussed below were previously published in separate papers, we do not present here any descriptions of the experimental procedures, conditions, or specifics of the experiments, but only give references to the corresponding papers.

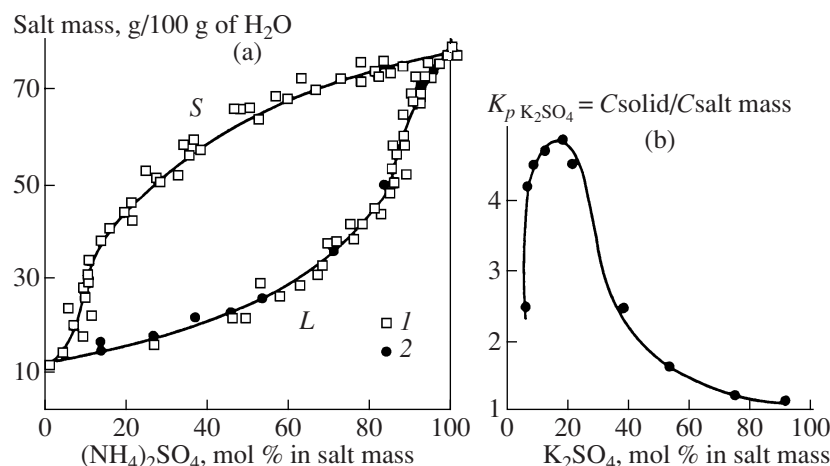


Fig. 1. Phase equilibria and admixture incorporation into crystals in the system K_2SO_4 – $(NH_4)_2SO_4$ – H_2O . (a) Solubility diagram (1—literature data, 2—our data); (b) K_2SO_4 partition coefficient between the solution and solid phase.

The admixtures incorporated in a growing crystal strongly differ by their “affinity” to this crystal (see, for example, Shearer and Larsen, 1994) and, correspondingly, the mode of their accommodation in this crystal. In this sense, it is expedient to distinguish three types of admixtures: (1) perfect isomorphic, (2) two-dimensional isomorphic, and (3) strongly adsorbed nonisomorphic. The capture of these three types of admixture will be discussed not separately, but in comparison with one another.

ISOMORPHIC ADMIXTURES

According to the widely known Pelikan rule, perfectly isomorphic structures cannot yield sectorial structures (Lemmlein, 1973; Grigor’ev and Zhabin, 1975). Nevertheless, sectorial distributions of isomorphic components in the crystals of solid solutions are known for a very broad spectrum of minerals: pyroxenes, feldspars, beryl, tourmaline, calcite, and others (Lemmlein, 1973, pp. 26–47; Grigor’ev and Zhabin, 1975). At the same time, generalized data on natural crystals indicate that the sectorial fractionation of major components is pronounced in minerals not as clearly as the fractionation of minor and trace elements (Leung, 1974). Regrettably, experimental data on the sectorial distributions in isomorphic systems remain very scarce.

We examined in much detail crystallization in the isomorphic system K_2SO_4 – $(NH_4)_2SO_4$ – H_2O , for which a strong nonideality of its behavior was established, even though its components are characterized by the absence of miscibility gaps. A refined diagram for the state of the system at 25°C is shown in Fig. 1a (Punin et al., 1999a). This diagram displays two compositional regions in which bimodal curves behave anomalously: inflections occur on the solidus lines at 8–10 mol % $(NH_4)_2SO_4$ in the crystal and on the solutus line at 90 mol % in the salt mass of the solution, which corresponds to 50–60 mol % in the crystal. The K partition

coefficient between the solution and solid phase is greater than one over the entire compositional range and has a sharp maximum at 10–20 mol % K_2SO_4 (Fig. 1b), which testifies to a significant deviation of the system from ideality. The mixed crystals $K_x(NH_4)_{2-x}SO_4$ show a clearly pronounced sectorial structure, which is manifested in a different birefringence in the growth sectors of the faces belonging to different simple crystal forms (Fig. 2). The interference colors and birefringence measured by a Berek compensator in the growth sectors of the faces {110} and {111} at the crystal top are always higher than in the growth sectors of the faces {010} and {021} in the side zone (Punin et al., 1999a). The compositions of the growth sectors were determined by three techniques (Punin et al., 1999b): (1) by the direct determination of the K concentration by flame photometry; (2) via the diffractometric estimate based on the unit cell volume; and (3) by an assessment based on the birefringence. The results of both the direct and the indirect measurements indicate that the growth sectors of the faces composing the top of the crystal are richer in the ammonium component than the sectors of the side zone. Correspondingly, the growth zones of the side zone are enriched in the potassic component. The difference is as great as 10–15%, which is much higher than the analytical error (Punin et al., 1999a, 1999b). It is worth mentioning that sectorial structures were observed only in the crystals of solid solutions of intermediate composition with 10–60 mol % $(NH_4)_2SO_4$, whose X-ray diffraction analysis reveals changes in the structural state of the solid solutions: ordering and, possibly, also exsolution (Punin et al., 1999c). With an increasing oversaturation, sectorial segregation weakens, as follows from a decrease in the percentage of sectorial crystals in the crystallizer.

The K_2SO_4 – $(NH_4)_2SO_4$ series of solid solutions is characterized by a remarkable morphological evolution of the crystals. For pure compositions with 0–10 and 60–100 mol % $(NH_4)_2SO_4$, the crystal morphologies are the same as for pure K_2SO_4 and $(NH_4)_2SO_4$, respec-

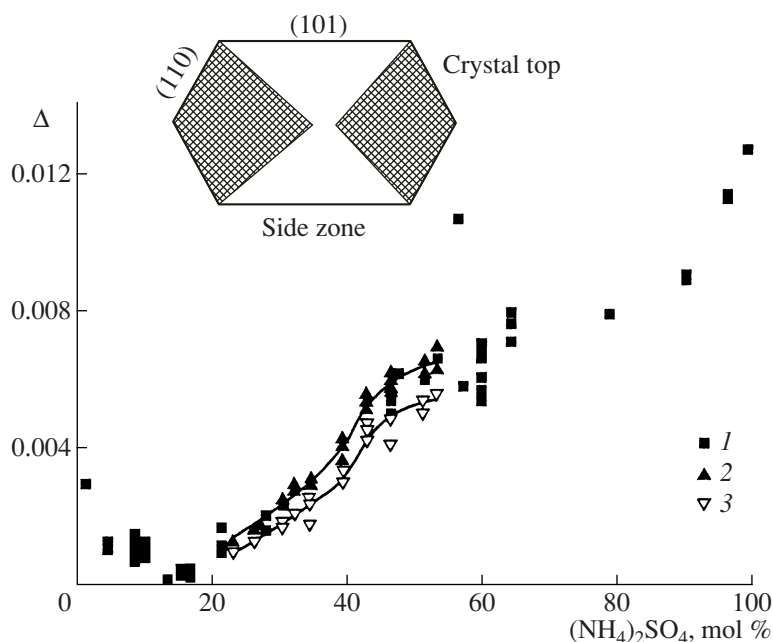


Fig. 2. Systematic variations in birefringence Δ with changes in the crystal composition. (1) Average birefringence in the section parallel to (010); (2) birefringence in the growth sectors of the faces of the crystal top; (3) birefringence in the growth sectors of the faces of the side zone. The analytical errors are proportional to the sizes of the symbols in the diagram.

tively. For intermediate compositions with 10–60 mol % ammonium sulfate, the crystals have morphologies basically different from those of the crystals of the end members, with the absolute predominance of prism {021}. Conceivably, the reason for this may be the excess adsorption of the less soluble potassic component on the {021} faces (according to the known Panet rule), which results in the preferable capture of this component by the faces. This idea finds support in the data on the dependence of the growth anisotropy on oversaturation (Fig. 3). For compositions with 0–10 and 60–100 mol % $(\text{NH}_4)_2\text{SO}_4$, this anisotropy increases with a greater oversaturation, as is also typical during crystal growth in admixture-free systems (Petrov et al., 1983). For intermediate compositions, the anisotropy of the growth rate is practically independent of the oversaturation, whose direct effect on the anisotropy is compensated by the weakening of the direct absorption of K on the {021} faces.

Hence, the systematic variations observed in the crystal habits of the solid solutions with changes in their composition and the oversaturation of the medium definitely testify to the selective adsorption of isomorphous components at the faces of various crystal forms. The deceleration of the growth of the side-zone {021} faces is associated with the enrichment of the growth sectors of these faces in the less soluble (and, hence, more actively adsorbed) potassic component. Both a sectorial structure and a change in the growth rate were detected in the same compositional region of the solid solutions, and both similarly weaken with an increasing oversaturation. It should be added that a correlation between changes in the habit of the crystals and the

development of a sectorial growth structure in them was observed in crystals of the glaserite solid solution in the system $\text{K}_2\text{SO}_4\text{--Na}_2\text{SO}_4\text{--H}_2\text{O}$ (Punin and Ivanova, 1998) and in minerals of variable composition (Grigor'ev and Zhabin, 1975). A good example is provided by polychrome tourmalines from eastern Transbaikalia in whose crystals the faces of pyramid {02 $\bar{2}$ 1}

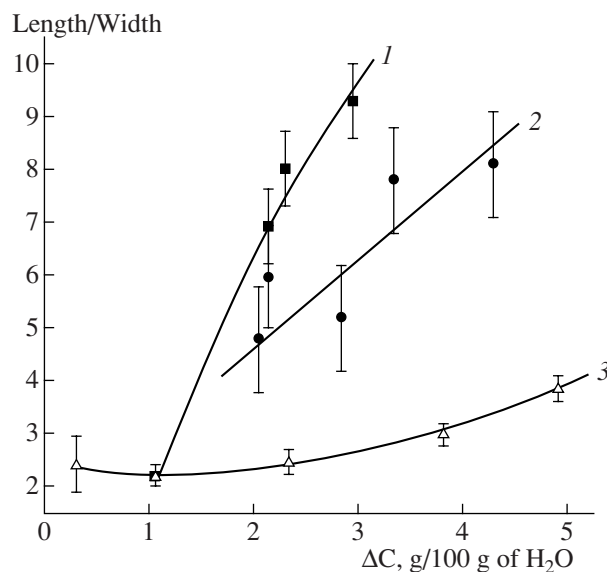


Fig. 3. Dependence of the growth rate anisotropy $V[100]/V[010]$ of $(\text{K},\text{NH}_4)_2\text{SO}_4$ crystals on the solution oversaturation. Compositional ranges of the solid phase: (1) 0–10, (2) 10–60, and (3) 60–100 mol % $(\text{NH}_4)_2\text{SO}_4$.

appear and enlarge (correspondingly to the deceleration of their growth) simultaneously with the active incorporation of the tsilaisite component in the growth sectors of these faces (Gorskaya et al., 1992). This testifies that the sectorial distribution of isomorphic components in crystals is controlled by the adsorption mechanism of their incorporation.

To justify this conclusion, we analyzed the diffusion mechanism of the sectorial incorporation of an isomorphic admixture as a consequence of the difference between the growth rates of various crystal forms. The equilibrium partition coefficient K_0 for the more soluble ammonium component is lower than one, and, hence, the higher the growth rate, the higher the degree of enrichment of this component in the boundary solution layer, and the higher the effective partition coefficient $K_{ef} > K_0$. In qualitative terms, this is consistent with the experimental results: indeed, the $(\text{NH}_4)_2\text{SO}_4$ concentration is higher in the growth sectors of the crystal tops, which are characterized by higher growth rates, than in those of the side-zone faces. However, the observed roughly twofold difference between the growth rates was calculated to be able to account for a mere 2% difference in the K_{ef} values, which corresponds to too low and experimentally undetectable differences between the compositions of various growth sectors, whereas the actual difference is, as was mentioned above, 10–15%.

Thus, the role of diffusion in the nonequilibrium sectorial incorporation of an isomorphic admixture is insignificant, and the sectorial structure of solid-solution crystals is controlled by the selective adsorption of isomorphic components on the faces of various crystal forms.

In conclusion for this section, it is pertinent to mention that the differences between the partition coefficients of the components for the growth sectors of various crystal forms are relatively small and do not exceed 25%, which is consistent with the literature data on both other water-soluble isomorphic crystals (Khaimov-Mal'kov et al., 1962) and natural minerals (Leung, 1974). This behavior is also consistent with the small differences in the adsorbability of isomorphic components.

TWO-DIMENSIONAL ISOMORPHIC MIXTURES

Systems with two-dimensional ("anomalous") isomorphism (Lemlein, 1973; Benedict et al., 2006) are spread not as widely as true solid solutions, but the adsorption-related nature of the nonequilibrium incorporation of an admixture into a growing crystal is pronounced very conspicuously in exactly these systems. In contrast to true isomorphic systems, the incorporation of admixtures during two-dimensional isomorphism was thoroughly enough studied in experiments. The situation with natural objects is, however, much worse. Grigor'ev and Zhabin (1975) and Pavlishin et al. (1988) presented numerous examples of syntaxy, a related phenomenon, which is, according to these researchers, widespread among minerals. However, syntaxy [the concurrent growth of mutually oriented crystals (Benedict et al., 2006)] is a phenomenon of a meso- and macroscopic scale. Although it is often asso-

ciated with two-dimensional isomorphism (Punin and Franke, 1998), these processes cannot be regarded as identical, and the latter is not a consequence of the former (an example is quartz–feldspar syntactic aggregates). The most widely spread and famous examples of natural objects with two-dimensional isomorphism are variably ordered polysomes (Ferraris, 1997), which are, however, most commonly produced by topotaxial reactions but not direct growth (Veblen, 1992) and are not related (in this case) to the adsorption mechanism. Nevertheless, following Lemlein (1973), we also believe that this mechanism of admixture incorporation should be widely spread among minerals, and the scarcity of information on it is explained by the poor understanding of and information on this problem. Arguments in support of this idea were provided in (Ferraris, 1997).

Systems with two-dimensional isomorphism are characterized by very strong relations between the capture of an admixture and its effect on the kinetics of crystal growth. Inasmuch as adsorption at two-dimensional isomorphism is epitaxial, this process is strongly selective, and correspondingly, the crystal habits are modified (Punin et al., 1993; Punin and Franke, 1998, 2000; Franke et al., 2003). For example, the epitaxial adsorption of admixtures in the systems NH_4Cl – $\text{CO}(\text{NH}_2)_2$ and NH_4Cl – CuCl_2 significantly suppresses the growth rates of the {100} faces of NH_4Cl (Figs. 4a and 4b), which, in turn, modifies the habit of the NH_4Cl crystals from rhombododecahedral to cubic and suppresses the skeletal growth of these crystals. A two-dimensional admixture of Mn^{2+} also suppresses the skeletal growth of NH_4Cl , but is selectively adsorbed on {110} faces, so that the habit of the holohedral NH_4Cl crystals remains rhombododecahedral. A noteworthy feature is a gentler slope (starting at a certain concentration of the admixture) of the dependences of the growth rate on the admixture concentration, the so-called saturation effect (Punin and Franke, 1998; Franke et al., 2003). This effect is clearly illustrated in Figs. 4a and 4b. Being epitaxially adsorbed on terraces between growth fronts, a two-dimensional admixture hampers and decelerates the expansion of the terraces. An echelon of terraces from a source becomes unstable, so that the terraces merge and enlarge away from the source. As the terraces merge, the distance between them increases, as also does their exposure time to the solution. This is associated with the further accumulation of the admixture in front of the terraces, whose expansion velocity catastrophically decreases, and the growth rate of the face also drastically diminishes (Punin et al., 2004). The images in Figs. 5a and 5b illustrate the morphology of crystal surfaces of KCl doped with an admixture of $\text{K}_3[\text{Fe}(\text{CN})_6]$ and NH_4Cl doped with a carbamide admixture. It can be clearly seen that the growth terraces merge and enlarge. Quantitative analyses of the concentrations of a two-dimensional admixture in the host crystal made it possible to calculate the effective partition coefficients K_{ef} for the admixture between the crystal and the solution (Punin and Franke, 1998; Franke et al., 2003). Of course, an

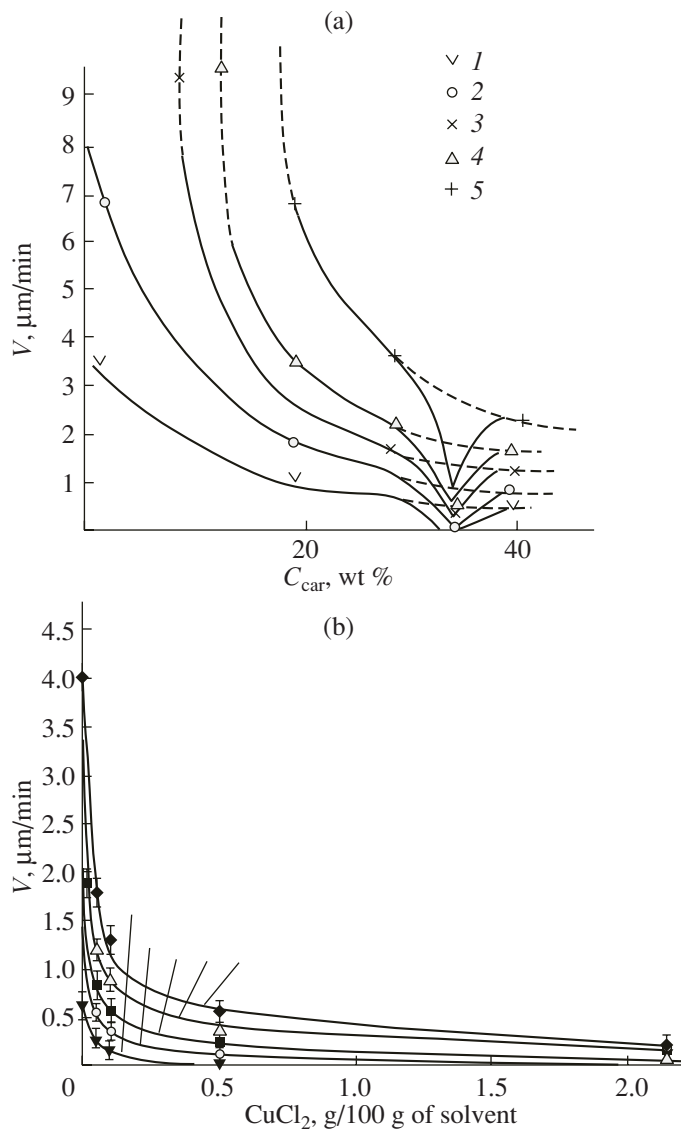


Fig. 4. Deceleration of the growth of {100} in NH_4Cl crystals by two-dimensional admixtures. (a) Carbamide admixture, undercooling for (1) 0.5, (2) 1.0, (3) 1.5, (4) 2.0, and (5) 3.0°C; (b) Cu chloride admixture, undercooling for (1) 1.0, (2) 2.0, (3) 3.0, (4) 4.0, and (5) 5.0°C.

increase in the concentration of the admixture in the solution intensifies its incorporation into the crystals. The partition coefficient, which is much higher than one at low concentrations of the admixture, decreases with an increasing concentration of the admixture, so that the dependence of K_{ef} on the admixture concentration acquires a gentler slope (Figs. 6a and 6b). Thus, the incorporation of an admixture highlights the same “saturation” effect as during the deceleration of the growth rate: the incorporation of an admixture becomes independent of the solution composition at high concentrations. Based on our data and the results obtained by other researchers (Draganova, 1960; Steinke, 1971), we arrived at the conclusion that high values of the parti-

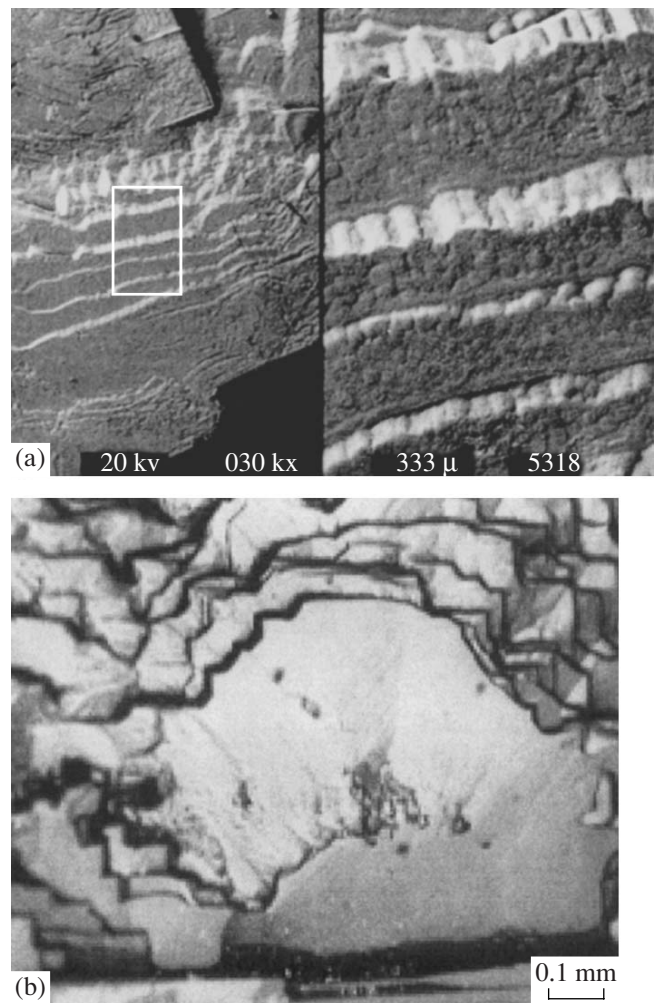


Fig. 5. Morphology of doped-crystal surfaces. (a) KCl with a $\text{K}_3[\text{Fe}(\text{CN})_6]$ admixture (2 wt % of the salt mass in the solution); (b) NH_4Cl with a carbamide admixture (20 wt %).

tion coefficient and the saturation effect are distinctive features of the adsorption incorporation mechanism of a two-dimensional isomorphous admixture.

Another characteristic of two-dimensional isomorphous systems is the heterogeneous structure of the crystals (Punin and Franke, 1998; Franke et al., 2003). At a drastic decrease in the growth rates, variably sized (ranging from microscopic lamella on the unit-cell scale to macroscopically discernible crystals) oriented ingrowths of the admixture pressure phase are captured (i.e., a combination of two-dimensional isomorphism and syntaxy). The phase heterogeneity of the crystals can be detected using single-crystal X-ray diffraction techniques by the appearance of reflections of the admixture phases near the reflections of the faces of the host crystal (Figs. 7a and 7b). We revealed a systematic orientation of the ingrowths in the matrix, as can be easily seen in Fig. 7, with the reflection indices of the admixture phases corresponding to the indices of the planes characterized by two-dimensional structural

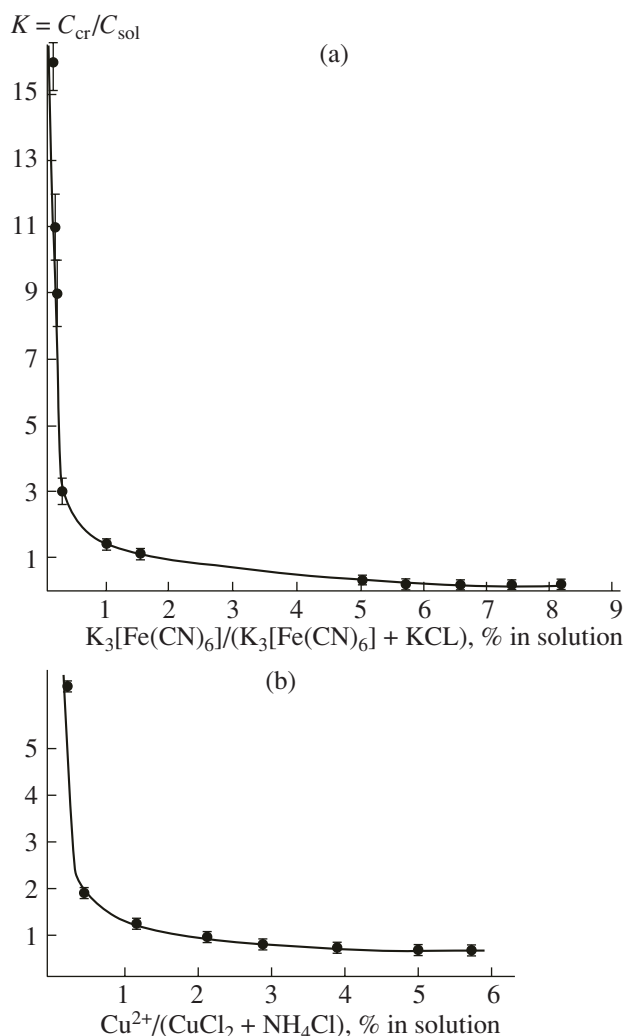


Fig. 6. Dependence of the partition coefficient of a two-dimensional isomorphous admixture between a crystal and a solution on the solution composition. (a) KCl– $K_3[Fe(CN)_6]$; (b) NH_4Cl – $CHCl_2$.

similarities with the faces of the host crystal (see the publications referred to above for the analysis of the structural correspondence). In complex systems, the phase composition of the ingrowths can vary with a varying concentration of the admixture in the solution. For example, in the system NH_4Cl – $CuCl_2$ – H_2O – CH_3ON at low Cu^{2+} concentrations in the solution, the admixture is accommodated in the form of systematically oriented ingrowths of the binary salt $(NH_4)_2CuCl_4 \cdot 2H_2O$. As the Cu concentration is increased, the admixture is incorporated simultaneously in the form of $(NH_4)_2CuCl_4 \cdot 2H_2O$ ingrowths and aqueous Cu chloride. At still higher concentrations, admixtures are additionally captured in the form of a phase of the composition $CuCl_2 \cdot 2CH_3ON$ (Fig. 7a) (Platonova et al., 1994; Franke et al., 2003). In the system KCl– $K_3[Fe(CN)_6]$, no individual three-dimensional phase of the composition intermediate between KCl and $K_3[Fe(CN)_6]$ exists, and only a two-dimensional phase

in a mixed crystal is formed. The diffractogram in Fig. 7b shows a peak of this two-dimensional phase near the peak 200 of KCl.

The phase heterogeneity of the crystals is also discernible thanks to their optics. Depending on the thickness of the layers of the admixture phase, various optical effects can be observed, from anomalous birefringence (NH_4Cl crystals in the presence of $CuCl_2$) or anomalous biaxiality [$(NH_2)_2CO$ in the presence of NH_4Cl] at the thicknesses of the layers of less than the light wavelength through distorted conoscopic interference figures at thicker layers to megascopically discernible systematically oriented phases in the host crystal (Shtukenberg and Punin, 2004). Optical methods confirm that the intergrowth planes correspond to the two-dimensional structural similarity of the matrix crystal and admixture phases (Punin et al., 1993; Kotelnikova et al., 1996).

The capture of microscopic-sized lamellae and syntactic ingrowths ceases with an increasing oversaturation (Punin and Franke, 1998; Franke et al., 2003). This is explained by the fact that an increasing oversaturation induces a greater material flux onto a crystal face and, thus, the time decreases during which the face “is available” for the adsorption of admixture particles. The effect of the duration of face exposure to the solution on the adsorption of an admixture can be illustrated by the example of the system KCl– $K_3[Fe(CN)_6]$. The concentration of the Fe^{3+} determined by a microprobe at the surface of KCl crystals is remarkably higher in regions of hampered growth than outside these areas at a finite growth rate (the time is insufficient for adsorption equilibrium to be established). In addition to a decrease in the amount of the adsorbed admixture with an increasing oversaturation (growth rate of the face), the possibility of the two-dimensional condensation of the adsorbed admixture also decreases. Indeed, at a constant induction time of the nucleation of an epitaxial phase, the nucleation probability of a two-dimensional phase decreases. This establishes a rigorous feedback between the concentration of the syntactic ingrowths, as well as the incorporation coefficient of the admixture, and the growth rate of the crystal, as is the case in nature (Figs. 8a and 8b).

NONISOMORPHIC STRONGLY ABSORBABLE ADMIXTURES

The incorporation of nonisomorphic minor admixtures into crystals is, of course, the most widely spread variant of crystal “contamination” with solution components (Watson, 1996). These admixtures are characterized by a very significant (sometimes as much as by several orders of magnitude) increase in the effective partition coefficient compared to the equilibrium coefficient (at very low absolute concentrations of the admixtures in the crystal), as well as highly significant differences in the incorporation of admixtures into various growth sectors of the crystal (Northrup and Reeder, 1994). Urusov et al. (1997) referred to this effect as the “capture” of a minor admixture by crystal

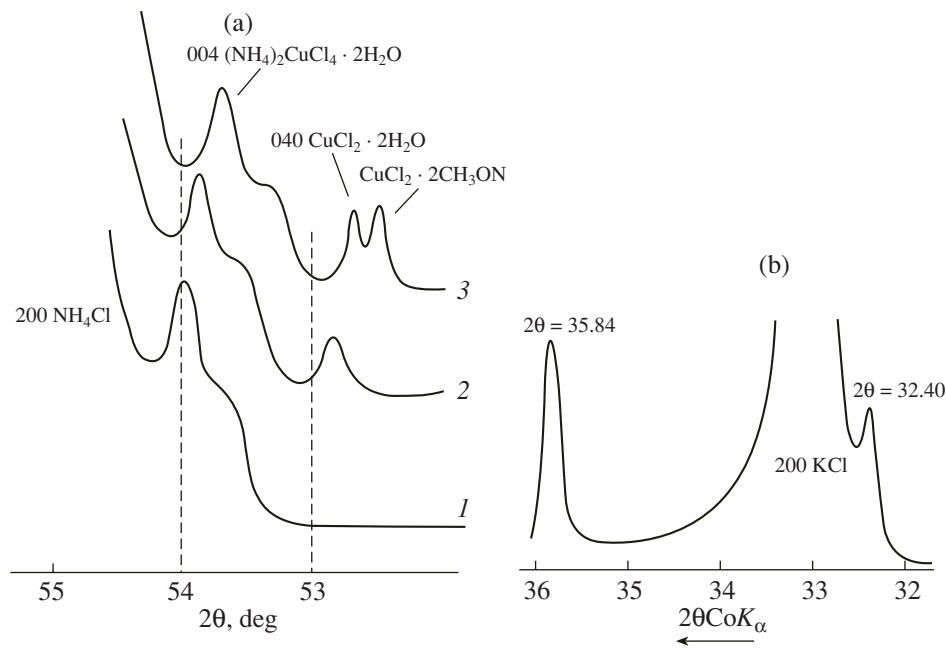


Fig. 7. X-ray diffraction characteristics of crystals grown from solutions with admixtures. (a) Position of the peaks of the admixture phases relative to the peak 200 of NH_4Cl ; concentrations of the CuCl_2 admixture: (1) 0.1–0.24, (2) 1.39–2.13, and (3) 5–7 g per 100 g of solvent. (b) Position of the 200 reflection of KCl; the concentrations of the $\text{K}_3[\text{Fe}(\text{CN})_6]$ admixture in the salt mass of the solution is 2 wt %.

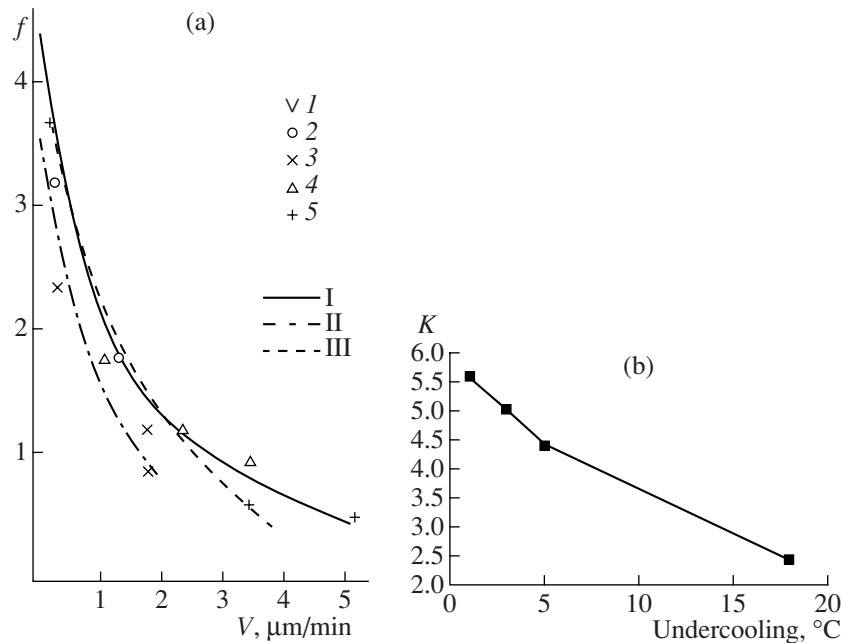


Fig. 8. Effect of oversaturation (growth rate) on the incorporation of a two-dimensional isomorphic admixture. (a) Concentration of the ingrowths of the guest phase in the NH_4Cl host crystal: (I) 28.2, (II) 33.8, and (III) 39.3 wt % carbamide in the solution; solution oversaturation: (1) 0.21, (2) 0.42, (3) 0.63, (4) 1.05, (5) 1.68 g/100 g of H_2O . (b) Partition coefficient of the admixture in the system $\text{NH}_4\text{Cl}-\text{CuCl}_2-\text{H}_2\text{O}-\text{CH}_3\text{ON}$; the concentration of CuCl_2 in the solution was equal to 0.5 g/100 g of solvent.

defects. However, concentrating on the defects is merely one of the possible accommodation mechanisms of nonisomorphic admixtures in a crystal structure. The “capturing” effect fails to explain, for exam-

ple, the sectorial and subsectorial incorporation of admixtures (Reeder and Grams, 1987). Indeed, there is neither theoretical justification of nor experimental data on the sectorial or subsectorial distribution of thermal

defects in crystals with which minor admixtures could form associates when “captured.” Most researchers believe that the mechanism of admixture incorporation in this case is also adsorption (Reeder and Grams, 1987; Shearer and Larsen, 1994; Watson, 1996).

Convenient systems that are traditionally used to examine the incorporation of minor admixtures are systems of a soluble salt plus coloring pigment (Kahr and Gurney, 2001; Benedict et al., 2006). According to some data (Leung, 1974), the behavior of these systems shows a close analogy with naturally occurring systems of a mineral and minor admixture. We examined the incorporation of nonisomorphic strongly adsorbed admixtures into aluminum potassium sulfate as the matrix crystals, with the dyes of direct pure blue (DPB) $C_{34}H_{24}O_{16}Na_4S_4N_6$ and fuchsin (FC) $C_{20}H_{17}O_9Na_2S_3N_3$ as the admixtures. The advantage of the selected system stems from the fact that, along with the strong and selective adsorption of the dyes on the faces of the host crystals, the incorporation of even very low concentrations of these pigments can be visually detected and quantitatively determined by photocolometric techniques.

All of the systems exhibited a strongly selective deceleration of crystal growth under the effect of the adsorption of admixtures with the modification of the crystal habits. With an increasing DPB concentration, the habits of the Al–K sulfate crystals changed from octahedral to cubic (Kenunen et al., 2002). It is worth mentioning that this phenomenon was pronounced particularly strongly at a low oversaturation. Under the effect of DPB and FC, K_2SO_4 crystals became strongly flattened parallel to {010} with the nearly complete disappearance of prisms and pyramids from their faceting (Punin et al., 2004).

A distinctive feature of the growth kinetics at doping with strongly absorbable admixtures is the occurrence of a so-called “dead zone,” i.e., an oversaturation range in which no growth takes place. The width of this zone increases with an increasing concentration of the admixture and a decreasing crystallization temperature, so that the growth surface may be passivated within a broad range of degrees of oversaturation. Note that a dead zone was also detected in some systems with two-dimensional isomorphism, for example, $KCl-K_3[Fe(CN)_6]$. At a strong doping, the surpassing of the critical oversaturation results in a new material overgrowth only for some areas at the surface, whereas adjacent portions of the same crystal face remain inert: so-called local or insular growth (Punin et al., 2004).

In all three of the examined systems, pigments were actively captured by the growing crystals, but the selectivity of this incorporation was expressed variably. The Al–K sulfate crystals captured the DPB admixture only at their cube faces. This resulted in a sectorial distribution of the admixture: the growth sectors of $\langle 100 \rangle$ were blue, whereas those of $\langle 111 \rangle$ remained colorless. The admixture was captured by exactly those faces whose growth was hampered by the adsorbed admixture. The incorporation of the admixture was discernible even at the lowest of the used concentrations of the admixture (0.002g/100 ml of H_2O) (Kenunen et al., 2002). In the

system K_2SO_4 –DPB, this admixture more strongly decelerated the growth of the {010} faces. The crystals grew thereby completely dyed, i.e., the pigment was also strongly enough adsorbed at other faces, except the second pinacoid. This also follows from the complete doping of the seed crystal surface at high concentrations of the admixture (>0.001 g/100 ml of H_2O), which results, as was already mentioned above, in a local character of growth. The system K_2SO_4 –fuchsin is an exception. This pigment is incorporated into the crystals sectorially (at the faces of the crystal tops), but suppresses the growth of other faces (in the [100] zone), whose growth sectors remain colorless, i.e., devoid of the pigment. This effect, which was previously also identified in other systems (Buckley, 1951), is still poorly understood and calls for further investigation.

Quantitative analyses of an admixture captured by crystals generally confirm the relationship and tendencies typical of the behavior of minor admixtures, regardless of their nature (Urusov et al., 1997). The absolute concentrations of the dye admixtures in the crystals are low, because these are nonstructural admixtures for these crystals. The partition coefficients are anomalously high in all systems (Figs. 9a, 9b, and 9c). For example, the effective partition coefficient for the system K_2SO_4 –DPB reaches 50. Thus, minor admixtures can be very significantly concentrated in crystals (up to the discoloration of the matrix solution). This type of admixtures displays the tendency toward their weaker incorporation with an increasing oversaturation and temperature (Kenunen et al., 2002), but these tendencies are weak and are often camouflaged by the strong scatter of the partition coefficient values. The reason for the latter phenomenon is not so much the insufficient accuracy of the analyses of the admixture minor component as the principal instability of the crystallization process in the presence of strongly absorbable admixtures (Punin et al., 2004), with this instability being of both a morphological and kinetic nature.

Potassium sulfate and alum crystals with DPB dye were determined to exhibit pleochroism, which testifies that admixtures are systematically oriented in the crystals. The character of the pleochroism suggests that linear molecules of the dye in the K_2SO_4 crystals are oriented parallel to [100]. Because the distances between sulfogroups in the pigment are divisible into the distances between SO_4^{2-} groups along [100] in the K_2SO_4 structure, DPB is epitaxially adsorbed on the faces of this zone. Judging from the character of the pleochroism of the alum crystals, admixtures are oriented perpendicularly to the cube faces, i.e., are adsorbed at their polar ends (SO_3 groups), which is in conflict with the scheme proposed by Portnov and Nikolaeva (1973). Obviously, this is a less strong adsorption, and this results in the weak doping of the crystal growth and lower incorporation coefficients of the pigment in this system. Fuchsin is adsorbed even less strongly on potassium sulfate crystals. The molecule of the pigment

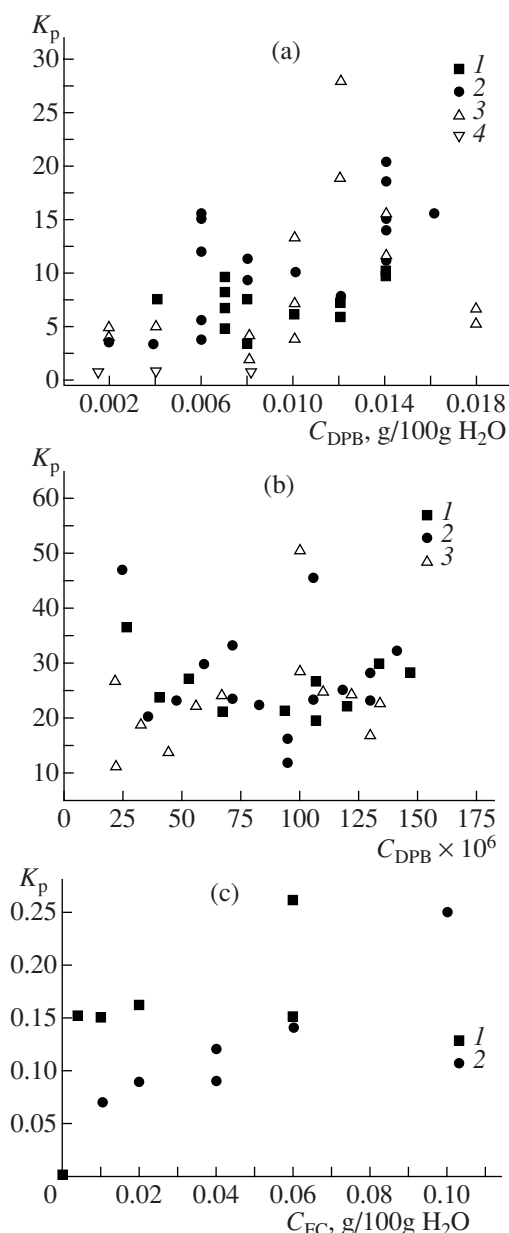


Fig. 9. Dependence of the partition coefficient of minor admixtures of pigments on their concentration in the solution. (a) System Al-K alum-DPB: (1-3), crystallization temperature equal to 20°C, oversaturation of 2.6, 4.6, and 6.6 g/100 g of H_2O , respectively; (4) crystallization temperature 35°C, oversaturation 6-8 g/100 g of H_2O . (b) System K_2SO_4 -DPB, oversaturation (1) 2, (2) 4, (3) 6 g/100g of H_2O . (c) System K_2SO_4 -fuchsin, crystallization temperature: (1) 6, (2) 18°C; oversaturation 3.0 g/100 g of H_2O .

is planar and can be adsorbed on the {111} faces of the top of K_2SO_4 crystals at its plane parallel to the plane of the crystal face. At the same time, the position of the three sulfogroups in the molecule plane does not correspond to the arrangement of the SO_4^{2-} groups in plane {111}, and hence, adsorption cannot be strong enough.

This is consistent with the much lower incorporation coefficients of FC than DPB in the growth sector {111} of K_2SO_4 crystals (the former coefficients are still anomalously high, considering the nonstructural character of the admixture).

The very high values of the partition coefficients and the significant scatter of their values because of the instability of the crystal growth are natural consequences of the adsorption mechanism of admixture incorporation. Analogous dependences were identified for other systems of ionic crystals and organic admixtures (Pritula et al., 2004). Furthermore, as was mentioned above, the incorporation coefficients are prone to diminish with an increasing crystallization temperature and oversaturation. This directly follows from the adsorption cocrystallization mechanism proposed by A.A. Chernov (*Modern...*, 1980). Indeed, a temperature increase is known to decrease the adsorption constant, and an increasing oversaturation diminishes the time during which the surface of a growing crystal is available for the adsorption of an admixture.

CONCLUSIONS

The capture of all three types of admixtures, which are characterized by basically different mechanisms of their incorporation into the crystal structure, was determined to be controlled predominantly by the adsorption effects at a subordinate role of the diffusion-related processes. This is pronounced particularly conspicuously for systems of the third type and results in much higher (by several orders of magnitude) effective partition coefficients than the equilibrium ones. The intensity of their capture is correlated with a decrease in the growth rates of the crystal faces in systems with isomorphic and two-dimensional isomorphic admixtures, whereas the systems with nonisomorphic minor admixtures can exhibit similar or opposite behaviors. The latter has still not received any rational explanation. The deviations of K_{ef} from K_0 for admixtures of all types usually decrease with an increasing oversaturation, and the extent of the sectorial segregation of admixtures behaves in a similar manner. The tendencies in the adsorption incorporation of admixtures are controlled by the interaction of three currently known mechanisms: the statistical selection of familiar and foreign (admixture) particles at the growth terraces of a crystal, the diffusion relaxation of compositional gradients in the solution layer near the crystal surface, and the slow adsorption of admixtures (*Modern...*, 1980; Punin, 2004). These effects can differently influence the incorporation of an admixture, with the final result depending on the "strength" of the adsorption. Regrettably, this is the only conclusion that can be drawn as yet. In contrast to the admixture-controlled deceleration of crystal growth, no theory is as yet developed for the adsorption incorporation of admixtures, and this precludes the quantitative description of this widespread phenomenon.

ACKNOWLEDGMENTS

This study was financially supported by the Russian Foundation for Basic Research, project no. 05-05-64289.

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