Emergence and development of crystallization nucleus structure in a supersaturated solid solution

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The problem of the development of a dissipative structure of spherical nuclei of a stable phase in a supersaturated solid solution is considered. On the initial stage, when all the nuclei have close dimensions, the obtained analytical solution indicates that the structure period monotonically decreases with time as $1/t$, then as $1/\sqrt{t}$. The numerical calculation indicates that later a fraction of nuclei are dissolved, and a structure of growing spherical nuclei with a period tending to a constant emerges. © *1996 American Institute of Physics.* [S1063-7761(96)02807-7]

1. INTRODUCTION

The emergence of a dissipative structure during a phase transition in a solid was first reported by Evans,[1] who detected a superlattice of vacancy pores generated in molybdenum by 2-MeV nitrogen ions at a high temperature. The superlattice period was several hundred angströms. Similar phenomena are observed in chemical reactions in solids.[2–4] All these processes include growth of clusters (nuclei of a new phase, vacancy pores, etc.) due to absorption or evaporation of atoms or point defects on their surfaces. The concentration of the supersaturated solution of atoms around each nucleus is not uniform (a "diffusion cloud" is formed). The overlap of diffusion clouds around different nuclei leads to the long-range diffusion interaction between them.[5,6] Screening takes place in the ensemble of nuclei interacting through diffusion.[7] In our previous publications[8,9] we suggested that this dissipative interaction may be responsible for the emergence of the pore superlattice and determine its final configuration.

The aim of this work was to go beyond the qualitative description of the process[5–9] and develop a kinetic theory of the emergence and development of a structure in a supersaturated solid solution. We have considered as a specific example a system initially containing nuclei of a stable phase inside a sphere with a radius L. Section 2 reconsiders the equation system[9] describing the kinetics of a pattern of nuclei. In Sec. 3 we investigate using analytical techniques a linearized equation system applicable to a dissipative structure on the initial stage, when dimensions of all nuclei are close to each other. We demonstrate that a structure with a gradually decreasing period is generated. In Sec. 4 the basic equation system is solved with due account of nonlinearity. The resulting quasi-stationary structure consists of spherical layers in which nuclei either evaporate and vanish or grow indefinitely. We have found that on the advanced stage the structure period is independent of time.

2. BASIC EQUATIONS

Following the generally accepted classic theory by Lifshitz and Slezov,[10] let us express the time derivative of the ith nucleus radius R_i in terms of diffusion of dissolved material with a concentration $c(\mathbf{r})$:

$$\frac{dR_i}{dt}=D\left.\frac{\partial c}{\partial r}\right|_{r=R_i}, \tag{2.1}$$

where D is the diffusion coefficient of the dissolved material. We assume that the nuclei grow slowly, and the solvent distribution in the space between clusters is quasi-steady:

$$c(r)=c_\infty+\sum_j \frac{q_j}{|r-r_j|}, \tag{2.2}$$

where r_j is the coordinate of the jth nucleus center and c_∞ is the concentration far from the nuclei. Equations (2.1) and (2.2) yield an expression for the growth rate of the ith nucleus:

$$\frac{dR_i}{dt}=-D\frac{q_i}{R_i^2}. \tag{2.3}$$

The concentration near the nucleus surface is determined by the thermodynamic equilibrium conditions and is a function of the surface curvature radius:

$$c(R_i)=c_T\left(1+\frac{R_T}{R_i}\right), \tag{2.4}$$

where c_T is the solvent concentration in equilibrium with a plane interface between the two phases, $R_T=2\sigma\omega_0/T$ (σ is the surface tension, ω_0 is the volume per molecule of the stable phase, and T is the temperature). From Eq. (2.2) we derive

$$c(R_i)=c_\infty+\frac{q_i}{R_i}+\phi_i, \tag{2.5}$$

where ϕ_i is the concentration "Coulomb field" at the point r_i generated by the system of growing nuclei with "charges" q_j:

$$\phi_i=\sum_{j\neq i}\frac{q_j}{|r_i-r_j|}=\sum_{j\neq i}\frac{q_j}{\rho_{ij}}. \tag{2.6}$$

Equations (2.4) and (2.6) are valid under the condition $\alpha\ll R_i\ll\rho_{ij}$.

Let us consider a system of nuclei whose radius is a continuous function of the coordinate r_i. In this case, the discrete equations (2.3)–(2.6) can be replaced by differential

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equations in which the nucleus dimension R, "charge" q, and "field" ϕ are continuous functions of the coordinate $\mathbf{r}$:

$$\frac{dR}{dt}=-\frac{q}{R^2}, \tag{2.7}$$

$$1-\eta R=q+R\phi, \tag{2.8}$$

$$\Delta\phi=-q\theta(R). \tag{2.9}$$

The step function $\theta(R)$ is introduced to exclude those nuclei which have evaporated. In this equation system, we have introduced the dimensionless variables

$$\tilde{R}=R/R_*, \quad \tilde{q}=q/R_T c_T, \quad \tilde{t}=tDR_T c_T/R_*^3,$$
$$\tilde{\phi}=\phi R_*/R_T c_T, \quad \tilde{r}=r\sqrt{4\pi R_* n_{\text{nuc}}} \tag{2.10}$$

and the tilde sign is omitted. The parameter n_{nuc} is the density of nuclei. The factor η is

$$\eta=\frac{R_*}{R_T}\left(\frac{c_\infty}{c_T}-1\right). \tag{2.11}$$

If the system of nuclei is immersed in a supersaturated solution ($c_\infty>c_T$), it is convenient to define R_* as the critical nucleus dimension

$$R_c=R_T\left(\frac{c_\infty}{c_T}-1\right)^{-1}. \tag{2.12}$$

Then $\eta=1$. If the nuclei are surrounded by saturated solution ($c_\infty=c_T$), it is convenient to define R_* as the average initial dimension of the nuclei and take $\eta=0$. In what follows, we take for definiteness $\eta=1$ (the nuclei are in a supersaturated solution).

The field $\phi(\mathbf{r})$ describes the effect of the diffusion clouds of surrounding nuclei on the growth rate of a nucleus at the point $\mathbf{r}$. The growing nuclei ($q<0$) reduce the solvent concentration and $\phi(r)$ [Eq. (2.6)], therefore they reduce the growth rate at the point $\mathbf{r}$ by virtue of Eqs. (2.7) and (2.8). The effect of the evaporating nuclei has the opposite sign.

In the next section we will demonstrate that the field ϕ leads to an instability in the uniform distribution of nuclei and to a development of a dissipative structure.

3. EVOLUTION OF SPHERICALLY SYMMETRICAL SYSTEM OF NUCLEI IN LINEAR APPROXIMATION

Let us consider the evolution of a system of nuclei whose dimensions at the initial moment are equal, $R\simeq 1$, and whose density in a spherical region with a radius $L\gg 1$ is constant. In such a system, all the parameters are functions only of the distance to the center of the sphere. Let us express the field ϕ as

$$\phi=\frac{L\chi}{r} \tag{3.1}$$

and instead of the three-dimensional Poisson equation (2.9) solve the one-dimensional equation

$$\frac{d^2\chi}{dr^2}=-\frac{r}{L}q \tag{3.2}$$

with the boundary conditions

$$\chi|_{r=0}=0, \quad \left.\frac{d\chi}{dr}\right|_{r=L}=0. \tag{3.3}$$

The first condition is obvious, the second derives from the continuity of ϕ and $d\phi/dr$ on the boundary $r=L$ and the condition

$$\phi=\frac{\text{const}}{r}, \quad r>L. \tag{3.4}$$

Let us investigate the initial stage of the evolution by linearizing Eqs. (2.7) and (2.8) with respect to small deviations of the parameters from the steady state described by the conditions $q_0=0$, $R_0=1$, and $\phi_0=1-\eta$. Substituting into Eqs. (2.7)–(2.9) the expressions

$$R=1+\xi, \quad \phi=\phi_0+\frac{L\chi}{r}, \tag{3.5}$$

we obtain the sought linear equation system:

$$\frac{d^2\chi}{dr^2}=-\frac{rq}{L}, \quad \dot{\xi}=-q, \quad \xi+q+\frac{L\chi}{r}=0. \tag{3.6}$$

This equation system can be simplified by taking the initial conditions

$$\xi\Big|_{t=0}=\xi_0(x)=C\exp(-\alpha x), \quad |C|\ll 1,$$
$$x=L-r, \quad \alpha L\gg 1. \tag{3.7}$$

Let us assume for definiteness that $\alpha>1$. In this case all the processes occur near the system boundary ($x\ll L$), and instead of Eq. (3.6) we can take the equation system with constant coefficients:

$$\frac{d^2\chi}{dx^2}=-q, \quad \dot{\xi}=-q, \quad \xi+q+\chi=0. \tag{3.8}$$

These equations indicate that the initial uniform distribution of nuclei is unstable. After substituting the wave function $\exp(pt+ikx)$ into Eq. (3.8), we easily obtain

$$p=\frac{k^2}{k^2+1}. \tag{3.9}$$

If the field χ in Eq. (3.8) is omitted, we obtain instead of Eq. (3.9) the growth increment independent of the wave vector ($p=1$). In this case, perturbations of all wavelengths grow at equal rates, and no periodic structure can emerge. If the field χ is included, the long-wave perturbations ($k<1$) grow slower than short-wave ones ($k>1$). Hence the resulting structure should have a period λ approximately equal to unity, or in dimensional units [see Eq. (2.10)]

$$\lambda\sim(4\pi n_{\text{nuc}}R_*)^{-1/2}. \tag{3.10}$$

This result was reported in Refs. 8 and 9.

Let us consider the effect of nonspherical perturbations. Let us expand the initial perturbation in terms of spherical harmonics:

$$\xi\Big|_{t=0}=\sum_{l,m}\xi_{lm}(r,t)Y_{lm}(\theta,\phi). \tag{3.11}$$

Then the equation system (2.7)–(2.9) splits into the subsystems

$$\dot{\xi}_{lm}=-q_{lm}, \quad -q_{lm}=\xi_{lm}+\phi_{lm}, \tag{3.12}$$
$$\frac{1}{r^2}\frac{\partial^2}{\partial r^2}(r^2\phi_{lm})-\frac{l(l+1)}{r^2}\phi_{lm}=-q_{lm}.$$

Let the amplitudes $\xi_{lm}(r,0)$, as well as the conditions in Eq. (3.7), be nonzero only near the system boundary $r=L$. Then the "centrifugal energy" in the last equation of the system (3.12) can be replaced with the constant $l(l+1)/L^2$. Then instead of Eq. (3.9) we obtain the following equation for the growth increment p_{lm} of the lm harmonic:

$$p_{lm}=\frac{k^2}{k^2+1+l(l+1)/L^2}. \tag{3.13}$$

This means that the harmonics with small angular momenta ($l\ll L$) grow at the same rate as the spherically symmetrical perturbation. Hence the ratio of the amplitudes of the spherical and nonspherical perturbations remains constant on the linear stage of the evolution. On the nonlinear stage the harmonics are not separated, and a layered structure with spherical interfaces between them is produced. Thus, the nonspherical perturbations do not have a great impact on the system evolution.

Usually[10] the spectrum of the instability exponent has a maximum at some k_0, and the period of the dissipative structure is determined by the position of this maximum ($\lambda\sim 1/k_0$) irrespective of the initial perturbation. In our case, all the waves with $k\geqslant 1$ grow at the same rate, hence the shape of the resulting dissipative structure is largely controlled by both boundary and initial conditions. The effect of the initial condition (3.7) can be illustrated by a particular solution of Eq. (3.8):

$$\xi_N(t,x)=C\exp(p_\alpha t-\alpha x), \quad p_\alpha=\frac{\alpha^2}{\alpha^2-1},$$
$$\chi_N=\frac{\xi_N}{\alpha^2-1}, \quad q_N=p_\alpha\xi_N. \tag{3.14}$$

But this solution does not satisfy the boundary condition in Eq. (3.3):

$$\frac{\partial\chi}{\partial x}\Big|_{x=0}=0. \tag{3.15}$$

Below we will see that the "mirror reflection" from the boundary $x=0$ leads to a layered structure. But let us first discuss the application domain of the linearized equation system (3.8).

According to Eq. (3.14), the perturbations are small at $t\ll t_1$, where

$$t_1\simeq|\ln C|. \tag{3.16}$$

If the initial perturbation amplitude $|C|$ is sufficiently small, the time t_1 is sufficiently long that a complex dissipative structure can develope in the linear stage of the evolution.

Let us use the Laplace transform to study this structure:

$$f(p)=\int_0^\infty e^{-pt}f(t)dt, \quad \mathrm{Re}\,p>0. \tag{3.17}$$

Equation (3.8) takes the form

$$p\xi(p,x)-\xi_0(x)=-q(p,x)=\xi(p,x)+\chi(p,x), \tag{3.18}$$
$$\frac{\partial^2\chi(p,x)}{\partial x^2}-\beta^2\chi(p,x)=\frac{\xi_0(x)}{p-1}, \tag{3.19}$$

where β is defined as

$$\beta(p)=\sqrt{\frac{p}{p-1}}, \quad \mathrm{Re}\,\beta\geqslant 0. \tag{3.20}$$

Equation (3.19) is solved with the boundary conditions

$$\chi(p,\infty)=0, \quad \frac{\partial}{\partial x}\chi(p,0)=0. \tag{3.21}$$

The particular solution of Eq. (3.19) is the Laplace transform of the functions defined by Eq. (3.14):

$$\chi_N(p)=\frac{1}{p^2-1}\xi_N(p), \quad \xi_N(p)=\frac{C}{p-p_\alpha}e^{-\alpha x},$$
$$q_N(p)=p_\alpha\xi_N(p). \tag{3.22}$$

In order to satisfy the boundary conditions (3.21), we must add to the functions in Eq. (3.22) the homogeneous solution

$$\chi_H(p)=\frac{C}{\alpha^2-1}\frac{1}{p-p_\alpha}\left(-\frac{\alpha}{\beta}e^{-\beta x}\right), \tag{3.23}$$
$$\xi_H(p)=C\left(\frac{1}{p-p_\alpha}-\frac{1}{p-1}\right)\left(-\frac{\alpha}{\beta}e^{-\beta x}\right), \tag{3.24}$$
$$q_H(p)=C\left(\frac{p_\alpha}{p-p_\alpha}-\frac{1}{p-1}\right)\left(-\frac{\alpha}{\beta}e^{-\beta x}\right). \tag{3.25}$$

The evolution of the nucleus structure is described by the inverse Laplace transform

$$f(t,x)=\frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty}f(p,x)e^{pt}dp, \quad \sigma>p_\alpha. \tag{3.26}$$

At small times, $0<t\ll 1$, and large coordinates, $x\gg 1$, the region of large increments $|p|\gg 1$ makes the largest contribution. In this region

$$\beta=\left(1-\frac{1}{p}\right)^{-1/2}\simeq 1+\frac{1}{2p} \tag{3.27}$$

and the function in Eq. (3.23) is expressed as

$$\chi_H(t)\simeq-\frac{\alpha Ce^{-x}}{\alpha^2-1}\int e^{pt}\frac{1}{p}e^{-x/2p}dp$$
$$=-\frac{\alpha Ce^{-x}}{\alpha^2-1}J_0(\sqrt{2xt}), \tag{3.28}$$

where J_0 is the Bessel function.

We can see than even after a short time a periodic structure with a period

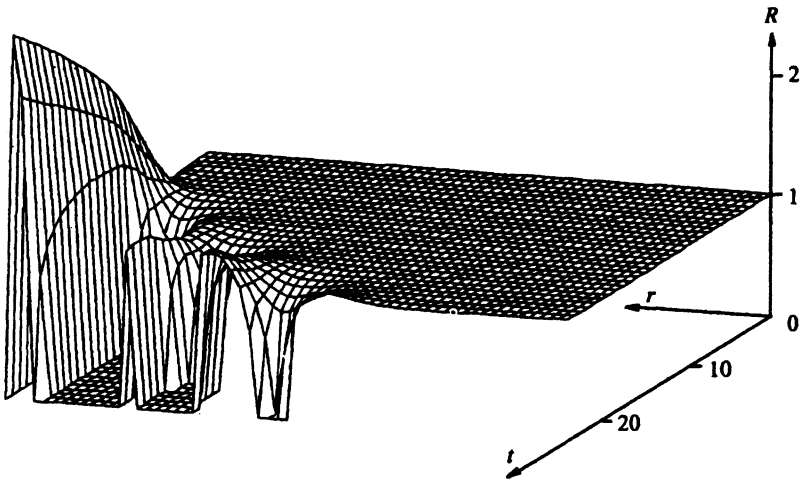

FIG. 1. Evolution of a spherically symmetrical system of nuclei. The system parameters are $L=20$, $C=-0.001$. At the moment $t=24$, three layers free from nuclei are seen.

$$x \simeq 1/t, \tag{3.29}$$

and an amplitude exponentially decreasing with the distance from the boundary is generated.

After a longer time, $1 \ll t \ll t_1$, the structure of the nucleus system is determined by the asymptotics of the functions in Eq. (3.26). Let us shift, as is usually done, the integration path to the left in order to bypass the pole at p_α and the cut along the segment (0,1). The comparison between Eqs. (3.23)–(3.25) and Eq. (3.22) demonstrates that the contribution to the full solutions

$$\chi_N+\chi_H, \quad \xi_N+\xi_H, \quad q_N+q_H \tag{3.30}$$

due to the pole at p_α is zero since $\beta(p_\alpha)=\alpha$. Around the segment (0,1), where $p=u+iv$, $0<u<1$, and $|v| \ll 1$, we have

$$\beta = \sqrt{\frac{u}{1-u}}[|v| - i \operatorname{sign}(v)] \tag{3.31}$$

and the integral in Eq. (3.26) is reduced to the integral over the segment of the unit length:

$$f(t) = \frac{1}{\pi}\int_0^1 \operatorname{Im} f(u-i0)e^{ut}du. \tag{3.32}$$

At $t \gg 1$, most of this integral is the contribution due to the integration over the region near the upper limit. By taking $u=1-z^2$, $0<z \ll 1$, we obtain, for example,

$$q(t) \simeq 2\alpha \frac{C}{\pi} e^t \operatorname{Re}\int_0^\infty \exp\left[-\left(tz^2+\frac{ix}{z}\right)\right]dz$$

$$\simeq \frac{2\alpha C}{\sqrt{3\pi}} e^{t-\mu}\cos(\sqrt{3}\mu), \tag{3.33}$$

where $\mu = 3(2tx^2)^{1/3}/4$. One can see that after a longer time the structure scale changes with time as

$$\Delta x \sim 1/\sqrt{t} \tag{3.34}$$

and the perturbation front ($\mu = t$) propagates from the boundary to the center at a constant speed ($x \propto t$). At times beyond the limit defined by Eq. (3.16) or from the start of the process if the initial condition is more complex than that described by Eq. (3.7), the linearized equation system (3.8) cannot be applied, and the nonlinear equation system (2.7)–(2.9) must be analyzed using numerical techniques.

4. COMPUTER SIMULATION OF THE SYSTEM EVOLUTION

In order to find a numerical solution of the equation system (2.3)–(2.6), let us transform it to the integro-differential form. In dimensionless variables, Eq. (2.10) takes the form

$$\frac{dR}{dt} = -\frac{q}{R^2}, \tag{4.1}$$

$$q + R_c\sqrt{4\pi R_c n}R\sum_{j\neq i}\frac{q_j}{r_{ij}} = 1-R. \tag{4.2}$$

Let us replace the sum in Eq. (4.2) with an integral and transform it using the spherical symmetry. Then we obtain the nonuniform Fredholm equation of second kind for the flux q:

$$q(r,t) + \int_0^L q(r',t)\mathscr{K}(r,r',t)dr' = 1-R(r,t) \tag{4.3}$$

with the kernel $\mathscr{K}(r,r')$:

$$\mathscr{K}(r,r',t) = R(r,t)\frac{r'}{r}\frac{r+r'-|r-r'|}{2}\theta[R(r')]. \tag{4.4}$$

At the initial moment of time $t=0$, the nucleus radius R_0 was defined as a function of the distance to the sphere center r, i.e., $R_0(r)$. Then Eq. (4.3) was solved and the flux $q(r)$ was determined. The technique for solving the Fredholm equation is described in Ref. 11. The function $R(r,t)$ on the next time layer was derived from the flux using Eq. (4.1). The step function is introduced to take into account the fact that some nuclei evaporate on the nonlinear stage of the evolution.

Figure 1 shows the function $R(r,t)$ calculated at $L=20$, $C=-10^{-4}$, and $\alpha=10$. You can see that by the time $t=24$ three shells with growing nuclei separated by gaps where the nuclei have evaporated have developed. The formation of the fourth shell has started. Note that after evapo-

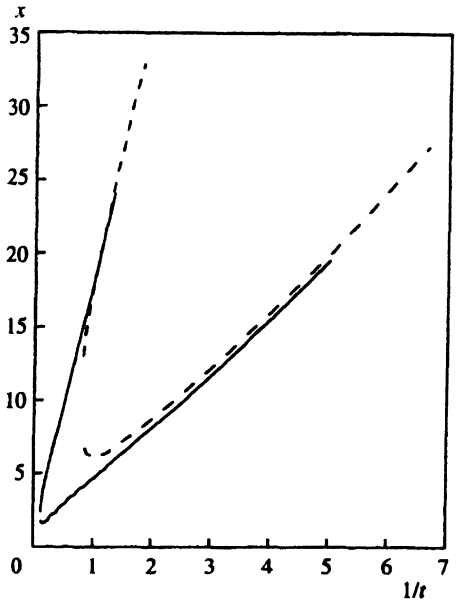

FIG. 2. Characteristic dimensions of the structure vs reciprocal time at different initial conditions. The dashed lines correspond to $C=-0.1$, the solid lines to $C=-0.0001$; $L=35$.

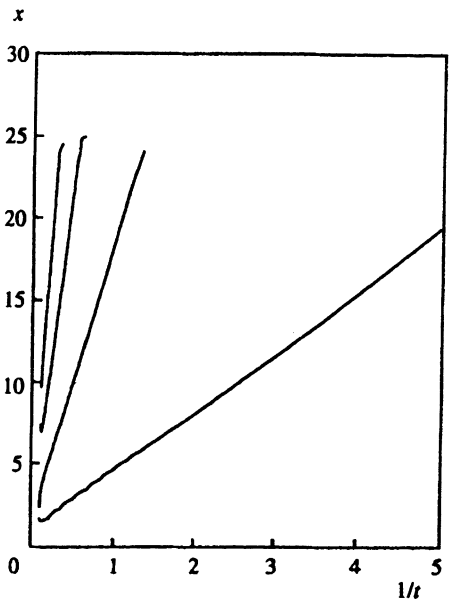

FIG. 3. Characteristic dimensions of the structure vs reciprocal time at a small initial perturbation. The system parameters are $L=35$, $C=-0.0001$. The graph indicates that at a small perturbation the relation $x \propto 1/t$ is valid.

ration of nuclei in the gaps, the positions of the growing shells are steady. The numerical solution yields the structure period defined by Eq. (3.10): $\lambda \simeq 6(4\pi n_{\text{nuc}} R_*)^{-1/2}$.

The structure evolution as a function of the initial conditions (3.7) was studied by tracing the positions of zeros of the function $q(r,t)$. Figure 2 shows the positions of the first two zeros of this function versus reciprocal time at the initial perturbation amplitude $C=-0.1$ (dashed lines) and $C=-0.0001$ (solid lines). The parameter L in this calculation was 35. One can see that on the initial stage, when the linear approximation (3.6) applies, the structure period changes proportionally to $1/t$, according to Eq. (3.29), the positions of zeros being independent of the initial perturbation amplitude, as follows from Eq. (3.26). The calculations deviate from this curve in the nonlinear region, in this case, when the first gap free from nuclei is formed.

Figure 3 shows the evolution of the structure at $L=35$ and $C=-0.0001$. Given the small amplitude of the initial perturbation, the positions of four zeros of the function $q(r,t)$ can be traced. The curves are rectilinear throughout the studied time interval. The slope of the nth line is proportional to the square of the nth root of the zero-order Bessel function, as follows from Eq. (3.29).

To sum up, we have proposed a theory describing the formation of a modulated structure from nuclei of a new phase. The stratification of the growing system of new phase nuclei is caused by diffusion among nuclei on the stage of their evaporation and growth. As a result of the overlap of diffusion clouds, the growing (supercritical) nuclei accelerate the evaporation of subcritical nuclei at a distance of the order of the screening radius λ. The resulting wave of the growth and evaporation rates leads to the formation of a layered structure in the distribution of nuclei.

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