

# Quantitative analysis based on the pair distribution function for understanding the anomalous liquid-structure change in $\text{In}_{20}\text{Sn}_{80}$

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The temperature-induced anomalous liquid-structure change in melt  $\text{In}_{20}\text{Sn}_{80}$  observed by Zu *et al.* [Phys. Rev. Lett. **89**, 125505 (2002)] has been studied. The structure transition in  $\text{In}_{20}\text{Sn}_{80}$  is further confirmed by the presence of an exothermic peak in the differential-scanning-calorimetry (DSC) curve. From experimental data of pair distribution functions, we calculated the viscosity ( $\eta$ ) and the excess entropy ( $S$ ) and found that there is a valley of viscosity in the  $\eta$ - $T$  curve and a valley of excess entropy in the  $S$ - $T$  curve, which are consistent with the internal-friction ( $Q^{-1}$ ) peak in the  $Q^{-1}$ - $T$  curve and the exothermic peak in the DSC curve, respectively. We decomposed  $S$  into two parts,  $S(1)$  and  $S(2)$ , which are related to the total potential and the isothermal compressibility, respectively. The behaviors of  $S(1)$  and  $S(2)$  tell us that the atomic bonds vary twice and the microstructures transform twice in the temperature range from 300 to 900 °C for liquid  $\text{In}_{20}\text{Sn}_{80}$ . The similar analyses of liquid  $\text{In}_{80}\text{Sn}_{20}$  and liquid Sn reveal that Sn plays a crucial role in the discontinuous structure change in liquid  $\text{In}_{20}\text{Sn}_{80}$ .

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First-order phase transitions in crystals induced by pressure and/or temperature constitute a class of phenomena which has been thoroughly studied both experimentally and theoretically. Compared to crystals, liquids have been investigated very insufficiently. Can there be first-order phase transitions in a single-component liquid when the pressure and/or temperature change is applied? This is one of the most interesting and challenging problems in the field of liquid science. Recently, growing experimental and theoretical evidence suggests that pressure-induced liquid-liquid phase transitions (LLPTs) do exist in some one-component systems, including  $\text{H}_2\text{O}$ ,  $\text{SiO}_2$ , P, C, Si, Ge, Cs, Se, Bi, and I.<sup>1</sup> These transitions are characterized by two different densities related to different atomic configurations. And, there is a general argument that the best candidates to exhibit LLPT are liquids having open molecular coordination environments, especially those with a locally tetrahedral molecular structure. For example, P, the low-pressure phase, consists of tetrahedral  $\text{P}_4$  molecules; the high-pressure phase with higher density has the polymeric form. Interestingly, in recent experiments, Zu *et al.*<sup>2,3</sup> reported a discontinuous temperature-induced liquid-structure change at the ambient pressure in some binary alloys, e.g., PbSn, PbBi, InSn, and InBi. This anomalous discontinuous structural change is suggested on the basis of the experimental results of internal friction, differential thermal analysis (DTA), and x-ray diffraction: There is a notable peak in the curve of internal friction ( $Q^{-1}$ ) as a function of temperature, and the features of this peak are in agreement with those exhibited during solid-solid phase transformations verified by previous investigators.<sup>4</sup> A thermal absorption peak occurs in the DTA curve at the corresponding temperature range. The coordination number and mean nearest-neighbor distance, derived from the pair distribution functions, undergo an abnormal minimum. This phenomenon is quite astonishing and of counterintuitive nature for the following reasons. (i) It has been widely accepted that

liquid-alloy structures change gradually with temperature increasing from the melting point to the critical point. (ii) There are no defined phase lines above the melting point in their temperature-composition phase diagrams as in most binary alloys. (iii) At the corresponding region of both temperature and composition there seems no possibility of the conventional phase separations. (iv) It does not fall into any other up-to-date recognized structural changes as mentioned above. Such a transition should be further confirmed and remains itself an interesting research subject.

The intent of this Letter is to prove this counterintuitive phenomenon in  $\text{In}_{20}\text{Sn}_{80}$  and shed light on this baffling issue. Specifically, we have performed a series of analyses based on the results of the x-ray diffraction in the melt  $\text{In}_{20}\text{Sn}_{80}$ , and present experimental evidence supportive of an exothermic peak in the differential-scanning-calorimetry (DSC) curve in liquid  $\text{In}_{20}\text{Sn}_{80}$ . Our quantitative estimation on the basis of pair distribution functions produces a valley of excess entropy ( $S$ ) in the  $S$ - $T$  curve and a valley of viscosity ( $\eta$ ) in the  $\eta$ - $T$  curve, which are in good agreement with the exothermic peak and the  $Q^{-1}$  peak observed in DSC and internal-friction experiments, respectively. Through x-ray diffraction, DSC measurement, and the similar estimation of the excess entropy of liquid  $\text{In}_{80}\text{Sn}_{20}$ , however, we do not observe an exothermic (or endothermic) peak and a valley of excess entropy.

The pair distribution function  $g(r)$  plays a central role in the physics of liquids. It is directly measurable and, in principle, various properties of liquid materials can be estimated from the structural data  $g(r)$  when coupled with an appropriate theory. This quantity is proportional to the probability of finding a particle at a distance  $r$  from a reference particle and is the ratio of local to bulk density at distance  $r$ . The function  $g(r)$  goes to 1 for large  $r$  and is always 1 for a random spatial distribution of particles. The total pair correlation function,  $h(r) = g(r) - 1$ , represents deviations from randomness. A fun-

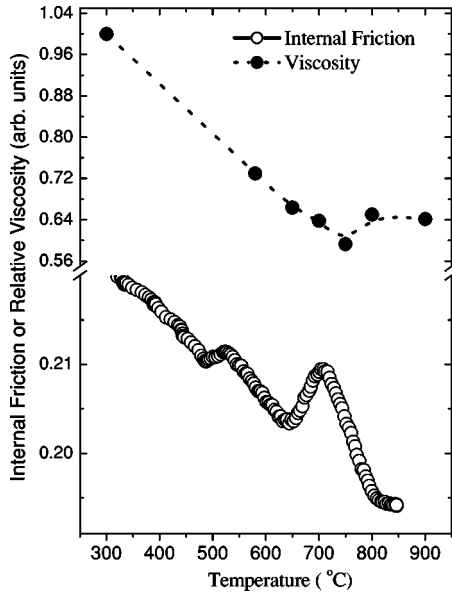


FIG. 1. Experimental measured internal friction and calculated relative viscosity as a function of temperature.

fundamental relation between structure and thermodynamics is given by

$$\kappa_B T \rho K_T = 1 + 4\pi\rho \int h(r)r^2 dr. \quad (1)$$

Here,  $\rho$  is the number density,  $K_T = (\partial\rho/\partial P)_T/\rho$  is the isothermal compressibility,  $P$  is the pressure, and  $\kappa_B$  is the Boltzmann constant.

The excess entropy  $S$ , the difference between the system thermodynamic entropy and that of the equivalent ideal gas, is a measure of the number of accessible configurations of the system and given as  $S = S_2 + S_3 + \dots$ , where  $S_2$  is the pair correlation entropy,  $S_3$  the triplet correlation entropy, and so on. The two-particle entropy is defined by

$$S_2 = -2\pi\rho \int_0^\infty \{g(r)\ln[g(r)] - [g(r) - 1]\}r^2 dr. \quad (2)$$

It is found by Baranyai and Evans<sup>5</sup> that the two-body entropy contributes at least 85% of the excess entropy at liquid densities; the difference between the actual excess entropy and the two-body entropy is nearly constant over a wide of range of densities, and the constant offset will merely translate into a constant shift of data on the figures with respect to the excess entropy. So, in the present work, the excess entropy is approximated and discussed by the two-body approximation, as in Refs. 6 and 7. For a binary mixture of two components  $\alpha$  and  $\beta$ , the excess entropy is given by  $S = \chi_\alpha S_\alpha + \chi_\beta S_\beta$ , where  $S_\mu$  is the partial molar entropy for the  $\mu$ th component as given by  $S_\mu = -2\pi\rho_\mu \int_0^\infty \{g_{\mu\nu}(r)\ln[g_{\mu\nu}(r)] - [g_{\mu\nu}(r) - 1]\}r^2 dr$  via the similar two-body approximation.<sup>8</sup> For convenience of the following analysis, we define

$$S(1) = -2\pi\rho \int_0^\infty \{g(r)\ln[g(r)]\}r^2 dr, \quad (3)$$

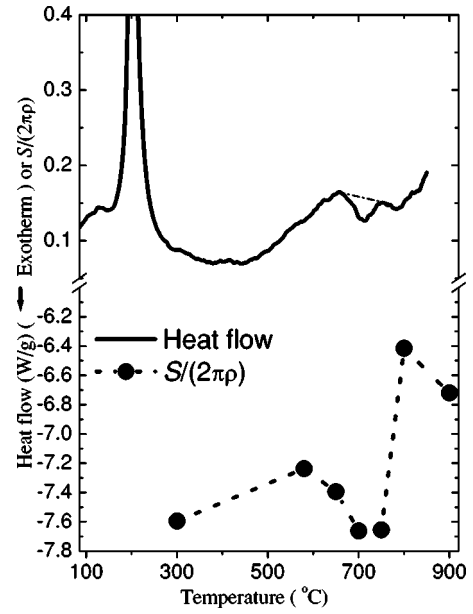


FIG. 2. Results of differential scanning calorimetry (DSC) and the calculated excess entropy (in unit of  $k_B$ ).

$$S(2) = 2\pi\rho \int_0^\infty h(r)r^2 dr. \quad (4)$$

The excess entropy is the sum of  $S(1)$  and  $S(2)$ . The pair potential of mean forces,  $\omega_2(r)$ , is defined in terms of the pair correlation functions by<sup>9</sup>

$$\omega_2(r) = -\kappa_B T \ln g(r). \quad (5)$$

According to Eqs. (1) and (3)–(5),  $S(1)$  and  $S(2)$  are, respectively, related to the total potential and the isothermal compressibility. Due to there not being a position to gain the partial structure factors, we cannot calculate the partial molar entropy and then obtain the excess entropy as Samanta suggested.<sup>8</sup> Here, we approximately calculate the excess entropy of  $\text{In}_{20}\text{Sn}_{80}$  in terms of the pair correlation entropy, which may be reasonable because, near the melting point, liquid In and Sn share similar structure properties for packing density, the nearest-neighbor notes distance, and the height of first peak of  $g(r)$  (see Tables 3.1, 8.15, and 8.17 of Waseda<sup>9</sup>).

Iida *et al.*<sup>10</sup> have proposed an expression for the viscosity of liquid metals in terms of the pair distribution function and the average interatomic frequency

$$\eta = (8\pi/9)v_0 P(T)m\rho^2 \int_0^a g(r)r^4 dr, \quad (6)$$

here  $v_0$  is a constant, corresponding to the frequency of oscillation when there is no net displacement,  $P(T)$  is the probability that the atom will stay in a state of oscillation around a fixed coordinate position, and  $a$  is the distance over which the transfer of momentum takes place. It can be assumed that momentum interactions occur between the neighboring atoms. In Ref. 10, the nearest-neighbor distance is estimated as representing the minimum between the first and second

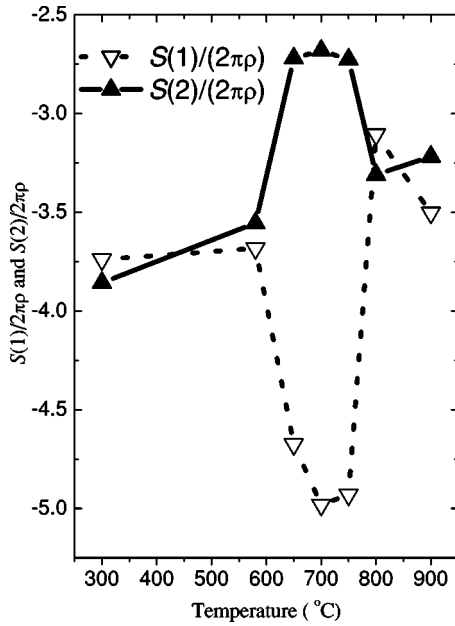


FIG. 3. Two parts  $S(1)$  and  $S(2)$  of excess entropy (in unit of  $k_B$ ) vs temperature.

peaks in the  $g(r)$  curve, and this distance is used as the upper limit  $a$  of the integral in Eq. (6). In our present work we use 15 Å as the upper limit  $a$  of the integral. According to the well-known Enskog theory of atomic transport, the collision frequency  $\Gamma$  is given by  $\Gamma = 4\sigma^2 g(\sigma) \rho \sqrt{\pi k_B T / m}$ .<sup>6</sup> Here,  $m$  is the atomic mass and  $\sigma$  is the position of the first peak of  $g(r)$ . Assuming that  $P(T)$  is inversely proportional to  $\Gamma$  due to the fact that the atom will move to another position once the collision occurs, we can write Eq. (6) approximately as

$$\eta \sim \frac{1}{\sigma^2 g(\sigma) \sqrt{T} \rho} \int_0^a g(r) r^4 dr. \quad (7)$$

To make a sharp comparison, we present the internal friction and the relative viscosity calculated from Eq. (7) in Fig. 1. Note that the internal friction is macroscopically measured, and the relative viscosity is obtained from the diffraction-experiment result,  $g(r)$ . In the temperature region (600–800 °C), there is a notable peak in the  $Q^{-1}$ - $T$  curve and an observable valley in the  $\eta$ - $T$  curve. The presence of the  $Q^{-1}$  peak and the  $\eta$  valley is coincident. A similar phenomenon occurs in the glass transition and crystallization for the amorphous alloy and in the eutectoid change for ZnAl alloy.<sup>11</sup> Thus, according to the above macroscopic and microscopic results, the structure transition does take place.

Both the DSC curve obtained at a heating rate of 20 °C/min and the curve of the excess entropy calculated from the diffraction experiment results are shown in Fig. 2. Based on the thermodynamics of phase transitions, the exothermic peak appearing around 700 °C suggests that it is a first-order LLPT peak. Note that the exothermic peak is piling up the high endothermic background. Corresponding to the exothermic peak in the DSC curve, a remarkable  $S$  valley appears in the  $S$ - $T$  curve at the same temperature range, i.e., the entropy first decreases abnormally and then increases abruptly with

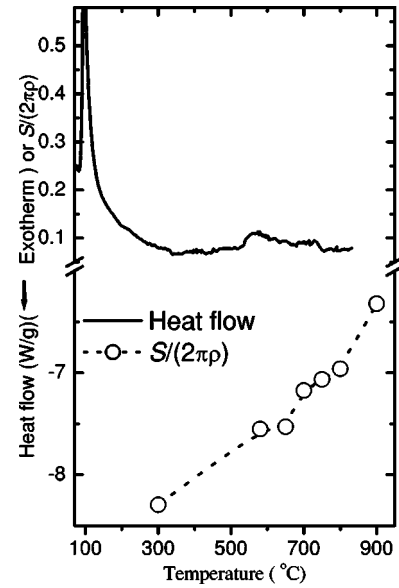


FIG. 4. Results of differential scanning calorimetry and the calculated excess entropy (in unit of  $k_B$ ) for  $\text{In}_{80}\text{Sn}_{20}$ .

rising temperature, which demonstrates that the phase transition is entropy driven. It is interesting to note that the temperature range of the  $S$  valley is in agreement with that of the exothermic peak. Thermodynamics tells us that the entropy of the high-temperature phase should be larger than that of the low-temperature phase at the transition temperature. However, the entropy shown in Fig. 2 suddenly decreases at around 650 °C accompanied by the exothermic peak in the DSC measurement, which seems to violate thermodynamics. So, it might be likely that liquid  $\text{In}_{20}\text{Sn}_{80}$  may exist a metastable structure at around 700 °C. This metastable phase gives rise to the abnormal decrease of the entropy at around 650 °C, and will change to stable phase with larger entropy at higher temperature. Further work is needed to explore this matter and the concrete change of structure in the process of the whole transition.

In order to better understand the mechanism of the LLPT, the calculated  $S(1)$  and  $S(2)$  are illustrated in Fig. 3. As shown in Fig. 3, first there is a step-down for  $S(1)$  and a step-up for  $S(2)$  at 580–650 °C; then, there is a step-up for  $S(1)$  and a step-down for  $S(2)$  at 750–800 °C, which leads to a net  $S$  valley in the  $S$ - $T$  curve. According to Eqs. (1) and (5), the behaviors of  $S(1)$  indicate that the total pair potential energies of mean force first go down suddenly and then go up sharply, i.e., a minimum of potential energies appears which results in the appearance of the exothermic peak; the behaviors of  $S(2)$  indicate that the isothermal compressibility first goes up and then goes down, i.e., a compressibility maximum occurs. Interestingly, similar behavior is found in supercooled water by the extensive molecular dynamics simulations, which points out that there is maximum in the curve of  $K_T$  as a function of temperature.<sup>12</sup> So, these behaviors of  $S(1)$  and  $S(2)$  clearly tell us that, as the temperature rises, the atomic bonds vary twice; the microstructures transform twice in liquid  $\text{In}_{20}\text{Sn}_{80}$ .

Motivated by the internal friction results of liquid BiSn

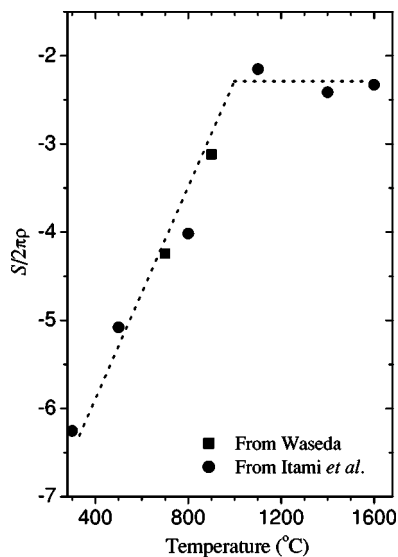


FIG. 5. The calculated excess entropy (in unit of  $k_B$ ) for pure Sn based on the  $g(r)$  data in Refs 9 and 14. The dotted line is a guide to the eyes.

alloys,<sup>13</sup> we carried out the x-ray diffraction and DSC measurement of liquid  $\text{In}_{80}\text{Sn}_{20}$ . The DSC curve measured at a heating rate of  $20^\circ\text{C}/\text{min}$  and the  $S$ - $T$  curve calculated from the x-ray diffraction results are presented in Fig. 4. In contrast with Fig. 2 for liquid  $\text{In}_{20}\text{Sn}_{80}$ , the exothermic peak nearly disappears in the DSC curve of liquid  $\text{In}_{80}\text{Sn}_{20}$ , and so does the valley of excess entropy. These findings tell us that Sn may play an important role in the occurrence of a temperature-induced discontinuous structural change in the liquid  $\text{In}_{20}\text{Sn}_{80}$ . Therefore, it is desired to study the structure properties of liquid Sn in an extremely wide temperature range. Fortunately, Itami *et al.* have recently studied the structures of liquid Sn over a wide temperature range by neutron scattering experiments.<sup>14</sup> Using  $g(r)$  data of Refs. 14 and 9, we have obtained the excess entropy at different temperatures, shown in Fig. 5. We have also measured the internal friction of pure Sn with different oscillating frequencies, shown in Fig. 6. A discontinuous change of excess entropy at around  $1000^\circ\text{C}$  and an internal-friction peak at  $800$ – $900^\circ\text{C}$  suggest that a discontinuous structure change happens at  $800$ – $1000^\circ\text{C}$  in liquid Sn, which is in good agreement with the  $P$ - $T$  diagram of liquid and solid Sn shown in Fig. 4 of Ref. 15. Therefore, the above-mentioned results of liquid  $\text{In}_{80}\text{Sn}_{20}$  and liquid Sn suggest that Sn may play a crucial role in the structural changes in liquid  $\text{In}_{20}\text{Sn}_{80}$  and PbSn.

In summary, the temperature-induced anomalous liquid-structure change in melt  $\text{In}_{20}\text{Sn}_{80}$  observed in recent experiments has been studied. The presence of an exothermic peak

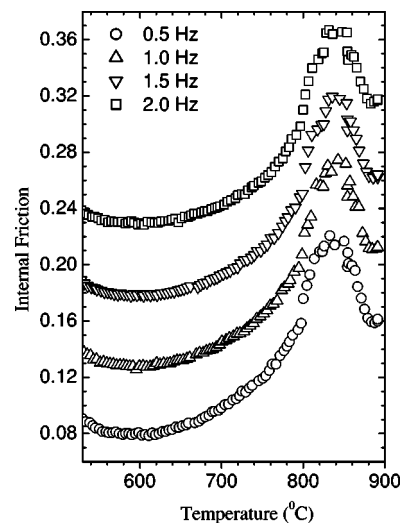


FIG. 6. Internal friction as a function of temperature for pure Sn measured with four oscillating frequencies.

in the DSC curve provides direct evidence of liquid-structure change in  $\text{In}_{20}\text{Sn}_{80}$ . The quantitative analysis based on the pair distribution functions produces an observable valley of viscosity and a deep valley of excess entropy. The presence of this viscosity valley is in agreement with the appearance of the internal-friction peak, and the presence of the entropy valley is consistent with the appearance of the exothermic peak. We decompose  $S$  into two parts,  $S(1)$  and  $S(2)$ , which are related to the total potential and the isothermal compressibility, respectively. The behaviors of  $S(1)$  and  $S(2)$  clearly indicate that the atomic bonds vary twice and the microstructures transform twice in liquid  $\text{In}_{20}\text{Sn}_{80}$ . The further experimental results, namely the absence of the exothermic peak in the DSC curve and the absence of the  $S$  valley in the  $S$ - $T$  curve in liquid  $\text{In}_{80}\text{Sn}_{20}$ , and the discontinuous change of the excess entropy and the appearance of internal-friction peak in  $Q^{-1}$ - $T$  curve for liquid Sn, enlighten us to the anomalous structure change in  $\text{In}_{20}\text{Sn}_{80}$  and PbSn liquids. So, further theoretical and experimental studies on the Sn-based alloys may help us explore this counterintuitive phenomenon. We believe that the present attempt at studying liquid-liquid phase transitions in liquids, in terms of the two-body approximation of the excess entropy, should be applicable to other liquid-liquid phase transitions.

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- <sup>13</sup>The systematic measurements of internal friction for liquid BiSn series show that internal friction peak height decreases with the decrease in Sn contents when other conditions such as the heating rate and the torsion frequency are fixed, and internal friction peak disappear in liquid BiSn<sub>20</sub>. The results will be published elsewhere.
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