Journal of Statistical Physics, Vol. 90, Nos. 5/6, 1998

Computer Simulation of Nonequilibrium Growth of Crystals in a Two-Dimensional Medium with a Phase-Separating Impurity

L. M. Martiouchev,[1,2] **V. D. Seleznev,**[2] **and S. A. Skopinov**[1]

Received February 21, 1997; final November 24, 1997

Two-dimensional nonequilibrium growth of crystals (quasistable faceted and dendritic) in the presence of a phase separating impurity is studied by computer simulation. It is shown that there is a gradual modification in this system from quasistable faceted growth to the formation of dendrites when the impurity concentration increases. If there is dendritic growth in the presence of a phase-separating impurity, the cyclic changes in the morphology, expressed through the periodic occurrence of tertiary branches of a dendrite, are observed when the phase-separating impurity concentration is raised. This behavior of the morphology is considered as a reentrant nonequilibrium phase transition.

KEY WORDS: Computer simulation; cellular automata; nonequilibrium forms of growth; dendrites; morphology; nonequilibrium phase transitions.

1. INTRODUCTION

There is great interest in theoretical and experimental questions on the formation of complex space-time structures appearing in nonequilibrium processes. Various systems (e.g., hydrodynamic, chemical, biological) have been discussed in which a sudden change of properties and symmetry occurs at critical values of thermodynamic flows and forces (so-called nonequilibrium phase transitions).(1-3) One of the most interesting, practically important and complex systems involves the nonequilibrium growth of crystals from a solution/melt at significant supersaturations/undercoolings, which results in skeletal and dendritic forms.(4) The influence of an impurity on such a nonequilibrum crystal growth is not well understood, because

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[1] Institute of Industrial Ecology UB RAS, Ekaterinburg, Russia.

[2] Ural State Technical University, Ekaterinburg, 620002, Russia.

0022-4715/98/0300-1413$15.00/0

there are two types of effects: thermodynamic (the impurity changes solubility, freezing temperature, etc.) and kinetic (the impurity influences the processes occurring at the crystal–solution interface).

In the present work, the morphological aspects of two-dimensional nonequilibrum growth of a crystal from solution in the presence of an impurity is studied with the help of a computer model. Initially this work was stimulated by the development of methods for medical diagnostics based on the crystallization of salts from biofluids (see, for example, ref. 5). A similar system was discussed by the authors earlier using the computer τ-model.(6) In that work it was shown that both a continuous change of the morphology and a sudden nonequilibrium phase transition occur during the growth of a skeletal crystal in a phase-separating medium. The present work considers quasistable faceted growth and the growth of a dendrite (a structure which forms at large deviations from equilibrium in comparison with skeletal) in a phase-separating medium, with the aid of the same model.

2. BRIEF REVIEW OF EXISTING APPROACHES TO CRYSTAL GROWTH SIMULATION

Because of the mathematical difficulties of the analysis, the morphological peculiarities of forming dendritic structures have been studied mainly by computer simulation. There are two basic approaches to the simulation of these phenomena. In the first,(7) researchers base their computer models, as far as possible, on a strict theoretical description of these phenomena, including both the basic diffusion/heat equations and Gibbs–Thomson equation, the anisotropy of the surface energy and the kinetic coefficient of crystallization, the phase diagram of the system, etc. This approach is useful for describing quantitatively rather simple, thoroughly experimentally investigated systems. The second approach to simulation uses cellular automata.(8) In this approach the investigated area is considered as a set of cells, each of them characterized by a definite set of variables. These variables, depending on the condition of the neighboring cells, vary their values in discrete time steps. The calculation rules are only indirectly built on theoretical models of the phenomenon, and are mainly defined by intuition. Such models are useful for studying complex systems. They give some qualitative understanding of the process, and allow one to test and to put forward new hypotheses, but it is difficult to use them for quantitative estimations.

The τ-model,(6, 9) used in this work occupies an intermediate position between these two approaches to modeling, embracing, as far as possible, the best aspects of each.

3. EXPERIMENTAL RESULTS STIMULATING THIS RESEARCH

The kinetic action of an impurity combines the influence on the processes of the transfer in volume and the influence on the phenomena of crystallization on the surface, of which the latter is the most essential.(10) It is possible to divide the effect of the impurity on the crystallization processes on the surface into two groups.

1. The adsorption of the impurity in the form of atoms, molecules, or complexes on the surface. The physical and chemical parameters of the

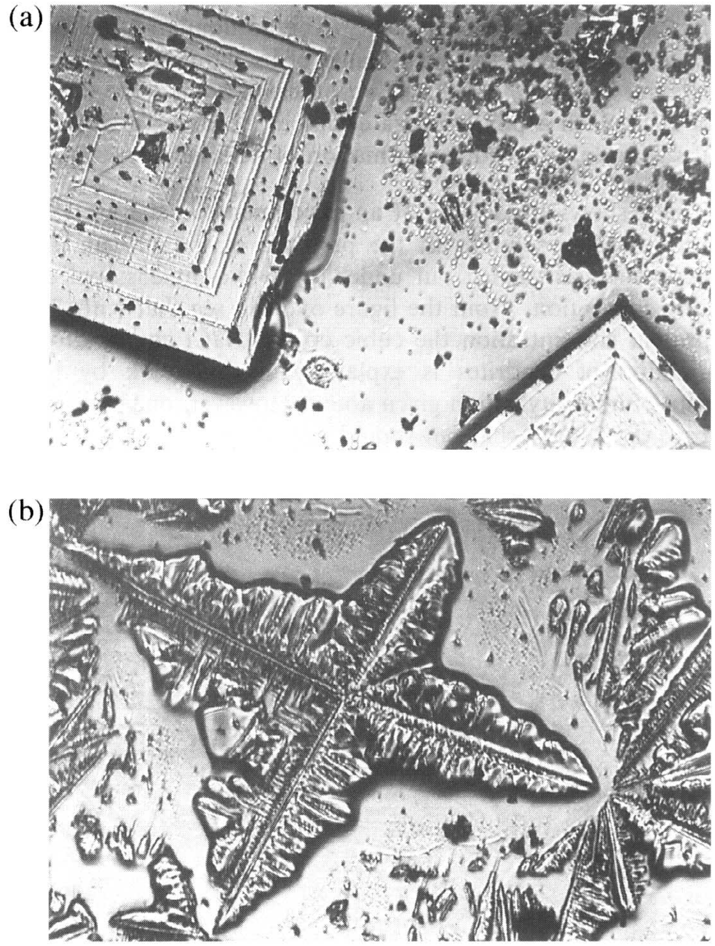

Fig. 1. The morphology of NaCl growing from an aqueous solution in the presence of albumin. The initial concentration of albumin: (a) 2 mg/ml, (b) 8 mg/ml, (c) 15 mg/ml.

impurity prevent it from entering the crystal. Impurities that accumulate on the surface of the crystal are usually the reason for either a gradual reduction of the growth rate or an end to crystal growth at a critical concentration.(10) Such a behavior of the impurity results in a change of the crystal morphology and in particular in the development of dendrites.(11)

2. The impurity (usually in the form of macromolecules, such as proteins, lipids, etc.) displaced by the growing crystal surface reaches a certain concentration and has a transition to another phase, thus creating local obstacles to the growth. Examples of such phase transitions are those from solution to gel in the case of proteins(12) or from vesicles to the lamellar phase in the case of lipids.(13) The accumulation of the impurity becomes possible due to the small value of its diffusion coefficient (about 10^{-7} cm/s^2 for proteins, which is two orders less than the diffusion coefficient of salt). Such a phase-separated impurity, creating various films on a crystal substrate, leads to the formation of dendritic structures.(14)

Figure 1 shows the results of an experiment on the growth of NaCl crystals from water solution in the presence of the protein albumin.(15) The experiment was carried out under quasi-two-dimensional conditions, eliminating convection. From the figure one can see that with the increase of the protein concentration the cubic crystal NaCl changes to dendritic. The formation of dendrites is explained in this work by the second mechanism of impurity action given above. However, one can suppose that in this case the first mechanism should not be neglected, because proteins (albumin in particular) are surface-active.(16)

(c)

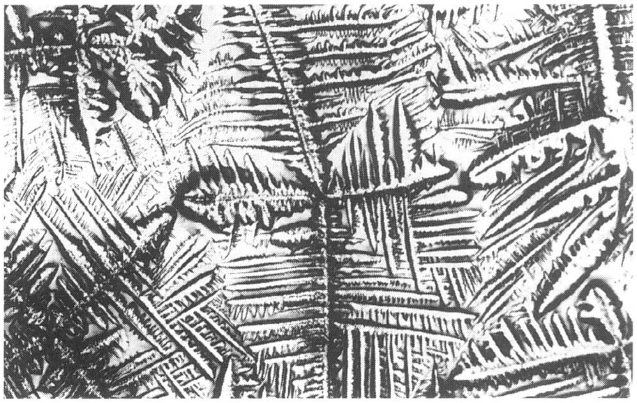

Fig. 1. (*Continued*)

4. MODEL

The model (named by the authors as the τ-model) was created on the principles of a cellular automaton. The following rules (see ref. 9 for details) were used.

4.1. General Rules

a. The calculation is carried out on a 100×100 square grid with thickness L, where the size of each square is L. The choice of a square grid presupposes that the growth of crystals having a cubic symmetry can be simulated. The size L is selected to be approximately the same as the resolution of the proposed device to observe the growing crystal of salt. It is supposed that each cell has four nearest neighbors.

b. As the interval of time through which the calculation of the concentration fields is made, the time for the relaxation of the concentration between two neighboring cells $\tau = L^2/(2D_s)$ is chosen, where D_s is the diffusion coefficient of a component (salt).

c. Each cell is characterized by two numbers: the concentration of the salt C_s and the concentration of the second component (impurity) C_p. At the initial moment of time the concentrations in all cells are identical and are respectively equal to $C_{s.\text{in}}$ and $C_{p.\text{in}}$.

d. All the cells are divided into the following groups:

(i) cells of the crystal (black color). For these cells $C_s = C_{s.\text{sol}}$ ($C_{s.\text{sol}}$ is the density of the solid salt), $C_p = 0$.

(ii) Cells with the phase-separated impurity (grey color). For these cells $C_p = C_{p.\text{sol}}$, where $C_{p.\text{sol}}$ is the concentration of impurity gelling.

(iii) cells of the solution (white color) $C_s \neq C_{s.\text{sol}}$, $C_p \neq C_{p.\text{sol}}$.

(iv) Border cells (white color). These cells of the solution are the nearest to the cells of the crystal (see details below).

e. It is postulated that there appears a viable crystal seed (cell of a crystal) at the center of the square grid which initiates the growth.

4.2. Rules Relating to Border Cells

a. The density of salt flux I at each interval of time τ coming into these cells is calculated from the assumption that the surface kinetics is quasi-isotropic and the growth rate is linear in the supersaturation$^{(10)}$:

$$I = \sum_i b(C_{s,i} - C_{\text{sat}})(C_{s.\text{sol}} - C_{s,i})/C_{s.\text{sol}}$$

where $C_{s,i}$ is the current concentration of salt in a cell i of the solution, being in the neighborhood of a border cell, C_{sat} is the saturation concentration of the solution, and b is the kinetic coefficient of crystallization (related to the nature and structure of the crystal surface, its nearest neighborhood, and temperature$^{(10)}$). The sum is carried out only for cells of the solution which are nearest neighbors of the border cells.

b. The density of the impurity flux from border cells is determined from the assumption of its complete displacement by the growing crystal into the nearest cells of the solution.

c. Choosing new border cells beside a newly painted (black) cell, such cells of the solution are not considered where there is already one border cell in the neighborhood. This feature of the algorithm has the physical rationale that crystal seeds are at a disadvantage in arising in the vicinity of one another because the energy of nucleation in these locations is bigger (the supersaturation is smaller).

4.3. Rules Relating to Cells of the Solution

a. It is considered that the fluxes of salt and of the second component in the solution are not connected, and therefore the calculations of the density of salt and of impurity fluxes are done independently.

b. The rule for the calculation of the concentration in the cell of the solution (for example, for a salt) has the following form:

The concentration in the cell changes due to the influx of salt from the nearest cells in which the concentration is greater (positive flux) and due to the outflow of salt to the nearest cells with lower concentration (negative flux). The general positive density of salt flux I_p^l into a given cell of the solution during the l-iteration is

$$I_p^l = \sum_{i,\{C_{s,i}>C_s\}} I_{p,i}^l = L(C_{s,\max} - C_s)/2$$

$$I_{p,i}^l = 0.5L(C_{s,\max} - C_s)(C_{s,i} - C_s) \Big/ \sum_{i,\{C_{s,i}>C_s\}} (C_{s,i} - C_s)$$

where $C_{s,\max}$ is the maximal salt concentration among the nearest solution cells, $C_{s,i}$ is the current concentration in the i nearest solution cell, and C_s is the concentration of the given cell. The sum is carried out only for cells where the concentration is greater than in the given cell.

The general negative flux I_n^l of salt from the given cell is

$$I_n^l = \sum_{i, \{C_{s,i} < C_s\}} I_{p,i}^{l-1}$$

The sum is carried out only for cells where the concentration is lower than in the given cell.

This rule follows directly from Fick's first law in dilute solutions and from using τ as interval of time, i.e., the time of the relaxation of the concentration between two cells. In applying the given rule, the diffusion coefficient of the impurity (D_p) is used for the impurity.

4.4. Rules for Cells with a Phase-Separated Impurity

It is supposed that the impurity diffusion coefficient is sufficiently small, and the displacement of the impurity results in its accumulation near the crystal surface. We shall consider here that when the impurity concentration in the cell reaches a value $C_{p.\mathrm{sol}}$, the impurity transfers to another phase, in which any flux through this cell is forbidden and salt crystallization in it is impossible.

4.5. Rules for Cells of a Crystal

Having achieved the concentration $C_{s.\mathrm{sol}}$ in a border cell, it is transformed to the cell of a crystal. These cells do not take part in subsequent calculations.

5. RESULTS AND DISCUSSION

5.1. Quasistable Faceted Growth in the Presence of a Phase-Separating Impurity

The following parameters were chosen for the simulation: $b = 2.2 \times 10^{-4}$ cm/s; $L = 10^{-4}$ cm; $D_s = 1.5 \times 10^{-5}$ cm^2/s, $C_{s.\mathrm{sol}} = 2.2$ g/cm^3, $C_{\mathrm{sat}} = 0.36$ g/cm^3 (corresponding to parameters for NaCl). Thus, $b\lambda/D_s \approx 1.5 \times 10^{-2}$, where λ is a characteristic size of the crystal ($\lambda \sim 10L$). The value of relative supersaturation $(C_{s.\mathrm{in}} - C_{\mathrm{sat}})/C_{\mathrm{sat}}$ was selected so that on the one hand faceted growth occurred, and on the other hand, the calculation of the structure by computer was as rapid as possible. We chose the value 0.9. Since $b\lambda/D_s$ is much less than one, then, according to ref. 10, the supersaturation on the surface is practically equal to the supersaturation in the bulk. The crystal in general keeps a faceted form in the absence of the impurity during growth (Fig. 2). The curvature of the phase boundary periodically arising during the growth (Fig. 2b), because the tops "eat" from a greater solid angle, is compensated by the geometrical peculiarities of the square grid used in the simulation (Fig. 2c).

The morphology of the crystals becomes extremely complicated if we add the impurity to the solution according to the rules described above (Fig. 3). At relatively small concentrations of the impurity $C_{p.\text{in}}/C_{p.\text{sol}}$, the crystal heterogeneously holding the impurity still keeps a faceted form (Fig. 3a). The crystal becomes more and more friable and its surface gets some typical fractal outlines$^{(3)}$ (Fig. 3b) for increasing relative concentration of the impurity up to 0.2–0.25. For a concentration of the impurity of about 0.30 the morphology of the crystal begins to resemble the cellular dendrites (Fig. 3c) described in the literature.$^{(17)}$ A further increase of impurity concentration results in typical dendrites with branches up to the fifth order (Fig. 3d). The picture shows the process of coarsening of branch spacings (double and fourfold) which is typical for dendrites.$^{(18)}$ This

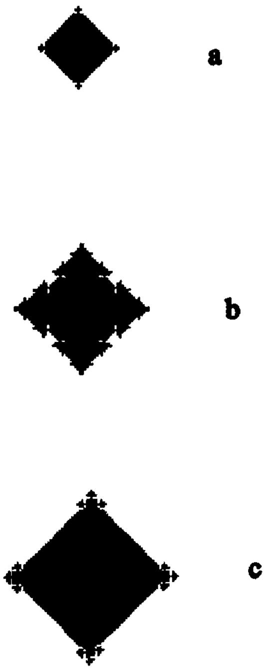

Fig. 2. The morphology of quasistable faceted growth. (a–c) The consecutive stages of development of a crystal.

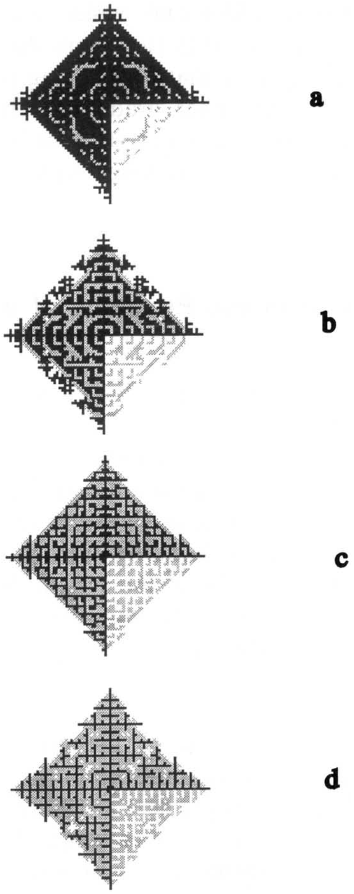

Fig. 3. The morphology of faceted growth upon the change of relative initial impurity concentration $C_{p.\mathrm{in}}/C_{p.\mathrm{sol}}$: (a) 0.10, (b) 0.25, (c) 0.33, (d) 0.45. The black color shows the distribution of salt, grey the distribution of the phase-separated impurity; the distribution of the impurity is shown (the distribution of salt is not shown) for convenience in the right bottom quarter. The fractal dimension of the resulted structures is equal, respectively, to 1.94 ± 0.02, 1.80 ± 0.02, 1.73 ± 0.05, and 1.65 ± 0.06.

process is obviously connected with the mechanism of pressing back the impurity. The structures found by computer experiment (Figs. 3a, 3b, 3d) qualitatively agree with structures found in experiments (Fig. 1). It is necessary to emphasize that the morphology of crystals is continuously changed along with the increase of the impurity concentration. Such changes are typical for quasistable systems. The fractal dimension of the resulting structures decreases linearly from two (corresponding to the absence of the impurity) to 1.65 ± 0.06, which corresponds to a relative concentration of the impurity of 0.45 (for more details see the caption to Fig. 3). The mass of the impurity that is changing phase, and the mass of the salt crystals, also change rather gradually. The growth rate of the crystal is constant at any impurity concentration because the kinetic-controlled regime of crystal growth is examined with the extremely simplified algorithm.

5.2. Dendritic Growth in the Presence of a Phase-Separating Impurity

The following parameters were chosen for the simulation: $b = 2.2 \times 10^{-2}$ cm/s; $L = 10^{-4}$ cm; $D_s = 1.5 \times 10^{-5}$ cm^2/s, $C_{s.\text{sol}} = 2.2$ g/cm^3, $C_{\text{sat}} = 0.36$ g/cm^3; the relative supersaturation was 0.9, i.e., only the value of the kinetic coefficient of the crystallization was changed. In this case the parameter $b\lambda/D_s$ was about 1.5 and, as shown in ref. 9, at such a choice of parameters in the absence of the impurity there is a growth of dendrites with branches up to the third order in the system. Note that the necessary condition for the accumulation of the impurity is $b\lambda/D_p > 1$ and, as the kinetic coefficient of crystallization differs greatly between the previous and the present experiment, the impurity diffusion coefficient used in each of these experiments will differ.

The sequence of structures due to the growth of dendrites in the presence of an increased concentration of impurity $(C_{p.\text{in}}/C_{p.\text{sol}})$ is shown in Fig. 4. The morphological changes here are more delicate in comparison with the previous case, and are more interesting. At first there is a gradual filling of intervals between branches by the impurity having a transition to another phase, and this does not practically influence the structure of the growing dendrite (Fig. 4a). The growth rate at this stage increases slowly and the mass of the impurity having a transition to another phase increases exponentially (see Fig. 5). At a relative concentration of the impurity in the region of 0.56, the presence of the impurity results in the occurrence of dendrites mainly with only secondary branches (Fig. 4b). Earlier research$^{(6)}$ shows that a simplification of the structure beginning from this moment gradually proceeds, namely there is a gradual increase of the intervals between branches. Now, however, the dendrite again has tertiary branches in the region of relative impurity concentration 0.58–0.63 (Fig. 4c). But at the impurity concentration 0.64 the dendrite morphology has only secondary branches (Fig. 4d). With further addition of the impurity the dendrites get branches up to the third order again (Fig. 4e), and then there is a very fast transition to the underdeveloped crystal structures.

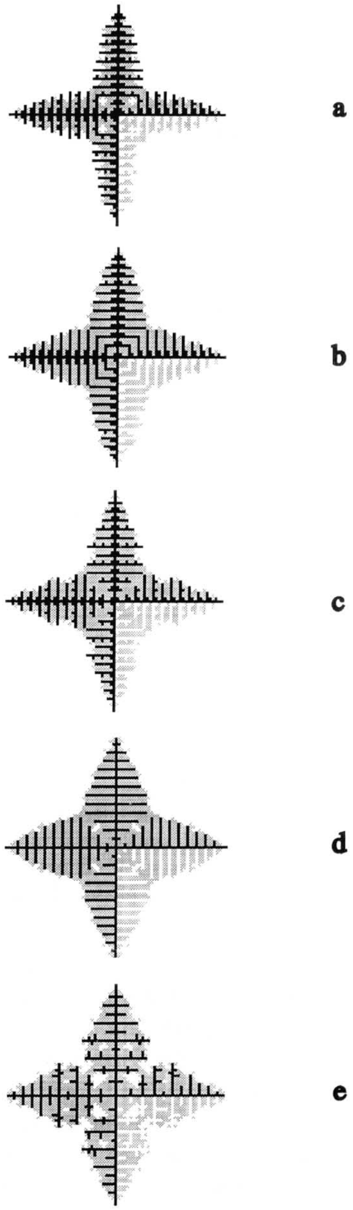

Fig. 4. The morphology of dendritic growth upon the change of relative initial impurity concentration $C_{p,\mathrm{in}}/C_{p,\mathrm{sol}}$: (a) 0.53, (b) 0.56, (c) 0.59, (d) 0.65, (e) 0.67. The black color shows the distribution of salt, grey the distribution of the phase-separated impurity; the distribution of the impurity is shown (the distribution of salt is not shown) for convenience in the right bottom quarter.

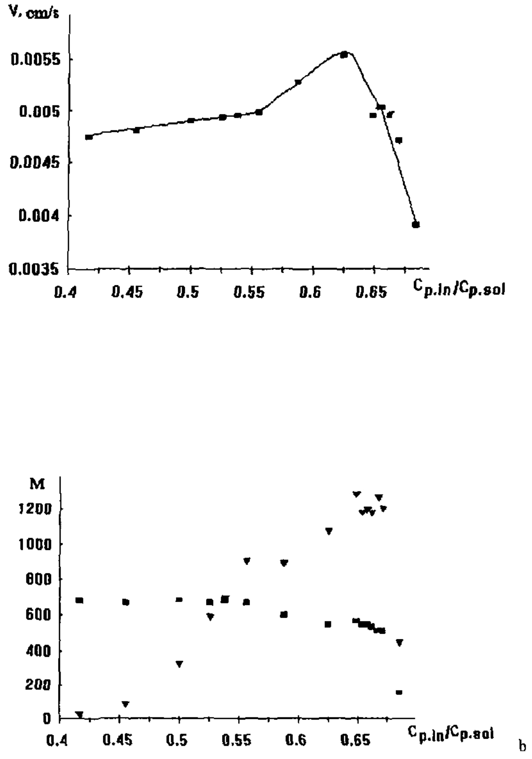

Fig. 5. (a) The dependence of the average (for the interval of time considered in the model) growth rate V of a crystal in direction ⟨100⟩ on the relative initial impurity concentration $C_{p.\mathrm{in}}/C_{p.\mathrm{sol}}$; (b) the dependence of the area (mass) M (dimensionless units) of a crystal (■) and the impurity having a transition to the other phase (▼) on the relative initial impurity concentration $C_{p.\mathrm{in}}/C_{p.\mathrm{sol}}$.

Such a cyclic reappearance of structures is explained by the highly unstable growth and the phase-separating medium. Two interconnected causes influence the morphology of the formed structure: the supersaturation on the crystal–solution boundary and local obstacles to the growth arising due to the nonuniform transition of impurity to the other phase (a typical negative feedback). Indeed, the transition from the structure represented in Fig. 4a to the structure in Fig. 4b takes place because the phase separation of the impurity near the formed secondary branches occurs practically simultaneously with the growth of these branches and prevents diffusion (a similar effect occurs at the transition from the structure with tertiary branches to the structure with secondary branches in Fig. 4c and 4d). The transition from the dendrite in Fig. 4b to the dendrite in Fig. 4c is explained by the fact that secondary dendritic branches, due to the early phase separation of the impurity, become thinner and the conditions at the available concentration fields of the salt and the impurity promote the formation of the tertiary branches. The last transition (Fig. 4d and 4e) caused by the change of the impurity concentration in the system occurs because of the increase of intervals between branches and the coarsening of the branch spacings during growth. As a result, the density of the crystal structure decreases, and the conditions promote the free movement of the impurity from the growing crystal surface, and simultaneously the solution near the crystal is more saturated by the salt. This results in an intensive branching of the dendrite with the development of tertiary branches.

Such a morphological reorganization is accompanied by an interesting behavior of the other growth parameters. The mass as a function of $C_{p.\mathrm{in}}/C_{p.\mathrm{sol}}$ for the impurity undergoing a transition to another phase (Fig. 5b) has two bends, at 0.56 and 0.65, that about correspond to the points of the disappearance of the dendrite tertiary branches. Such a nonlinear behavior can be explained as follows: with an increase of the relative impurity concentration and crystal growth, the amount of the impurity undergoing transition to the other phase increases, and so obstacles for crystal growth arise at the given locations. Thus the impurity modifies the crystal structure and the transition from the tertiary to the secondary branches leads to the gradual disappearance of tertiary branches with the formation of areas with the phase-separated impurity in these positions (tertiary branches arise at a later stage of the growth; they are less steady and accordingly they disappear more easily due to impurity influence). After the disappearance of the tertiary branches a more essential reorganization of the dendrite is required, because it is necessary to change the thickness or the location of the secondary branches, and so the relative concentration of the impurity is increased, but the mass of the impurity undergoing a transition to the other phase does not change. The dendrite with the tertiary branches arises again after such a reorganization and the process is repeated. At a relative concentration of the impurity in the region of 0.68, the impurity blocks the growth in the early stage and the mass of the impurity decreases sharply.

The general behavior of the average growth rate in the direction $\langle 100 \rangle$ (Fig. 5a) under the conditions of crystallization considered in this work is similar to the results found by the authors earlier.(6) The concentration fields of the growing secondary and tertiary branches of the dendrite influence indirectly the growth rate of the primary branches in the direction $\langle 100 \rangle$. The more developed these branches are, the more they contribute to the fall of the concentration near the primary branches they cause.

Therefore, the increase of the growth rate of a crystal for an increase of the relative impurity concentration up to 0.63 is explained by the fact that the general mass of the secondary and tertiary branches decreases because of the additional phase separation of the impurity. It is seen from the comparison of Fig. 5a and Fig. 5b that the most significant increase of the growth rate after 0.55 coincides with a more appreciable decrease of the mass of the crystal salts. The uneven decrease of the growth rate ($C_{p.\mathrm{in}}/C_{p.\mathrm{sol}} > 0.63$) is explained by the fact that the primary branches begin "to eat" from a smaller solid angle because of the phase separation occurring already at the early stages in the system.

The results of the computer simulation mentioned above allow us to conclude that cyclic changes of morphology take place in the present system (the appearance and disappearrance of tertiary dendritic branches), which are accompanied by the change of properties. One may say, that there are some cyclic nonequilibrium phase transitions in the extremely unstable system under consideration. The nonequilibrum phase transitions considered here are typical representatives of nonequilibrum phase transitions, as investigated by synergetics (Benard instability, transition to turbulence, etc.).(1, 2) This class is characterized by the extraordinary richness of structure arising as a result of the development of the instabilities at the growth of the crystal from various solutions. A feature of this class of nonequilibrum phase transition is that the space-time structure fixes itself ("solidifies itself") in space and time with the growth of the crystal. Another characteristic feature of this class of phenomena is the existence of two simultaneous transitions: the usual thermodynamical transition (solution–crystal) and the nonequilibrum phase transition.

It is known(1, 2) that the terminology and approaches available in the physics of equilibrium (thermodynamic) phase transitions are widely used for the description of nonequilibrium phase transitions (for example, the concept of the order parameter, Landau theory, and others). The phenomena known as reentrant phase transitions was found by Cladis for organic substances forming a liquid crystal phase.(19) These reentrant equilibrium transitions are characterized by a cyclic sequence of phases consecutively replacing each other at the gradual change of temperature. This phenomenon has not received a complete description, though it is qualitatively explained by the presence of two interacting orientation and translation order parameters.(20) In the present work, using a qualitative analogy, we may say that the sequence of morphologies at the change of impurity concentration can be called a nonequilibrium reentrant phase transition. The quantitative changes of structure during these nonequilibrium reentrant transitions are not so significant (for example, there is practically no change of the fractal dimension for the structures in Fig. 4,

1.61 ± 0.02); however, a periodic change of the symmetry of the morphotypes takes place, and it can be connected with the cyclic change of the symmetry at the nonequilibrium reentrant phase transition.

ACKNOWLEDGMENT

Our special thanks go to Zh. Khramushina.

REFERENCES

1. H. Haken, *Synergetics* (Springer-Verlag, Berlin, 1978).
2. P. Glansdorff and I. Prigogine, *Thermodynamic Theory of Structure, Stability and Fluctuations* (Wiley, New York, 1971).
3. J. Feder, *Fractals* (Plenum Press, New York, 1988).
4. J. S. Langer, Instabilities and pattern formation in crystal growth, *Rev. Mod. Phys.* **52**:1 (1980).
5. A. Sole, *Stagoskopie* (Franz Deuticke, Vienna, 1960).
6. L. M. Martyushev, V. D. Seleznev, and S. A. Skopinov, *Tech. Phys. Lett.* **22**:648 (1996).
7. P. K. Galenko and V. A. Zhuravlev, *Physics of Dendrites* (World Scientific, Singapore, 1994); R. Sasikumar and R. Sreenivasan, *Acta Metall. Mater.* **42**:2381 (1994); Shu-Zu Lu, J. D. Hung, P. Gilgien, and W. Kurz, *Acta Metall. Mater.* **42**:1653 (1994).
8. S. G. R. Brown, T. Williams, and J. A. Spittle, *Acta Metall. Mater.* **42**:2893 (1994); D. B. Berg, S. A. Skopinov, *et al.*, *Izv. Akad. Nauk. SSSR Ser. Fiz.* **55**:175 (1991).
9. L. M. Martyushev, V. D. Seleznev, and S. A. Skopinov, *Tech. Phys. Lett.* **22**:146 (1996); L. M. Martiouchev, V. D. Seleznev, and S. A. Skopinov, *Crystallogr. Rep.* **42**:735 (1997).
10. A. A. Chernov, *Modern Crystallography III: Crystal Growth* (Springer-Verlag, Berlin, 1984).
11. D. D. Saratovkin, *Dendritic Crystallization* (Metallurgizdat, Moscow, 1957).
12. W. N. Izmailova and P. A. Rehbinder, *The Formation of Structures in Protein Systems* (Nauka, Moscow, 1974).
13. G. H. Brown and J. J. Wolken, *Liquid Crystals and Biological Structures* (Academic Press, New York, 1979).
14. R. I. Mints, S. A. Skopinov, *et al.*, *Russ. J. Phys. Chem.* **66**:183 (1992); R. I. Mints and D. B. Berg, *Russ. J. Phys. Chem.* **69**:48 (1995) [in Russian]; R. I. Mints and D. B. Berg, In *Surface Phenomena*, SPIE Proceedings, Vol. 2731, p. 74; R. I. Mints, S. A. Skopinov, S. V. Yakovleva, *et al.*, *Studia Biophys.* **133**:221 (1989); M. Yasui and M. Matsushita, *J. Phys. Soc. Jpn.* **61**:2327 (1992).
15. R. I. Mints, S. A. Skopinov, and S. V. Yakovleva, *Tech. Phys. Lett.* **14**:12 (1988).
16. K. Shinoda, T. Nakogawa, B. Tamamushi, *et al.*, *Colloidal Surfactants. Some Physicochemical Properties* (Academic Press, New York, 1963); W. N. Izmailova, G. P. Jampolskaia, and B. D. Summ, *Surface Phenomena in Protein Systems* (Chemistry, Moscow, 1988).
17. B. Chalmers, *Principles of Solidification* (Wiley, New York, 1964).
18. S.-C. Huang and M. E. Glicksman, *Acta Metall.* **29**:717 (1981).
19. P. E. Cladis, *Phys. Rev. Lett.* **35**:48 (1975); P. E. Cladis, R. K. Bogardus, and D. Aadsen, *Phys. Rev. A* **18**:2292 (1978).
20. P. E. Cladis, *Mol. Cryst. Liquid Cryst.* **67**:177 (1981).