Explosive crystallization of amorphous substances

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This review provides an analysis of the theoretical and experimental aspects of explosive crystallization of amorphous substances (glasses). Quantitative criteria are formulated for thermal bistability of quasisteady crystallization of glasses and for the absence of explosive crystallization. Expressions are derived for the critical parameters and the velocity of an explosive crystallization front allowing for the heat transfer conditions and for the geometry of the crystallization front (which may be plane, spherical, or circular). A systematic account is given of thermophysical characteristics and of the parameters governing the thermal stability of practically all the materials in which explosive crystallization has been discovered so far. Data on the velocity of propagation and temperature in an explosive crystallization front are also given. A classification of glasses is proposed on the basis of their stability against explosive crystallization and a quantitative analysis is made of the published experimental data on explosive crystallization of metallic, semiconducting, and insulating glasses. It is shown that there is a satisfactory qualitative and quantitative agreement between the theory and experiment.

CONTENTS

1. INTRODUCTION

One of the interesting (and important from the point of view of applications) topics in the physics of the amorphous state of matter (glassy state)[1] is the problem of thermal stability of this state against crystallization under the influence of homogeneous or local heating. Recent investigations have shown that many problems of the stability of glasses belong to the general physical range of problems of nonlinear nonisothermal macrokinetics which is traditionally investigated in the physics of combustion and explosion.[1,2]

The solution of these problems with the aid of ideas and methods employed in the theory of crystallization[3,4] makes it possible to progress further in the theory of nonisothermal precipitation of glasses than in qualitatively similar problems in chemical kinetics. Therefore, the interaction of two apparently independent branches of nonlinear macrokinetics has proved to be mutually fruitful. However, it should be stressed that the very possibility of such an interpenetration of ideas and results is due to the specific nature of glasses, which we shall now consider in greater detail.

According to the generally accepted ideas (see, for example, Refs. 5 and 6), amorphous substances are configurationally frozen metastable (and sometimes also labile[7]) states of matter without any long-range order and below the glass-forming temperature T_g they are stabilized by a "kinetic" factor which is a high viscosity (exceeding 10^{13}–10^{15} P). In view of their thermodynamic quasiequilibrium, glasses are subject also to another factor which is destabilizing and proportional to the difference between the thermodynamic potentials of the amorphous and equilibrium (crystalline) states. Even in the absence of external perturbations, this factor is responsible for relaxation of amorphous substances to a state closer to equilibrium. Two types of such relaxation, homogeneous and heterogeneous, are known.[5,8]

Homogeneous relaxation (frequently known as structural) occurs uniformly throughout a sample so that its amorphous state is retained, which naturally means that the concept of the "amorphous state" loses its unambiguous thermodynamic meaning which is associated with an equilibrium state of a crystal. Structural relaxation alters the short-range order and this is usually accompanied by a slight

reduction in the degree of nonequilibrium of glass. The heat of transformation to a stable phase, which can be regarded as a measure of such nonequilibrium, changes only slightly.

Heterogeneous relaxation creates regions with a long-range order and is characterized by the presence of phase boundaries. It involves nucleation and growth of equilibrium or metastable crystalline phases and is accompanied by the release of the latent heat of the phase transition. It is important to stress that the rate of these "elementary" processes of appearance of a new phase increases strongly (in an activational manner) on increase in the temperature of an amorphous sample.

It is for this reason that in the case of slow ("oven") heating of glasses they all become crystallized at some temperature T_c, which depends relatively weakly on the rate of heating as long as the rate of dissipation of the heat of transition is high and we can ignore the influence of this rate on a possible self-acceleration of the slow crystallization process.

However, such self-acceleration becomes possible when the removal of heat is sufficiently slow. Then the rapid evolution of the latent heat of the transition at an interface between two phases (when the experiments are designed suitably) may result in considerable self-heating of the crystallization front which assumes the form of a thermal domain moving at a velocity up to several tens of meters per second. Crystallization of a sample under these conditions is usually called "explosive" or "avalanche."

In recent years the process of explosive crystallization has been the subject of intensive experimental and theoretical investigations. In addition to the obvious physical interest in this phenomenon, studies of the nature of explosive crystallization are important also because of the increasing applications of amorphous materials in modern technology. In fact, explosive crystallization initiated by a sufficiently strong local energy pulse (mechanical or thermal) may propagate throughout the whole volume of an amorphous material at a high rate and, what is very important, this may happen at temperatures well below (by hundreds of degrees) the crystallization temperature under oven annealing conditions. This must be allowed for in, for example, the selection of amorphous materials in practical applications.

It therefore follows that the specific nature of nonisothermal precipitation of glasses is that under constant external conditions, depending on the method of initiation of the transition to the stable phase, an amorphous sample may exhibit both slow (practically isothermal) and fast explosive (practically adiabatic) steady-state crystallization. This feature of the crystallization of glasses will be called the thermal bistability of the process of growth of a new phase and it will be considered in greater detail in Sec. 3.

Reviews have already been published on explosive crystallization of semiconductors.[9,10] However, in addition to amorphous semiconductors, explosive crystallization is observed also in some amorphous metallic alloys,[11] pure amorphous metals,[12,13] and insulators.[6] A recently developed theory[14-19] makes it possible to consider all these cases from a unified standpoint, which is the main purpose of our theoretical and experimental review. It differs from the published reviews both in respect of its approach and content.

A special feature of our approach is a unified analysis of both fast (explosive) and slow processes of crystallization of glasses, demonstrating the possibility of thermal bistability

of this process. This makes it possible to compare the experimental results and critical parameters of explosive crystallization with the theory.

The content of this review (particularly in the presentation of theoretical results) is governed primarily by the nature of the original publications, but it includes also a fairly detailed analysis of the most interesting (primarily experimental) work of other authors.

2. EXPERIMENTAL INVESTIGATIONS OF CRYSTALLIZATION OF AMORPHOUS SUBSTANCES

2.1. Some characteristics of the microstructure of amorphous films

Although there is no long-range order in amorphous substances, they do have a short-range order in which the distribution of atoms around any other atom in a system can be described by a radial distribution function of the atomic density. The radial distribution functions are found experimentally using diffraction of x rays, electrons, and neutrons. The positions of peaks on the radial distribution curves and the areas under them give, respectively, the average radius and the average number of atoms in a coordination sphere. Problems in determination of the structure of amorphous substances have been reviewed in detail in many papers and monographs (see, for example, Refs. 20–22). We shall consider only some characteristics of the microstructure of amorphous films and, in particular, we shall consider the microscopic isotropy of amorphous films formed by condensation in vacuum or by quenching of a melt. It has been established that such films are not homogeneous. They are characterized by fluctuations of the density, representing regions of free and "antifree" volume found in a number of amorphous alloys by low-angle scattering of x rays and neutrons.[21,23] For example, fluctuations of the atomic plane in Fe–P amorphous alloys are 1–2% (Ref. 23). Such fluctuations are associated with "frozen" crystallization centers in amorphous films. These frozen centers are very small, do not have the regular structure, and can become effective crystallization nuclei only after some modification.[5,8] It seems that microcrystalline "domains" (of ~ 1 nm size) observed in electron-microscopic studies of amorphous $Fe_{84}B_{16}$ alloys[24] can be regarded as frozen crystallization centers. The existence of such centers has been demonstrated experimentally in studies of the nature of nucleation during heating of amorphous metallic alloys.[8] It has been shown that the density of frozen centers decreases on increase in the rate of cooling when a melt is quenched. This accounts in particular for a nonuniform distribution of frozen centers across the thickness of a film. When a free surface of an amorphous ribbon is formed by quenching a melt, the density of such frozen centers is higher than on a surface adjoining the drum supporting a film[8] because the rate of heat transfer from the latter is greater. The situation is clearly similar in the case of amorphous films formed by the condensation of a vapor on a cold substrate in vacuum. An indirect proof of the existence of frozen crystallization centers in such films is provided by a change in the Hall coefficient R_H, observed on increase in the thickness of amorphous Yb and Bi films.[25] The value of R_H changes in the direction of the crystalline state and in the case of Yb there is even a change in the sign. This is also attributed[25] to an increase in the concentration of frozen centers on increase in the thickness of a condensed film be-

cause of a reduction in the rate of heat removal from its surface.[14]

2.2. Crystallization of amorphous substances during heating

Amorphous substances are known to crystallize by nucleation and growth. The fullest information on the micromechanisms of crystallization of amorphous metallic alloys can be found in the review of Köster.[8] We shall not deal with nucleation, which is described in detail in Refs. 5 and 8, but mention only some of the more important laws governing the growth of crystals in an amorphous substance which will be needed in the subsequent discussion of explosive crystallization. Slow (under oven annealing conditions) growth of crystals may be the dominant eutectic or polymorphic process, and it is always thermally activated.[5,8] From our point of view the most interesting is polymorphic crystallization, when only one phase forms and it is of the same composition as the amorphous material. This type of crystallization can occur only in the region representing pure elements or compounds in equilibrium phase diagrams and it involves single jumps of atoms across a crystallization front, i.e., it occurs as a result of a diffusion-free mechanism. The occurrence of this mechanism is obviously a necessary condition for explosive crystallization.

It has been found experimentally that, in agreement with the theory, the growth velocity u of crystals during heating of many amorphous substances [Si,[26] Sb,[27] GaSe,[28] (Fe, Co, Ni)–B metallic alloys[8]] can be described satisfactorily by the Arrhenius dependence

$$u = u_0 e^{-E/RT}, \tag{1}$$

where $u_0 = \mathrm{const}$, E is the activation energy, and R is the universal gas constant.

It follows from Eq. (1) that the crystallization temperature T_c is not rigorously defined: the transition may occur (although very slowly) even in the case of isothermal storage at a temperature several degrees (for pure amorphous metals) or tens of degrees (in the case of amorphous metallic alloys) below the value accepted as T_c. The crystallization

temperature T_c is usually understood to be the temperature at which the transition occurs at a significant rate (10^{-3}–10^{-1} of the volume of a sample per minute).

The activation energy and the latent heat of a transition Q play the dominant role in the kinetics of crystallization of amorphous films. The values of T_c, E, and Q are given in Table I for some of the amorphous substances. The large scatter of the values of these quantities in the case of Si, Ge, and Sb is due to the different conditions of preparation of the samples (and, consequently, their purity). The relationship is unambiguous: the purer the sample, the lower the values of T_c and E and the higher the values of Q. Moreover, the values of these parameters may depend also on the substrate material.[60,61]

2.3. Initiation of explosive crystallization by a local energy pulse

Explosive crystallization was first observed back in 1855 for Sb films prepared by electrochemical deposition.[62] However, the nature of this effect was not understood at the time and the report in Ref. 62 was forgotten for a long time. The processes of explosive crystallization observed in amorphous Sb films formed by vacuum condensation[27,63,64] have made it possible to identify the explosive process in Sb formed by electrochemical deposition.

Systematic studies of explosive crystallization began in 1972 using amorphous Ge films prepared by hf cathodic sputtering.[65] Explosive crystallization was initiated in Ge films at room temperature by a local energy pulse (pricking with a needle, laser pulse, electron beam).[65,66] A self-maintained circular[65] or nearly linear[66] crystallization front propagated from the initiation point. In the former case the radius of the crystallized region[65] reached several centimeters. In the latter case[66] the process of explosive crystallization took place without damping and spread over the whole sample, which was a rectangular film 7 cm long and 2 cm wide. The velocity of the explosive crystallization front, determined in Refs. 65 and 66 by high-speed cinematography, reached 1.2 m/s and was independent of the method of ini-

TABLE I. Thermodynamic and kinetic characteristics of some materials forming amorphous phases.

Material	T_c, K	E, kJ/mol	Q, kJ/mol	ΔH, kJ/mol
Ge	473—603 [29–31] 743—774 [32,33]	125 [34,35] 145 [36]	15,9 [37] 11,5 [38] 12,1 [32]	37,3 [38] 31,8 [39]
Si	723—1014 [32,40–43]	260 [36] 280±10 [43] 320 [26]	9,51 [32] 11.3±0,8 [44]	50,7 [45]
Sb	240—270 [46–48] 313 [46]	55 [86] 84 [27] 96,5 [35] 30,9 [49]	10.2 [27] 12,3 [50]	20,1 [39]
Bi	13—15 [25,51]	3,4±0,4 [13] 3,77 [52]	6,07 [52]	10,9 [39]
Ga	15—20 [25,51]	3.8±0,6 [13]	1,21 *) [52]	5,59 [39]
Yb	13—14 [53,54]	3,4±0,4 [13]		7,66 [55]
Y	38 [56]	7,9±1,3 [57]		16,75 [58]
H_2O	160 [6]	41,6 [6]	1,8 [6]	5 [59]

*This value corresponds to the transition of amorphous Ga to a metastable monoclinic modification β-Ga. The transition of β-Ga to a stable phase as a result of further heating is accompanied by an additional release of the latent heat of the transition amounting to ~ 2.47 kJ/mol (Ref. 52).
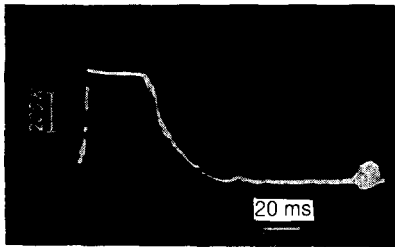
FIG. 1. Oscillogram showing an increase in the temperature of a Ge film in the course of explosive crystallization.[67]

tiation. A study of the evolution of heat in the course of explosive crystallization of germanium at room temperature with the aid of an InSb infrared detector[67] showed that the temperature in the crystallization front T_f was approximately 500 K higher than the initial temperature of the sample T_0 (Fig. 1). This was in satisfactory agreement with calculations[68] predicting

$$Q = \int_{300\mathrm{K}}^{T_f} c \, dT \tag{2}$$

(where c is the specific heat) on the assumption that $Q = 12.5 \, \mathrm{kJ/mol}$ (which is the average value in Table I) and that the heating by the heat of transition was adiabatic.

Investigations of explosive crystallization of amorphous Ge films established[65,67] the existence of two related parameters d^+ and T_0^+, which limited the possibility of undamped explosive crystallization (see Sec. 3). The minimum critical thickness d^+ is that thickness of an amorphous film below which self-maintained explosive crystallization becomes impossible at a given temperature and the critical temperature T_0^+ is that at which undamped explosive crystallization does not occur in a given amorphous film. The relationship between the parameters T_0^+ and d^+ for Ge films has been found experimentally[69]:

$$T_0^+ = 287 + \frac{5.2 \cdot 10^{-2}}{d} \ ; \tag{3}$$

here, the temperature is in kelvin and the thickness is in centimeters.

In addition to Ge, much work has been done on explosive crystallization in amorphous Si films.[70–73] For example, samples used in Ref. 70 were Si wafers 80–100 μm thick with an amorphous layer 350 nm on the surface. This layer was formed by phosphorus ion implantation (7×10^{14} P/cm^2) or condensation of Si vapor in ultrahigh vacuum. Undamped explosive crystallization occurred in these samples as a result of laser heating to $T > T_0^+$ at a rate of $\sim 10^6$ K/s. The process was initiated by a short pulse from a second laser. The velocity of the explosive crystallization front was independent of the traversed distance and amounted to 15–16 m/s. The temperature in the explosive crystallization front was $T_f = 1150$–1250 K.

Explosive crystallization had been investigated also in detail in amorphous films of ($\mathrm{In}_{1-x}\mathrm{Ga}_x$)$_{50}\mathrm{Sb}_{50}$ ($0.52 < x < 1$) alloys.[74] The temperature of glass substrates during condensation was 100 ± 25 °C. Explosive crystallization was initiated by pricking with a needle or by a laser pulse. As in the case of Ge and Si, a critical temperature T_0^+ was observed. For example, in the case of a freshly con-

densed $\mathrm{Ga}_{50}\mathrm{Sb}_{50}$ film of thickness $\sim 4 \, \mu$m this critical temperature was $T_0^+ \approx 90$ °C. The velocity of the crystallization front was 2–5 m/s. This front stopped always when the thickness of a wedge-shaped film decreased below a certain value, which was a clear manifestation of the existence of a minimum critical thickness d^+.

In the above cases of amorphous substances stable at temperatures well above the room value the critical temperature T_0^+ was also higher than the room value. In the case of pure amorphous metals and some amorphous metallic alloys characterized by low values of T_c the process of explosive crystallization occurred even at $T_0 = 4.2$ K. For example, undamped explosive crystallization was initiated in amorphous Yb and Bi films by a local current pulse[13] at $T_0 = 1.5$–6 K. The minimum critical thickness of amorphous Yb films, determined at $T_0 = 4.2$ K, was 35–45 nm and the corresponding thickness of Bi films was 25–35 nm. In addition to pure metals, explosive crystallization was initiated at $T_0 = 4.2$ K (by an electron beam pulse in an electron microscope) in $\mathrm{Fe}_{70}\mathrm{Ni}_{30}$ films.[12] It was found that during explosive crystallization of this amorphous metallic alloy some crystallites grew quite uniformly at a velocity of 10–20 m/s.

Apart from the substances mentioned above, explosive crystallization was observed in amorphous films of ice,[6] CdTe,[75] and possibly $\mathrm{Zr}_{70}\mathrm{Pd}_{30}$ (Ref. 76). In these cases it was again found that the temperature in the crystallization front increased strongly and the front traveled at a high velocity.

2.4. Spontaneous explosive crystallization

An important parameter of explosive crystallization is the maximum critical thickness[2] of amorphous films d^- (Sec. 3), which is the thickness above which a film becomes stable against explosive crystallization. An experimental manifestation of this instability is spontaneous explosive crystallization during condensation of an amorphous film when a thickness reaches the critical value $d_c^- < d^-$. The origin of this inequality is discussed in Sec. 4.

The critical thickness was first found in Ref. 63 and investigated thoroughly later[64,77] in amorphous Sb films. It was then observed in Fe and V films[78] and also in other metals and alloys[25] (Table II). It is clear from Table II that even in the case of the same substance the scatter of the values of d_c^- was quite considerable. This was primarily due to the presence of a number of foreign atoms (mainly gases) captured by the film during its condensation.[25]

The critical thickness of amorphous films of some metals was found by the electrical resistance method[25] (Table II). The behavior of the electrical resistance of Yb and Bi films condensed on liquid-helium-cooled substrates exhibited the following special features.[84] From the moment when a Yb film became continuous, its electrical resistance fell smoothly on increase in the thickness (Fig. 2a). When the film reached its critical thickness, the resistance R fell abruptly by 75–80%, corresponding to the difference between the resistivities of the amorphous and crystalline phases of Yb. Subsequent condensation resulted in a continuous fall of R because of an increase in the film thickness which was now in the crystalline state. Crystallization of an amorphous Bi film, which reached its critical thickness during condensation, revealed an abrupt appearance of an electrical resis-

TABLE II. Values of the critical thickness of the purest films of some amorphous materials.

Material	Investigation method*	Substrate material	d_c^-, nm	Ref.
Bi	R	glass	30—60	13, 25
	IS	AL	120	79
Ga	R	glass	180—230	13, 25
V	R	»	30	56
	R	»	20	78
Yb	R	»	60—120	13, 25
Fe	R	»	5	25, 78
	R, ED	sapphire	15	80
Ni	EM	amorphous C	3	81
	ED	Formvar	3	82
$Bi_{50}Sb_{50}$	R	glass	250	25
$Fe_{50}Ni_{50}$	EM	amorphous C	100	81
Sb	R	glass	160—240	86
Ge	R, EM	»	10	83

*Here, R is the electrical resistance method, ED is electron diffraction, EM is electron microscopy, and IS is the method of internal stresses.

All materials, except Ge, were condensed on substrates cooled with liquid helium. In the case of Ge, we have $T_0 = 250\,°C$.

tance (Fig. 2b), since crystalline Bi (in contrast to the amorphous material) was not superconducting.

On the basis of Table II it is difficult to determine whether the critical thickness of amorphous films depends on the substrate material, since these films had been condensed under various vacuum conditions and these conditions are known[25] to have a strong influence on the parameter d_c^-. Nevertheless, such a dependence undoubtedly exists. This is demonstrated by the results[85] an investigation of the influence of the substrate material (other conditions being kept constant) on the critical thickness of amorphous Bi films. For example, it was established that in the case of a copper substrate the value of d_c^- is 5 times greater than for a glass substrate. It seems that this is mainly due to the high thermal diffusivity of copper, compared with that of glass.

The velocity of the crystallization front in a film which reached its critical thickness was estimated to exceed 2.5 m/s (Ref. 27) and determined accurately to be ∼32 m/s (Ref. 27) by the method of high-speed cinematography of amorphous Sb films condensed at room temperature. Explosive crystallization appeared locally and spread to the whole

FIG. 2. Changes in the electrical resistance R during condensation of Yb and Bi films on liquid-helium-cooled substrates[84]: a) Yb film; b) Bi film.

sample by a self-maintained process. The value of d_c^- was about 200 nm (Refs. 27 and 64). Explosive crystallization also appeared spontaneously during condensation of Sb films on substrates cooled with liquid helium.[86] Again the value of d_c^- was 200 ± 40 nm and the average velocity of the explosive crystallization front was 35 ± 5 m/s. In contrast to the case of higher substrate temperatures[27,64] it was found that explosive crystallization of Sb films at $T_0 = 4.2$ K was damped at a distance of 2–3 mm from the point where it appeared.

Spontaneous crystallization during condensation of Bi, Yb (Ref. 84), and V (Ref. 86) films (when $d = d_c^-$) on liquid-helium-cooled substrates is also due to explosive crystallization. It was shown in Ref. 84 that once more the explosive crystallization front propagated spontaneously over the whole sample at a velocity equal to the velocity of the explosive crystallization front initiated by a local energy pulse.[13] Figure 3 shows typical oscillograms of spontaneous explosive crystallization of Yb and Bi films[84] which appeared when $d = d_c^-$. The sloping parts of the oscillograms in Fig. 3, corresponding to a change in the potential across the samples during their crystallization, identify the transition time. Similar behavior was reported for amorphous V (Ref. 86) and for Bi–Sb (Ref. 25) and Fe–Ni (Ref. 81) amorphous metallic alloys. When the critical thickness was reached during condensation of films of variable thickness, the process of explosive crystallization, which began in the thickest part of the film ($d = d_c^-$), was rapidly arrested on reaching a region where the thickness was $d = d^+$. This was observed in the case of Sb (Ref. 64), Yb, Bi (Ref. 13), and V (Ref. 86) films.

A different manifestation of the critical thickness was observed in the case of amorphous Ga. Figure 4 shows how the electrical resistance of a Ga film changed during its condensation on a liquid-helium-cooled substrate.[84] Up to the part of the curve identified by the arrow (where $d = d_c^-$) the resistance decreased smoothly on increase in the amorphous film thickness. When the critical thickness was reached, there was a slight fall of R. Similar abrupt falls of different magnitudes appeared at different time intervals up
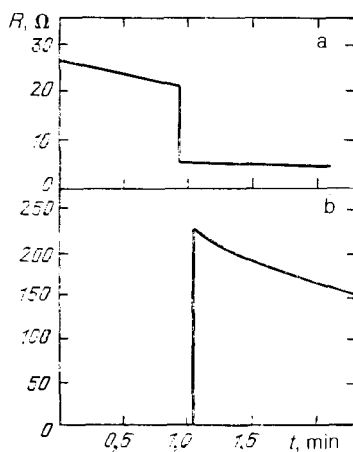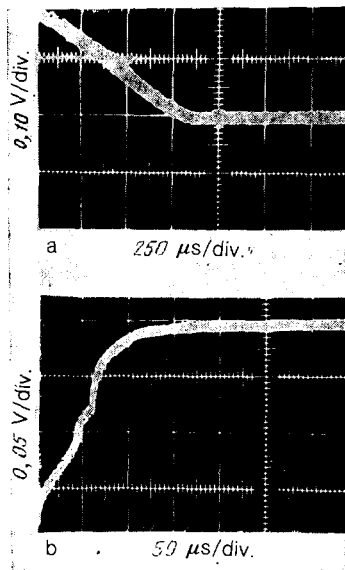
FIG. 3. Oscillograms demonstrating spontaneous crystallization of amorphous Yb (a) and Bi (b) films when they reached a critical thickness during condensation. The sloping parts of the oscillograms correspond to the vertical parts of the curves in Fig. 2 (Ref. 84).
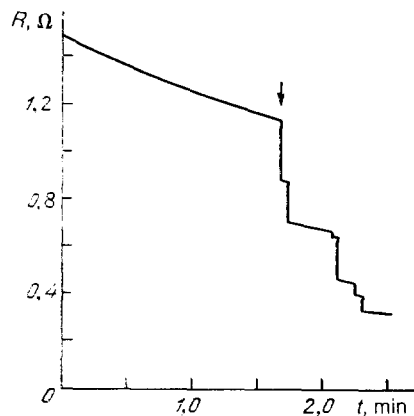

FIG. 4. Changes in the electrical resistance during condensation of a Ga film on a liquid-helium-cooled substrate. The arrow identifies the moment at which the film reached its critical thickness.[84]

to values $d > d_c^-$. It was found[84] that these abrupt changes corresponded to crystallization of small volumes of the amorphous phase of Ga. Therefore, in the case of Ga (and also Sb at low temperatures) we encountered the process of damping of explosive crystallization and the reasons for this effect will be discussed in Sec. 4.

Table III lists the known velocities of explosive crystallization fronts in various substances. In the majority of these substances (Yb, Bi, V, Sb, $Fe_{70}Ni_{30}$, CdTe) the process of explosive crystallization can appear spontaneously or after initiation of a local energy pulse. Reliable information on spontaneous explosive crystallization in Ge, Si, and H_2O films is not yet available.

It is at present thought that one of the sufficient conditions for explosive crystallization is the formation of a sufficiently large crystalline "domain" with a high temperature ($T \gg T_c$), which is an explosive crystallization center in an

amorphous film.[6,15,87] An explosive crystallization center clearly forms from a region of an amorphous matrix characterized by a short-range order and a density closest to the crystalline phase. This may be a region of free or antifree volume.[21] The appearance of an explosive crystallization center may be due to a local energy pulse. This was precisely how explosive crystallization was initiated in the majority of the substances discussed above (Table III). In the case of spontaneous explosive crystallization when a film reached its critical thickness during condensation the mechanism of formation of explosive crystallization centers was not clear. It was most likely that these centers form as a result of cooperative jumps of a group of atoms when each of them is displaced by a fraction of the interatomic distance.[88]

2.5. Dependences of the parameters of explosive crystallization on the experimental conditions

The density, heat of transition, and activation energy of crystallization of amorphous films may depend strongly on the conditions during their preparation. For example, in the case of amorphous Ge prepared by a variety of methods the density varies within the range 4.6–5.9 g/cm^3 and the latent heat of crystallization is 10.9–21.8 kJ/mol.[69] Consequently,

TABLE III. Velocities of an explosive crystallization front and increase in the temperature $\theta_f \equiv T_f - T_0$ in the front.

Material	T_0, K	u, m/s	θ_f, K	Ref.
Yb	1.5—11	6—10		13
Bi	6	~ 20		13
V	4.2; 20.4	50±10		86
$Fe_{70}Ni_{30}$	4.2	10—20		13
$(In_{1-x}Ga_x)_{50}Sb_{50}$	363	2—5		74
Sb	~ 293	32		77
	4.2	35±5		86
	~ 293		OF*	82
Ge	~ 293	1—1,2		65, 66
	~ 293	1	500	67
Si		15—16		70
		10—20		72
CdTe	~ 293		OF	75
H_2O	~ 150	$(0.2—1)\cdot10^{-2}$	60—80	6

*A considerable increase in the temperature of the front was obvious also in the case of explosive crystallization of amorphous CdTe films and electrodeposited antimony. In these films the process of explosive crystallization, initiated by an external energy pulse, was accompanied by an optical flash (OF).
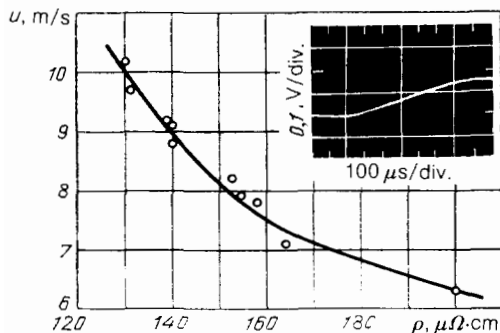
FIG. 5. Dependence of the velocity of an explosive crystallization front on the purity (represented by the value of ρ) of amorphous Yb films.[13] The inset shows a typical oscillogram of explosive crystallization initiated by the application of a current pulse to a Yb film.

the parameters of explosive crystallization u, T_f, $d^{\pm}$, and $T_0^{\pm}$ should depend on the method and conditions during preparation of an amorphous substance. For example, it was shown that the values of d^+ (Ref. 13) and d_e^- (Ref. 25) for amorphous Yb and Bi films increase on increase in the number of random impurities. Heat treatment of amorphous $Ga_{50}Sb_{50}$ (Ref. 74) and Ge (Ref. 67) films at temperatures $T < T_c$ increases the values of T_0^+ and d^+, which could be due to a reduction in the energy stored in the films as a result of their relaxation.[89,90] In the experimental investigations it was found that the velocity of explosive crystallization front depends on the degree of contamination of a film with impurities. For example, when the concentration of nitrogen and oxygen in amorphous $Fe_{70}Ni_{30}$ films[12] was less than 2 at.%, the velocity was $u = 10$–20 m/s. However, in films of the same amorphous metallic alloy containing ~ 7 at.% of air, the velocity was only $u \approx 1$ m/s and the crystallization did not extend over the whole volume of the film. The strong dependence of the velocity of the explosive crystallization front on the purity was also reported for Yb films.[13] Figure 5 shows the dependence of u on the electrical resistivity ρ (which can be used as a measure of the purity of the metal) and it demonstrates that the purer the Yb film, the higher the value of u. It seems that at some degree of contamination, which prevents diffusion-free crystallization, the process of explosive crystallization does not occur at all. For example, in the case of CdTe films containing ~ 1 at.% of oxygen it is found that explosive crystallization is spontaneous when air is admitted to the vacuum chamber.[75] If oxygen in the films reaches a concentration of 2–5 at.%, the spontaneous transition does not occur, but it is possible to initiate explosive crystallization by a local energy pulse. In the case of films with ~ 14 at.% of oxygen the process of explosive crystallization does not occur at all.

The dependence of the velocity of an explosive crystallization front on the film thickness and the substrate temperature was investigated only for Yb (Ref. 13), Ge (Ref. 91), and V (Ref. 86). In the case of Yb it was found that, within the limits of experimental error ($\sim 10\%$), the value of u is independent of the film thickness (in the range 45–80 nm) and of the substrate temperature (1.5–11 K). The critical thickness of amorphous V films and the velocity of the explosive crystallization front in these films are independent of the initial substrate temperature (4.2 or 20.4 K) within 10% (Ref. 86). The velocity of the spontaneous crystallization

front in amorphous Ge films is again independent of the substrate temperature (in the range 293–673 K) and of the film thickness.[91]

Various materials (both metals and nonmetals) have been used as substrates in the preparation of amorphous films of Ge (Ref. 65), Bi (Ref. 85), and CdTe (Ref. 75) in which explosive crystallization has been observed. However, these papers or any other literature known to us does not contain concrete evidence that the velocity of the explosive crystallization front depends on the substrate material. However, it is not clear whether stresses affect the explosive crystallization front. It has simply been mentioned in Ref. 65 that explosive crystallization in Ge occurs in the presence of internal stresses (which may be tensile or compressive) or in the absence of such stresses (in films separated from the substrates).

2.6. Characteristics of explosive crystallization maintained by external energy sources

Much work has been done recently on explosive crystallization of amorphous Ge and Si films subjected to a scanning laser beam.[9,71,92,93] It follows from these investigations that if the amorphous film temperature is less than T_0^+ and the laser scanning rate is less than the velocity of spontaneous explosive crystallization in Ge (or Si), the crystallization front moves in rapid jumps between points of rest. This behavior is observed because when the explosive crystallization front moves away from the laser beam, the contribution of the laser heating to the temperature at the interface between the phases decreases strongly. Although the continuing release of the latent heat maintains the motion of the front, its temperature eventually falls because of the loss of heat below the value needed to maintain explosive crystallization. Consequently, the phase boundary stops until the laser beam approaches it. This supporting effect of a laser beam has been observed also for an electron beam used in studies of explosive crystallization of Ge, Si (Ref. 94) and Sb (Ref. 95) in an electron microscope.

A simplified theoretical model[76] deals not only with solid-phase spontaneous crystallization (from the amorphous to the crystalline phase), but also postulates the possibility of melting of an amorphous substance directly before crystallization (amorphous phase $\rightarrow$ melt $\rightarrow$ crystalline phase). In other words, an explosive crystallization front may be a narrow ($\sim 10^{-1}\, d$) molten zone. In fact, the possibility of existence of a liquid layer at the explosive crystallization front in Ge and Si films is supported by several experiments.[72,73,96] However, it is shown clearly in Ref. 73 that the appearance of a liquid layer (in the case of Si) is entirely due to the laser power and is related to its scanning rate, but it is not necessary to achieve explosive crystallization. Such crystallization of amorphous Si (or Ge—see Ref. 97) may occur in the solid phase if the relevant parameters of a scanning laser beam are selected optimally. A direct electron-microscopic study of explosive crystallization in amorphous Ge, Si (Ref. 94), and Sb (Ref. 95) films has confirmed that melting does not occur in this case.

We have thus considered an experimental manifestation of a new phase transition which is explosive crystallization of amorphous substances. We have not dealt with specific accelerated crystallization processes in some

amorphous insulators, which are discussed in the book by Aleksandrov.[10]

3. THERMAL BISTABILITY OF CRYSTALLIZATION OF AMORPHOUS SUBSTANCES. PHENOMENOLOGICAL APPROACH

In this section we shall deal with theoretical ideas on the nature and main manifestations of a possible thermal bistability of nonisothermal crystallization of glasses. We shall use a fairly general and effectively model-free quasisteady approach which combines the known[3] phenomenological ideas on the relationship between the velocity of a crystallization front and its temperature and, moreover, the widely used concept[16–19] of heat transfer from a crystallization front of arbitrary geometry moving at a given velocity.

The phenomenological approach makes it possible to identify clearly those general aspects which are not related to the specific mechanism of heat removal and to the geometry of the crystallization (transition) front. These include the following: a) formulation of the ideas on a possible thermal bistability of quasisteady crystallization of glasses and on critical and singular parameters of explosive crystallization (Sec. 3.1); b) discussion of quantitative criteria of thermal bistability and absence of explosive crystallization using quasi-isothermal and quasi-adiabatic approximations (Sec. 3.2). In Sec. 3.3 we shall give the results of a model analysis of a number of problems on heat transfer away from the crystallization front allowing for the geometry of this front and for the method by which it is established, whereas in Sec. 3.4 we shall discuss briefly the transient effects.

3.1. Thermal instability and bistability of crystallization of glasses. Qualitative analysis

Experiments show (Sec. 2) that in spite of the existence of slow (effectively isothermal) crystallization in the case of all amorphous substances, explosive crystallization occurs only in few glasses. However, when explosive crystallization is possible in a given substance, at least in principle, we have to know also the range of values of the parameters d and T_0 in which such crystallization occurs.

A phenomenological analysis (confirmed in Sec. 4 by a quantitative discussion of the known experimental data on explosive crystallization) shows that the characteristics of slow and fast (explosive) crystallization are mutually related. A qualitative expression of this relationship is the concept of a possible thermal bistability of the process of crystallization of glasses.

A phenomenological description of quasisteady crystallization of a supercooled liquid (including a glass) given below is based on a simultaneous analysis of two nonlinear phenomenological relationships, of different origin, between the crystallization front velocity u and the front temperature T_f.

The first (kinetic) relationship is governed by an "intrinsic" kinetics of propagation of a front which depends on the actual crystallization mechanism. In theoretical estimates it is usual to employ the following dependence of u on T_f, which is known from the theory of crystallization from a melt,[3]

$$u = \eta\,(T_f) = u_0 e^{-E/T_f}\{1 - \exp[-\Delta H\,(T_f^{-1} - T_{mp}^{-1})]\}, \quad (4)$$

where ΔH is the heat of crystallization per particle expressed

in kelvin at $T = T_{mp}$ (T_{mp} is the melting point), E is the activation energy (again in kelvin), and u_0 is a preexponential factor.

The second relationship, associated with the concept of a local rate of heat removal from a crystallization front (for details see Sec. 3.3), should be found by solving the problem of quasisteady heat removal from a crystallization front moving at a given velocity (allowing for heat evolution in the front). In the cases discussed below (see Sec. 3.3) this relationship can always be represented in the form[19]

$$\theta_f \equiv T_f - T_0 = T_Q \psi\left(\frac{u}{v}\right), \quad (5)$$

where $T_Q \equiv Q/c$ is the temperature effect of crystallization (Q is the heat of the transition and c is the specific heat), T_0 is the initial temperature, and the actual form of the function $\psi(\mu)$ depends on the mechanism of heat removal and the geometry of the crystallization front (Table IV). It follows from physical considerations that $\psi(0) = 9$, $\psi(\infty) = 1$, $\psi' > 0$, and $\psi'' < 0$. The parameter v in Eq. (5) represents the rate of heat removal from the crystallization front and its relationship to the thermophysical characteristics is also given in Table IV.

The required dependence of the self-consistent velocity of the crystallization motion of the front $u(T_0, v)$ is found by eliminating T_f from Eqs. (4) and (5). The possible behavior of the function $u(T_0, v)$ can be identified by considering first the qualitative features of the functions η and ψ which follow from their physical meaning.

The dependence (4) is a bell-shaped curve (Fig. 6) which vanishes at the points $T_f = 0$ and $T_f = T_{mp}$ for different physical reasons. In the limit $T \to 0$ the driving force of the phase transition is practically independent of T and the viscosity of glass rises exponentially as a result of cooling, so that

$$\eta\,(T_f) = u_0 e^{-E/T_f} \quad (T_f \to 0). \quad (6)$$

The kinetic parameters (u_0, E) can be determined in experiments involving low-temperature $(E/T_f \gg 1)$ annealing of glasses.[8,98] If $T \to T_{mp}$, then $u \to 0$ because the driving force of the transition vanishes (since at the melting point the thermodynamic potentials of the crystal and melt are equal) and the viscosity depends weakly on T.

In those cases when practically isothermal crystallization with $u = \mathrm{const}$ can be established experimentally (which is true, for example, of many organic liquids), the bell-shaped dependence of Eq. (4) can be determined experimentally throughout the temperature range from 0 to T_{mp} (Ref. 99). However, in the majority of one-component metals because of their viscosity and considerable heat of crystallization it is possible to investigate experimentally by familiar methods only the conditions corresponding to narrow temperature intervals outside the bell-shaped kinetic curve ($T \to 0$ in the annealing experiments and $T \to T_{mp}$ in the crystallization of the melt).

It should be stressed that Eq. (4) represents the simplest approximation of the real kinetic dependence with a minimum number of the fitting parameters (u_0 and E) and it agrees with the main principles of statistical physics. Equation (4) is usually deduced using the theory of absolute reaction rates by calculating the resultant flux of particles across an interface between phases with the potential relief of the

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TABLE IV. Solution of the problem of heat removal from a crystallization front.

	$\psi(\mu)$	$\psi(\mu \to 0)$	$\Delta(\mu \to \infty)$	$F(\mu_0)$	$\delta(\mu)$	υ
Plane front: relaxation heat removal[14]	$\Psi_r = \mu\,(1+\mu^2)^{-1/2}$	μ	$1/2\mu^2$	0,38	μ^2	$v_r = 2\,(\varkappa/\tau_\theta)^{1/2}$
diffusion heat removal[19]	$\Psi_d = \dfrac{2}{\pi} \times$ $\times \left[\displaystyle\int_0^\mu K_0(x)\,dx \right.$ $\left. + K_1(\mu) - \mu^{-1}\right]$	$\dfrac{\mu}{2}\,\lvert \ln \mu \rvert$	$2/\pi\mu$	0.25	$(\ln \mu)^{-1}$	$v_d = \varkappa/d$
Spherical front* (Ref. 17)	$\Psi_3 = \mu e^\mu E_2(\mu)$	μ	$2/\mu$	0,18	$\mu \ln \mu$	$v_3 = \varkappa/R$
Circular front* (Ref. 18b)	$\Psi_2 = \mu e^\mu E_1(\mu)$	$\mu\,\lvert \ln \mu \rvert$	$1/\mu$	0,20	$(\ln \mu)^{-1}$	$v_2 = \varkappa/R$

*Quasistationary solutions; K_0 and K_1 are the modified Bessel functions; E_1 and E_2 are the integral logarithm functions (see, for example, Ref. 114); τ_θ is the thermal relaxation time of a film.

type shown in the inset in Fig. 6 (see, for example, Ref. 3). This approximation corresponds to the mechanism of normal growth and can be used to describe quite satisfactorily the experimental data on the crystallization of many molecular liquids[99] and metals,[100] and also polymorphic crystallization of metallic glasses.[5,8]

In the case of the function ψ of Eq. (5) the values $v \to 0$ correspond to the absence of heat transfer away from the crystallization front (adiabatic crystallization), whereas $\psi(u)$ tends to a limit represented by a segment on the ordinate in the interval (0, 1) for $u = 0$ and equal to 1 for all $u > 0$. The values $v \to \infty$ correspond to isothermal crystallization (best heat removal) and in this case the limiting form of the $\psi(u)$ curve is the abscissa.

Physical concepts of the rate of heat evolution in a crystallization front and the rate of removal of heat from this front can be usefully associated with the functions η and ψ and introduced by means of Eqs. (4) and (5). Since the amount of heat released per unit time in a crystallization front is proportional to its velocity, the ordinate of the de-
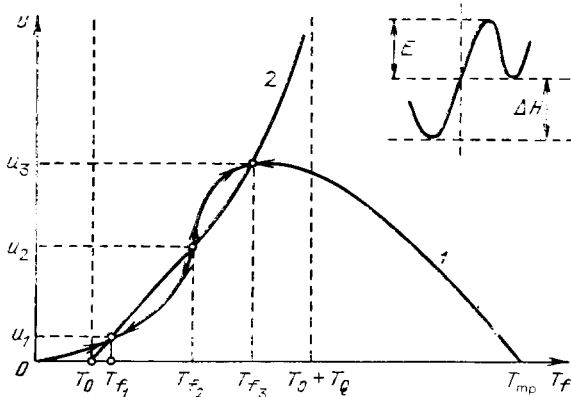

FIG. 6. Schematic representations of the kinetic dependence (1) and of the curve representing heat removal (2). The inset shows the average potential relief at an interface between phases; u_1 and u_3 are the stable values of the self-consistent velocity of a crystallization front (arrows pointing inward) and u_2 is an unstable value (arrows pointing outward).

pendence $\eta(T_f)$ in Fig. 6 can be interpreted as the rate of heat evolution in the front. Consequently, the ordinate of the function

$$u = v\,\Psi^{-1}\left(\frac{\theta_f}{T_Q}\right) \tag{7}$$

can be regarded as the rate of removal of heat from the front. In fact, if the temperature rise inside the front $\theta_f \equiv T_f - T_0$ is fixed, the value of the above function increases on increase in v, i.e., it increases on improvement in heat removal.

We shall now consider the physical meaning of the ordinates of the graphs of the functions represented by Eqs. (4) and (7) in order to carry out a clear graphical analysis of the self-consistency of the problem.[14,16] With this in mind we note that the motion of a crystallization front characterized by $u = \text{const}$ corresponds to equality of the rates of heat evolution and removal. Therefore, if we represent both dependences of Eqs. (4) and (7) in the same graph, the ordinates of the points of intersection of these dependences give the required stationary values of the self-consistent velocity $u(T_0, v)$. If the quantity T_0 is varied from 0 to T_{mp} [in this case the curve representing heat removal of Eq. (7) shifts parallel to itself], we can plot the dependences of the ordinates $u(T_0)$ and the abscissas $T_f(T_0)$ of the points of intersection of curves 1 and 2 in Fig. 6 on the value of T_0 (when the other parameters are fixed). Such a plot shows that, depending on the parameters governing the actual behavior of the graphs of Eqs. (4) and (7), we can distinguish two qualitatively different cases.

In the former case the dependences $u(T_0)$ and $T_f(T_0)$ are single-valued and the main task is to find the scale of nonisothermal effects from the renormalization of the self-consistent values of the temperature of the crystallization front and its velocity reduced to T_0 (Ref. 14). In this case the special features of the crystallization of glasses are not manifested.

The second and main case is that when the dependences $u(T_0)$ and $T_f(T_0)$ are not single-valued, which is precisely the criterion of thermal bistability of the glass crystallization process. This bistability appears because of thermal instabil-

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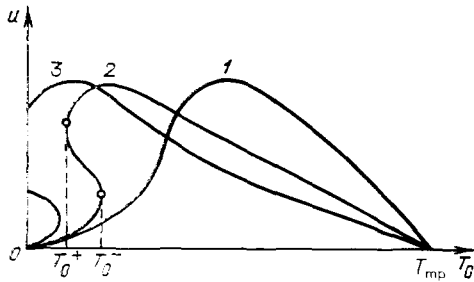V. A. Shklovskiĭ and V. M. Kuz'menko   171

FIG. 7. Schematic temperature dependence of the self-consistent velocity $u(T_0)$ plotted for three different values of the rate of heat removal: 1) ideal rate; 2), 3) multivalued dependences (curve 3 corresponds to the worst heat removal rate).

ity of a crystallization front, investigated in detail theoretically by one of the present authors[14] considering, by way of example, the motion of a plane phase-transition front in the case of precipitation of configurationally frozen metastable states, particularly glasses.

The physical reason for the appearance of this instability in the case of glasses is as follows: in contrast to the case of a slight supercooling $(\Delta T \equiv T_{mp} - T_f \ll T_{mp})$, when $\partial\eta/\partial T_f < 0$ and the evolution of the heat of transition hinders the crystallization process, in the case of glasses $(T \ll T_{mp})$ we always have $\partial\eta/\partial T_f > 0$ and the evolution of heat accelerates crystallization. Such a positive feedback and the activated nature of precipitation of glasses [Eq. (3)] establishes conditions for manifestation of a thermal instability of the explosive type when relatively small changes in the easily controlled parameters can alter greatly the rate of crystallization of glasses.

We shall now consider qualitatively the appearance of a thermal instability in the case of single-valued dependences $u(T_0)$ [and, correspondingly, $T_f(T_0)$] and a transformation into multivalued dependences as the conditions for removal of heat from a crystallization front deteriorate. We shall do this by graphical analysis of the initial single-valued dependences of Eqs. (4) and (7).

If the removal of heat is an ideal process $(v \to \infty)$, then $u(T_0)$ reproduces $\eta(T_0)$ as T_0 is varied, i.e., $u(T_0)$ is single-valued (compare curve 1 in Fig. 6 and curve 1 in Fig. 7). Deterioration of the removal of heat from a crystallization front bends the heat removal curve of Eq. (7) to the right and downward (Fig. 6) and the dependence $u(T_0)$ is deformed so that its rising branch becomes increasingly steeper. Finally, when the removal of heat has deteriorated sufficiently, the single-valued self-consistent solution $j(T_0)$ becomes unstable and further deterioration in heat removal makes the dependence $u(T_0)$ multivalued. Initially $u(T_0)$ is S-shaped (curve 2 in Fig. 7) and then even becomes discontinuous (curve 3 in Fig. 7). In the multivalued region for each temperature T_0 in the interval (T_0^+, T_0^-) there are three stationary values of the crystallization front velocity (these are u_1, u_2, and u_3 in Fig. 6).

An analysis of these values of the velocity for stability against small changes in the crystallization front temperature shows (for details see Sec. 3.4) that u_1 and u_3 are stable, whereas u_2 is unstable. This can be understood qualitatively if we bear in mind that for small changes of T_f the relationships between the corresponding increments in the rates of heat removal and heat evolution are such that the "mapping

point" of the crystallization front in Fig. 6 (which is always "bound" to the kinetic curve) returns to the initial states u_1 and u_3 (as identified by arrows towards them), whereas in the case of the state u_2 this point moves away from it (arrows away from it).

Therefore, in the temperature interval (T_0^+, T_0^-) the motion of a crystallization front is bistable, i.e., it is stable on the lower $(-)$ and upper $(+)$ branches of the hysteretic dependence $u(T_0)$. The $(-)$ branch usually corresponds to slow practically isothermal $(\theta_f \ll T_0)$ crystallization, but on increase in T_0 it becomes unstable at the right-hand limit of bistability characterized by T_0^-. The $(+)$ branch usually represents hot and practically adiabatic $(T_f \approx T_a \equiv T_0 + T_Q)$ cases of fast (explosive)crystallization and as T_0 is reduced, this branch becomes unstable at the left-hand boundary of bistability T_0^+. In some cases it may happen that $T_0^+ < 0$. Since only the values $T_0^+ > 0$ are physically meaningful, this corresponds to the appearance of discontinuities in the dependence $u(T_0)$ (curve 3 in Fig. 7) and demonstrates stability of the crystallization states belonging to the upper $(+)$ branch at all values of T_0 (right up to $T_0 = 0$). The values of T_0^+ dependent on the other parameters (u_0, E, T_Q, v) are critical and they correspond to catastrophes representing abrupt changes in the velocity and temperature of a crystallization front.

The values of the parameters at which the bistable range contracts into a point (i.e., $T_0^+ = T_0^-$) are called singular (index s). At these points the bistability disappears (or appears), i.e., the dependence $u(T_0)$ becomes single-valued. It follows from geometric considerations that at these critical points the functions $\eta(T_f)$ and $v\psi^{-1}(\theta_f/T_Q)$ are equal and so are their first derivatives with respect to T_f. At the singular points we have to supplement these conditions by the equality of the second derivatives of these functions.

3.2. Quantitative criteria of thermal bistability of explosive crystallization of glasses

There is considerable interest in the functional dependence of the critical and singular parameters of glasses on the kinetic and thermophysical characteristics of the crystallization process. Introducing variables $w \equiv u/u_0$ and $\tau \equiv T/E$, we obtain a system of two nonlinear equations for the determination of $w(\tau_0, \tau_Q, V)$, which is the self-consistent velocity of a crystallization front considered as a function of three dimensionless parameters (initial temperature $\tau_0 \equiv T_0/E$, temperature effect of crystallization $\tau_Q \equiv T_Q/E$, and rate of heat removal $V \equiv v/u_0$):

$$w = e^{-1/\tau}, \tag{8}$$

$$\tau - \tau_0 = \tau_Q \psi \ (\mu), \tag{9}$$

where $\mu = w/V$. An investigation of this system of equations; shows that in the plane of the parameters (τ_0, τ_Q) we can find a region bounded by a monotonic dependence $\tau_0^s(\tau_Q)$ where bistable motion of a crystallization front is possible. It is found[19] that if $\tau_Q \to 0$, then

$$\tau_0^s (\tau_Q) \approx [F \ (\mu_0) \ \tau_Q]^{1/2} \propto \tau_Q^{1/2}, \tag{10}$$

where μ_0 is a root of the equation $F'(\mu) = 0$ and $F(\mu) \equiv \mu\psi'$. In the limit $\tau_Q \to \infty$, we have

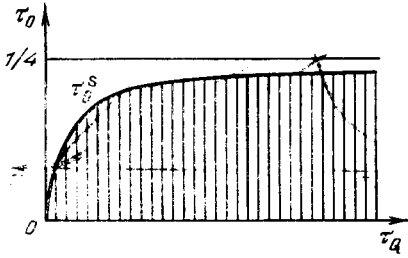$$\tau_0^s (\tau_Q) \approx \frac{1}{4} [1 - \delta \ (\mu)], \tag{11}$$

FIG. 8. Plot of the function $\tau_0^s(\tau_Q)$ representing the boundary of thermal bistability (identified by vertical shading).
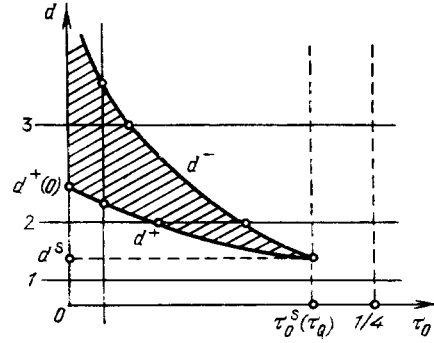

FIG. 9. Schematic representations of critical thicknesses $d^{\pm}(\tau_0)$ plotted for $\tau_Q = $ const. The thermal bistability region is shaded.

where $\delta(\mu) \equiv [\psi/\mu\psi') - 1] \to +0$ in the limit $\mu \to 0$ and in the main approximation the relationship between $\varepsilon = \frac{1}{4}\tau_Q$ and μ is $\varepsilon \approx \psi(\mu)$.

Using these asymptotes, we can readily represent the overall nature of the dependence $\tau_0^s(\tau_Q)$, shown schematically in Fig. 8 where the range of realization of bistable regimes lies between the $\tau_0^s(\tau_Q)$ line and the τ_Q axis. Therefore, if heat evolution in the crystallization front is not sufficiently rapid $[\tau_0 > \tau_0^s(\tau_Q)]$, thermal bistability becomes impossible and the dependence $w(\tau_0)$ becomes single-valued.

Using Eqs. (8) and (9) and the conditions of tangency of the kinetic dependence and the curve representing heat removal, we find that in the bistable case we obtain explicit expressions for the critical parameters and the velocity of a crystallization front in two approximations important in the interpretation of the experimental results (Sec. 4): quasi-adiabatic ($\mu \gg 1$) and quasi-isothermal ($\mu \ll 1$). In these two cases it is sufficient to know the asymptotic behavior of $\psi(\mu)$ (Table IV).

If $\mu \gg 1$ and $\psi \equiv 1 - \Delta$, where $\Delta(\mu) \approx \Delta_n/\mu^n$ with $n > 1$, and $\tau_a \equiv \tau_0 + \tau_Q \ll n/2$, the critical heat removal rate for the (+) branch can be obtained from

$$V^+(\tau_0, \tau_Q) = w_a \left[\frac{\tau_Q}{\tau_a^2} en \Delta_n \right]^{-1/n}, \tag{12}$$

where $w_a \equiv w(\tau_a)$ is the adiabatic velocity of the front. If $V < V^+$, then in the same approximation the velocity of the crystallization front for the (+) branch is

$$w^+(\tau_0, \tau_Q, V) = w_a e^{-z/n}, \tag{13}$$

where $0 < z < 1$ is found from the equation

$$\gamma^+ z = e^z, \quad \gamma^+ \equiv e\left(\frac{V}{V}\right)^n > e. \tag{14}$$

Therefore, the maximum difference between w^+ and w_a [by a factor $\exp(-1/n)$] occurs at the critical point ($V = V^+$).

In the quasi-isothermal approximation ($\mu \ll 1$) we have to distinguish two cases (Table IV): $\psi \propto \mu$ and $\psi \propto -\mu \ln \mu$. If $\tau_0 \ll 1$, then the critical value of the heat removal rate for the (−) branch is

$$V^-(\tau_0, \tau_Q) = ew_0 a, \quad \psi \approx A\mu, \tag{15a}$$

$$= ew_0 a \ln a, \quad \psi \approx -A\mu \ln \mu, \tag{15b}$$

where $a \equiv A\tau_Q/\tau_0^2$. Calculation of $w^-(\tau_0, \tau_Q, V)$ for $V > V^-$ gives

$$w^-(\tau_0, \tau_Q, V) = w_0 e^z, \tag{16}$$

where z is the solution of an equation of the (14) type in which γ^+ is replaced with $\gamma^- \equiv e(V/V^-) > e$ (in the case when $\psi \approx A\mu$). However, if $\psi \approx -A\mu \ln \mu$, then an equation analogous to (14) is somewhat more complex, but the result is qualitatively similar to that obtained in the preceding case: the maximum value of w^- is reached at $V = V^-$, where $w^-(\tau_0, \tau_Q, V) = ew_0$ and $w_0 \equiv w(\tau_0)$ is the isothermal growth velocity.

We shall now discuss how to apply these results to the behavior of the "critical thickness" of amorphous layers of films. For example, many glasses can be prepared in the form of films of thickness $d < d^-$, where d^- is the maximum critical value above which a sample becomes unstable against explosive crystallization. There is always also a minimal thickness d^+ below which the explosive processes are unstable.[84] The values of $d^{\pm}$ generally depend both on τ_0 and on the heat removal conditions. Equations (12) and (15) allow us to study the general nature of these dependences since the parameter V proportional to the rate of loss of heat from a film increases on reduction (other conditions being constant) of the film thickness d (see, for example, the expressions for v in Table IV). We can therefore plot a graph of $d^{\pm}(\tau_0)$ for $\tau_Q = $ const (Fig. 9) where the thermal bistability range is shown by slanted shading. In Fig. 9 we have $d^-(\tau_0) \to \infty$ in the limit $\tau_0 \to 0$ and $d^+(0) > d^s$, where d^s is the ordinate of the point of merging of the $d^+(\tau_0)$ and $d^-(\tau_0)$ lines; on increase in τ_Q this point shifts to the right and downward (Fig. 8).

Several horizontal lines (1, 2, 3) with $d = $ const are plotted in Fig. 9 to demonstrate the qualitatively different (depending on the fixed film thickness) variants of the change $d(\tau_0)$. For example, if $d < d^s$ (horizontal line 1), there is no thermal instability and for any value of τ_0 we can only have single-valued dependences $u(T_0)$. If $d^s < d < d^+(0)$ (horizontal line 2), bistability is observed only at temperatures within the interval $\tau_0^+(d) < \tau_0 < \tau_0^-(d)$ and outside this interval the dependences $u(T_0)$ are single-valued. Finally, in the range $d > d^+(\tau_0)$ (horizontal line 3), bistability occurs at temperatures defined by $0 \leqslant \tau_0 < \tau_0^-(d)$. However, if we assume that $\tau_0 = $ const, it must be stressed that if $\tau_0 < \tau_0^s(\tau_Q)$, we always have $d^+(\tau_0) < d^-(\tau_0)$, i.e., the critical thickness d^+ for the upper (+) branch of the dependence $u(d)$ is less than the critical thickness d^- for the lower (−) branch.

It should also be pointed out that the expressions for the critical thicknesses $d^{\pm}(\tau_0, \tau_Q)$ [and the analogous critical
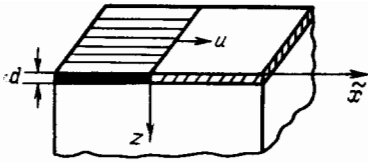
FIG. 10. Plane crystallization front in the film geometry; here u is the velocity of the crystallization front and d is the film thickness.

FIG. 11. Schematic dependence of the velocity of a spherical crystallization front w on the radius of a center ρ under explosive growth conditions $[\tau_0 < \tau_0^s(\tau_Q)]$. The dashed part of the curve is the unstable branch of w; $\rho^{\pm}$ are the upper and lower critical radii; $w_0 \equiv w(\tau_0)$.

radii $R^{\pm}$ (τ_0, τ_Q) in the case of two- and three-dimensional crystallization—see Sec. 3.3] can readily be obtained from the expressions for $V^{\pm}$ (τ_0, τ_Q) given by Eqs. (12) and (15) allowing for the relationship between v and d or R (Table IV).

3.3. Heat removal from a crystallization front

In contrast to the results of the phenomenological approach (Secs. 3.1 and 3.2), an analysis of heat removal from a crystallization front has to be based on a model and the results are specific, on the one hand, because of the geometry of the crystallization front (plane, circular, or spherical) and, on the other, because of the conditions of heat removal from the front. For example, in the "film" geometry shown in Fig. 10, depending on the method of defining T_0, we can have two qualitatively different limiting cases of allowance for heat removal: relaxation and diffusion.[19]

The former (and simpler) method involves supplementing the heat conduction equation with a "relaxation" term of the $\mathscr{P} = (\alpha/d)(T - T_0)$ type, where $\mathscr{P}$ is the power of a thermal sink per unit volume of the film with a local temperature T, α is known as the heat removal coefficient, and T_0 is the fixed temperature of the substrate ("thermostat"). This relaxation heat removal mechanism implies physically that the thermal conductivity of the substrate is infinite, so that all the thermal resistance of the sink is in the form of a temperature jump $\delta T = T - T_0$ localized at the film-substrate interface and proportional to the heat flowing into the substrate. The thermal problem of a plane phase-transition front then becomes one-dimensional and the temperature profile of the crystallization front falls exponentially on both sides of the front.[76,14,19]

However, under experimental conditions we almost always have the second case (Sec. 2) corresponding to heat removal by diffusion.[19] In this limit the main contribution to the thermal resistance of the sink comes from the finite thermal diffusivity of the substrate $\varkappa$ and the temperature jump at the film-substrate interface is negligible. In this case the dependence $\psi(\mu)$ is governed essentially by the two-dimensional distribution of temperatures in the substrate and T_0 is defined only at infinity. The following main characteristics of heat removal by diffusion in explosive crystallization experiments are discussed in Ref. 19:
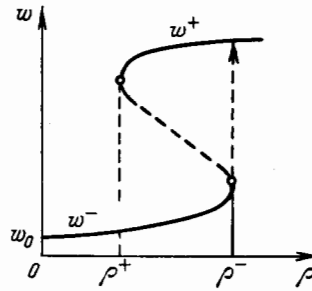
a) a slowly falling ($\propto 1/|\tilde{x}|^{1/2}$, where $\tilde{x}$ is the distance from a crystallization front in a reference system at rest) surface temperature profile behind the front (in the relaxation heat removal case this is an exponentially falling profile);

b) the time for establishment of a steady state in slow regimes increasing on reduction in the crystallization front velocity u proportionally to $1/u^2$ (in the relaxation heat removal case this time reaches saturation);

c) a high (compared with the relaxation case) sensitivity of the critical parameters to a change in the film thickness d (as described by the expressions for v_d and v_r in Table IV).

In studies of heat removal from spherical[17] and circular[18] phase transition centers in glasses we have to allow for the fact that the radius of a growing crystallization center is an additional "internal" (i.e., varying during growth) parameter which governs the rate of heat removal $v(R)$ which is now a bulk quantity. In the self-consistent problem we have to find the dependences of the growth velocity u on the radius R and in analyzing them in the case of explosive growth we can use the phenomenological approach employed earlier in the present section. The analytic forms of the functions $\psi(\mu)$ and $\tau_0^s(\tau_Q)$ are summarized in Table IV.

The solutions of the problem of heat removal from spherical and circular crystallization fronts presented in Table I are quasistationary. They are derived assuming that the front velocity u is a parameter and ignoring the term $\partial/\partial t$ in the heat conduction equation written down in a system in which the crystallization front is at rest. A special feature of these solutions is a local (on the time scale) relationship between θ_f and u of the type given by Eq. (5). An analysis of bistable crystallization regimes based on this local behavior predicts the possibility of "catastrophes" representing abrupt changes in the velocity of quasistationary growth of a crystallization center when its radius has the critical value (Figs. 11 and 12).

It is shown in Ref. 17 that quasistationary growth of a

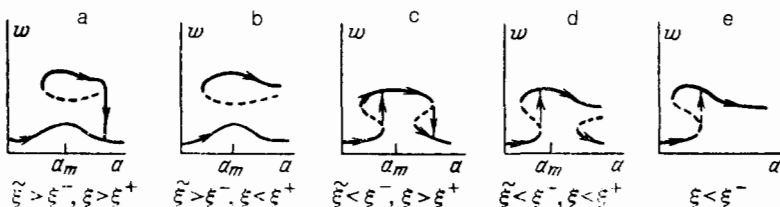FIG. 12. Schematic dependences of the observed velocity of a circular crystallization front w on the radius a plotted for different relationships between the parameters $\xi \equiv V/\tau_Q$ and $\xi^{\pm} = V^{\pm}/\tau_Q$ (Ref. 18). The dashed lines are the unstable branches; a_m are the values of the radius at which the heat removal rate is minimal and the velocity of a crystallization front is maximal.

spherical crystallization center in bulk amorphous samples, allowing for the evolution of heat in the phase transition front, is a self-accelerating process and can be explosive. The function $\psi_3\,(\mu)$ found in Ref. 17 has asymptotes (Table IV) suitable for calculating the upper and lower critical radii $R^{\pm}$. An expression for the preexplosion heating time is also obtained in Ref. 17.

It was shown in Ref. 18 that in the case of quasistationary nonisothermal growth of a circular crystallization center in an amorphous film in the presence of a sink transferring heat to the substrate we can expect a nonmonotonic (on increase in the radius of the center) change in the rate of heat removal from the phase-transition front and we can then expect either explosive growth or practical stoppage of a center. As the thermal conductivity and specific heat of the crystalline phase increase, the rate of removal of heat becomes even more nonmonotonic and this enhances the effects of the nonmonotonic dynamics of the front, but when the front velocity increases, these effects become weaker.[18]

3.4. Transient effects

The mechanism of heat removal from a crystallization front influences greatly the nature and scale of the various transient effects during nonisothermal motion of the front, such as the time taken to establish steady-state motion or the thermal and morphological stability, and also the possibility of spontaneous oscillatory and damped motion of the front. The growth velocity jumps in the case of two- and three-dimensional crystallization (catastrophes) mentioned above are possible also in the case of a plane crystallization front when the "external" parameters (for example, T_0 or d) are varied continuously.

It should be stressed that these jumps appear precisely because of quasisteady idealization of conditions and are absent (smoothed out) when the term $\partial/\partial t$ is included in the heat conduction equation. In the latter case the relationship of θ_f to R and $\dot{R}$ is nonlocal even in the heat removal problem [when $R(t)$ is a given function], i.e., the quantity $\theta_f(t)$ depends on the coordinate and velocity of a crystallization front not only at a given moment t but also at earlier moments. Therefore, an analysis of the self-consistent nonlinear problem of nonisothermal crystallization under transient conditions (and also allowing for an external heat source) is quite difficult even when a computer is used (see, for example, Refs. 101 and 102).

In a qualitative discussion of the stability of self-consistent steady-state and quasisteady solutions it is convenient to introduce the concept of dynamic rates of heat evolution in a crystallization front and of heat removal from the front defining them as the slopes of the tangents $\xi_\eta \equiv \partial\eta/\partial T_f$ and $\xi_\mu \equiv v\partial\psi^{-1}/\partial T_f$ to the kinetic curve of Eq. (4) and to the curve representing heat removal [Eq. (7)], respectively. At the stable points of intersection of these curves (points 1 and 3 in Fig. 6) we should have $\xi_\mu > \xi_\eta$. By definition, we have $\xi_\mu = \xi_\eta$ at critical points (points of contact), i.e., in the first approximation (in terms of the amplitudes of the deviations δT_f and δu from the values of T_f and u for the steady state), the evolution of heat in a crystallization front and the removal of heat from the front balance out fully. This is the reason why the critical points are "suspect" in the sense of the possibility of appearance of spontaneous oscillatory crystallization regimes.

A linear analysis of the thermal and morphological stability of steady-state motion of a plane crystallization front under relaxation heat removal conditions, carried out in Ref. 14, has identified the range of parameters where the motion of the front can exhibit spontaneous oscillations.

A dispersion equation describing the growth increments of transverse perturbations of a crystallization front was also derived in Ref. 14.

In a subsequent paper[36] these results were obtained by a different method and were used to explain a "wave-like" morphology of amorphous (In, Ga)Sb films[74] crystallized as a result of self-oscillatory explosive process. Subsequent numerical solution of this problem demonstrated[103] that lowering the substrate temperature below T_0^+ gives rise also to a cascade of bifurcations doubling the period of spontaneous oscillations with critical exponents corresponding to the familiar analysis of Feigenbaum.[104] It should be noted that the instability criteria of steady-state fast crystallization deduced in Refs. 14, 36, and 103 are in some cases more stringent than in quasisteady criteria. Unfortunately, the physical reasons for this discrepancy are not yet clear.

We shall mention also a simple physical factor responsible for the morphological stability of a crystallization front in the course of nonisothermal precipitation of glasses. In fact, in the case of amorphous substances we have $\partial\eta/\partial T_f > 0$ (Fig. 6), so that the appearance of a "projection" on a crystallization front reduces its velocity compared with the rest of the front because it penetrates a colder region (for details see Refs. 14 and 36).

4. COMPARISON OF THEORY AND EXPERIMENT

We shall now compare quantitatively the theoretical results of Sec. 3 with experiments.

Such a quantitative comparison is in our opinion justified at present only for steady and quasisteady crystallization of glasses when the theoretical results are in fact independent of the model (Secs. 3.1 and 3.2). The phenomenological nature of the theory postulates that all six dimensional parameters used in the calculations (both "kinetic" quantities u_0 and E and thermophysical properties τ_Q, T_0, $\varkappa$, and d) are known from independent measurements, i.e., there are no fitting parameters. It is shown in Sec. 3 that these six parameters can be reduced to three dimensionless parameters: the temperature effect of crystallization τ_Q, the initial temperature τ_0, and the rate of heat removal V. Two relationships between them, $\tau_0^s(\tau_Q)$ and $V^{\pm}(\tau_0, \tau_Q)$, can be used to obtain quantitative quasisteady criteria: a) the existence of bistability [$\tau_0 < \tau_0^s(\tau_Q)$]; b) the absence of explosive crystallization [$V > V^{\pm}(\tau_0, \tau_Q)$]. Equations (13) and (16) make it possible to determine the dependences of the velocity of a crystallization front on any one of the parameters. For example, it is found that the dependence $w^{\pm}(\tau_0, \tau_Q, V)$ on V is very weak: the minimum value of w^+ corresponds to $V = V^+$ and it is by a factor of $\exp(-1/n)$ lower than w_a [Eq. (13)], whereas the maximum value of w^-, realized for $V = V^-$, is e times greater than w_0 [Eq. (16)].

4.1. Classification of glasses on the basis of their stability against explosive crystallization

An analysis of the experimental values of T_Q, T_0, T_c, and E for different glasses (Tables I and III) shows that in

TABLE V.

Material	τ_Q	τ_K	τ_0	u, m/s	T_f, K	$10^{-2}\frac{\varkappa}{}$, cm²/s*	d^+, nm	d_0^+, nm	Ref.
Ga	0,11	0,039	0,009	—	54	1,5	900	> 200	84
Yb	0,38	0,034	0,010	10	155	1,0	290	35—45	13
Bi	0,55	0,033	0,014	20	240	0,86	100	25—35	13
V	0,34	0,040	0,020	50	340	0,83	50	25—40	86
Sb	0,046	0,032	5·10⁻⁴	35	375	0,80	310	200	86
		0,037	0,038	32	660	0,76	98	90—140	64
Ge	0,030	0,047	0,019	1	780	0,76	6200	(5—10)·10³	33, 66
		—	0,029	1	950	0,76	4200	2900	69
		—	0,034	1	1030	0,76	3600	2200	69
Si	0,013	0,029	0,022	15	1200	1,65	740	350	70
H₂O	0,011	0,032	0,029	(0,2—1)·10⁻²	250	2,0	1,5·10⁶	10⁶	6

*In all cases (with the exception of Si and H_2O) the films were condensed on glass. The values of $\varkappa$ are taken for quartz glass[105] at T_f, estimated as the sum of T_0 and Q/c (values of c taken from Refs. 36 and 39).

the majority of cases the values of τ_Q are very small (the maximum values of $\tau_Q \sim 0.5$ are obtained only for some pure metals) and the maximum values of τ_0 are in all cases limited from above to a fairly small quantity $\tau_c \sim 0.03$–0.04 (Table V). Hence, it follows that the Arrhenius approximation applies to $w(\tau)$ [Eq. (8)] and the asymptotic ($\mu \gg 1$) representation is valid in the case of $\psi(\mu)$, as used in the derivation of Eqs. (12) and (13) for $V^+(\tau_0, \tau_Q)$ and $w^+(\tau_0, \tau_Q, V)$. A qualitative analysis of these expressions makes it possible to divide arbitrarily, on the basis of the relationship between τ_Q and τ_c, all the glasses into three groups in accordance with the degree of their thermal stability against explosive crystallization.

The first group comprises glasses with $\tau_Q \gg \tau_c$. Its typical representatives are pure metals: V, Yb, Bi. They are characterized by the lowest thermal and size stability against explosive crystallization [such crystallization may be initiated right down to 0 K and characteristic dimensions $d_0 \equiv d^+(0)$ are less than 0.1 μm]. The former can be explained by the fact that if $\tau_0 \lesssim \tau_c$ the dependence $d^+(\tau_0)$ is so weak [$d^+(\tau_0) \approx d_0$; see Fig. 9] that it cannot be resolved experimentally, whereas the latter is due to relatively high values $\tau_Q \sim 0.5$. Typical velocities of an explosive crystallization front are fairly high (in excess of 10 m/s) and practically independent of τ_0 and d. The experimental values of d_e^- are only about twice as high as d^+ and many orders of magnitude less than the geometric values d^- at helium temperatures (Sec. 3.2). Steady-state explosive crystallization is characterized by a relatively high dynamic stability and because $d^+(\tau_0) \approx d_0$, it is difficult to observe oscillatory explosive crystallization.

The second group comprises glasses characterized by $\tau_Q \sim \tau_c$. Typical examples are the majority of pure semiconductors (Ge, Si, Sb) and one-component insulators (H_2O, D_2O). They are characterized by moderate thermal and size stabilities against explosive crystallization, and they have a definite temperature τ_0^+ (of the order of several hundreds kelvin) at thicknesses of the order of 1–10 μm (in the case of H_2O up to $10^3 \mu$m). The dependence $d^+(\tau_0)$ for $\tau_0 \ll \tau_c$ is quite steep. Typical velocities of an explosive crystallization front cover a very wide range from 10^{-2} m/s (H_2O) to tens of meters per second (Sb). In the case of glasses belonging to this group we can expect an instability of steady-state explo-

sive crystallization tending to become oscillatory and even tending to a chaotic hot crystallization front. The dependence $\tau_0^s(\tau_Q)$ is quite accurately described by the asymptotic form (10) with $F(\mu_0)$ from Table IV.

Finally, the third group consists of glasses characterized by $\tau_Q \ll \tau_c$. These are usually multicomponent (including metallic) glasses. They are characterized by the highest thermal and size stabilities against explosive crystallization. Only in the case of this group can we expect a situation when, on the one hand, we have $\tau_0 \gg \tau_Q$ and, on the other, we find that $\tau_0 < \tau_0^s(\tau_Q)$, when—as in the case of glasses of the second group—we can use the asymptote described by Eq. (10). In this case the dependences $d^{\pm}(\tau_0)$ for $\tau_0 \lesssim 0.8\tau_c$ (i.e., for τ_0 comparatively far from τ_c) are sufficiently close to one another and are not very likely to be within the range of bistability with respect to τ_0 (Fig. 9). In view of the relatively low value of τ_Q the velocities of an explosive crystallization front should be low (of the order of 10^{-3} m/s). We can easily show that at the bistability limit $\tau_0 = \tau_0^s(\tau_Q)$ the maximum renormalization of the velocity is $w(\tau_a)/w(\tau_0^s) \approx \exp[F^{-1}(\mu_0)] \sim 10^2$, i.e., it is slight (Table IV).

4.2. Critical thicknesses and radii. Theory and experiment

Table V, together with Tables I, III, and IV, provides systematic data needed in a comparison of the experimental (identified by the subscript "e") and calculated values of d^+ under diffusion heat removal conditions ($\Delta_1 = 2/\pi$; Table IV) only in the case of the first two groups of glasses, whereas the information on explosive crystallization and glasses of the third group is at present only of preliminary (basically qualitative) nature,[11,76,106] and the parameters needed in theoretical estimates are known only partly.[3]

Since in most cases there are no experimental values of u_0, we can use instead the experimental velocities of a crystallization front on the (+) branch in the vicinity of the critical point $u_c^+(\tau_0, \tau_Q)$ allowing for the fact that $u_c^+ = u_0/\exp(-\tau_c^+)$, because we can show that for $n = 1$ (diffusion heat removal) we have $\tau_c^+ = \tau_a(1 + \tau_a)/(1 + 2\tau_a)$. The value of d^+ was calculated from Eq. (12) using $V = \varkappa/du_0$, which gives

$$d^+(\tau_0, \tau_Q) = \frac{2}{\pi} \frac{\varkappa}{u_c^+} \frac{\tau_Q}{\tau_a^2}(1 + 2\tau_a). \qquad (17)$$

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It follows from Table V that the agreement between the values of d^+ calculated from Eq. (17) and the experimental values d_e^+ is quite satisfactory if we bear in mind some indeterminacy in the selection of $\varkappa$ for the hot regime; this is true in all cases with the exception of Ga. There is also a correct correlation between the experimental and calculated values of the ratios of the critical thicknesses (for example, d_{Bi}^+/d_{Yb}^+) for Bi, Yb, and V (when they crystallize on the same substrates) from which the experimental value of $\varkappa$ drops out.

Gallium is a pure metal, but it must be assigned to glasses of the second rather than the first group because of the relatively low (compared with pure metals) values of τ_Q and some other features of crystallization of this element (Sec. 2.4). If we assume that $u \sim 10$ m/s (which is the most optimistic estimate), then even in this case the value of $d^+ \approx 1$ μm obtained for Ga from Eq. (17) is still considerably higher than d_e^-. This can clearly explain why Ga exhibits damped explosive crystallization in the thickness range $d < d^+$.

We shall also consider a possible quantitative relationship between T_0^+ and d, as observed in Ref. 69 for Ge films [see Eq. (3)]. The appropriate theoretical dependence $d^+(\tau_0)$ can be obtained from Eq. (17) if we know the experimental values of $u_c^+(\tau_a)$ for Ge, missing from Ref. 59. If we assume that in the range of temperatures investigated in Ref. 69 ($450 < T_0 < 550$ K) the average velocity of a crystallization front is 1 m/s (Table III), we find that the theoretical values of $d^+(\tau_0)$ effectively fit the experimental dependence described by Eq. (3).

We shall now consider whether we can compare the experimental values of d_c^- observed in the case of spontaneous crystallization of films during their evaporation (Sec. 2.4 and Table II) with the theoretical values of d^- predicted by the expressions in Eq. (15) for the diffusion heat removal case ($A = \frac{1}{2}$; Table IV):

$$d^-(\tau_0, \tau_Q) = \frac{\varkappa}{eu(\tau_0)} \frac{\tau_Q}{2\tau_0^2} \ln \frac{\tau_Q}{2\tau_0^2}. \qquad (18)$$

It follows from Eq. (18) that in the limit $\tau_0 \to 0$ the value of d^- rises exponentially (see also Fig. 9). At first sight this is in conflict with the finite values of d_c^- obtained experimentally (in any case these values are fairly small at liquid helium temperatures; see Table II). However, we must bear in mind that the calculated values of $d^-(\tau_0)$ obtained from Eq. (18) represent thermal stability against quasiisothermal crystallization of already deposited films of thickness $d < d^-$, whereas d_e^- determines thermal stability against "spontaneous" explosive crystallization [self-maintained if $d > d^+(\tau_0)$ and damped if $d < d^+(\tau_0)$] during evaporation of the films.

Among the obvious physical factors that can provoke "premature" (because if $\tau_0 \ll \tau_c$, then $d_e^- \ll d^-$) spontaneous crystallization one should mention first of all the release of heat of condensation of atoms, which is unavoidable even if atoms are deposited one by one and it is particularly important as τ_0 decreases. In fact, the condensation energy per particle is usually one or two orders of magnitude greater than the corresponding heat of fusion,[3] i.e., each condensation event is accompanied by the appearance of several tens or hundreds of thermal excitations (phonons or electrons) with energies of the order of the Debye value. An increase in the thickness of the deposited film results in an increase in the probability that these thermal excitations initiate fluctuation-induced (homogeneous or heterogeneous) appearance of crystalline centers in the amorphous matrix and in the final analysis this leads to the conversion of one of them (if $d > d^+$) or some of them ($d < d^+$) into explosive crystallization centers (Sec. 2.4). However, a theoretical estimate of the value of d^- based on this reasoning is outside the scope of the quasisteady approach adopted in the present review.

The dependences $d^-(\tau_0)$ predicted by Eq. (18) imply homogeneous heating of a film and they should be determined experimentally under conditions avoiding possible appearance of large local fluctuations of the film temperature. Therefore, a deposited amorphous film with $d < d_c^-$ should be heated rapidly and as homogeneously as possible to a temperature $\tau_0 > \tau_0^-(d)$, as in the case of differential thermal analysis.[108] However, interpretation of the "explosive" response of such an indirect experiment should allow for the concentration and the average size of crystalline centers already existing and those created in a sample during an experiment, and also for the transient conversion of one or several of them so as to induce explosive crystallization.

We shall consider briefly possible methods for experimental investigation of explosive crystallization of a spherical center. It follows from Table IV, that the quantity $R^+(\tau_0, \tau_Q)$ is identical, apart from a factor of the order of unity, with the corresponding quantity $d^+(\tau_0, \tau_Q)$. Physical realization of R^+ is possible only in an experiment under transient conditions utilizing a spherical T flash of suitable intensity, duration, and initial radius.[109] Direct observation of the dependences $w^\pm(\rho, \alpha_0, \tau_Q)$ and of the dependences of the preexplosion heating time $t_1(\tau_0, \tau_Q)$ given in Ref. 17 is possible only in transparent glasses as their optical properties begin to differ from those of the crystalline phase. In the case of metallic glasses, when direct optical observations are impossible, it is convenient to control the growth of the crystallization centers by rapid heating of a bulk sample to a temperature T_0 by passing an electric current pulse of suitable magnitude and duration. To the best of our knowledge, explosive crystallization of a spherical center has not yet been observed directly. Similar observations in the case of two-dimensional crystallization are facilitated by the possibility of visualization of this process.

In discussing the experimental aspects of the removal of heat from a crystallization front in the film geometry, we must stress that experiments of this kind make it possible to visualize the process of explosive crystallization by direct measurements of the shape and characteristic dimensions of the temperature profile associated with a crystallization front of a thermal domain. The physical interpretation of such measurements depends on a satisfactory description of the experiments on removal of heat from a crystallization front (Sec. 3.3). It should be pointed out that, although in the case of diffusion heat removal (in contrast to the relaxation process), the thermophysical characteristics of the substrate determine explicitly the rate of removal of heat from a crystallization front, this does not complicate, but just the opposite it simplifies (for a number of reasons), the design of experiments intended to study explosive crystallization of glasses and a comparison with the theory. In fact, quartz glass substrates are used in low-temperature experiments,[13,14] i.e., the conditions for diffusion heat removal are

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satisfied. At these temperatures we can expect relaxation heat removal characterized by $\tau_\theta \sim 10^{-8}$ s or less (in the case of single-crystal quartz and sapphire substrates[110]) and this not only may result in damping of steady-state explosive crystallization because the rate of removal of heat is too high, but also sets fairly stringent requirements in respects of the resolution of the apparatus used to record the temperature profile of a thermal domain of relatively small size ($l \sim u\tau_0 \sim 10^{-5}$ cm)[14] traveling at a velocity $u \sim 10^3$ cm/s.

In the case of diffusion heat removal, such measurements simplify greatly because in this case the observed dimensions of a thermal domain should increase by several orders of magnitude because of the very slow fall of the temperature profile behind a crystallization front. A temperature profile of explosive crystallization in amorphous Ge reported in Ref. 67 was in qualitative agreement with the theory of Ref. 19 (Fig. 1).

4.3. Influence of crystalline centers and impurities on explosive crystallization

It must be stressed that our theoretical description of slow ($\tau \approx \tau_0$) and fast ($\tau \approx \tau_a$) crystallization is literally valid only in the case of a homogeneous amorphous medium with just one crystallization front. The real situation is different, as pointed out already: even during preparation of an amorphous sample there may be a large number of frozen crystallization centers (Sec. 2.1). The role of these centers differs in slow and fast crystallization.

In contrast to self-maintained explosive crystallization, slow crystallization cannot be observed in the form of a single crystallization front crossing the whole sample because of the presence of frozen centers. The experimental observations are most likely to yield the integrated effects of slow crystallization which generally mask the theoretically predicted thermal instability of a crystallization front of a single center on the (−) branch of $w(\tau)$.

The processes of fast crystallization are practically insensitive to the presence of frozen centers because of the small volume fraction of these centers. However, processes of spontaneous nucleation (both homogeneous and heterogeneous, including that involving frozen centers) may be important in explosive crystallization because such nucleation can occur at distances of the order of $\varkappa/u$ ahead of a hot ($\tau \sim \tau_a$) crystallization front. The frequency of nucleation may be so high for $\tau \approx \tau_a$ that the approximation of an infinitesimally thin (compared with the thermal length) crystallization front, which underlies our theoretical analysis, is no longer physically justified. In spite of the morphological stability of a crystallization front pointed out earlier (Sec. 3.4), the true interface between phases may be strongly regular ("fractal") and the dependence of its average (over the scale of irregularities) velocity on the parameters of the problem may be different. Although an attempt to provide a qualitative analysis of this problem can be found in Ref. 111, a correct analysis (even at the "physical" level of rigor) is still lacking.

As pointed out already, in view of the fundamentally kinetic nature of the processes used in fabrication of glasses and a consequent strong nonequilibrium of the amorphous state, the quantities u_0, E, and T_Q may depend strongly on the method used to prepare a sample, and on the duration and temperature of storage (with the amorphous state being retained). All this requires a certain care in theoretical interpretation of the experimental data: independent measurements of parameters of importance in theory should be carried out on samples made under identical conditions.

The stabilizing role of impurities in amorphous substances is manifested by an increase in their crystallization temperature T , critical thickness d_c^-, and activation energy of crystallization E.[25] Introduction of a small number of impurities can affect also the quantities u_0 and $\varkappa$, which like E are of "kinetic" nature. However, the value of T_Q (thermodynamic property of the sample) should then change only slightly. According to Eq. (13), the value of w^+ decreases on increase in E (or on reduction in u_0) or rises on reduction in $\varkappa$. Therefore, the reduction in the velocity of an explosive crystallization front observed in amorphous Yb films[13] (Fig. 5) and in $Fe_{70}Ni_{30}$ films[12] on increase in the impurity concentration may be attributed to an increase in E or a reduction in u_0. A reduction in the values of d_c^+ in the case of purer Yb and Bi films[13] can also be explained by a reduction in the activation energy E of these films [see Eq. (17)]. In a quantitative comparison with the theory one requires the experimental dependences of the parameters E, u_0, d_c^-, and u on the amounts of impurities in the samples. Unfortunately, investigations that would yield such information have not yet been carried out.

5. CONCLUSIONS

Although the majority of the experiments discussed above have been planned without considering the possibility of a comparison with a quantitative theory, we can draw the conclusion that in those cases when the necessary experimental quantities are known, they are in satisfactory qualitative and quantitative agreement with the calculated values. Nevertheless, it is desirable to carry out a more extensive and deliberate quantitative check of the predictions of the quasisteady approach for all three groups of glasses (Sec. 4).

On this basis one can then carry out a systematic, supplemented by allowance for nucleation processes, investigation of more complex topics in transient explosive crystallization (Sec. 3.4) including the process of initiation. One of the attractive possibilities of such investigation would be to provide a consistent and if possible quantitative interpretation of the characteristics of thermograms obtained by differential thermal analysis of amorphous substances.[108]

We must also draw attention to the fact that nonisothermal effects similar to explosive crystallization of glasses may also be observed in precipitation of structurally frozen metastable phases in other objects (for example, in liquid crystals[112] or polymers[113]), and some of the theoretical results for two- and three-dimensional heat removal may be useful in studies of qualitatively similar phenomena of "gas-free" combustion of condensed substances considered in the approximation of a narrow reaction zone.[1,2]

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[1]In spite of the differences encountered in the literature, we shall use the terms "amorphous substance" and "glass" as synonyms.
[2]Later in this section we shall simply say "critical thickness."
[3]In the review given in Ref. 8 only the values of u_0 and E are given for some of the alloys, whereas T_c and T_Q are not provided. In Ref. 107

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there are values of T , T_Q, and E for some other alloys, but no values of u_0.

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