

# Spinodal decomposition and glass transition in eutectic alloys

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(Submitted 6 March 1985)

Zh. Eksp. Teor. Fiz. **91**, 1074–1081 (September 1986)

A theory is derived for the behavior of alloys of eutectic composition during quenching from the liquid phase. Several structures may form, depending on the quenching rate: a lamellar structure, a crystalline alloy of homogeneous composition which is unstable with respect to spinodal decomposition, and an amorphous alloy. Several experiments which could provide information on the mechanism by which alloys of eutectic composition convert to an amorphous structure are proposed.

1. The crystallization of eutectic alloys has been studied theoretically and experimentally for many years now.<sup>1–8</sup> When a liquid is cooled sufficiently slowly, the crystallization front retains a fixed shape as it moves, at velocities  $v \sim 10^{-2} - 1$  cm/s. A "lamellar structure" forms, in which layers of the *A* and *B* phases making up the eutectic alloy alternate periodically in the direction perpendicular to the growth direction. These layers may be plates or rods. In the simplest case of a binary alloy, the phases *A* and *B* may consist of pure elements, either metals or nonmetals. Some typical alloys are Al–Zn, Al–Cu, Pb–Cd, and Sn–Zn in the first case and Al–Si, Pb–Bi, and Sn–Bi in the second.

It has been found that the period  $\lambda$  of the lamellar structure depends on the front velocity  $v$ :  $\lambda^2 v = \text{const}$ . The first arguments in favor of such a dependence appeared in Refs. 1–3. It has recently been shown that this relation keeps the steady-state growth of a lamellar structure stable.<sup>9–11</sup>

As the quenching rate is increased, the period  $\lambda$  of the steady-state structure decreases. For the alloy Al–Al<sub>2</sub>Cu, for example, the period changes from a few microns to something on the order of 100 Å (Refs. 6 and 7) as this rate is increased to  $\sim 1$  cm/s. In order to produce structures of this sort in the case of a stable, steady-state crystallization front, it is necessary to produce a high temperature gradient ahead of the front. This was done in Refs. 6 and 7 by scanning a CO<sub>2</sub> laser beam over a thin layer of the alloy of eutectic composition.

With a further increase in the quenching rate, a single-phase alloy forms.<sup>12–14</sup> The single-phase Ag–Cu alloy which is produced in quenching as the molten material is sprayed onto a cold substrate was studied in more detail in Ref. 15, where it was found that as a homogenous alloy of this type ages its composition acquires a periodic modulation. This behavior was interpreted as a spinodal decomposition in the two-phase system.

On the other hand, there is a wide range of research on eutectic alloys at even higher cooling rates, at which an amorphous structure forms (e.g., Refs. 16 and 27). A characteristic difference between eutectic alloys and alloys of other compositions is the relatively low cooling rate at which an amorphous structure occurs.

In the present paper we attempt to describe from a unified standpoint the entire set of events which are observed during a systematic increase in the rate at which a eutectic melt is cooled.

In particular, we explain the existence of a limit on the interval of cooling rates in which a lamellar structure can form. We show that at rates higher than this interval a solid alloy forms; its composition is homogeneous, and it decomposes behind the front by a mechanism of spinodal decomposition, in accordance with observations. Even this solidification, however, occurs only at rates up to a certain limit, above which the eutectic alloy begins to acquire an amorphous structure. We offer a possible explanation for the circumstance that this limiting rate is significantly lower than the cooling rate required for the conversion of alloys of other compositions to an amorphous structure.

We also propose some experiments which could permit a more detailed study of the mechanism for the decomposition and glass transition of alloys of eutectic composition.

2. The steady-state growth of a lamellar structure as a eutectic alloy is cooled slowly was studied in detail by Jackson and Hunt<sup>2,3</sup> (see also Ref. 18). It was suggested that a two-phase system of this sort grows due to diffusive redistribution of the melt components in the liquid phase near the crystallization front. The diffusion equation is written as follows in a coordinate system which moves at the front velocity:

$$D_L \nabla^2 c_L + R \partial c_L / \partial z = 0, \quad (1)$$

where  $D_L$  is the diffusion coefficient of the liquid phase,  $c_L$  is the concentration of one of the components in the liquid phase, and  $R$  is the velocity of the crystallization front, which is moving in the  $z$  direction.

Imposing the boundary conditions

$$c_L = c_E + c_\infty = c_0 \quad (2)$$

at  $z \rightarrow \infty$ , far from the front, and the boundary conditions

$$\begin{aligned} \frac{\partial c_L}{\partial z} &= -\frac{R(c_E - c_A)}{D_L}, & 0 \leq x \leq S_A, \\ \frac{\partial c_L}{\partial z} &= -\frac{R(c_E - c_B)}{D_L}, & S_A \leq x \leq S_A + S_B, \end{aligned} \quad (3)$$

at  $z = 0$ , at the crystallization front ( $c_E$  is the concentration of the eutectic composition;  $c_A$  and  $c_B$  are the concentrations of the *A* and *B* phases at the melting point of the eutectic,  $T_E$ ; and  $S_A$  and  $S_B$  are the dimensions of the plates of the lamellar structure), we find a solution for the distribution of the concentrations of the components in the liquid phase ahead

of the crystallization front:

$$c_L - c_0 = (c_B - c_0) e^{-(R/D_L)z} + \sum_{n=1}^{\infty} B_n \cos\left(\frac{2\pi n x}{\lambda}\right) \times \exp\left[\left(-\frac{R}{2D_L} - \left\{\left(\frac{R}{2D_L}\right)^2 + \left(\frac{2\pi n}{\lambda}\right)^2\right\}^{1/2}\right)z\right], \quad (4)$$

where

$$B_n = \frac{\lambda R}{(\pi n)^2 D_L} (c_B - c_A) \sin \frac{2\pi S_A n}{\lambda}, \quad \lambda = 2(S_A + S_B).$$

For growth to occur with a concentration distribution of this sort, at a given velocity  $R$  and with a steady-state shape of the front, we would need the following supercooling at the front:

$$\Delta T = T_E - T_f = \Delta T_c + \Delta T_\sigma + \Delta T_K, \quad (5)$$

where  $\Delta T_c$  depends on the local deviation of the concentration of the liquid at the front from the eutectic composition ( $\Delta T_c \propto \lambda R / D_L$ ),  $\Delta T_\sigma$  is related to the finite curvature of the front ( $\Delta T_\sigma \propto 1/\lambda$ ), and  $\Delta T_K$  is the kinetic supercooling of the liquid, whose meaning will become clear below.

3. To determine how relations (1)–(4) transform as the front velocity increases, we examine the phase diagram in Fig. 1, which is typical of eutectic alloys. A diagram of this sort can be constructed in, for example, the simple model of a lattice gas.<sup>19</sup> Assuming  $N = N_A + N_B$  atoms of the solid phase occupy sites of the regular lattice and that the atoms of the two components  $A$  and  $B$  interact only with their nearest neighbors, we can find the following expression for the free energy of the system:

$$F(c) = Gc(1-c) + kT[c \ln c + (1-c) \ln(1-c)], \quad (6)$$

where  $G$  is the energy of the mixing of the alloy components. For  $G > 2kT$ , the plot of  $F(c)$  is a two-trough curve like curve 1 in Fig. 2. Curve 2 in Fig. 2 shows  $F(c)$  for the liquid phase. As the temperature changes, there are changes in the relative positions of curves 1 and 2 and, accordingly, in the equilibrium concentrations of the liquid and solid phases. By analyzing the behavior of the free-energy curves in Fig. 2, we can determine the range of applicability of the Hunt-Jackson theory for the solidification of eutectic alloys. Specifically, there is always a range of concentrations of the liquid phase in which this phase loses its stability with respect to the solid phase. In our simple model, this region is the exterior of the

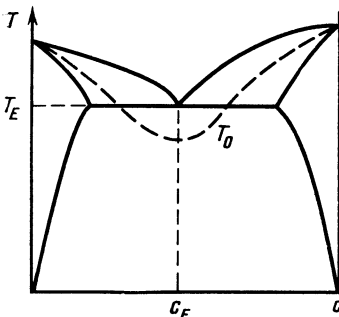


FIG. 1.

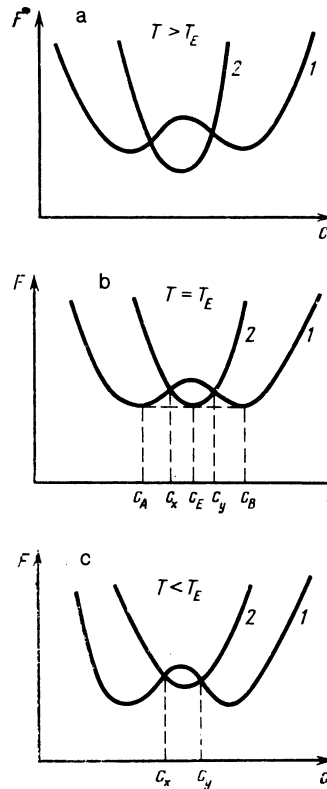


FIG. 2.

interval  $[c_x, c_y]$ , whose magnitude decreases with decreasing temperature. In Fig. 1, this concentration region is bounded by the curve  $T_0$ , defined as the equilibrium curve of the liquid and solid phases with identical concentrations. This curve is usually regarded as a thermodynamic limit,<sup>20</sup> which determines the maximum solubility of an impurity in the solid phase<sup>21</sup> (various types of behavior of this curve are discussed below). For high front velocities [and, accordingly, when the supercooling at the front,  $\Delta T$  in (5), is large], so that the concentration of the components of the liquid phase, described by the estimate

$$c_L - c_B \propto \frac{\lambda R}{D_L} (c_B - c_A), \quad (7)$$

derived from Eq. (4), goes outside the stability interval  $[c_x, c_y]$ , the Hunt-Jackson theory no longer describes the crystallization of a eutectic alloy.

It is not difficult to estimate the velocity of the crystallization front at which this event occurs. Under the assumption that there exists a minimum dimension  $\lambda$ , bounded by the width of the interfacial region between the  $A$  and  $B$  phases,  $d \sim 10\text{--}100 \text{ \AA}$  (Ref. 22), and taking  $D_L 10^{-4} - 10^{-5} \text{ cm}^2/\text{s}$  to be a typical value of the diffusion coefficient, we find  $(c_L - c_E)/c_B - c_A > (0.1 - 1)$  from (7) for velocities  $R > 10 \text{ cm/s}$ ; i.e., the value of  $c_L$  is clearly beginning to go outside the stability interval of the liquid phase. This estimate agrees with the limiting velocity given in Ref. 7 for the eutectic  $\text{Ag-Ag}_2\text{Cu}$ , i.e., the velocity above which one no longer observes a lamellar structure, whose minimum period  $\lambda$  is  $\sim 100 \text{ \AA}$ .

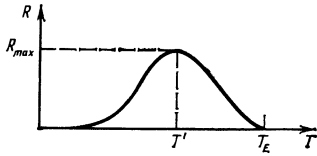


FIG. 3.

This discussion has been based on a model; it ignores the more complex behavior of the alloy of a given concentration at the transition from the liquid state to the solid state. In particular, account should have been taken of the existence of energy barriers of a kinetic nature at this transition. These barriers could enlarge the stability interval of the liquid phase,  $[c_x, c_y]$ , and ultimately increase the limiting velocity. However, in order to derive an estimate we will assume that these arguments are completely justified.

In view of the importance of this conclusion that there exists a limiting velocity, we will show how to reach a similar result on the basis of other considerations, which were used in Ref. 23 in a study of the glass transition of a eutectic alloy (below we offer some criticism of that approach for explaining the glass transition). As we have already seen, one of the results of the Hunt-Jackson theory is a relation between the period  $\lambda$  of the lamellar structure and the front velocity  $R$ :  $\lambda^2 R = D_L (T_f) A_2 / A_1$ , where  $R = D_L (T_f) (\Delta T)^2 / 4 A_1 A_2$ ,  $\lambda^2 = 2 A_2 / T$ , and  $A_1$  and  $A_2$  are constants. Allowing for the temperature dependence of the diffusion coefficient of the liquid phase,  $D_L = D_0 \exp(-A_0/kT)$ , we can derive a non-monotonic dependence of the velocity of the crystallization front of the lamellar structure on the supercooling at the front (Fig. 3). For the Pb-Sn eutectic system, the calculated value of the maximum attainable front velocity is  $R_{\max} \approx 12$  cm/s, which reached when the front is supercooled by an amount  $\Delta T = T_f - T_E \approx 100^\circ$ .

We thus reach the conclusion that as the crystallization front propagates faster the diffusion of the components in the liquid phase is not fast enough to support the growth of the plates of the  $A$  and  $B$  components in the solid phase. We note, however, that the solid phase which forms behind the front may retain a concentration composition which is modulated in the direction perpendicular to the motion of the front, at a modulation amplitude smaller than  $c_B - c_A$ . In this case, the continuity equation (3) becomes

$$D_L \left. \frac{\partial c_L(x)}{\partial z} \right|_{z=0} = R(c_s(x) - c_L(x)). \quad (8)$$

Assuming

$$c_s = c_E + \sum_k c_k^s e^{ikh} e^{-q_k^s z}, \quad c_L = c_E + \sum_k c_k^L e^{ikh} e^{-q_k^L z},$$

we find the following results for the amplitudes of the modulations of the liquid and solid phases at the front:

$$c_k^L = c_k^s \left( \frac{R}{D_L q_k^L + R} \right). \quad (9)$$

Here  $q_L$  is determined from the diffusion equation in the liquid phase, (1):

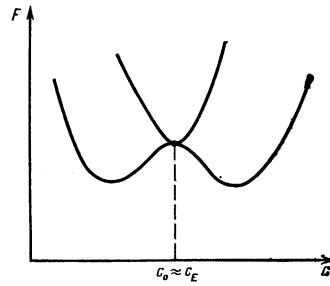


FIG. 4.

$$q_L = \frac{R}{2D_L} + \left[ \left( \frac{R}{2D_L} \right)^2 + k^2 \right]^{1/2}. \quad (10)$$

For a complete description of the crystallization process in this case, the system of equations should be supplemented with an equation for the distribution of the concentrations of the components in the solid phase (in a coordinate system which is moving with the front):

$$\frac{\partial c_s}{\partial t} - R \frac{\partial c_s}{\partial z} = D_s \nabla^2 c_s + \kappa \nabla^4 c_s, \quad (11)$$

where  $D_s$  is the diffusion coefficient in the solid phase, and the last term in this equation reflects the energy of the non-uniform composition distribution.

4. A study of equations (8)–(10) shows that as the front velocity increases after the end of the growth of the lamellar structure the temperature at the front changes abruptly to  $T_* < T_0$  ( $T_0$  is defined in Fig. 4), when the supercooling which is reached becomes capable of maintaining the given front velocity.

Actually, as we see from (8) and (9), as  $R$  increases the amplitude of the modulation of the solid phase,  $c_k^s$ , approaches twice the value of  $c_k^L$ , which vanishes along with the stability interval  $[c_x, c_y]$  in the limit  $T \rightarrow T_0$ . At  $T_0$ , however, the liquid and homogeneous solid phases (to simplify the discussions, we assume  $c_E \approx c_0$  in Fig. 4) are found to be in equilibrium at the front; this result means that the front is not moving ( $R \rightarrow 0$ ). A further kinetic supercooling to a temperature  $T_* < T_0$  causes motion of the front at a given velocity; the compositions of the liquid and solid phases at the front are nearly homogeneous.

This state of the solid phase is unstable, however, and a decomposition of the spinodal type begins in the system behind the front, by virtue of the relation  $\partial^2 F / \partial c^2 < 0$ . Correspondingly, we have a diffusion coefficient  $D_s < 0$ , and Eq. (11) describes an "ascending" diffusion (cf. Ref. 24). As in Cahn's theory,<sup>24</sup> it can be shown for a spinodal decomposition that the growth rate of the instability in a system of this sort peaks at  $k_0 \approx 0.7(D_s/2\kappa)^{1/2}$ , so that we easily find the following expression for  $q_{k_0}^s$  from (11) in the steady state:

$$q_{k_0}^s \approx \frac{D_s k_0^2 + \kappa k_0^4}{R} \ll k_0. \quad (12)$$

Consequently, a solid alloy which is nearly homogeneous in composition at the front (it should be assumed that there is a small but nonzero modulation of the composition at the

front because of the energy barriers of a kinetic nature) becomes progressively more inhomogeneous with distance from the crystallization front into the interior of the sample. As usual, a description of this sort is suitable only for the initial (linear) stage of the decomposition. It is interesting to note that since the spinodal decomposition is greatly retarded by the small value of  $D_S$ , no significant modulation of the concentration appears until several hours have passed.<sup>15</sup> In the early stage, in contrast, the solid phase in an experiment should be observed to be homogeneous.

We would like to also stress the following circumstance: In examining spinodal decomposition in an ordinary binary alloy one cannot eliminate the competing growth of nucleating regions of new phases which form as the system passes through a metastable region as it cools.<sup>24</sup> For eutectic systems, our arguments show that it is possible to eliminate a competition of this sort and to deal with "pure" spinodal decomposition.

5. With a further increase in the cooling rate, this analysis remains valid until the kinetic supercooling of the front reaches the level at which the alloy begins to become amorphous. Since the solid phase at the front forms with a nearly homogeneous composition, so that the transition to the solid phase is diffusionless, the picture of the phase transition at high front velocities is no different from the ordinary (diffusionless) picture for alloys of arbitrary composition. Accordingly, the standard arguments for single-component substances are valid for determining the limiting velocity at which the substance becomes amorphous.<sup>25-27</sup> These arguments can be summarized by saying that in the case of a diffusionless phase transition to the solid state the front velocity is described approximately as a function of the supercooling by<sup>25,28</sup>

$$R \propto \omega \exp\left(-\frac{E}{kT}\right) \exp\left(-\frac{\Delta s}{k}\right) \left\{ 1 - \exp\left[-\frac{\Delta H}{k} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \right\}, \quad (13)$$

where the notation is explained in Fig. 5 (see also Ref. 29).

In equilibrium at  $T = T_0$ , with  $R = 0$ , we have  $\Delta \epsilon = \epsilon_L - \epsilon_s = T_0 \Delta s = \Delta H$ . The front velocity begins to decrease at some front temperature  $T < T_0$ , and at  $T = T_{gl}$  the material becomes amorphous.

There is, however, an important distinction for eutectic alloys: The temperature  $T_0$  for a eutectic alloy may be far lower than its melting point. For the eutectic alloy Ag-Cu, for example, the difference  $T_e - T_0$  is on the order of 100° (Ref. 30), while that for the alloy Zn-Cd is about 200° (Ref. 31). This result means that in order to achieve approximately the same temperature  $T_{gl}$  for the glass transition for alloys

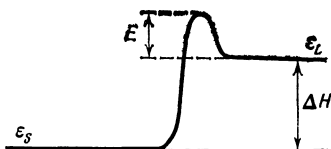


FIG. 5.

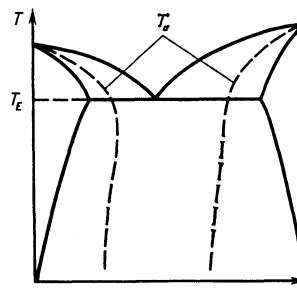


FIG. 6.

of eutectic and noneutectic compositions,<sup>17</sup> the eutectic alloy must be cooled at a rate significantly lower, since for equal velocities of the crystallization front the supercooling at the front of the eutectic alloy may be far greater (by an amount of order  $T_e - T_0$ ).

In a recent effort<sup>23,32</sup> to explain the relatively small cooling rates required for the glass transition of a eutectic Pd-Cu-Si alloy, a state diagram of the alloy with a curve of  $T_0$  as in Fig. 6 was examined. Using the results of the Hunt-Jackson theory for the growth rate of a lamellar structure,

$$R \propto D_L (\Delta T)^2, \quad \lambda^2 R \propto D_L,$$

and estimating the behavior of this quantity as the temperature is lowered, Boettinger<sup>23,32</sup> concluded that there is a decrease in  $R$  with decreasing temperature beginning at a certain  $T' < T_E$  (Fig. 3). Boettinger concluded that this circumstance should ultimately give rise to the transition to an amorphous alloy. In fact, the front velocity above which the Pd-Cu-Si eutectic alloy becomes amorphous has also turned out to be very low,  $R \approx 2.5$  mm/s (!). As Boettinger<sup>23,32</sup> mentioned, however, the temperature at which this transition to an amorphous state occurs,  $T_{gl}$ , is very high for this alloy (apparently because of its high viscosity). We believe that the latter circumstance is the primary reason for the rapid glass transition of the Pd-Cu-Si alloy. For many alloys of eutectic composition for which  $T_{gl}$  is substantially lower than for this alloy, the existence of a limiting velocity  $R_{max}$  above which a lamellar structure cannot form does not imply the onset of a glass transition. As we showed above, this behavior of  $R$  as a function of the front supercooling leads to only the formation of a solid alloy of homogeneous composition (not necessarily amorphous!). In contrast with alloys with a state diagram of the type in Fig. 1, a homogeneous crystalline structure of this sort could not be in equilibrium with the liquid phase at  $T < T_E$  (in the limit  $R \rightarrow 0$ ). Accordingly, such alloys do not appear to us to represent any special case among alloys of various compositions from the standpoint of a rapid glass transition. We believe that the alloys of primary interest from this standpoint are the eutectic alloys for which the  $T_0$  curve shows the behavior in Fig. 1—the alloys which we have been discussing here.

6. We turn now to a discussion of some possible experiments which might yield a more detailed understanding of the mechanism for the decomposition and glass transition of eutectic alloys. Such experiments might also serve as tests of

some assertions which follow from the arguments above.

It would obviously be very worthwhile to pursue Cline's experiments<sup>6,7</sup> involving the scanning of a laser beam over thin layers of eutectic alloys. By raising the power of the laser beam and the scanning velocity, i.e., by increasing the temperature gradient along the crystallization front of the eutectic alloy, it might be possible to reach high front velocities at which the solid-liquid interface would remain stable. In this situation it might become possible to move continuously through the entire range of cooling rates at which lamellar, single-phase, and amorphous structures of the eutectic alloy form in succession.

Furthermore, we believe it would be interesting to carry out an experiment to observe the structure of a eutectic alloy, e.g., Ag-Cu, as it is heated out of the amorphous state. Some experiments of this sort which have already been carried out (e.g., Refs. 33 and 34) have revealed some new crystalline structures in the alloys. However, that is not what we are interested in. If our arguments regarding the mechanism for the glass transition of a eutectic alloy are correct, then as the alloy is heated slightly above  $T_{gl}$  it may go into a homogeneous phase which is unstable with respect to spinodal decomposition. Accordingly, after such an alloy has aged for a few hours it should exhibit a periodic structure of the type observed in Ref. 15.

The initial alloy might be produced by a method other than quenching of a melt. Another possibility is to deposit atoms of the alloy with the concentrations of components corresponding to the eutectic composition on a cold substrate. The resulting amorphous film might exhibit a similar behavior when heated above  $T_{gl}$ . This method would also be interesting in that it would become possible to study the spinodal decomposition in other binary alloys, whose melting points lie above the two-phase region in the state diagram.

We wish to thank V. G. Vaks for a useful discussion of these results.

<sup>1</sup>C. Zener, *Trans. Met. Soc. AIME* 167, 550 (1946).

<sup>2</sup>J. D. Hunt and K. A. Jackson, *Trans. Met. Soc. AIME* 236, 843 (1966).

- <sup>3</sup>K. A. Jackson and J. D. Hunt, *Trans. Met. Soc. AIME* 236, 1129 (1966).
- <sup>4</sup>B. E. Sundquist, *Metall. Trans.* **4**, 1919 (1973).
- <sup>5</sup>M. Hillert, *Acta Metall.* **30**, 1689 (1982).
- <sup>6</sup>H. E. Cline, *Appl. Phys. Lett.* **37**, 1098 (1980).
- <sup>7</sup>H. E. Cline, in: *Laser-Solid Interactions and Transient Thermal Processing of Materials* (ed. J. Narayan, W. L. Brown, and R. A. Lemons), New York, 1983, p. 727.
- <sup>8</sup>M. B. Gellikman and D. E. Temkin, *Kristallografiya* **29**, 643 (1984) [*Sov. Phys. Crystallogr.* **29**, 381 (1984)].
- <sup>9</sup>J. S. Langer, *Phys. Rev. Lett.* **44**, 1023 (1980).
- <sup>10</sup>J. S. Langer, *Phys. Rev.* **B24**, 4155 (1981).
- <sup>11</sup>J. S. Kirkaldy, *Phys. Rev.* **B30**, 6889 (1984).
- <sup>12</sup>P. Duwez, R. H. Willens, and W. Klement, Jr., *J. Appl. Phys.* **31**, 1136 (1960).
- <sup>13</sup>W. A. Elliot, *Met. Trans.* **4**, 2031 (1973).
- <sup>14</sup>P. G. Beck, S. M. Copley, and M. Bas, *Met. Trans.* **A12**, 1687 (1981).
- <sup>15</sup>P. G. Boswell and G. A. Chadwick, *J. Mat. Sci.* **12**, 1687 (1977).
- <sup>16</sup>M. Takahashi, Y. Tateno, and M. Koshimura, *Jpn. J. Appl. Phys.* **19**, 2334 (1980).
- <sup>17</sup>B. Predel, *Physica* **103B+C**, 113 (1981).
- <sup>18</sup>M. Flemings, *Solidification Processes* (Russ. transl. Mir, Moscow, 1971).
- <sup>19</sup>G. Schulze, *Physics of Metals* (Russ. transl. Mir, Moscow, 1971).
- <sup>20</sup>J. W. Cahn, S. R. Coriell, and W. J. Boettinger, in: *Laser and Electron Beam Processing of Materials* (ed. C. W. White and P. S. Peercy), New York, 1980, p. 89.
- <sup>21</sup>C. W. White, in: *Laser and Electron Beam Interactions with Solids* (ed. B. R. Appleton and G. K. Celler), New York, 1982, p. 109.
- <sup>22</sup>J. W. Cahn and S. M. Allen, *Acta Metall.* **27**, 1085 (1979).
- <sup>23</sup>W. J. Boettinger, in: *Rapid Solidification Processing*, (ed. R. Mehrabian), 1980.
- <sup>24</sup>J. W. Cahn and J. E. Hilliard, *J. Chem. Phys.* **31**, 688 (1958).
- <sup>25</sup>M. von Almen, in: *Laser-Solid Interaction and Transient Thermal Processing of Mat.* (ed. J. Narayan, W. L. Brown, and R. A. Lemons), New York, 1983, p. 691.
- <sup>26</sup>D. R. Uhlman, *J. Non-Cryst. Solids*, **7**, 337 (1972).
- <sup>27</sup>V. I. Motorin, *Phys. Stat. Sol.* **a80**, 447 (1983).
- <sup>28</sup>J. W. Cahn, W. B. Hillig, and G. W. Sears, *Acta Met.* **12**, 1421 (1964).
- <sup>29</sup>A. A. Chernov, *Sovremennaya kristallografiya* (Modern Crystallography), Vol. 3, Nauka, Moscow, 1980.
- <sup>30</sup>W. J. Boettinger, in: *Rapidly Solidified Amorphous and Crystalline Alloys* (ed. B. H. Kear), 1982.
- <sup>31</sup>P. G. Boswell and G. A. Chadwick, *J. Mat. Sci.* **14**, 1269 (1979).
- <sup>32</sup>W. J. Boettinger, in: *Rapidly Solidified Amorphous and Crystalline Alloys*, (ed. B. H. Kear), 1982.
- <sup>33</sup>J. L. Walter, in: *Rapid Solidification Processing*, (ed. R. Mehrabian), 1980, p. 79.
- <sup>34</sup>K. S. Tan, T. Wahl, and R. Kaplow, in: *Rapid Solidification Processing* (ed. R. Mehrabian), 1986, p. 112.

Translated by Dave Parsons