Size effects at a crystal-liquid phase transition

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A size dependence resulting in a change in the nature of a crystal-liquid phase transition has been observed. A study of the supercooling of vacuum condensates (island films) of various metals has revealed how the maximum supercooling of the particles of the island films depends on their size. The extent of the supercooling decreases with decreasing particle radius. For a particle with a radius smaller than a critical value the supercooling vanishes. It is therefore concluded that a first-order phase transition becomes continuous in a sufficiently small particle.

1. INTRODUCTION

The phase transitions which occur in small particles and thin films have distinctive features because of the finite dimensions of the systems. Size effects are therefore inherent in these transitions. Particles containing on the order of ten atoms or more are tiny pieces of a condensed phase. In addition to their crystal structure they have a band structure, which, depending on the particular substance and the particular conditions, may or may not reproduce the structure of the bulk material. The properties of small particles are usually studied in island films synthesized by condensing molecular beams in high vacuum. These properties are thus generally influenced by a variety of factors: the state of the substrate, the cooling rate, the presence of impurities, etc. The actual physical properties of small particles are masked by these factors. Nevertheless, recent research has revealed conditions under which it is possible to avoid the effects of these secondary factors and to obtain reliable information on the properties of small particles. It has thus become possible to establish certain results regarding the displacement of the phase stability boundaries in small particles and, in particular, to observe the peculiar critical phenomena which occur at crystal-liquid phase transitions. For particles larger than the critical size the nature of the phase transition is the same as in the bulk material, although the transition temperature, the extent of the supercooling, the latent heat, and the volume effect all exhibit size dependence. For particles smaller than the critical size the nature of the transition changes: The volume effect of the supercooling disappears, and the latent heat vanishes. The crystal-liquid phase transition becomes continuous in particles smaller than the critical size.

That such a change occurs in the nature of the transition is indicated by two series of studies which have been carried out independently in different systems: an electron-microscopy study of the supercooling during the crystallization of liquid metals in island films[1] and a study of the anomalous temperature dependence of the specific heat of atomic clusters of argon and nitrogen and films of water.[2,3] It was shown convincingly in Ref. 1 that the extent of the supercooling decreases with decreasing particle radius and tends toward zero at a certain radius. It was also shown there that a law of corresponding states applies, according to which the melting temperature and the maximum crystallization supercooling depend in a similar way on the size of the particle for different metals.

Sheng *et al.*[2] ascribe the maximum in the temperature dependence of the specific heat of atomic clusters to the existence of a continuous phase transition which occurs at the temperature corresponding to the position of this maximum. Taken together, these two series of experiments thus explain the essence of this new critical size effect from different directions (the first series of experiments offers an explanation for the large-size side, and the second series explains the small-size side): The nature of the phase transition changes from discrete to continuous. This result implies that the size of a particle is not simply a formal parameter which characterizes the geometric extent of the particle. With decreasing particle size, more profound changes occur in the structure and lead to qualitatively new properties.

In the present paper we report a study of the properties of small particles near the point of a crystal-liquid transition in experiments on island films. We discuss the relationship between these new results and the results of other studies.

2. EXPERIMENTAL PROCEDURE

The test samples are island metal films synthesized by condensation on various substrates in vacuum. Since the properties of the films depend on many physical and technological parameters of the preparation (the pressure and composition of the residual gas, the condensation rate, the temperature and material of the substrate, and the thickness of the condensate, i.e., the size of the islands), part of our problem was to study how the condensation conditions affect the properties of the small particles, in order to determine whether it is possible to extract objective information about the actual size-dependent physical properties of the small particles. Another reason for studying metals and these particular film-substrate pairs was the need to obtain the results required for generalizing conclusions.

We used island films of the metals In, Sn, Bi, Pb, Au, Cu, Fe, Co, and Ni. The purity of the initial metals was greater than or equal to 99.999%. The films are synthesized in an ultrahigh-vacuum apparatus with oil-free pumping in which a vacuum up to 10^{-10} torr can be achieved. The residual gas pressure during the film condensation is varied over the range 10^{-3}–10^{-9} torr in different experiments. The substrates are amorphous films (graphite, SiO, Al_2O_3, ZrO_2, and MgO), polycrystalline films (W, Ni, and Cu), and cleaved faces of KCl and NaCl single crystals. The substrate films are synthesized by evaporation and condensation on polished plates (stainless steel, copper, tantalum, "Polikor," etc.) before the deposition of the metal. The thickness of the substrate films is 300–500 Å and is monitored by a quartz resonator directly during the synthesis. The size of the islands varies over the range $(20–30) \cdot 10^4$ Å in different experiments. The size of the particles in the island films is determined from electron micrographs; for particles smaller than 200 Å the size is determined by a photometry method.[4] The relative error in the determination of the particle sizes is estimated to be less than 10%.

One of the most important parameters determining the state of the particle (or island), its structure, and its properties is the substrate temperature. It has been found that there are several characteristic temperatures at which changes occur in the condensation mechanism and in the growth kinetics of the films.[5] In connection with our study of the crystal-liquid transition in small particles we will be interested in that temperature (T_g) at which the vapor-crystal condensation mechanism gives way to a vapor-liquid mechanism. To determine this boundary temperature T_g we use the following procedure. The island films are condensed on a substrate in which a temperature gradient is produced by simultaneously heating and cooling ends of the substrate; the temperature drop (δT) along the substrate is $0.5T_s < \delta T < T_{cr}$, where T_s is the melting point of the bulk metal, and T_{cr} is a critical condensation temperature, above which a film does not form on the substrate at the given density of the molecular beam. The temperature distribution along the substrate is measured by differential Chromel-Alumel thermocouples welded to the back side of the substrate. The temperature is determined to within ± 1 K.

The boundary temperature T_g, which corresponds to the transition from the vapor-crystal mechanism to the vapor-liquid mechanism as the substrate temperature is raised, is determined from the change in the morphological structure of the condensate on the substrate. This transition occurs in a narrow temperature interval of 0.05 K (Ref. 6), so that the value of T_g is determined very accurately (within $\approx 1\%$). The differences between the morphological structures of the films above and below T_g cause a change in the optical scattering of the film, so that the position of the boundary at which the condensation mechanism changes can be determined visually for films $\geqslant 500$ Å in thickness. For thinner films, the temperature T_g is determined by electron microscopy. These measurements underlie the system according to which the film morphology corresponds to the film synthesis mechanism.[6,7]

As a parameter characterizing the effect of the substrate material on the formation and stability of the liquid phase in the island films we selected the edge angle (θ) in the wetting of the substrate by the liquid island film. This choice has a natural physical basis and, in particular, makes it possible to determine the maximum extent of supercooling during homogeneous crystallization. The edge angles θ are measured for the same samples as are used for the measurements of the temperature T_g. Several methods involving electron and optical microscopy which have been developed[4,8] for determining θ can be used for particles ranging in size from 50 to 10^5 Å.

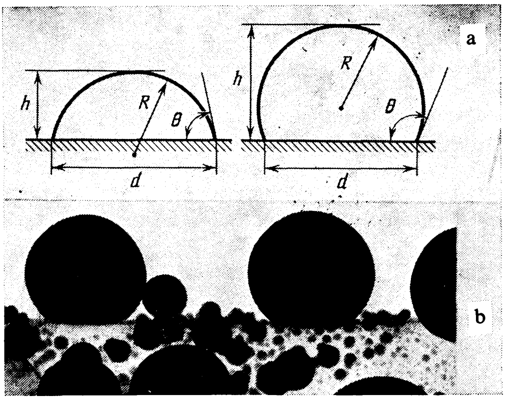

FIG. 1. a—Geometric diagrams of droplets on the substrates for the cases $\theta < 90°$ and $\theta > 90°$; b—electron micrograph ($10^5 \times$) of a tin island film on a graphite substrate ("convolution").

The shape of the small droplets on the substrate is a spherical segment, so that the edge angle can be determined from

$$\cos\theta = 1 - \frac{h}{R} = \left[1 - \left(\frac{D}{2R}\right)^2\right]^{1/2} = \frac{1-(2h/D)^2}{1+(2h/D)^2},$$

where h is the height of the segment, R is the radius of curvature, and $D/2$ is the radius of the base of the droplet. The parameters h, R, and D can be found from photomicrographs of the droplet profiles. Figure 1 shows electron micrographs of the profile of tin microscopic droplets on a graphite substrate (convolution method), along with a geometric diagram of the droplet for the cases $\theta < 90°$ and $\theta > 90°$. The convolution method makes it possible to find the values of θ for particles more than 200 Å in diameter within an error of 2–3° (Ref. 8). For smaller droplets, it is preferable to use a photometric method based on a quantitative analysis of the blackening profile of the electron-microscopy image of a particle in plan view.[4] The photometric method can be used to measure θ for particles with diameters in the range 30–50 Å.

3. EXPERIMENTAL RESULTS

3.1. Effect of the film thickness

The electron microscopy of the microstructure of the In, Sn, Bi, Pb, and Au island films synthesized in a vacuum of 10^{-8} torr by condensation on amorphous graphite films showed that the liquid phase is observed in the films of these metals at temperatures down to 285, 336, 361, 408, and 891 K, respectively. For metals of the iron group condensed on amorphous aluminum oxide films the values of T_g are 1140 (Fe), 1170 (Co), and 1150 K (Ni). These boundary temperatures T_g for the various metals are significantly lower than the melting points of these metals even if we allow for a size-dependent decrease in the melting points at the corresponding sizes of the islands in the films.

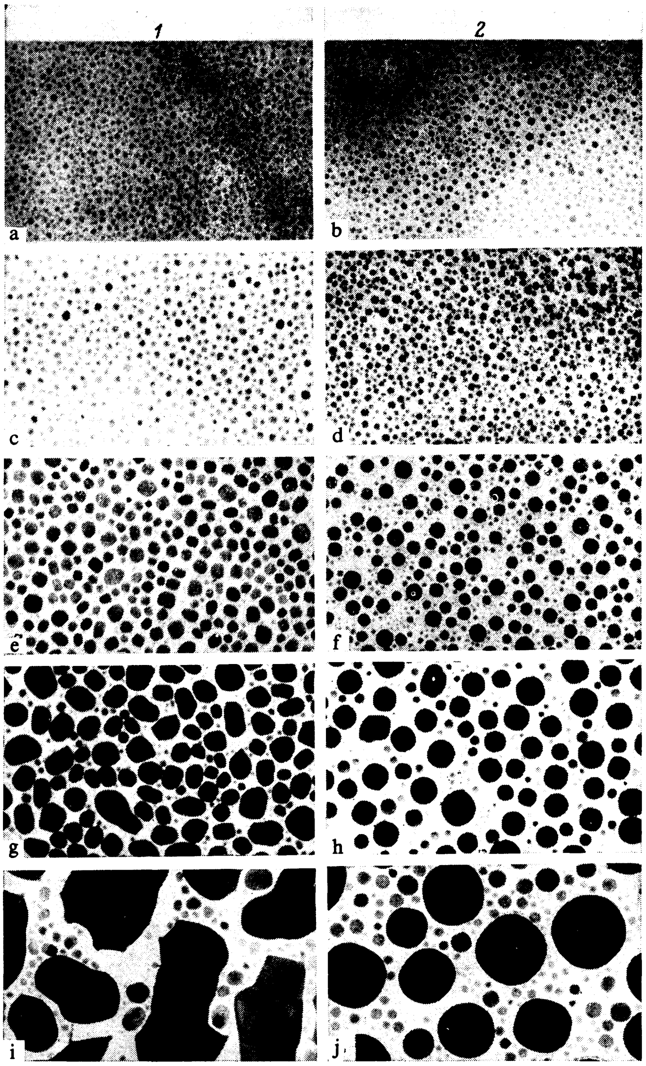

FIG. 2. Electron micrographs $(10^5\times)$ of tin island films on graphite substrates. 1: Vapor-crystal mechanism (320 K). 2: Vapor-liquid mechanism ($T = 350$ K). The film thicknesses are: a, b—20 Å; c, d—35 Å; e, f—50 Å; g, h—120 Å; i, j—300 Å $(10^5\times)$.

Varying the film thickness (the island size) from 10^2 to 10^4–10^5 Å again has no effect on T_g, i.e., on the temperature interval in which the liquid phase exists. Electron microscopy of films of various thicknesses reveals the following features: In the early stage of the growth of the island films (e.g., at film thicknesses 20–30 Å for Sn) we observe essentially no difference between the microstructures above and below T_g. Typically, the particles in both regions are nearly spherical. At thicknesses above 50 Å, differences in the microstructure of the condensates above and below T_g begin to become apparent, and these differences become more pronounced as the thickness of the island film increases. Figure 2 shows the growth stages of a tin island film on a graphite substrate at $T < T_g$ and $T > T_g$. The liquid islands typically grow to large dimensions in the temperature interval $T_g < T < T_s$ (the upper limit on the dimensions in these experiments was 10^4–10^5 Å), but the value of T_g does not depend on the size of the islands.

Since a liquid phase persists in the island films at temperatures $T_g < T < T_s$ for particles with sizes much larger than would follow from the size dependence of the melting point, the liquid phase is probably supercooled in this temperature interval. This conclusion agrees with the results of electron microscopy of the phase state of the condensates directly during the synthesis for In, Bi, Pb (Ref. 9), Ag, and Cu (Ref. 10). According to data on the size dependence of the melting point of the small particles, particles with a radius of 20–30 Å melt at temperatures near T_g (Refs. 11–15).

If the condensation by the vapor-liquid mechanism at $T > T_g$ involves the formation and growth of particles of supercooled liquid, the magnitude of the supercooling, $\Delta T = T_s - T_g$, will therefore depend on the factors which determine the crystallization conditions for these particles. For island films, one such factor is the presence of soluble impurities from the residual atmosphere in the vacuum chamber. Another is the substrate, which may act as a catalyst in the formation of nucleating regions of crystalline phase. The experimental results show that the values of T_g and ΔT depend on these factors.

3.2. Effects of the residual gas pressure and the condensation rate

A change in the residual gas pressure (P) during the condensation has different effects on the boundary temperature T_g for different metals.[16–18] For condensates of gold on graphite films, for example, raising P from 10^{-8} to 10^{-3} torr does not change the value of T_g. For Sn films at $P \geqslant 10^{-4}$ torr we find that T_g rises from 340 to 400 K (Fig. 3), but we do not observe a single-valued relationship among P, the condensation rate ω, and the boundary temperature. For island films of Bi and Pb at $\omega = \text{const}$ we clearly detect a dependence of T_g on the pressure P (Fig. 3). At a certain P_{cr} we observe a sharp increase in T_g, to 430 and 518 K, in these two cases, respectively. The value of P_{cr} is determined by the condensation rate, increasing as the latter increases. It follows from Fig. 3 that the upper values of T_g (at $P > P_{cr}$) for Pb do not depend on the condensation rate or on the substrate material. These values are approximately equal to the magnitudes of the supercooling determined from the crystallization of droplets of micron size in a vacuum of 10^{-5}–10^{-4} torr (Ref. 19).

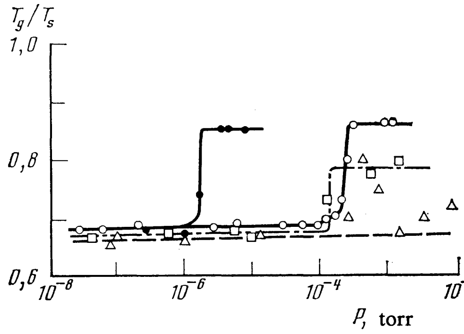

FIG. 3. T_g versus the resideual gas pressure P. ●, ○—Lead; □—bismuth; △—tin.

According to electron microscopy of the phase composition of the Sn, Bi, and Pb condensates synthesized at $P<P_{cr}$ and $P>P_{cr}$, the increase in T_g with increasing P or with decreasing ω results from the formation of corresponding metal oxides (e.g., SnO_2 or γ-Bi_2O_3). The oxides which form during the condensation and growth of island films at $P>P_{cr}$ are additional crystallization centers and accordingly alter the temperature interval in which the liquid phase is stable in the island film, so that ΔT decreases. This conclusion is confirmed by the experimental observation that the temperature T_g for Bi on a substrate in the form of the oxide Bi_2O_3 at $P<P_{cr}$ corresponds to the value of T_g for Bi on a graphite substrate, but at $P>P_{cr}$. The same factor probably explains the agreement of the upper values of T_g with the temperatures to which small droplets of Sn, Bi, and Pb can be supercooled in a vacuum of 10^{-5}–10^{-4} torr in Ref. 19. These results show that heterogeneous crystallization was observed in Refs. 19 and 20, not the homogeneous crystallization which was assumed in Refs. 21 and 22; this point is still under discussion (see Refs. 23–25, for example).

We can thus conclude that, under conditions such that the effect of impurities from the residual gases is minimized, the temperature T_g is the temperature which corresponds to supercooling in the crystallization of liquid islands on the substrate. In this case the only solid "impurity" is the substrate on which the island film grows and whose material affects the supercooling of the liquid islands.

3.3. Dependence of T_g and ΔT on the substrate material

To determine the quantitative relationship between T_g and the substrate material we measured the temperatures at which the condensation mechanism changes on various substrates. At the same time, we measured the edge angles θ of the wetting of the substrate material by the liquid islands. Figure 4 shows the results. We conclude from these results that in switching from amorphous to crystalline substrates we reduce the temperature interval in which the liquid phase is stable in the island films. A comparison of the data on the temperature T_g on different substrates with measurements of the edge angles θ reveals a relationship between T_g and θ.

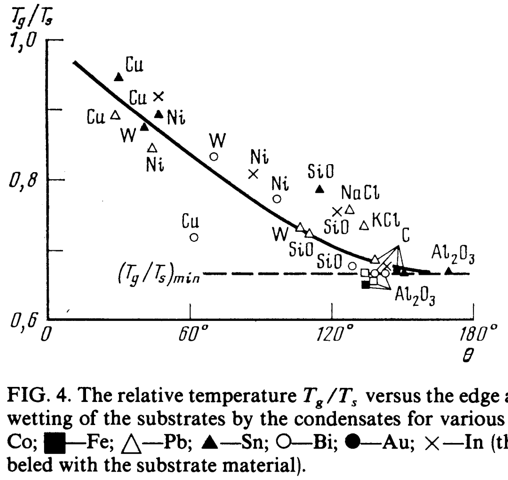

FIG. 4. The relative temperature T_g/T_s versus the edge angle (θ) for the wetting of the substrates by the condensates for various metals: □—Ni, Co; ■—Fe; △—Pb; ▲—Sn; ○—Bi; ●—Au; ×—In (the points are labeled with the substrate material).

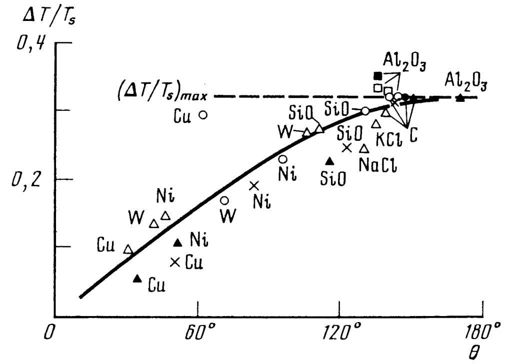

FIG. 5. The relative magnitude of the supercooling versus the wetting edge angle for various metals. The notation is the same as in Fig. 4.

Specifically, as the extent of the wetting increases, the boundary temperature T_g rises, approaching T_s, and in the case of absolutely no wetting ($\theta \to 180°$) we have $T_g \to (2/3)T_s$ (Refs. 8–10, 26).

Consequently, the extent of supercooling required for the crystallization of liquid islands on a substrate decreases with increasing extent of wetting, and in the case of absolutely no wetting ($\theta \to 180°$) we have $\Delta T \to (1/3)T_s$ (Fig. 5). Essentially the limiting degree of supercooling, $\Delta T \approx (1/3)T_s$, is reached for the various metals at wetting angles $\theta > 150°$ (Refs. 1 and 26).

4. DISCUSSION OF RESULTS

From these experimental results we can draw a conclusion regarding the physical nature of the boundary temperature T_g, at which the condensation mechanism changes; we can explain why the ratio $(T_g/T_s) \approx 2/3$ is the same for different metals; and we can plot a temperature-(particle size) diagram for crystal-liquid phase transitions for island films.

4.1 Constancy of the limiting ratios $(T_g/T_s)_{min}$ and $(\Delta T/T_s)_{max}$ for different metals

Measurements of the boundary temperature T_g for metals on substrates with $\theta \to 180°$ yield the value of $(T_g)_{min}$, which corresponds to $(\Delta T)_{max}$. In order to realize these values it is necessary to completely eliminate the effects of impurities and the substrate. It is thus natural to suggest that these quantities correspond to the conditions for homogeneous nucleation during the crystallization of the island films. Proof of homogeneity in this case comes from the satisfaction of the main experimental criterion for homogeneous crystallization—reproducibility of the results— and also from the constancy of the ratio $(T_g/T_s) \approx 2/3$ which is observed during the condensation of metal island films on amorphous substrates when the angle θ is close to 180°.

We can thus draw a conclusion of fundamental importance. The limiting value $(T_g)_{min}$ measured on an unwettable substrate is an intrinsic characteristic of the material under study: It is the temperature T_g which corresponds to the maximum supercooling (the critical temperature) and which does not depend on the particle size. This is the physical meaning of the constancy of the ratios $(T_g/T_s)_{min}$ and $(\Delta T/$

$T_s)_{\max}$. At the maximum-supercooling temperature T_g, metals behave in a similar way. Characteristically, the vacuum-condensation method makes it possible to achieve significantly greater extents of supercooling of metals than is possible when other methods are used to observe the crystallization of supercooled melts.[25]

4.2 Thermal hysteresis in the melting and crystallization of the particles

Analysis of the results on the size dependence of the melting point of small particles and on the formation and thermal stability of the liquid phase in the island films, together with the present theoretical understanding,[1] based on a thermodynamic approach with allowance for the size effect, makes is possible to identify the regions of the liquid phase, the supercooled phase, and the crystalline phase in the island films.[17]

Figure 6 shows a diagram of the crystal-liquid phase transitions in the variable temperature and particle size. This diagram was plotted in the following way. We take the dependence of the melting point of the small particles, T_R, on their size R from the expression in Refs. 27 and 28:

$$T_R(R)=T_s(1-3\Delta\Omega/\lambda\rho R) \tag{1}$$

(ρ is the density, λ is the heat of fusion, and $\Delta\Omega$ is the change in the surface energy upon melting). Also plotted here are the temperature T_s and T_g. We have distinguished three regions in this diagram. The melting curve for the small particles, *AOB*, is the lower boundary of the region in which a thermodynamically equilibrium liquid phase exists (region I); the temperature T_g is the crystallization temperature of the supercooled liquid phase, so that the region between lines *OC* and *OB* is the interval in which the supercooled liquid exists (II); correspondingly, below *OC* and to the right of *AO*, the phase state of the condensate is crystalline (III). Using this diagram, we can predict the state of the particles in the island films on unwettable substrates both during condensation and in existing films as the particle size and the temperature are changed. As examples, we show in this diagram the sequence of transitions which occur at the temperatures T_1 and T_2 as the particle size is varied and also the sequence of transitions for particles of a given size R as the temperature is varied.

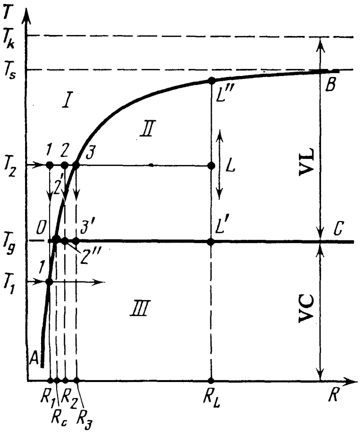

FIG. 6. Diagram of crystal-liquid phase transitions for condensed island films and small particles. VL—Vapor-liquid condensation mechanism; VC—Vapor-crystal condensation mechanism.

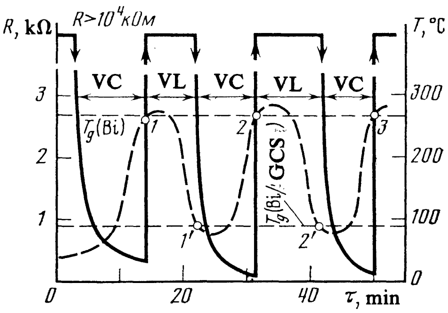

FIG. 7. Electrical resistance (solid line) of Bi films versus the substrate temperature (dashed line) during continuous condensation in a vacuum of 10^{-8} torr. 1, 2, 3—Melting of the films; 1', 2'—crystallization. GCS is a glass ceramic substrate.

It follows from this diagram that if the particle size satisfied $R > R_c$ the melting and crystallization of the particle will occur at different temperature; i.e., thermal hysteresis will occur in melting and crystallization. The magnitude of this hysteresis $(T_r - T_g)$ varies over the interval $0<(T_R - T_g)<(T_s - T_g)$, depending on the particle size. At $R < R_c$, the melting and crystallization temperatures are the same: the supercooling during crystallization vanishes. The thermal hysteresis in melting and crystallization of island films was determined directly from measurements of the electrical resistance of the films during continuous condensation on a substrate while the temperature was periodically toggled between $T < T_g$ and $T > T_g$ (Fig. 7).

The experimental procedure is based on the following picture: During condensation by the vapor-liquid mechanism a film on a substrate with $\theta > 90°$ has an island structure for all thicknesses, so that its resistance is infinite. During condensation by the vapor-crystal method, the resistance of the film has a finite value at thicknesses ≈ 100 Å. The melting of a solid film is accompanied by accumulation of its material into small balls (liquid drops) and, correspondingly, by a sharp increase in the resistance. Figure 7 shows the resistance of a Bi film on a glass ceramic substrate versus the condensation time as the temperature is toggled periodically between $T < T_g$ and $T > T_s$. Analysis of this behavior[1] reveals the melting and crystallization temperatures of bismuth films as functions of the film thickness and the substrate temperature. It also becomes possible to construct a diagram of the crystal-liquid phase transitions (Fig. 8). Similar results were obtained for Sn island films on a glass ceramic substrate.

The magnitude of the thermal hysteresis during melting and crystallization of small particles has been found to depend on the size of these particles in measurements by *in situ* dark-field electron microscopy of island films of In, Hg, and Sn (Refs. 21 and 23). These results agree with the results of the present study for Sn. Zhdanov's conclusion[21] that a heterogeneous crystallization of In particles occurs on a graphite substrate was probably due to the effect of an impurity in

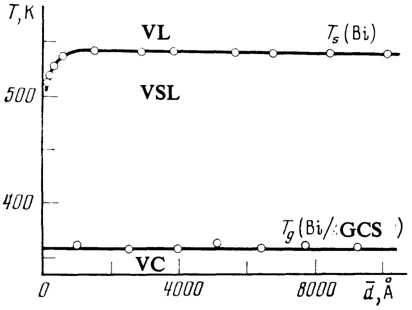

FIG. 8. Diagram of crystal-liquid transitions for Bi constructed from measurements of the resistance. VSL—Vapor-supercooled liquid condensation mechanism.

the low vacuum, 10^{-5} torr. In the present experiments, for In island films synthesized in a vacuum of 10^{-8} torr, we observed considerably greater supercooling.

4.3 Diagram of crystal-liquid phase transitions in small particles

Combining the experimental data on the dependence of the melting point on the size of the particles for the various metals[11-15] and the limiting relative boundary temperature is a constant, $T_g/T_s = 2/3$, we can construct a generalized diagram of the crystal-liquid phase transition for small particles. The melting point (T_R) of a particle of radius R is naturally expressed in units of the melting point (T_g) of the bulk material, and the radius of the particle is naturally expressed in units of the atomic radius R_a ($v_a = 4\pi R_a^3/3$ is the atomic volume). The ratio R/R_a is equal to the cube root of the number (N) of atoms in a particle. Figure 9 shows the most comprehensive of the experimental results available[11-15] in a plot in terms of the relative coordinates T_R/T_s and R/R_a. The results of the measurements of the melting points of these four metals conform well to a common curve

$$T_R/T_s=1-C(R/R_a)^{-1}, \tag{2}$$

where C is a constant for all of these metals. This generalized diagram is an analog of the law of corresponding states in the reduced coordinates T_R/T_s and R/R_a. The fact that Eq. (2) describe the behavior of several metals with various lattice types (fcc and tetragonal) indicates a similarity in the characteristics of small particles near the critical state.

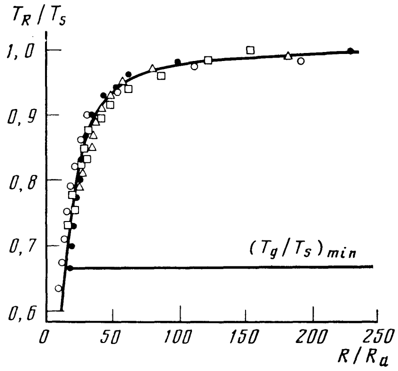

FIG. 9. Generalized diagram of crystal-liquid transitions. ○—Au; ●—Pb; □—In; △—Sn.

According to Fig. 9, there exists a critical particle size $R = R_c$ at which we have $T_R = T_g$ and at which the supercooling during the crystallization of the liquid vanishes. The temperature difference $(T_R-T_g)/T_s$ is the relative supercooling during the crystallization of a particle. The limiting value of this difference in a bulk medium is 1/3; with decreasing particle size, the difference $(T_R - T_g)/T_s$ decreases, vanishing at the point $R = R_c$. Below R_c, T_R decreases, again in accordance with (2), but the transition occurs without any supercooling and thus becomes continuous. To conclude this discussion we should point out that experimental data on the melting of small particles of In, Sn, Pb, and Au (Refs. 11-15) put the value of the parameter R_c at 20–30 Å.

5. CONCLUSION

The experimental data discussed above show that as the size of the particle decreases the distinction between the liquid and the crystalline states of the particle disappears. The radius of a critical particle is approximately equal to the size of the region of short-range order in the liquid phase, so that the observations may be interpreted as follows. The nature of the phase transition changes with the size of the particle. Large particles ($R \gg R_c$) have two thermodynamically stable states near the melting point, with different degrees of order—liquid and crystalline states. These large particles are thus similar to an infinite medium. Small particles ($R \ll R_c$), in contrast, have only a single stable state, with an ordering which corresponds to the short-range order in the liquid phase. Consequently, the phase transition which occurs in large particles proceeds as a first-order transition, while that in small particles is continuous. Together, the experimental results discussed here constitute thermodynamic proof of the existence of a well-defined size for the correlation region (or ordering region) of the distribution of atoms in a small system.

Studies of small particles usually contrast small particles with clusters, although no criteria have been formulated to distinguish between these concepts. The results of the present study cast some light on this question. The critical radius R_c apparently identifies the boundary between particles and clusters. In particles, the phase transition discussed above retains the characteristics of a discrete transition in a bulk material, while in clusters the transition is continuous.

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