Thermal expansion mechanism of liquid metals

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Liquid tin has been studied by x-ray diffraction over the temperature range from 300 to 1700 °C. The mechanism for the thermal expansion of the molten metal is primarily an increase in the free volume of "holes," without an increase in interatomic distances. This mechanism is thus fundamentally different from the familiar mechanism for the thermal expansion of crystalline phases.

Diffraction methods have been used to study most liquid metals near their melting point.[1–5] It has been established experimentally that the melting of typical metals with closely packed atoms in the crystalline phase not only does not increase the shortest interatomic distances but in fact reduces them somewhat, with a simultaneous increase of 3–5% in the specific volume. In the case of a semimetal or semiconductor whose crystal lattice has a loose packing, melting leads to increases in the shortest interatomic distances and also the coordination number. The specific volume may either increase (Bi, Sn) or decrease (Ga, Si) in the process.[3]

As the temperature of a liquid metal is increased, there is a further increase in the specific volume, amounting to about 1% per 100° (Ref. 3). The information available on the nature of the changes in the interatomic distances is not completely unambiguous, and in some instances it is in fact contradictory.[2,4,6–11] The reason for this situation apparently lies in the relatively narrow temperature intervals in which the studies have been carried out, which have been mandated by serious methodological difficulties in high-temperature x-ray diffraction of molten materials. There has accordingly been essentially no discussion of the mechanism for the thermal expansion of liquid metals; only in Refs. 12 and 13 do we find some qualitative considerations.

In the present paper we report experiments in which temperatures of 1700 °C were reached and in which liquid tin was studied by x-ray diffraction in an atmosphere of pure helium. The temperature range over which tin is in the liquid phase is one of the widest among pure metals. The material can be heated 1465° above the melting point in this case. This study has become possible thanks to a refinement of the experimental apparatus of Ref. 14 and the use of reliable techniques in the x-ray diffraction.[15,16]

Working from the experimental scattering functions, we calculated the structure factors (interference functions) $i(s) = I_{ke}/f^2$ by the standard methods, where I_{ke} is the intensity in electron units of the x radiation scattered by the sample, f^2 is the independent (gas) scattering, $s = 4\pi\lambda^{-1}\sin\theta$ is the absolute value of the diffraction vector, λ is the wavelength, and 2θ is the scattering angle. We used molybdenum radiation, rendered monochromatic with a graphite monochromator in the primary beam, and an optimized detection arrangement. Numerical values of the structure factors over the temperature range 400–1700 °C were published in Ref. 17. From those factors we calculated the radial atomic profiles $4\pi r^2\rho(r)$ and the relative atomic distribution $g(r) = \rho(r)/\rho_0$, where ρ_0 is the average atomic density.[3] The structure factors and radial atomic distributions found experimentally for some of the temperatures studied are shown in Figs. 1 and 2.

The shape of these functions and the structural features on them (the secondary maxima and bumps) agree well with published results on liquid tin[1,2,7,9,11,18] (the highest temperature which has been achieved previously has been 1100–1140 °C, Refs. 7 and 18). The scatter in the values reported by different investigators for the position r_1 of the first maximum on the radial atomic distribution and for the coordination number Z lies within the usual limits.

First, our experimental data show that over a wide temperature range (up to 1700 °C) the short-range spatial order of the atoms remains the same, since diffraction effects are seen clearly up to large scattering angles, and the radial atomic distribution deviates from its mean value $4\pi r^2\rho_0$ over distances greater than 0.8 nm.

The behavior of several of the structural characteristics can be followed quite well over a wide temperature range. Table I shows structural characteristics for two series of experiments; the results of one series are marked with an asterisk. In each series of experiments it was possible to hold constant maximum number of experimenal conditions (through adjustment of the sample and the heating conditions). This constancy improved the accuracy of the observation of relative changes in the characteristics with the temperature. As the temperature is raised, the position (s_1) of the first diffraction maximum in the structure factor remains essentially constant for the liquid tin. We do see a tendency of the remote diffraction maxima to shift toward larger scattering angles. This behavior stands in contrast with the shift of the diffraction maxima toward smaller scattering angles which is observed during the heating of the crystalline phase. The height of the first diffraction maximum decreases significantly (by ~30%), while its width increases [$\Delta s_{1/2}$ is the half-width, and Δs_1 is the width at $i(s) = 1$]. For the remote diffraction maxima the changes in height are weaker. For example, the height of the second maximum, at $s_2 = 44$ nm^{-1}, decreases from 1.29 to 1.16 (by ~10%). Beginning at 1300 °C, $i(s_2)$ remains essentially constant. The third maximum, $i(s_3)$, at $s_3 = 67$ nm^{-1}, decreases by 3%, while the fourth, at $s_4 = 87$ nm^{-1}, remains fixed, within the experimental errors. There is a substantial decrease in the overall coordination number Z, calculated as the area under the first maximum on the radial atomic distribution, up to $r = 0.39$ nm.

Note in particular that the most probable distance between neighboring atoms found from the position r_1 of the

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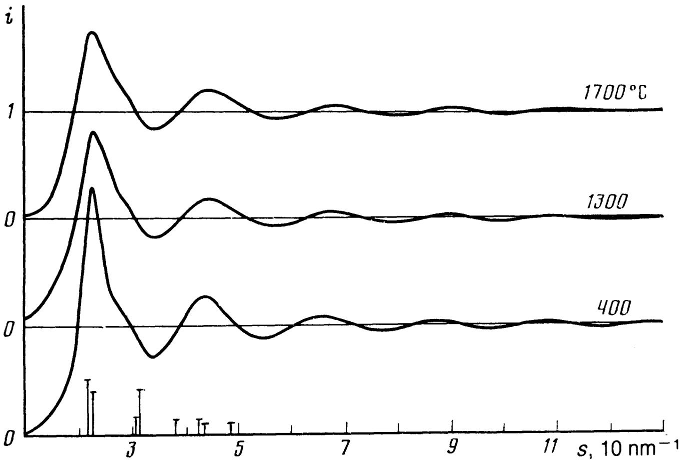

FIG. 1. Structure factors of liquid tin. The vertical bars mark diffraction reflections of tetragonal crystalline white tin.

first maximum on the radial atomic distribution and that on the $g(r)$ curve (r_1') does not increase; in fact, it shows some tendency to decrease. Whether this behavior is a consequence of the significant asymmetry and complex shape of the first maximum on the radial atomic distribution can be tested by calculating the mean square values of the interatomic distances, $\bar{r}_k$, within the first maximum on this distribution, from r_0 $[4\pi r_0^2(r_0) = 0]$ to $r_2 = 0.39$ nm.

Calculations of $\bar{r}_k$ from the expression

$$\bar{r}_k = \left[\int_{r_0}^{r_2} r^2 g(r)\,dr\right]^{1/2} \left[\int_{r_0}^{r_2} g(r)\,dr\right]^{-1/2} \tag{1}$$

show (Table I) that the change in the mean square interatomic distance with the temperature is similar to the behavior of the most probable interatomic distance.

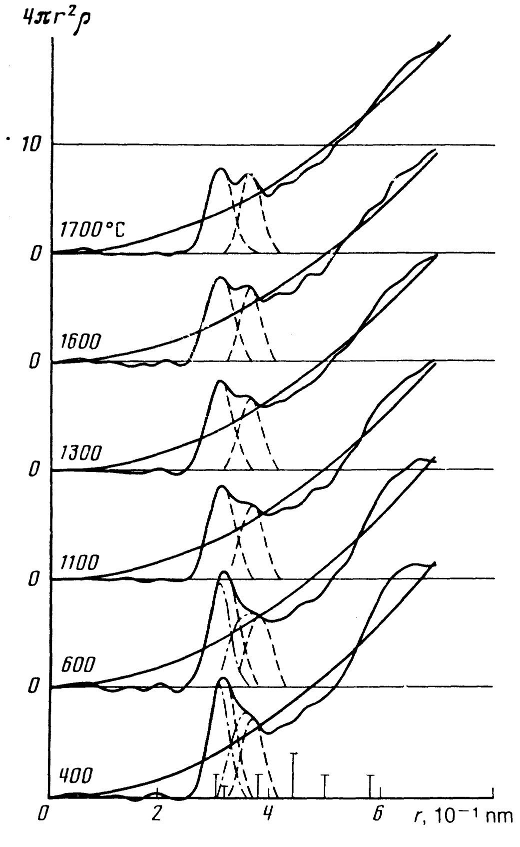

FIG. 2. Radial atomic profiles of liquid tin. The dashed and dot-dashed lines show decompositions of the first maximum by two techniques (explained in the text proper). The vertical bars show the coordination spheres in the tetragonal crystal lattice of white tin.

The first maximum on the radial atomic distribution has a complex structure. We are actually seeing two principal interatomic distances, r_1' and r_1'', which correspond to the absolute maximum and a secondary maximum. The latter becomes sharper in the temperature interval 1600–1700 °C, in fact emerging as a distinct maximum (Fig. 2). We can follow the changes in these principal distances with increasing temperature through a symmetry decomposition of the first maximum into two subpeaks, carried out by two techniques. In the first technique, the first subpeak is constructed for all temperatures under the assumption that its crest is at $r_1' = 0.308$ nm (its area is Z_1'). The crest of the second subpeak appears at a distance $r_1'' = 0.36$ nm (its area is Z_1''). This decomposition is the most obvious one for the situation prevailing in the interval 1600–1700 °C. Even at other temperatures, however, the position of the second subpeak is close to that given above. The areas under the subpeaks, Z_1' and Z_1'', correspond to low coordination numbers (~ 4) (columns 3, 4, and 5 in Table II).

The second technique for decomposing the first maximum on the radial atomic distribution can be outlined as follows: The position of the first subpeak for each temperature is taken to be the distance r_1 listed in Table I. Its area, Z_2', decreases from 6.4 to ~ 4. The second subpeak appears at distances r_1'' of about 0.37 nm; its area, Z_2'', oscillates over the range 3–3.5 (columns 6, 7, and 8 in Table II).

Analysis shows that the second principal interatomic distance also fails to increase with the temperature, and the subpeaks are characterized by low coordination numbers, regardless of the technique used to separate them. These results are evidence that the interatomic interaction in liquid tin is of a directed nature.

Returning to the structure factor, we note that the experimental fact that right-hand branch of the first maximum remains highly asymmetric is clearly of interest (Fig. 1). At low temperatures we see a secondary maximum, which becomes a bump at higher temperatures. While there is a gen-

TABLE I. Structural characteristics of liquid tin.

$T°$, C	$s_1 \cdot 10^{-1}$ nm^{-1}	$i(s_1)$	$i(s')$	$\Delta s_1 \cdot 10^{-1}$ nm^{-1}	$\Delta s_{1/2} \cdot 10^{-1}$ nm	Z_{min}	$r_1 \cdot 10^{+1}$ nm	$r_1' \cdot 10^{+1}$ nm	$\bar{r}_k \cdot 10^{+1}$ nm	V, $\frac{cm^3}{mole}$
300 *	2.25	2.5	1,06	0.75	0.66	9.4	3.17	3,12	3.30	17.10
400	2.24	2.3	1.21	0,99	0.74	9.1	3,15	3,11	3,25	17,25
500 *	2.24	2.2	1,12	0,87	0.73	9.3	3.15	3.11	3.30	17.42
600	2.25	2.2	1,25	1,02	0.90	8.9	3,16	3,12	3,22	17,58
700 *	2.23	2,0	1.14	0.91	0.85	8.6	3,12	3,07	3,19	17.74
800	2,25	2.0	1.25	1.02	1.01	9.0	3.15	3.11	3.32	17.92
900 *	2,25	1.9	1.15	0.93	1.06	8.4	3.13	3.09	3.22	18.09
1000	2.24	2.0	1.12	1.03	1.06	8.5	3.16	3.15	3.38	18.27
1100 *	2.23	1.9	1,21	0.99	1.09	8.1	3.11	3.07	3.27	18.42
1200	2.25	1.8	1.28	1.08	1.22	8.1	3.11	3.06	3.23	18.63
1300	2.25	1.8	1,31	1.12	1.26	7.6	3.09	3.05	3.16	18.83
1400	2.27	1.8	1.30	1.10	1.28	8.1	3.16	3.12	3.19	19.01
1500	2.27	1.7	1.28	1.10	1.34	7.7	3.11	3.08	3.22	19.20
1600	2.25	1.8	1.29	1.11	1.26	7.8	3.09	3.05	3.23	19.42
1700	2.26	1.7	1,29	1.13	1.40	7.6	3.08	3,04	3.16	19.61
δ, %	0.5	2	2	2	2	1	1	1	>1	3

eral decrease in the height of the first maximum, however, the ordinate of this bump does not decrease. Table I shows values of $i(s')$ at $s' = 28$ nm^{-1} which illustrate this conclusion. The nature of this bump has been discussed in the literature, and several opinions have been expressed. Furukawa *et al.*[11] have suggested that there are some atoms in the melt for which the distance is smaller and corresponds to the first coordination sphere of grey tin ($r = 0.285$ nm). That suggestion is not supported by the present study. Orton[19] constructed an explanation on the basis of a two-structure model for the short-range atomic order. There has been the further suggestion that the existence of this bump might be explained for several liquid metals in terms of a common structure on the basis of energy considerations, if increasing structural complexity, with a transition from a spherically symmetric interaction to a directional interaction, were accompanied by a reduction in the distance from the first maximum in the structure factor to the zero of the pseudopotential form factor.[20]

An idea common to these approaches is that this bump is caused by the preservation of a certain fraction of directed interatomic bonds in the liquid. The preservation of this bump up to high temperatures which we have established in the present study, on the one hand, and the values found for the coordination numbers Z' and Z'' (Table II), on the other, constitute unambiguous evidence that the interatomic interaction in liquid tin is directional.

There is obviously the further question of the relationship between the short-range atomic order in liquid tin and the structure of its crystalline phases. Danilov[1] has shown that near the melting point the statistical distribution of the interatomic distances in liquid tin is similar to that of the atoms in the tetragonal crystal structure of white tin, for which the radii of the coordination spheres and the coordination numbers (given in parentheses) near the melting point are $r_1 = 0.303$ nm (4), $r_2 = 0.319$ nm (2), $r_3 = 0.378$ nm (4), and $r_4 = 0.443$ nm (8).

We know that when low-symmetry crystal structures melt one observes a certain probability for an organization of more-symmetric directional bonds.[21] This tendency is manifested in the formation of the well-defined first maxima on the radial atomic distributions, with deep minima. These maxima are evidence of a decrease in the spread of coordination spheres characteristic of the crystal lattice. One might thus suggest that the secondary maximum (the second subpeak) on the right-hand branch of the radial atomic distribution of liquid tin (0.360 nm) forms as the results of a certain restructuring in the first three coordination spheres and is a superposition of the second and third coordination spheres (in crystalline white tin, their average distance is 0.358 nm).

TABLE II. Coordination numbers found by the two techniques for decomposing the first maximum on the radial atomic profile.

No.	T, °C	I			II		
		Z_1' for $r_1'=0{,}308$	Z_1''	r_1'', nm	Z_2' for r_1 (т. 1)	Z_2''	r_1'', nm
1	300	4.3	6.4	0,360	6.4	3.0	0.37
2	400	4.5	6.0	0.360	5.9	3.4	0.37
3	500	4.2	6.0	0.360	5.8	3.3	0.37
4	600	4.0	6.0	0.360	6.0	3.1	0.38
5	700	4.3	5.6	0.360	5.8	3.2	0.37
6	800	4.5	5.5	0.360	5.6	3.6	0.37
7	900	4.0	5.4	0.360	5.5	3.0	0.36
8	1000	4.0	5.2	0.360	5.0	3.5	0.35
9	1100	4.2	5.0	0.360	4.9	3.8	0.37
10	1200	4.0	4.9	0.360	4.9	3.3	0,37
11	1300	4.4	5.0	0.360	5.0	3.2	0.36
12	1400	4.0	4.8	0.360	4.9	3.3	0,37
13	1500	4.0	4.7	0.360	4.8	3.2	0.36
14	1600	4.2	4.8	0.360	4.8	3.1	0.36
15	1700	4.0	4.2	0,360	4.2	3.4	0,36

We thus see that the temperature increase does not substantially disrupt the correlation between the positions of the maxima on the radial atomic distribution of liquid tin and the set of coordination spheres of crystalline white tin. Comparison with the set of coordination spheres and diffraction reflections of other crystal structures—the fcc, bcc, diamond, etc., structures—shows that the most likely structure for liquid tin over a wide temperature range is a short-range-order structure of a single type, in which the distribution of interatomic distances is basically similar to that of the tetragonal structure of white tin. This conclusion agrees with results which were found in Refs. 1, 2, and 7 for narrower temperature intervals and also with the results found by Orton *et al.*,[22] who used the method of extended x-ray absorption fine structure, which is sensitive to the nearest atomic neighborhood. Orton *et al.* established that at a temperature slightly above the melting point liquid tin contains interatomic distances which correspond to the structure of white tin.

Let us use the x-ray diffraction data to examine the mechanism for the thermal expansion of liquid tin. Over the temperature range studied, 300–1700 °C, the specific volume of liquid tin increases by 14.6% (Ref. 6). If we assume that the mechanisms for the thermal expansion of the solid and liquid phases are the same, we would expect an increase of 4.7% in the interatomic distances in the melt. This figure is well outside the error in the experimental determination of these distances by diffraction methods. However, the data of the present study show quite convincingly that this behavior is not observed in the temperature dependence of the interatomic distances. The meaning here is that the mechanism for the thermal expansion of the liquid metal is not determined by an increase in the interatomic distances due to anharmonicity in the potential energy of the interatomic interaction.

If we were to invoke the ideas of Frenkel'[23] and suggest that the cause of the thermal expansion of the liquid is an increase in the free volume due to "holes," without a change in interatomic distances, we could describe the temperature dependence of the molar volume of the melt by the exponential function

$$V-V_0=V_0\exp(-U/kT), \tag{2}$$

where V_0 is the "ideal" model volume of a mole of atoms packed in the structure of the short-range order of the liquid in the absence of a free volume, and U is the hole formation energy. The isothermal compressibility would then be a consequence of the free volume. According to the ideas of Frenkel', the diffusion coefficient D, the viscosity η, the isothermal compressibility β, and the thermal expansion coefficient α of the liquid are given by[23]

$$D=(\delta^2/6\tau_0)\exp(-U_D/kT), \tag{3}$$

$$\eta=(\tau_0 kT/6\pi\delta^3)\exp(U_\eta/kT), \tag{4}$$

$$\beta=(1/V)(\partial V/\partial p)_T=(V_0/NkT)\exp(-U/kT), \tag{5}$$

$$\alpha=(1/V)(\partial V/\partial T)_P=(U/kT^2)\exp(-U/kT), \tag{6}$$

where δ is the mean square displacement of the atoms of the liquid, τ_0 is the duration of the "settled life" of an atom near the melting point, U_D and U_η are the corresponding activation energies, N is Avogadro's number, and T is the absolute temperature. If we assume in a first approximation that the mean square displacements of the atoms do not change, since the experiments demonstrate that the interatomic distances do not change with the temperature, and if we also assume that the activation energies in (2)–(5), which stem from the common (hole) mechanism differ only negligibly, then we find the following relations from (2)–(5):

$$\frac{V-V_0}{D}=B_D,\qquad \frac{(V-V_0)\eta}{T}=B_\eta,\qquad \frac{V-V_0}{\beta T}=B_\beta. \tag{7}$$

These relations can be used to determine the ideal molar volume from experimental data on diffusion, viscosity, and isothermal compressibility. The values found for B_D, B_η, and B_β in this way should remain constant over a wide temperature range if this understanding of the thermal expansion of the liquid is correct. Indeed, the values calculated for these properties from (7) and from experimental data on the diffusion,[24] viscosity,[3] and isothermal compressibility[25] of liquid tin turn out to remain constant over a wide temperature range, within 3.7% for B_D, within 0.9% for B_η, and within 1.8% for B_β. The values calculated for the ideal model volume from these data agree well with each other: $V_0^D = 16.62$ cm^3/mole, $V_0^\eta = 16.75$ cm^3/mole, and $V_0^\beta = 16.52$ cm^3/mole. The mean value is $\overline{V}_0 = 16.63$ cm^3/mole. The mean value of the ideal model volume is 2.8% greater than $V_0 = 16.16$ cm^3/mole, which is the value which we find by extrapolating the temperature dependence of the molar volume of liquid tin to 0 K. The some extent, this circumstance serves to illustrate the physical nature of the ideal model volume.

From the value found for $\overline{V}_0$ and from the packing coefficient of 0.53, which characterizes a structure like that of crystalline white tin, we can determine the distance between neighboring atoms in the ideal model volume. Specifically, we find 3.03 Å, in good agreement with the shortest interatomic distance in white tin near the melting point. In accordance with the arguments above, we can estimate the number of holes as a fraction of the total number of atoms at various temperatures in liquid tin. Near the melting point this quantity is about 3% and agrees well with the data in Ref. 23; at 1700 °C it is 18%. This increase in the free volume over the temperature range studied is accompanied by the experimentally observed decrease of 19% in the average coordination number.

These calculations show that the interpretation proposed here agrees well with several facts which have been established experimentally regarding liquid tin. This agreement suggests that the mechanism for the thermal expansion of the molten material is basically one of an increase in the free volume of holes, without an increase in interatomic distances. This mechanism is fundamentally different from the familiar mechanism for the thermal expansion of crystalline phases. It is a consequence of the nature of the liquid, which is characterized by a high mobility of atoms, while the densities are comparable to those of the solid phases.

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