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Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

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Fang-Qiu Zu^a; Zhi-hao Chen^a; Li Zou^a; Hong-sheng Chen^a

^a College of Materials Science and Engineering, Hefei University of Technology, Hefei 230009, China

To cite this Article Zu, Fang-Qiu, Chen, Zhi-hao, Zou, Li and Chen, Hong-sheng(2008) 'Kinetics of liquid-structure change of In-Sn and In-Pb melts', *Physics and Chemistry of Liquids*, 46: 4, 433 – 441

To link to this Article: DOI: 10.1080/00319100701716528

URL: <http://dx.doi.org/10.1080/00319100701716528>

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Kinetics of liquid–structure change of In–Sn and In–Pb melts

FANG-QIU ZU*, ZHI-HAO CHEN, LI ZOU and HONG-SHENG CHEN

College of Materials Science and Engineering, Hefei University of Technology,
Hefei 230009, China

(Received 19 September 2007; in final form 1 October 2007)

In this article, we investigate the kinetics of temperature-induced liquid–liquid structure changes in In–Sn80 wt% and In–Pb80 wt% alloy melts by measuring the electrical resistivity, and obvious kinetic phenomena are observed during isothermal and heating experiments. We found that the time evolution of the electrical resistivity could be described by the autocatalytic reaction model, which is an indication of nucleation growth type. The mechanism of autocatalysis and the kinetic phenomena have been roughly discussed. Using Kissinger's equation, their apparent activation energy (E_k) at transition beginning point has also been calculated.

Keywords: Liquid structure change; Electrical resistivity; Activation energy

1. Introduction

As a concerned field in liquid physics, liquid–liquid structure transition (LLST) has been revealed in a variety of liquids covering atomic to molecular liquids [1], the existence of which presents a challenge to our conventional picture of liquids as entities with continuously varying averaged structure. Tanaka [2] proposed that a LLST can, in principle, exist in any liquids, including atomic liquids such as C, P, Si, Ge, Se, Rb and Cs [3–10], network-forming liquids such as water, SiO₂, and GeO₂ [11–14], and ordinary molecular liquids. Up to now, for molecular liquids, there are detailed studies on the kinetics of LLST [15–18]. For example, Kurita studied the time evolution of the heat flux during LLST process in triphenyl phosphate, and found different transition mode: nucleation growth and spinodal decomposition type [17]. However, for atomic systems, research on the kinetics of the LLST is just at the beginning.

Recently, temperature-induced discontinuous LLST has been newly put forward in some binary melts at ambient pressure, e.g. In–Sn, Pb–Sn, Al–Cu and In–Sb [19–25], which is a convenient system to study LLST. We have studied the kinetic property of Pb–Sn61.9 liquid structure transition process [26], and found that fitted by

*Corresponding author. Email: fangqiuzu@hotmail.com

Johnson-Mehl-Avrami (JMA) transition model, the time evolution of heat flux and resistivity is nucleation growth type. However, more liquid alloys with LLST should have been investigated to extend the study area. In this article, we studied the kinetic process of liquid-liquid structure changes in In-Sn80 and In-Pb80 alloys. Their compositions are both single solutions in solid state, which could avoid the occurrence of the conventional phase separation. In our previous study [22,27], obvious structure changes have been found at hundreds of degrees above their liquidus by means of internal friction, X-ray diffraction and electrical resistivity. For example, the X-ray diffraction results of In-Sn80 reveal that around about 700°C, a remarkable valley of mean nearest neighbor distance (r_1) and coordination number (N_1) appears abnormally, and both the ordering range and the ordering degree decrease abruptly. It demonstrates evidently a discontinuous configuration reconstruction in the melt, and suggests that obvious order-disorder structure change occurs in the liquid transition process.

In this article, during isothermal experiments, we find that different with JMA transition model of Pb-Sn61.9 LLST, the time evolution of the electrical resistivity in In-Sn80 and In-Pb80 alloy melts could be described by the autocatalytic reaction model, which is an indication of nucleation growth type. At different heating rate, obviously kinetic phenomena are observed in the liquid structure transition process. Using Kissinger equation, their apparent activation energy at transition beginning point is calculated. The mechanism of autocatalytic effect and the kinetic phenomena have been roughly discussed.

2. Experiments and results

As a structure-sensitive physical quantity, electric resistivity (ρ) is sensitive to the liquid structural change. According to the nearly free electron (NFE) model [28], the electrical conductivity of liquid alloys is given by $\rho = hk_f/n_e e^2 L_0$, where h and k_f are the Planck constant and the Fermi wave number respectively. n_e and L_0 are electron density and mean free path of conduction electrons respectively. During the transition process, the change of L_0 that is induced by the change of short-range orders will lead to obvious change of resistivity. Our previous studies also testified the reliability of the electric resistivity method used for investigating the liquid structure transition [26]. So in this article, we select the electric resistivity method as the main experimental means.

DC 4-probe method has been used for measuring the electric resistivity. Weighted amounts of 99.99% pure In, Sn and Pb were melted at 400°C for over 30 min, then poured into measuring quartz cells, and cooled to room temperature for the following experiment. Tungsten wires with diameter 1 mm, the surface of which is polished by the mechanical polishing method, were employed as current and potential electrode. The quartz cell was placed in the homogeneous heat area of the furnace to eliminate thermal electromotive forces (EMFs) as possible. Furthermore, the DC current-reversal technique was used to cancel the thermal EMFs which may be brought with the connection points and temperature fluctuations in the test leads [29]. The potential drop was measured by KEITHLEY-2182 nanovoltmeter with the PF66M sourcemeter providing the constant current. The whole measuring process was under the shielding of argon gas. The error of our experiment is under 2% and by repeating the measurements, we come to reproducible results.

2.1. Isothermal experiments

During isothermal experiments, In–Sn80 and In–Pb80 samples are heated rapidly (about 300 K min^{-1}) and then held at the appointed temperatures: 650 and 730°C respectively. The curves of resistivity *versus* time (ρ – t) are recorded in figure 1.

In figure 1, the resistivity of In–Sn80 and In–Pb80 reveal similar changing rule. When the temperature is held at 650°C , their resistivity are almost unchanged, which reflects that the liquid structure is steady at low temperatures and the influencing factors such as composition segregation could be neglected. When temperature is held at 730°C , an S-shaped change in ρ – t curve occurs at 27 min for InSn80 and 162 min for InPb80 respectively. Through tangent method, we selected t_0 , t_e as the transition beginning time and ending time respectively. The anomalous resistivity changes indicate the existence of liquid structure change.

2.2. Heating experiments

At different heating rate $2.5, 5, 10, 15\text{ k min}^{-1}$, the In–Sn80 and In–Pb80 alloys have been heated from room temperature to 1200°C , and the curves of ρ – T have been shown in figure 2. The resistivity increases linearly with increasing temperature, and corresponding to liquid structure changes, evident turning points could be seen on the ρ – T curves. T_0 is the transition beginning point, T_h is the transition ending point, and $\Delta T (T_h - T_0)$ is the temperature region of transition. All these data have been listed in tables 1 and 2. It could be seen that both InSn80 and InPb80 binary alloys have revealed obvious kinetic phenomena in LLST process.

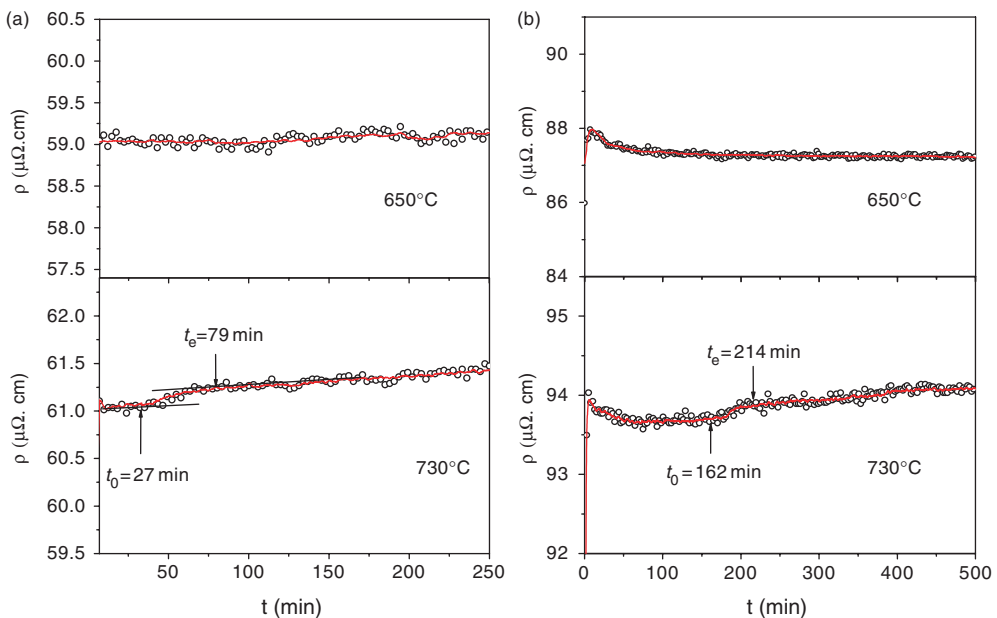


Figure 1. Curves of resistivity vs. time held at 650 and 730°C . (a) InSn80; (b) InPb80.

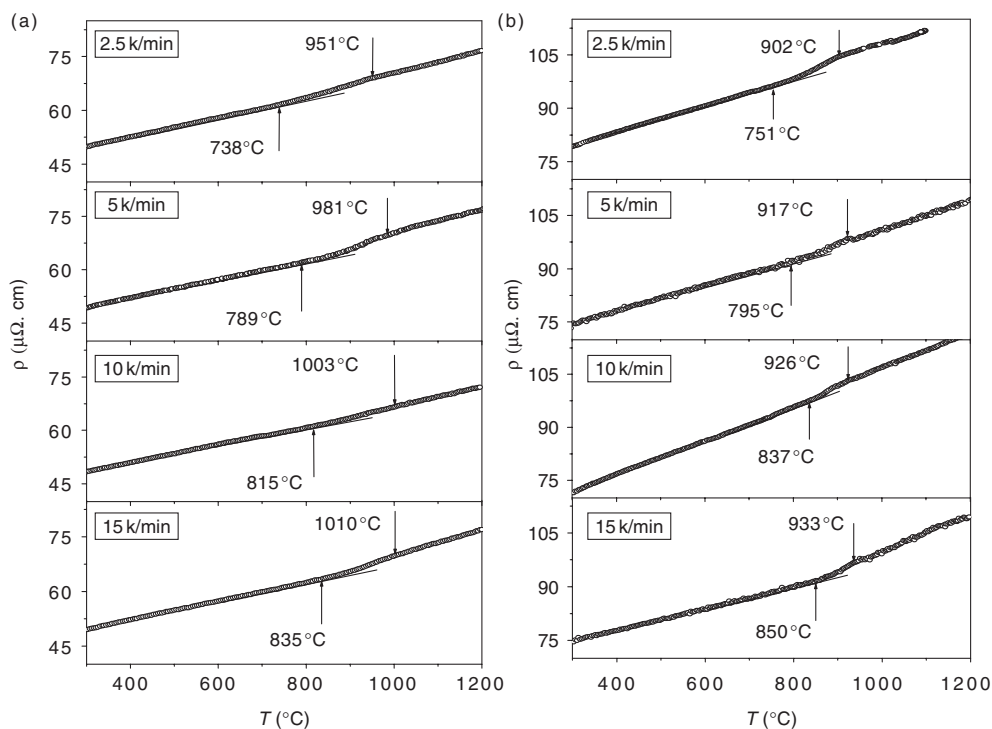


Figure 2. Resistivity vs. temperature curves at different heating rates. (a) InSn80; (b) InPb80.

Table 1. InSn80 starting temperature, ending temperature and temperature range of liquid structure transition.

$Q(K \text{ min}^{-1})$	2.5	5	10	15
$T_0(^{\circ}\text{C})$	738	789	815	835
$T_h(^{\circ}\text{C})$	951	981	1003	1010
$\Delta T(^{\circ}\text{C})$	213	192	188	175

Table 2. InPb80 starting temperature, ending temperature and temperature range of liquid structure transition.

$Q(K \text{ min}^{-1})$	2.5	5	10	15
$T_0(^{\circ}\text{C})$	751	795	837	850
$T_h(^{\circ}\text{C})$	902	917	926	933
$\Delta T(^{\circ}\text{C})$	151	122	89	83

Figure 3 is the curve of T_0 , T_h versus heating rate Q . With Q increasing, both T_0 and T_h move to higher temperatures. As an atomic diffusion and rearrangement process, liquid structure transition process needs enough time, so heating rate can affect T_0 and T_h greatly. With T_0 and T_h shift, the whole transition range also move to higher temperatures, and ΔT becomes narrower. It reveals that the transition speed of LLST

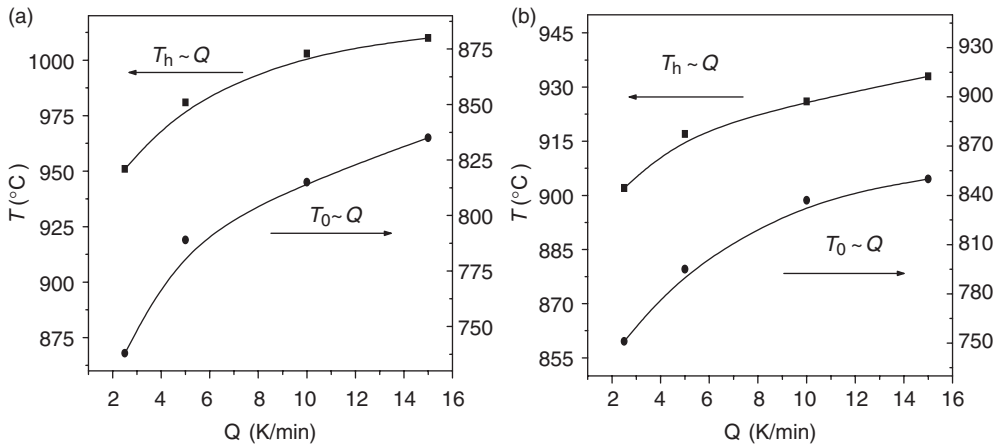


Figure 3. Curves of T_0 , T_h vs. Q in InSn80 and InPb80 heating experiments. (a) InSn80; (b) InPb80.

will become more rapid at higher temperatures. Furthermore, from figure 3 and tables 1 and 2, it could be seen that the variation amplitude of T_0 , T_h and ΔT decreased with the increase of heating rate, which means that heating rate could not affect liquid structure transition process unlimitedly.

3. Discussion

Now let us take brief account of what is taking place during the LLST reconstruction. As we know, liquid structure is mainly composed by atomic clusters and a few free atoms less than 10% [30,31]. It is generally accepted that the atomic bonds of crystals are only partly broken at melting stage and the atomic clusters with the crystal structure still remain in liquids. Therefore, one could take it for granted that, for binary alloy melts $A-B$ (such as In–Sn or In–Pb), liquid structure is metastable local ordering (liquid phase L_1) with lots of minor residual orders rich in either A or B at the temperature not too far above the liquidus. Within these minor zones the local microstructures and compositions remain almost constant in spite of long-range disorders and the energetic undulation. With temperature increasing, liquid structure will gain enough energy to overcome the energy barrier ΔE (which is mainly composed by atomic bonding forces), and the $A-A$ or $B-B$ atomic bonds are broken continuously. At the same time, the new $A-B$ atomic bonds build up, by which the relatively uniform melt (liquid phase L_2) nucleates and grows, and gradually substitute old liquid structure. Liquid phase L_2 is a true solution, a completely mixed liquid state.

From the above analysis, it could be seen that similar to normal solid-state phase transition, LLST process is also a kinetic process with new phase forming and old phase disappearing. From t_0 to t_e , the time evolution of structure transition fraction (x) could be deduced by the equation $x = (\rho_t - \rho_0) / (\rho_e - \rho_0)$, where ρ_0 is the resistivity at the time t_0 , ρ_e the resistivity at the time t_e , and ρ_t the resistivity at time t . Figure 4 shows the $x-t$ curve of InSn80 and InPb80 melts.

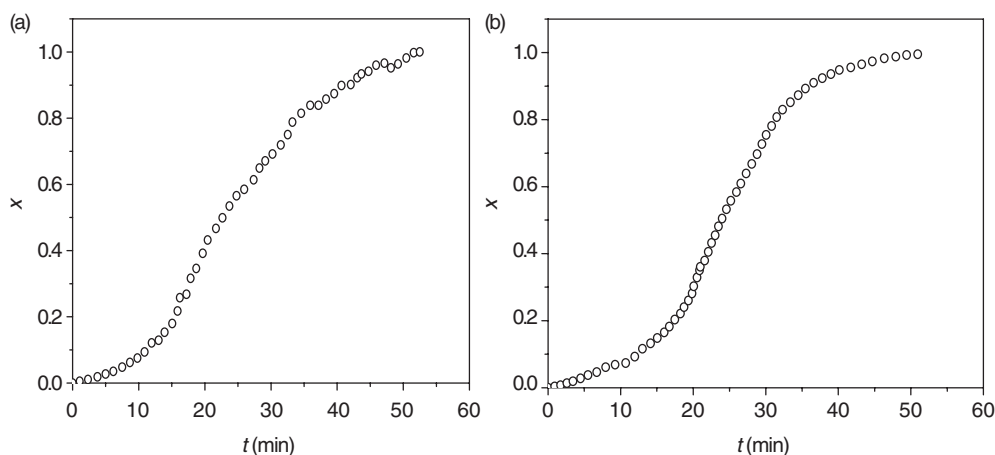


Figure 4. Curves of structure transition fraction vs. time of InSn80 and InPb80 held at 730°C. (a) InSn80; (b) InPb80.

Different with JMA transition model of PbSn61.9 LLST, we found that the time evolution of the electrical resistivity in InSn80 and InPb80 LLST process could be described by the autocatalytic reaction model well, the equation is as follows:

$$\ln\left(\frac{1-x}{x}\right) + \ln d = -K_T t \quad (1)$$

where K_T is reaction rate constant, the value of which reflects the transition speed, and d is initial catalyst concentration. The autocatalytic reaction model is also nucleation growth type and the new generated phase has catalysis effect on the transition process. With $\ln(1-x)/x$ and t as variants, the curve is plotted in figure 5, and maintains approximately linear when $\ln(1-x)/x < 2$. For InSn80 and InPb80, $\ln K_T$ are calculated as -2.03 and -1.70 respectively, and d are calculated as 0.046 and 0.014 respectively. Compared with PbSn61.9 LLST ($\ln K_T = -15.38$) [26], transition speed of the two liquid alloys are faster for catalysis, and $\ln K_T$ of the two liquid alloys are both larger correspondingly.

Now we will try to explain the catalysis mechanism during the liquid structure transition process. According to the above analysis, LLST process of binary alloy $A-B$ (In-Sn or In-Pb) could be simply described as $L_1(A-A + B-B) \rightarrow L_2(A-B)$ [19,32], which is also an atomic diffusion process. It could be seen that there are superfluous atom clusters (rich in $A-A$ or $B-B$) that do not take part in the transition process when the alloy composition leans to one component, and those superfluous clusters distribute in the melt homogeneously. Based on Daken's [33] atomic diffusion theory and Eyring thermoactivation energy theory, the activation energy required in atomic migration (ΔQ) is different with different compositions. Obviously, as the transition progresses, the existence of those superfluous clusters will lead to increasing proportion difference between $A-A$ clusters and $B-B$ clusters, and the proportion change will reflect rapidly in the local structure for the fluidity and diffusibility of liquid. It will reduce the value of ΔQ and accelerate the transition speed. So with the indirect catalysis

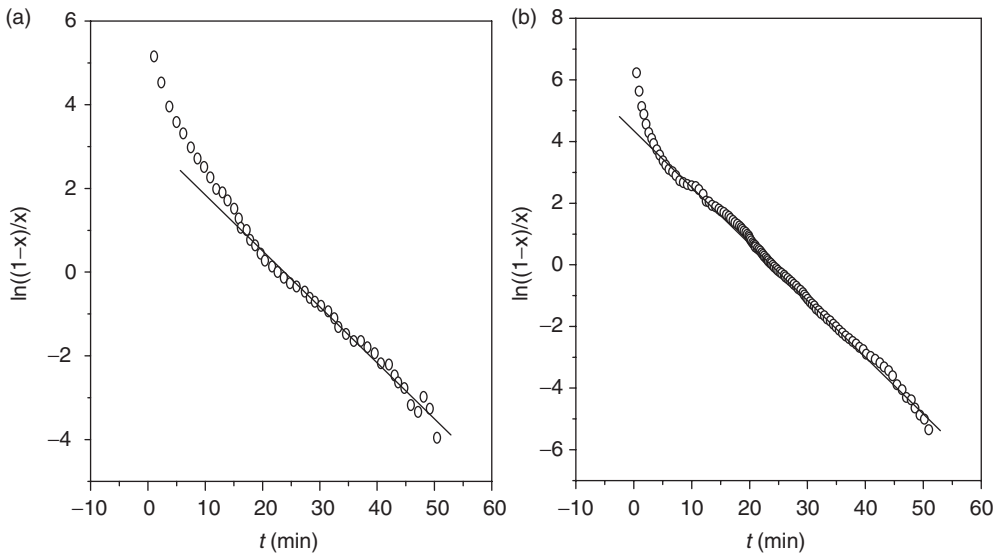


Figure 5. Curve of $\ln(1-x)/x$ vs. time in InSn80 and InPb80 held at 730 C. (a) InSn80; (b) InPb80.

of superfluous clusters, the whole LLST process of InSn80 and InPb80 melts reveal autocatalytic reaction model.

Using Kissinger's equation, the apparent activation energy E_k at T_0 could be calculated. The equation is described as [34]:

$$\ln \frac{T^2}{Q} = \frac{E_k}{RT} + A \quad (2)$$

where T is starting temperature of transition T_0 ; Q is the heating rate; R is gas constant; A is a constant; E_k is apparent activation energy, which reflects the energy needed to overcome energy barrier. Equation (1) could be considered as linear equation with $\ln(T^2/Q)$ and $1000/T$ as variants. Based on tables 1 and 2, we get linear lines of In–Sn80 and In–Pb80 (figure 6). Therefore E_k are calculated as 1.60 eV and 1.45 eV respectively. The small value of E_k reveals that mainly localized atomic structure rearrangement occurs in LLST process.

4. Conclusion

In summary, by means of electrical resistivity, we investigate the kinetic behavior of temperature-induced LLST process in InSn80 and InPb80 alloys through isothermal and continuous heating experiments. We found that the time evolution of the electrical resistivity could be described by the autocatalytic reaction mode, which is an indication of nucleation growth type. The mechanism of autocatalysis and the kinetic phenomena have been roughly discussed. Using Kissinger's equation, their apparent activation energy (E_k) at transition beginning point has also been calculated. Our work shows that the kinetic behavior is not an isolated phenomenon in temperature-induced LLST process, and may occur in other alloy systems. Through analysis of its mechanism,

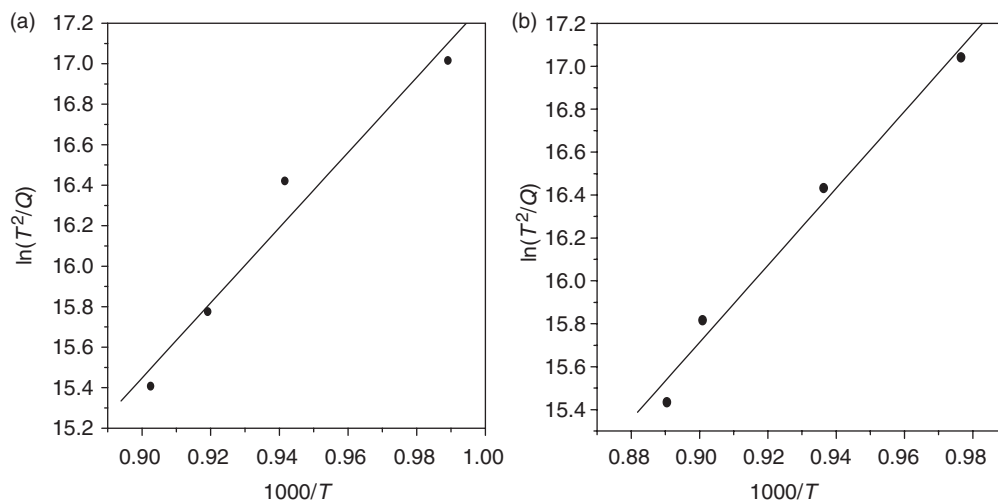


Figure 6. Curves of $\ln(T^2)/Q$ vs. $1000/T$. (a) InSn80; (b) InPb80.

it will be beneficial for further understanding the essence of liquid alloy structure transition.

Acknowledgements

This project is supported by the National Natural Science Foundation of China (grant no. 50371024, 50571033) and Natural Science Foundation of Anhui Province no. 070414178.

References

- [1] P.H. Poole, T. Grande, C.A. Angell, P.F. McMillan. *Science*, **275**, 322 (1997).
- [2] H. Tanaka. *Phys. Rev. E*, **62**, 5 (2000).
- [3] M. van Thiel, F.H. Ree. *Phys. Rev. B*, **48**, 3591 (1993); J.N. Glosli, F.H. Ree. *Phys. Rev. Lett.*, **82**, 4659 (1999).
- [4] M. Togaya. *Phys. Rev. Lett.*, **79**, 2474 (1997).
- [5] F.P. Bundy. *J. Chem. Phys.*, **38**, 618 (1963).
- [6] N.S. Fateeva, L.F. Vereshchagin. *Pis'ma Zh. E' ksp. Teor. Fiz.*, **13**, 168 (1971) [*JETP Lett.*, **13**, 110 (1971)].
- [7] Y. Katayama, T. Mizutani, W. Utsumi, O. Shimomura, M. Yamanaka, K. Funakoshi. *Nature (London)*, **403**, 170 (2000).
- [8] M.P. Grumbach, R.M. Martin. *Phys. Rev. B*, **54**, 15730 (1996).
- [9] K.H. Smith, E. Shero, A. Chizmeshya, G.H. Wolf. *J. Chem. Phys.*, **102**, 6851 (1995).
- [10] M. Yao, H. Endo. *J. Non-Cryst. Solids*, **205–207**, 85 (1996).
- [11] C.J. Roberts, A.Z. Panagiotopoulos, P.G. Debenedetti. *Phys. Rev. Lett.*, **77**, 4386 (1996).
- [12] S. Harrington, R. Zhang, P.H. Poole, F. Sciortino, H.E. Stanley. *Phys. Rev. Lett.*, **78**, 2409 (1997).
- [13] P.H. Poole, F. Sciortino, T. Grande, H.E. Stanley, C.A. Angell. *Phys. Rev. Lett.*, **73**, 1632 (1994).
- [14] O. Mishima, H.E. Stanley. *Nature (London)*, **392**, 164 (1998).
- [15] R. Kurita, H. Tanaka. *Science*, **306**, 845 (2004).
- [16] R. Kurita, H. Tanaka. *J. Phys.: Condens. Matter*, **17**, L293 (2005).
- [17] R. Kurita, H. Tanaka. *Phys. Rev. B*, **73**, 104202 (2006).
- [18] M.M. Koza, T. Hansen, R.P. May, H. Schober. *J. Non-Cryst. Solids*, **352**, 4988 (2006).

- [19] F.Q. Zu, Z.G. Zhu, L.J. Guo, B. Zhang, J.P. Shui, C.S. Liu. *Phys. Rev. B*, **64**, 180203(R) (2001).
- [20] F.Q. Zu, L.J. Guo, Z.G. Zhu, Y. Feng. *Chin. Phys. Lett.*, **19**, 94 (2002).
- [21] F.Q. Zu, Z.G. Zhu, Y. Feng, J.P. Shui. *J. Phys.: Condens. Matter*, **13**, 11435 (2001).
- [22] F.Q. Zu, Z.G. Zhu, L.J. Guo, X.B. Qin, H. Yang, W.J. Shan. *Phys. Rev. Lett.*, **89**, 125505 (2002).
- [23] L. Wang, X.F. Bian, J.T. Liu. *Phys. Lett. A*, **326**, 429 (2004).
- [24] K.Q. Lu, Q. Wang, X.M. Chen, C.X. Li, *et al.* *J. Non-Cryst. Solids*, **312–314**, 34 (2002).
- [25] U. Dahlborg, M. Calvo-Dahlborg, P.S. Popel, V.E. Sidorov. *Eur. Phys. J. B*, **14**, 639 (2000).
- [26] Z.H. Chen, F.Q. Zu, X.F. Li, J. Yu, Y. Xi, R.R. Shen. *J. Phys.: Condens. Matter*, **19**, 116106 (2007).
- [27] J. Yu, Y. Zhang, F.Q. Zu, Y. Xi, X.F. Li, W. Xu, H.M. Liu. *Phys. Chem. Liq.*, **44**, 401 (2006).
- [28] T.E. Faber. *An Introduction to the Theory of Liquid Metals*, Cambridge Univ. Press, Cambridge (1972).
- [29] Keithley Instruments, Inc Model 2182 Nanovoltmeter User's Manual, Cleveland, Ohio, U.S.A. Fifth Printing, April 2002.
- [30] H. Richter, G. Breitling. *Z. Metallkd.*, **61**, 628 (1970).
- [31] A.C. Mitus, A.Z. Patashinskii, B.I. Shumilo. *Phys. Lett.*, **A113**, 41 (1985).
- [32] F.Q. Zu, X.F. Li, L.J. Guo, H. Yang, X.B. Qin, Z.G. Zhu. *Phys. Lett. A*, **324**, 472 (2004).
- [33] L.S. Daken. *Trans. Am. Inst. Min. Eng.*, **175**, 185 (1948).
- [34] H.E. Kissinger. *J. Res. Natl. Bur. Stand.*, **57**, 217 (1956).