Observation of an Anomalous Discontinuous Liquid-Structure Change with Temperature

Fang-Qiu Zu,[1,2,*] Zhen-Gang Zhu,[1] Li-Jun Guo,[1] Xu-Bo Qin,[3] Hua Yang,[3] and Wen-Jun Shan[1]
[1]*Laboratory of Internal Friction and Defects in Solids, Institute of Solid State Physics, Chinese Academy of Sciences, P.O. Box 1129, Hefei 230031, China*
[2]*College of Materials Science and Engineering, Hefei University of Technology, Hefei 230009, China*
[3]*The Key Laboratory of Liquid Structure and Heredity of Materials, Ministry of Education, Shandong University, Jinan 250061, China*

(Received 4 April 2002; published 30 August 2002)

The nature of liquid structures with their changing behaviors remains an unsolved fundamental problem in many fields of science and technology. It has been widely accepted that liquid structures change gradually with temperature and/or pressure. With x-ray diffraction in the melt In-Sn80, however, we have confirmed that a temperature-dependent discontinuous structural change could occur in some binary liquids, which does not fall into any other up-to-date recognized liquid-liquid changes. This finding, together with the recently recognized pressure-induced liquid change, suggests that the conventional view on liquids should be revised.

DOI: 10.1103/PhysRevLett.89.125505 PACS numbers: 61.25.Mv, 07.90.+c, 83.10.Tv

It has been a widely accepted conventional view that the liquid structure varies gradually with temperature and/or pressure from the melting point to the critical point. However, growing evidence suggests that the pressure-induced discontinuous phase changes might happen in some one-component liquids, e.g., SiO_2, H_2O, C, Si, Cs, Ga, Bi, I_2, and Se [1–8]. Such liquid state polyamorphism (or named "polymorphism" as in crystalline solid state) has been recently verified by an *in situ* x-ray study, with an abrupt, pressure-induced structural change between two distinct forms observed in liquid phosphorus [9]. In addition, a temperature-induced phase transition was observed in the supercooled system Al_2O_3-Y_2O_3 [10]. Moreover, some liquid alloys such as S-Te [11], Se-Te [12], and Te-I [13] are newly added to the systems in which the well-known conventional liquid phase separations can occur in the region near the liquidus (T_L) with the chemical composition as the changing parameter. Because of the versatility of matter, the melting mechanisms and the liquid structural nature are versatile. Therefore, it is believed that novel phenomena and new knowledge will be uncovered as we probe liquid behaviors more deeply [1,14]. Up until now, however, it has not been considered seriously if a temperature-induced structural change could discontinuously occur, at ordinary pressure and far over the liquidus, in multiple component liquids with a constant chemical composition, although simulations [15] have already suggested its possibility.

The results of our earlier studies by the revised internal friction method, as well as differential thermal analysis and differential scanning calorimetry experiments, implied that the liquid structure might change discontinuously, hundreds of degrees above the liquidus, as a function of temperature at constant pressure in some binary alloys, e.g., Pb-Sn, Pb-Bi, In-Sn, and In-Bi [16–18]. The phenomenon is quite astonishing because there is no defined phase line above T_L in their temperature-composition phase diagrams [19] as in most other binary systems, and the features of the transitions as well as the corresponding region of both temperature and composition seem to exclude the possibility of the conventional phase separations. No doubt, however, it should be further confirmed if the results do reflect such structure changes and found out what ever happens structurally during the process. By means of x-ray diffraction, in the present study, we observed the occurrence of such a temperature-induced structural change in the melt In-Sn80. During the change, the coordination number and mean nearest neighbor distance underwent an abnormal minimum, and the interatomic bonds altered obviously. At the end of the change, the size of short-range orders and the ordering degree decreased abruptly. It does not fall into the well-known conventional phase separations in some binary melts [11–13,19]. This Letter gives solid confirmation for one case of the temperature-induced discontinuous structure changes in some binary melts, thus presenting a challenge again to our conventional picture of liquids as entities with continuously varying averaged structure.

The reasons for selecting In-Sn80 (wt %) in the diffraction study lie in the fact that it is within the composition region (single solution in solid state) [19] where the conventional phase separation can by no means occur and that the vapor pressure of the both elements is low so as not to stain the apparatus. The diffraction sample was previously prepared with tin and indium granules of high purity (5*N*), held at 600 °C (melted at about 195 °C) for 210 min under the shielding slag (B_2O_3), and then solidified for use. The x-ray diffraction measurements were carried out using a θ-θ diffractometer with Mo-Kα-radiation, the graphite monochromator, the tantalum heater, and the corundum crucible ($20 \times 15 \times 8$). The chamber was evacuated to 10^{-6} mm Hg and then filled with high pure Ar (4*N*) at 1.3 atm. The scanning step was 0.05 Å^{-1} for the wave number Q. Based on the internal friction (Q^{-1}-T) of the corresponding composition, the scattering temperatures were selected, respectively, as follows: 300, 580, 650, 700, 750, 800, and 900 °C. The sample was held at 300 °C for 2 h, then the scattering began. For the further scattering temperatures, the sample was held for 30 min before each measurement.

Based on the results of the diffraction experiment, Fig. 1 shows the mean nearest neighbor distance (r_1) and the coordination number (N_1) derived from the pair distribution function $g(r)$ and the radical distribution function at each temperature respectively. For comparison, the internal friction pattern Q^{-1}-T of the melt In-Sn80 is also shown in the same figure. Corresponding to the peak of the internal friction in the curve Q^{-1}-T, as can be seen in the figure, a remarkable valley appears abnormally around about 700 °C for both r_1 and N_1, demonstrating evidently a discontinuous configuration reconstruction in the melt, while r_1 and N_1 vary only slightly with temperature before and after the valley. Considering the diffraction temperature intervals, it is very likely for r_1 and N_1 to start falling between 580 and 650 °C. Therefore, the results of diffraction well agree with those of the internal friction experiment, which can also be regarded as a foolproof verification of the reliability for the results of both methods. As is well known, the atomic neighbor distance r_1 and the coordination number N_1 are both important structural parameters for liquids, whose above-mentioned peculiar behaviors reveal the occurrence of a temperature-induced discontinuous structural change in the melt In-Sn80.

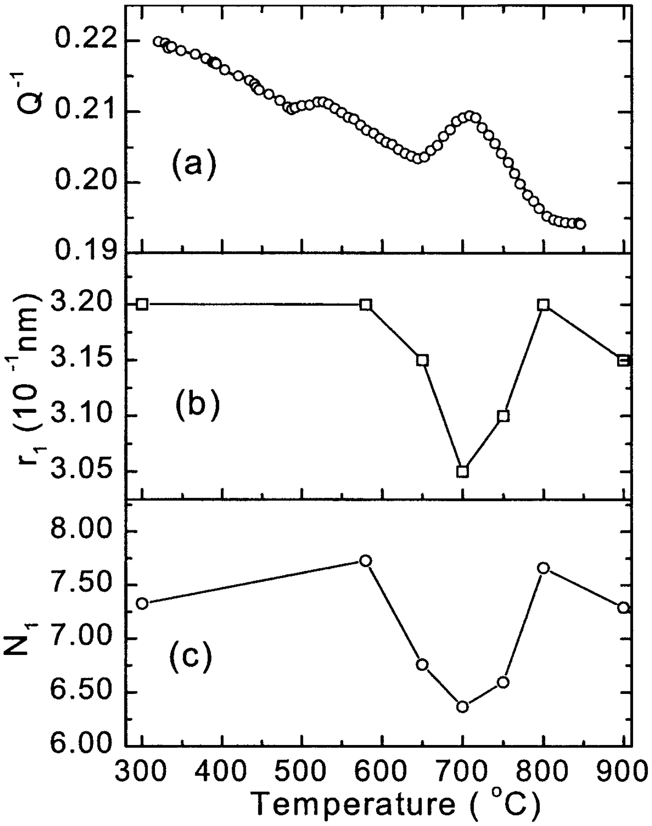

FIG. 1. Results of x-ray diffraction compared with those of the internal friction experiment for the melt In-Sn80: (a) internal friction (Q^{-1}) versus temperature; (b) mean nearest neighbor distance (r_1) versus temperature; (c) coordination number (N_1) versus temperature. Here r_1 corresponds to the position of the maximum of the first peak in $g(r)$, and N_1 is obtained by the integration [20] to the first minimum in the $4\pi\rho_0 r^2 g(r)$ curve, where ρ_0 is the average number density. For the definition and experimental method of the internal friction Q^{-1}, please refer to Refs. [16,17].

With respect to liquid structures, on the other hand, it is generally agreed that there are lots of minor short-range ordering domains, around which the ordering is lacking, although it is considered at present that they dissipate and engender always with time and space. For a definite liquid, the statistically averaged size (the radius r_C) of the domains and the atom numbers (N_C) within them must vary with the structural change due to the alteration of atomic interactions. Using a semiempirical approach [20], we got the functions of both r_C [beyond which $g(r)$ is always within 1 ± 0.01] and N_C versus temperature for the melt In-Sn80 based on the results of $g(r)$. From 750 to 800 °C, as illustrated in Fig. 2, the averaged ordering domain radius

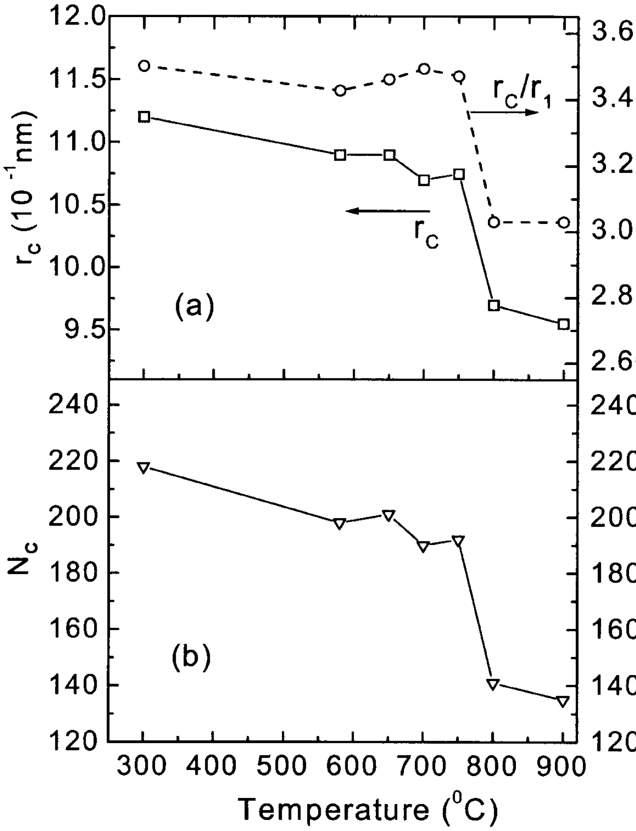

FIG. 2. Both the ordering range and the ordering degree of the melt In-Sn80 decrease abruptly at the end of the structure change. (a) Size of ordering domains r_C and the ratio (ordering degree) r_C/r_1; (b) atom number within the orders N_C.

r_C drops from 10.75 Å to 9.55 Å and the atom number N_C within the domains from 192 to 141, which indicate obviously that the ordering range becomes much smaller abruptly at the end of the structure change. In addition, Fig. 2 also shows the parameter ζ ($= r_C/r_1$) denoting the structural disorder [21], whose pattern signifies that the ordering degree of the melt In-Sn80 decreases evidently along with the change. Compared with Fig. 1, the temperature at the end of the change exhibited in Fig. 2 is in perfect accordance with that denoted by both structural parameters (r_1 and N_1) in the nearest atom shell and that illustrated by the peak in the internal friction pattern.

It should be noted that the values of both r_1 and N_1 after the valley are not much different from those before it (Fig. 1). The similar case exhibits in the behavior of the shoulder at the right side of the first peak of $g(r)$ too, as demonstrated in Fig. 3. Up to 580 °C the shoulder does not vary distinctly, while it starts to depress between 580 and 650 °C and disappears around 700 °C. Fascinatingly enough, a shoulder reappears at the higher temperatures. It is impossible that the structure of the melt remains the same after the structure change. So let us take a look at what is taking place during the reconstruction and what is different before and after that.

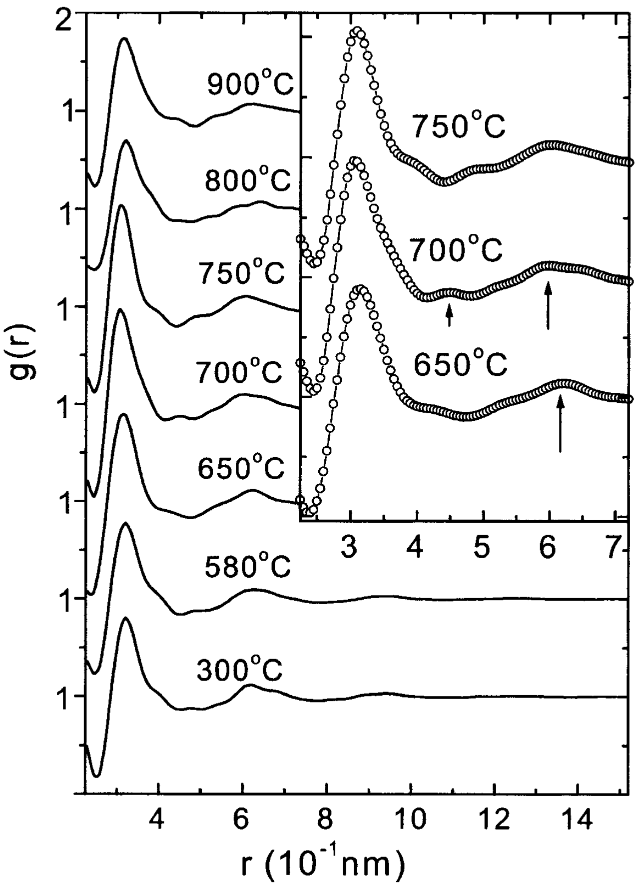

FIG. 3. Patterns of the pair correlation function $g(r)$ of the melt In-Sn80 at different temperatures. Inset: Magnification of $g(r)$ from the first peak to the second one at 650, 700, and 750 °C.

Former investigators have found that a similar shoulder appears in $g(r)$ for pure liquid tin near the melting point and vanishes between 300 and 700 °C (lack of definite data) [20,21], but does not reappear at the higher temperatures. This kind of shoulder is also found in the pair correlation functions of these liquid elements with covalent bonds in their solid state, e.g., silicon, carbon, and germanium [22–24]. The shoulder is attributed to the residual covalent bonds of solids in the liquids, by which it is manifested that the short-range ordering of tetrahedrons exists in these liquids. Evidently, the same reason applies for the shoulder of the melt In-Sn80 before it vanishes, and the fact that the shoulder disappears implies the breaking of the covalent bonds of tin around 700 °C in the melt. However, what about the shoulder at higher temperatures? We suppose, in the melt, the atoms of indium do not distribute uniformly with those of tin before the breaking of the covalent bonds of tin, whereas they aggregate to some extent in microscopic zones surrounded by the domains composed mainly of tin atoms, showing a kind of metastable local ordering. When temperature is elevated to the extent that the covalent bonds are broken, the kinetic energy of the atoms is high enough to drive them to diffuse into the opposite domains of each other. At the same time, new atomic bonds build up, with the relatively uniform melt forming. Since the melt is mainly composed of tin, after the reconstruction, a reference Sn atom is surrounded by the nearest shell made up of about five or six atoms of tin and one or two atoms of indium ($N_1 = 7.66$ at 800 °C), and the bond length difference between the Sn-Sn bonds (no longer the covalent bonds) and the In-Sn bonds leads to the recurrence of the shoulder in $g(r)$.

The assumption is supported by the experimental results. In Fig. 3, at about 700 °C, there is a small hump (rather than a shoulder) between the first peak and the second one, and the latter leans to the left. According to the physical meaning of the pair correlation function $g(r)$, the abnormal manners, compared with those at lower and higher temperatures, demonstrate that some atoms move amid the nearest atom shell and the next one around the reference atom, say, the atoms of tin outwards and those of indium inwards. Of course, the same moving takes place between the further shells. On the other hand, the mean nearest neighbor distance (r_1) shows fixedness after 300 °C for both pure tin and indium [20,25], while r_1 of the In-Sn80 undergoes an abnormal minimum around 700 °C, which indicates the variation of the atomic interaction and the adjustment of the atomic bonds.

An anomalous temperature-induced discontinuous liquid structural change was observed in In-Sn80 far over the liquidus, which is distinct from the up-to-date recognized liquid-liquid changes. It, from another aspect, proposes that our conventional views on the structural changing pattern and the nature of liquid should be revised.

In a more broad sense, it might be likely that there are more than one such changes for some binary melts and that such liquid state polyamorphism could take place in some liquid systems composed of more than two components. In the inverse course, consequently, the freezing microscopical mechanism may not be the same as a liquid alloy cooled from a different temperature with distinct local structures, and the frozen structures may be dissimilar, as reported in some cases [26,27].

This work has been supported by the National Natural Science Foundation of China Grant No. 19874067 and the Core-Teacher Foundation of China Ministry of Education.

---

*Corresponding author.
Electronic address: fangqiuzu@hotmail.com

[1] P. McMillan, Nature (London) **403**, 151 (2000).
[2] C. A. Poole, T. Grande, and P. McMillan, Science **275**, 322 (1997).
[3] D. J. Lacks, Phys. Rev. Lett. **84**, 2881 (2000).
[4] O. Mishima and H. E. Stanley, Nature (London) **392**, 164 (1998).
[5] K. Koga, H. Tanaka, and X. C. Zeng, Nature (London) **408**, 564 (2000).
[6] A. K. Soper and M. A. Ricci, Phys. Rev. Lett. **84**, 2881 (2000).
[7] J. N. Glosli and F. H. Ree, Phys. Rev. Lett. **82**, 4659 (1999).
[8] J. Y. Raty *et al.*, J. Phys. Condens. Matter **11**, 10 243 (1999).
[9] Y. Katayama *et al.*, Nature (London) **403**, 170 (2000).
[10] S. Aasland and P. McMillan, Nature (London) **369**, 633 (1994).
[11] M. V. Coulet *et al.*, J. Non-Cryst. Solids **252**, 463 (1999).
[12] Y. Tsuchiya, F. Kakinuma, and C. Bergman, J. Non-Cryst. Solids **207**, 143 (1996).
[13] I. Kaban, T. Halm, and W. Honyer, J. Non-Cryst. Solids **288**, 96 (2001).
[14] A. R. Ubbelohde, *The Molten State of Matter: Melting and Crystal Structure* (Wiley, New York, 1978).
[15] F. Shimojo, S. Munejiri, K. Hoshino, and Y. Zempo, J. Phys. Condens. Matter **12**, 6161 (2000).
[16] F. Q. Zu *et al.*, Phys. Rev. B **64**, 180203(R) (2001).
[17] F. Q. Zu, L. J. Guo, Z. G. Zhu, and Y. Feng, Chin. Phys. Lett. **19**, 94 (2002).
[18] F. Q. Zu, Z. G. Zhu, B. Zhang, Y. Feng, and J. P. Shui, J. Phys. Condens. Matter **13**, 11 435 (2001).
[19] *Binary Alloy Phase Diagram*, edited by T. B. Massalski *et al.* (American Society for Metals, Metals Park, Ohio, 1993).
[20] Y. Waseda, *The Structure of Non-Crystalline Materials* (McGraw-Hill, New York, 1980).
[21] Y. Marcus, *Introduction to Liquid State Chemistry* (Wiley, London, 1977).
[22] R. Brozel *et al.*, Naturwissenschaften **49**, 129 (1962).
[23] A. H. Narten, J. Chem. Phys. **56**, 1185 (1972).
[24] Y. Kita *et al.*, J. Phys. Condens. Matter **6**, 811 (1994).
[25] B. R. Orton and P. Smith, Philos. Mag. **14**, 873 (1966).
[26] X. F. Bian and W. M. Wang, Mater. Lett. **44**, 54 (2000).
[27] X. F. Bian, X. F. Liu, and J. J. Ma, *Heredity in Cast Metals* (Shandong Science & Technology Press, Jinan, China, 1998).