

Supercooling and Its Thermal Hysteresis of Pure Metal Liquids

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By using a recently developed adiabatic calorimeter, supercooling of gallium, bismuth, tin, lead and indium was measured. It was found that the metals which crystallize in lower symmetries supercooled more deeply and more stably than those which crystallize in the structure of higher symmetry. The degree of supercooling depended on the highest temperature experienced by the sample. This thermal hysteretic effect was examined from the standpoint of nucleation and precursory phenomenon of solidification.

1. Introduction

It is well-known that liquid metals and semiconductors often supercool before they solidify. Existence of the supercooled phase in the solidifying nucleation process is one of the essential factors that determine the texture and other characteristics of the material¹⁻¹⁵. Supercooling is also important for the formation of amorphous and quasi-crystalline substances. There are two theoretical approaches to the nucleation. One is the homogeneous nucleation theory which is based upon the relation between the solid-liquid interfacial energy and volume free energy. The other is the heterogeneous nucleation theory in which interactions with impurities and vessel walls are further taken into account¹⁶⁻²².

Turnbull²³ measured the degree of supercooling by using the droplet method. Although this method gives values of supercooling for droplets, thermodynamic properties of the supercooled state can not be determined by this method. It has also been

pointed out that the number of atoms in a droplet is too small to be reliably discussed in terms of macroscopic statistics²¹.

In spite of the importance of the phenomenon, there have not been detailed quantitative studies of the degree of supercooling of bulk metal liquids from the standpoint of the nucleation theory. Determination of the internal energy, heat capacity and other thermodynamic properties is indispensable for investigation of the meta-stable supercooled phase as the precursor of the phase transition.

In order to accumulate basic data for further calorimetric study of the normal and supercooled liquids, the author performed measurements of supercooling of bulk samples of several metals using a recently developed adiabatic calorimeter²⁴. The samples examined were high purity gallium, bismuth, tin, lead and indium.

It was found that the metals which crystallize in lower symmetries more deeply and more stably than those which crystallize in the structure of higher symmetry. The degree of supercooling depended on the highest temperature experienced by the sample. This thermal hysteretic effect was examined from the standpoint of nucleation and precursory phenomenon of solidification.

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2. Experiment

2. 1 Samples and crucibles

The purities, impurity elements, masses and surface treatment of the samples are shown in Table 1. As for these without description of surface treatment, the samples were used as ingots. All the samples were heated in the crucible at least to 200 K above the melting point for hours. Volatile impurities were removed by this treatment.

Table 1 Masses, purities, impurity elements and surface treatment of the samples.

	Weight	Purity	Impurity	Treatment
Ga	24.796g	5N	Zn, Sn	
Bi	90.846g	6N	Te, Sb	Chemical Polish. ²⁴⁾
Sn	45.550g	5N	Pb, Cu	
Pb	12.020g	6N	Bi	Chemical Polish. ²⁵⁾
In	13.434g	6N	Cd, Tl	Chemical Polish. ²⁶⁾

The crucibles were made of fused quartz. A piece of fine quartz tube was fused to the center of the bottom. It accepted a thermocouple junction. Constantan wire was wound bifilarly on the outer surface of the crucible. The even distribution of the joule heating thus generated over the large portion of the surface of the sample prevented local heating, thus avoiding breakdown of the supercooling due to temperature inhomogeneity. The sample shape, dimension and other experimental details were reported in the previous paper²⁴⁾. A crucible made of high purity (99.9999%) carbon was used for the measurement on lead because it was less reactive with the metal.

2. 2 Apparatus and experimental method

The apparatus used for the measurement was an adiabatic calorimeter developed for solid, liquid and supercooled liquid samples²⁴⁾. The thermostat in which the calorimeter was housed was evacuated to a vacuum of 10^{-4} Pa. For the measurement of the supercooling of gallium, the calorimeter was modified to enable liquid nitrogen to be used as the cooling agent.

The electromotive force of the chromel-constantan thermocouple inserted in a crucible was

measured with a digital voltmeter. The reading of the lowest three digits of the voltmeter was sent to a strip chart recorder via a digital to analogue converter. The output of the D-A converter was fed simultaneously to a differentiator (Model XE-20 of Rika Denki Kogyo K.K.) of an analogue computer in parallel with the recorder. The time derivative of the thermogram thus obtained increased the sensitivity of the detection of the formation of the solidifying nuclei.

The procedure of the measurement was as follows.

- 1) After the sample was melted, it was held for a certain period of time (t_{\max}) at a temperature T_m just above the melting point and cooled slowly.
- 2) The slow cooling was continued into the supercooling region. When the supercooling was broken by nucleation, the temperature at which the solidifying nucleation occurred was recorded.
- 3) The sample was then immediately heated to a temperature slightly higher than that at which the previous cooling was started, and kept there for a prescribed time.
- 4) Measurement repeating the operations 1)-3) as one cycle was carried out starting at the new value of T_m .
- 5) When the degree of supercooling did not change any more as indicated by a constant value of the crystallization temperature¹⁾, the temperature T_m of the next cycle was lowered.

The measurement was repeated until the temperature T_m reached the melting point.

3. Experimental Results

3. 1 Relation between the temperature T_m and degree of supercooling

The change of the degree of supercooling ΔT in the processes 1)-4) in which the highest temperature T_m was increased step by step is shown in Fig. 1. The abscissa $(T_m - T_{m,p})/T_{m,p}$ represents the separation of the highest temperature T_m from the melting point $T_{m,p}$ normalized with the latter. The

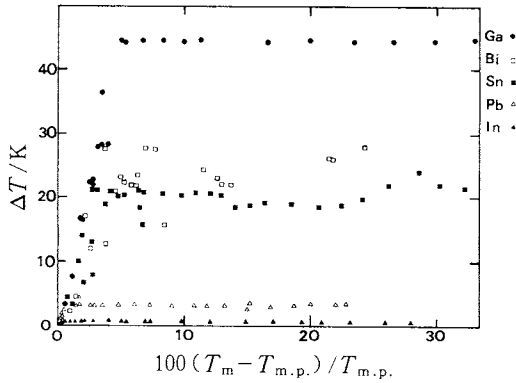


Fig. 1 The degree of supercooling ΔT plotted against the highest temperature T_m experienced by the sample for gallium, bismuth, tin, lead and indium. The data were collected in the *increasing* order of T_m . The abscissa is normalized relative to the melting point $T_{m,p}$.

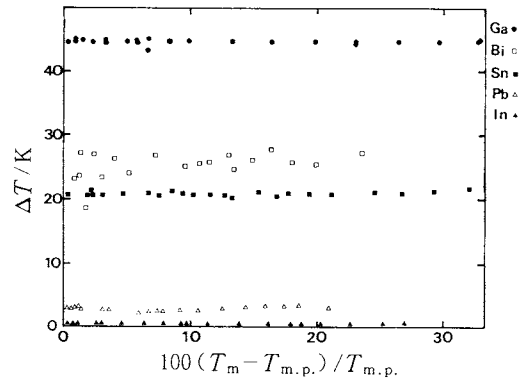


Fig. 3 The degree of supercooling ΔT plotted against the highest temperature T_m experienced by the sample for gallium, bismuth, tin, lead and indium. The data were collected in the *decreasing* order of T_m . The abscissa is normalized relative to the melting point T_m .

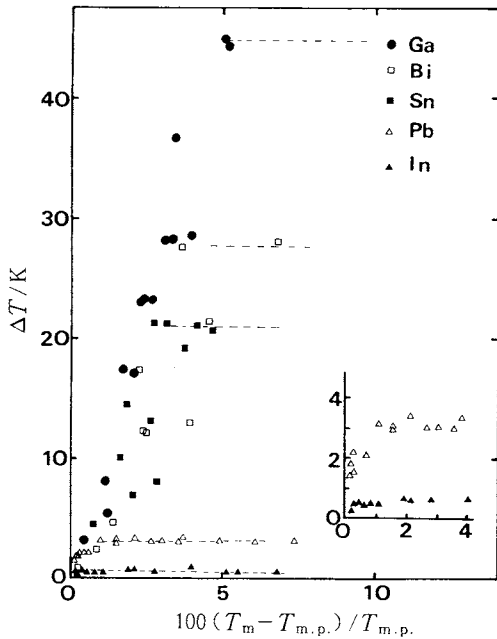


Fig. 2 An expanded representation of the region near the origin of figure 1.

ordinate is the degree of supercooling. Figure 2 shows the behavior of ΔT in the region just above the melting point in an enlarged scale. ΔT showed a clear tendency in all the samples to increase with increasing T_m until a certain limit was reached.

Beyond the limit it remained constant. It is noteworthy that gallium, bismuth and tin supercooled more deeply than lead and indium.

3. 2 Relation between the temperature T_m and degree of supercooling in the process of temperature lowering

For the process of lowering T_m as described in the procedure 5) in section 2-2, a different relation between T_m and ΔT was obtained as plotted in Fig. 3. It was found that even though T_m was decreased down to the temperature just above the normal melting points, ΔT remained constant at the value obtained for the highest value of T_m . The behavior was the same for all the samples. It shows that there is a thermal hysteresis in the relation between ΔT and T_m .

3. 3 Effect of the cooling rate and time for which the sample was held at T_m on the degree of supercooling.

In Table 2, the maximum degree of supercooling ΔT_{max} , the mean cooling rate dT/dt and the t_{max} for which the sample was kept at the temperature T_m are collected. The maximum degrees of supercooling are normalized with the melting point of the substance. The cooling rate and t_{max} were such that the samples remained sufficiently close to thermal

Table 2 Maximum degrees of supercooling ΔT_{\max} , their relative magnitude $\Delta T_{\max}/T_{m,p}$, normalized by the melting temperature $T_{m,p}$, the mean cooling rates dT/dt and the time t_{\max} for which the samples were kept at the highest temperature.

	ΔT_{\max} (K)	$100\Delta T/T_{m,p}$	dT/dt (Kh ⁻¹)	t_{\max} (min)
Ga	44.8	14.8	30	20
Bi	28.2	5.2	23	18
Sn	24.5	4.9	24	17
Pb	3.4	0.6	32	16
In	0.7	0.2	37	20

equilibrium throughout the experiment for the statistical description of the space-time structure to be adequate for the liquid^{27,28}.

In order to confirm this, the following experiment was carried out. First, ΔT was determined for different cooling rates between 12–120 Kh⁻¹. No significant difference was observed in the result. Next, the time for which the samples was held at the highest temperature T_m was changed in the range 0.1–4 h. Again no change was observed in the supercooling behavior. As a further variation of the experimental condition, the sample was held during cooling at an arbitrary temperature in the supercooled state for 1–13 h. Thereafter, the cooling was resumed at that temperature. The values of ΔT thus obtained were the same as those in the straight-forward experiment both for the process of the temperature rise and temperature lowering.

4. Discussion

4.1 Degree of supercooling and crystal structure

Turnbull *et al.* studied supercooling of metallic elements using the droplet method²³. The melting point of thin films and droplets is lower than the bulk value because of the surface free energy. A clear size effect is also found in ΔT ^{29,30}. Therefore the present author aimed at examining the maximum degree of supercooling $\Delta T/T_{m,p}$ of bulk samples. The results are given in Table 3 together with the enthalpy ΔH_f and entropy ΔS_f of fusion. Structure of metallic elements and the coordination num-

Table 3 The melting points $T_{m,p}$, enthalpies ΔH_f , entropies ΔS_f of fusion and maximum degrees of supercooling normalized by the melting point $\Delta T_{\max}/T_{m,p}$.

	$T_{m,p}$ (K)	ΔH_f (Jmol ⁻¹)	ΔS_f (Jmol ⁻¹ K ⁻¹)	$100\Delta T/T_{m,p}$
Ga	302.9	5.61	18.45	14.8
Bi	544.6	11.48	21.01	5.2
Sn	505.1	7.20	14.31	4.9
Pb	600.6	5.44	9.12	0.6
In	429.8	3.26	7.61	0.2

Table 4 The crystal structure and the numbers of nearest neighbors N_s and N_l in the solid and liquid phases.

	Structure	N_s	N_l	N_l	N_s
		Near. Neighbors (sol.)	Near. Neighbors (liq.)		
Ga	orthorhomb.	1-6	11		
Bi	rhomb.	3-3	7-8		
Sn	hexetrag.	4-2	8-9		
Pb	fcc.	12	8-9		
In	hexetrag.	4-8	8		

ber in the solid and liquid phases are given in Table 4^{27,28,36}.

As shown in the table, the elements which have large entropies of fusion supercool more readily than those whose entropies of fusion are small. Obviously the contribution of the volume change is included in ΔS_f , but in the metals investigated in the present work the fractional volume change is 2-3% at most. Therefore a major part of the entropy of fusion should be attributed to the configurational disordering that occurs upon melting, with an addition of a minor contribution arising from the volume change²⁸. With regard to the relation with the crystal structure, the elements which crystallize in the structures of low symmetries (gallium, bismuth and tin) supercool more than those which crystallize in higher symmetries, as Table 4 shows.

An interpretation of this observation is that in these liquids nuclei of the solid are formed less frequently than in the liquids of the elements crystallizing in higher symmetries because the atoms in constant random motion are less likely to arrange themselves in the more specific

configurations²⁾. Obviously less frequent formation of nuclei means a deeper supercooling. As one sees in Table 4, ΔT is large for those elements for which the number of the nearest neighbor (the coordination number) N_s in the solid is smaller than that N_L in the liquid^{3,27,18)}.

4. 2 Thermal hysteresis of supercooling and solidifying nucleation

It has been empirically known that there is a correlation between the nucleation temperature and the maximum temperature T_m experienced by the sample³⁷⁻³⁹⁾. This was explained by invoking a solid-like structure in the liquid^{1,38)}. It has been reported from X-ray⁴⁰⁾, electron beam⁴¹⁾ and neutron diffraction⁴²⁾ studies that solid-like structure exist in liquids at temperatures considerably higher than the melting point. Furthermore, the heat capacity of bismuth is anomalously large in the temperature region just above the melting point as reported by Grønvald⁴³⁾ and Bell *et al.*⁴⁴⁾. These results support the argument that the atomic cluster (embryo) in the liquid possessing solid-like structure starts the liquid-solid transformation as the nucleating agent. This agrees qualitatively with the results of the present study that the degree of the supercooling increases as the temperature to which the sample has been heated previously increases.

The thermal hysteresis of ΔT found in the present study cannot be explained by the homogeneous nucleation mechanism involving only the embryo in thermal equilibrium. It was shown above that even if some solid structure may remain after melting, it vanishes as the sample is heated to a certain temperature and when the temperature is lowered the nuclei are not formed again within the experimental time. This may probably be related with superheating at the site of micro-cracks of vessel wall or at the surrounding of impurities^{1,2)}. In these sites, the sample retains its local solid structure after melting and when the sample is heated to a high temperature the solid structure vanishes.

Discussion of the thermal hysteresis of nucleation is important for metallurgical application^{37-39,45)} and need be treated separately from the homogene-

ous nucleation. It may be added briefly that the heat capacity of bismuth measured recently by the author is a smooth function of temperature in the liquid as well as in the supercooled liquid state^{46,47)}. Thus, existence in thermal equilibrium of the embryo only in the region just above the melting point postulated previously^{43,44,48,49)} has not been substantiated by heat capacity measurement.

4. 3 Degree of supercooling and precursory phenomena of solidification

The solid-like structure or cluster of atoms (embryo) postulated in the liquid phase as precursor to solidification is discussed separately for the temperature region close to the melting point^{43,44,48,49)} and wide into the liquid phase^{40-42,51,52)}. As described in the previous section the supercooling behavior depends on the thermal history of the sample. The hysteretic property may probably be related with heterogeneous nucleation.

The nucleation theory^{2,16,17)} applied to embryos in liquid bismuth gives the relation between the radius r^* of critical embryo which cause phase transformation and the degree of supercooling ΔT as plotted in Fig. 4 by the solid curve. The critical radius r^* is related to ΔT by the following equation.

$$r^* = (2\sigma T_{m,p} V_m) / (\Delta T \Delta H_f) \quad (1)$$

where σ is the solid-liquid interfacial energy, ΔH_f enthalpy of fusion and V_m molar volume of the liquid. Taking $\sigma = 54.4 \text{ Jm}^{-2}$ given by Turnbull¹⁾ and $\Delta H_f = 11478 \text{ Jmol}^{-1}$ by the present author, one obtains $\sigma^* = 540 \text{ nm}$ for $\Delta T = 20 \text{ K}$. According to Chalmers²⁾, the maximum radius r of the embryo which can exist in liquid at $T = T_{m,p} - \Delta T$ depends on ΔT typically as indicated by the broken line in Fig. 4.

For heterogeneous nucleation the maximum size of the embryo for a given degree of supercooling is larger than for homogeneous nucleation. Therefore, the broken curve increases faster for heterogeneous nucleation than is shown in Fig. 4. Spontaneous transformation from the liquid to solid state occurs when the radius of the largest possible embryo

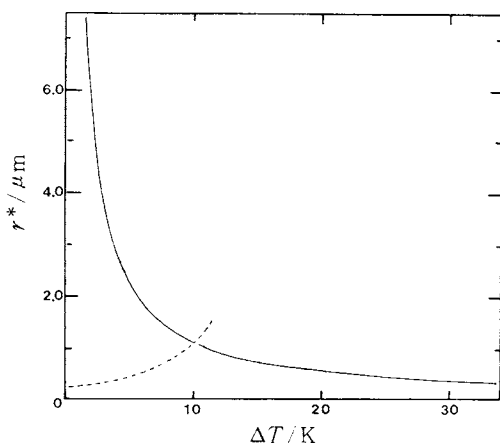


Fig. 4 The relation between the radius r^* of critical nuclei and the degree of supercooling ΔT (solid line). The broken line represents the relation between ΔT and the radius of the largest embryo which can exist in liquid.

becomes equal to the critical radius r^* . The degree of supercooling is thus given by the intersection of the solid and broken curves.

The above argument shows that the behavior of the solid like structure (embryo) in the stable and supercooled liquid phase is closely related to the precursory phenomena of solidification. Detailed calorimetric data on the solid, liquid and supercooled liquid phases of bismuth will be reported soon⁵³⁾.

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要 旨

バルク試料の液相から過冷却に至る領域で、熱量測定の可能性を探るために、新たに開発された断熱型熱量計と溶融石英製の坩堝を使用し、種々の金属試料の過冷却について測定、検討を行なった。用いた試料は、高純度ビスマス、ゲリウム、インジウム、錫、及び鉛である。結晶の対称性の低い金属ほど、深く安定した過冷却が得られ、過冷却液相に於いても十分に熱量解析が可能であることが示された。しかも、得られる過冷却度は、“試料が経験した最高温度に依存する”という、熱履歴現象が測定され、核生成と凝固前駆現象の立場から検討が加えられた。