

## Liquid-liquid phase transition in Pb-Sn melts

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A first-order liquid-liquid (LL) phase transition as a function of temperature in Pb-Sn melts is suggested by internal friction experiments and verified by differential thermal analysis with an entropy-driven order-disorder mechanism. It differs remarkably with other already found LL phase transitions in some aspects. The findings may throw light on the nature of viscous liquids in condensed state physics and be of significance in materials science. The present work makes a beneficial attempt at exploring internal friction as an experimental method for studying liquids.

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The nature of viscous liquids is recognized as an important, unsolved problem in condensed state physics.<sup>1</sup> Exploring the phenomena of melts near the liquidus ( $T_L$ ) is especially helpful for us to understand the nature of liquids and to elucidate melting and freezing mechanisms.<sup>2</sup> For liquid Sn, shoulders appear on the first peak of the scattering curves near  $T_L$ , but vanish around 750 °C, indicating a somewhat structural change.<sup>2</sup> With experimental results of scattering techniques it has been proposed that there are domains of both spherical close packing and layer lattice in the melts of Au, Ag, Pb, Tl, and Bi and the alkali metals.<sup>2-5</sup> In recent years, more significantly, even LL phase transitions have experimentally and theoretically proved to occur in some one-component liquids, e.g., Cs, Bi, Ga, Si, Se, Ge, C, S, P, H<sub>2</sub>O, and SiO<sub>2</sub>,<sup>6-12</sup> and in a few multiple component systems such as Y<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>.<sup>13</sup> These findings enrich and illuminate the phenomenology of liquid states and indicate that further candidates and new knowledge will be uncovered as we probe liquid behaviors more deeply.<sup>14</sup> It has long been observed that liquid phase separations could occur in some binary component systems, which have been recorded in their phase diagrams.<sup>15</sup> For most ordinary binary alloys, however, liquid structural changes and LL phase transitions have been seldom observed, because partial structure factors are hard to obtain, and the results from these are normally not as informative as expected.<sup>16</sup>

In this paper, a first-order LL phase transition in Pb-Sn melts is suggested by our experimental study. The significance of the finding lies in the following aspects. First, the transition takes place in a two-component liquid system, but as well known for over one hundred of years in condensed matter physics and materials science, there is no other defined phase line above  $T_L$  in phase diagrams of common binary systems such as Pb-Sn. On the other hand, there is an unsolved riddle in engineering practice that the structures and properties of many materials often depend on the thermal history of the original liquids. Therefore, the discovered phenomenon may throw useful light on understanding the nature of multiple component liquids and resolving the above riddle. In addition, LL transitions recognized to date are generally in either super-cooled or high-pressure conditions,<sup>6-14</sup> except in liquid sulphur (but  $\lambda$ -type),<sup>7</sup> and

liquid crystals,<sup>17</sup> while they occur in Pb-Sn at ordinary pressure as temperature is elevated up to hundreds of degrees over  $T_L$ . Moreover, there is general agreement that the study of the liquid state has made much slower progress in contrast to solid and gaseous states, hence new experimental and theoretical methods are in great demand for the study of liquids.<sup>2,16,18</sup> As is well known, internal friction is a structure sensitive physical property and is a powerful technique widely used for studying crystal structures, defects and phase transitions in solids.<sup>19</sup> In our work, an improved torsion pendulum internal friction apparatus was used to study liquids, i.e., Pb-Sn melts, and it was verified to be also valid and sensitive to liquid structures.

The difficulties in using the internal friction technique for studying molten materials lie in certain aspects. First, the temperature is usually quite high, which could cause the oxidation of samples, the interaction between samples and the sensor of apparatus. Second, the sensor linked to the pendulum rod may swing easily, leading to poor experiment results. The third problem is how to collect the data of internal friction signals for liquids, so as to make it sensitive to structures and physical properties of liquids. In order to overcome these difficulties, we took some steps as follows: Highly pure argon (5N) was used as a shielding atmosphere to prevent liquid samples from oxidation. Two different kinds of quartz tubes were specially manufactured, one used as the sample vessel and the other as the sensor, thus eliminating the interaction with the samples. A bearing guide device was built at the upper part of the pendulum rod to lessen the radial swing of the sensor. Similar to that in solid materials, the internal friction ( $Q^{-1}$ ) of liquid samples was expressed as the tangent of the so-called angel loss, by which the sample strain was lagging behind the given persistent oscillating stress. A computer controlled all the experimental conditions and data collection automatically. With this apparatus, as verification, the internal friction of the Zn-Sn melt was measured with the temperature elevated, and in each  $Q^{-1}$ - $T$  curve there appeared a peak, whose position was in good agreement with the LL separation temperature (see the Zn-Sn phase diagram).<sup>15</sup> It made us confident of the suitability of the apparatus for studying liquids. The details of the apparatus and its use in other liquid systems will be published elsewhere.

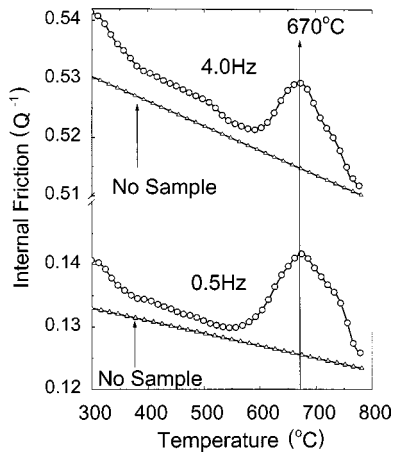


FIG. 1. Internal friction behavior of the melt Pb-Sn 61.9 wt%. Heating rate: 2.5 °C/min.

The Pb-Sn samples were prepared with pure (99.9 wt%) lead and tin. The raw materials were melted, held at a temperature of about 100 °C over  $T_L$  for 60 min, mixed mechanically, and then cooled to room temperature by blowing air. Afterwards, the sample was re-melted and shielded with argon at 0.08 MPa. With the given torsion frequencies and constant amplitude, then, the internal friction of the Pb-Sn melt was measured as the temperature was elevated at a given heating rate ( $dT/dt$ ).

Figures 1 and 2 show the internal friction experiment results of the liquid samples with eutectic composition (Pb-Sn 61.9 wt%). Surprisingly, there is a notable peak in each  $Q^{-1}$ - $T$  curve, around 670 °C at 2.5 °C/min (Fig. 1) and 712 °C at 6.0 °C/min (Fig. 2), respectively, hundreds of degrees above  $T_L$  (183 °C). The fact that peak position ( $T_p$ ) moves to higher temperature with ( $dT/dt$ ) raised is consistent with the kinetic nature of phase transitions.<sup>20</sup> In order to detect what the  $Q^{-1}$ - $T$  peak means for the Pb-Sn melt, the characteristics of the peak were analyzed. Figures 1 and 2 indicate clearly that  $T_p$  does not change with torsion frequencies ( $f$ ), which resemble the internal friction feature in

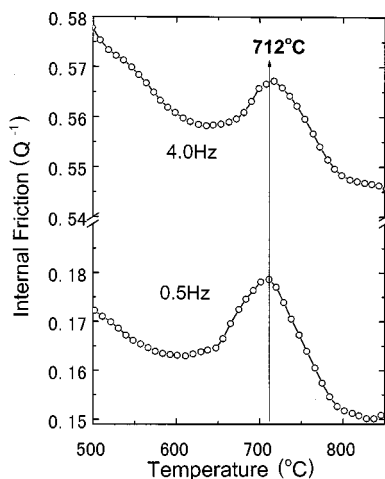


FIG. 2. Internal friction behavior of the melt Pb-Sn 61.9 wt%. Heating rate: 6.0 °C/min.

TABLE I. Relation of the magnitude  $Q_p^{-1}$  of the internal friction peak with frequencies and heating rates. Sample: Pb-Sr 61.9 wt%.

$Q_p^{-1}$	0.5 Hz	1.0 Hz	2.0 Hz	4.0 Hz
2.5 °C/min	0.0125	0.0111	0.0101	0.0088
6.0 °C/min	0.0143	0.0116	0.0104	0.0102

solid transitions.<sup>19</sup> On the other hand, the magnitude of the peaks, i.e.,  $Q_p^{-1} = Q_{\max}^{-1} - Q_{\min}^{-1}$  ( $Q_{\min}^{-1}$  refers to the minimum value of  $Q^{-1}$  before the peaks,  $Q_{\max}^{-1}$  the maximum value of the peaks), drops with increasing frequency, but rises with  $dT/dt$  (see Fig. 1, Fig. 2, and Table I). These features are perfectly in accordance with those of the first-order phase transitions in solid internal friction investigations, which have been theoretically interpreted by DeLorme's and Belko's models.<sup>21</sup> Both models deduced the same conclusion, i.e.,  $Q_p^{-1} = A(dT/dt)/f$ , in first-order phase transitions ( $A$  here is a constant in terms of materials). This proportional relation has been confirmed in many cases.<sup>22,23</sup> Figure 3 is obtained from the data of Pb-Sn 61.9 in Table I, with the linear relation suggesting that a first-order transition happens in the melt.

The internal friction characteristics in the eutectic Pb-Sn melt can be well repeated in other Pb-Sn melts with different compositions. However, peak position and magnitude change with Sn contents at the same heating rate and torsion frequency. The relevant data for  $T_p$  and  $Q_p^{-1}$  at 2.5 °C/min and 0.5 Hz are listed in Table II, each  $T_p$  with its composition shown in the Pb-Sn phase diagram (Fig. 5) for direct comparison.

The fact that the features of the internal friction pattern in Pb-Sn melts resemble quite well those of first-order phase transitions in solids implies that some kind of LL phase transformation takes place as a function of temperature. In order to make certain what kind of transition happened in the Pb-Sn melts, we carried out a series of differential thermal analyses (DTA) on Pb-Sn melts (PETDA-1700, heating rate 15 °C/min). For all tested compositions, a thermal absorption peak occurs in each DTA curve above  $T_L$ . Figure 4 is the result of DTA on a Pb-Sn 61.9 sample, which shows that the peak position corresponds roughly to that of the relevant internal friction peak but with a lagging to some extent due to a higher heating rate, e.g., the  $Q^{-1}$ - $T$  peak at 6 °C/min is

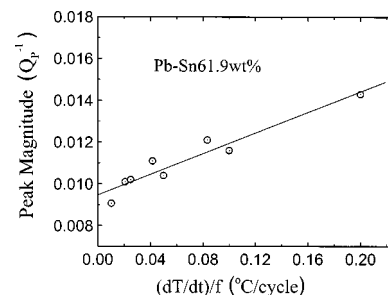


FIG. 3. Dependence of the internal friction peak magnitude  $Q_p^{-1}$  on heating rate  $(dT/dt)/f$  for the melt Pb-Sn 61.9 wt%, with the linear relation suggesting a first-order LL phase transition.

TABLE II. Peak positions  $T_p$  and magnitudes  $Q_p^{-1}$  of internal friction with different compositions,  $dT/dt=2.5^\circ\text{C}/\text{min}$ ,  $f=0.5\text{ Hz}$ .

Pb-Sn wt%	20	40	61.9	80
$T_p$ °C	620	740	670	650
$Q_p^{-1}$	0.0064	0.0155	0.0125	0.0185

around  $712^\circ\text{C}$ , the DTA peak at  $15^\circ\text{C}/\text{min}$  around  $778^\circ\text{C}$ . The calorific effect in the DTA curves means that the system entropy of Pb-Sn melts undergoes a discontinuous change during the LL transition, i.e., the transition is entropy driven, which confirms that it is a first-order LL phase transition in Pb-Sn melts, based on the thermodynamics of phase transitions. And it is reasonable to infer that microstructures of Pb-Sn melts have changed during the phase transformation, although no direct evidence has been obtained because we are right now not in a position to gain the partial structure factors and other relevant structure information.

It should be pointed out that the peak magnitude of the LL transition in DTA curves is much lower and less sharp than that of the SL one, e.g., in Fig. 4, the height of the SL peak is about  $3.62\text{ deg}$  (around  $183^\circ\text{C}$ ), while that of the LL peak is only  $0.31$ . On the other hand, the width of the LL peaks in DTA is quite broad, resembling that in  $Q^{-1}-T$  curves. Comparing Fig. 1, Fig. 2, and Fig. 4, it can be seen that the slower the heating rate, the broader the peak width, e.g., for Pb-Sn 61.9, the width of the  $Q^{-1}-T$  peak ( $0.5\text{ Hz}$ ) at  $2.5^\circ\text{C}/\text{min}$  is about  $200^\circ\text{C}$  and at  $6^\circ\text{C}/\text{min}$  about  $180^\circ\text{C}$ , that of the DTA at  $15^\circ\text{C}/\text{min}$  about  $140^\circ\text{C}$ , indicating that the result of internal friction is in agreement with that of DTA. The lower height and smaller area (related to the change of enthalpy  $\Delta H$ ) of the LL peak in DTA suggest that the change of the enthalpy, entropy, and density in Pb-Sn melts is relatively small across the LL transition, which is understandable because the phases before and after the change are both liquid.<sup>14,24</sup> The broad and nonsharp peak in DTA and the  $Q^{-1}-T$  curves indicates the other feature that the phase transformation rate is quite slow.

Now let us take a brief account of the transition mechanism in Pb-Sn melts. On the one hand, the existence of local crystal orderings in melts has been proposed based on results of experiments<sup>2-5</sup> and theoretical analysis from the stand-

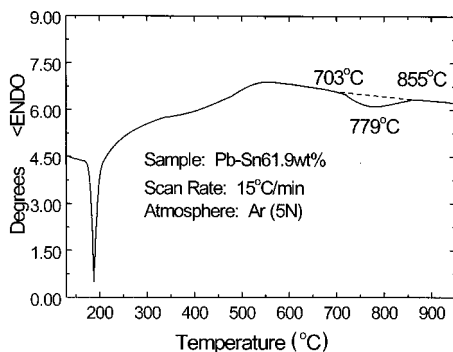


FIG. 4. Result of differential thermal analysis (DTA) on the melt Pb-Sn 61.9 wt%.

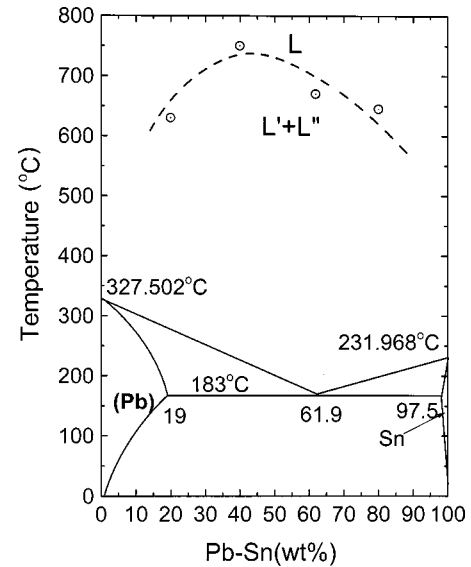


FIG. 5. Liquid-liquid transition temperature  $T_p$  of different compositions on the Pb-Sn phase diagram (Ref. 14):  $\odot$  indicates experimental results ( $dT/dt=2.5^\circ\text{C}/\text{min}$ ,  $f=0.5\text{ Hz}$ ), dashed line is fitted result.

point of thermodynamics.<sup>24</sup> As a matter of fact, the entropy of vaporization for most matters is many times larger than that of fusion,<sup>25</sup> which means atomic bonds in crystals are only partly broken when a matter melts. On the other hand, the positive excess enthalpy of Pb-Sn (Ref. 26) indicates repulsive interactions between Pb and Sn, i.e., the mutual solubility is small, especially for Pb into Sn, see Fig. 5. Therefore, one could take for granted that residual orders, namely, minor crystals rich in either Pb or Sn, still exist in Pb-Sn melts near  $T_L$  in spite of long-range disorders and the energetic undulation. Essentially speaking, there are still two different kinds of phases ( $L'+L''$ ) in the melts. They are, however, metastable and prone to homogenization. As temperature is elevated, the atoms within the residual crystals gain higher and higher energy. Once the critical temperature is reached, the energy is high enough to overcome the energy barrier so that the Pb-Pb and Sn-Sn atomic bonds in original phases are broken continuously. At the same time, the new Pb-Sn atomic bonds build up, by which the relatively homogeneous liquid phase (L) nucleates and grows. That is, the phase transition  $L'(\text{Pb})+L''(\text{Sn})\rightarrow L(\text{Pb-Sn})$  takes place, shown in Fig. 5. In short, we assume it is an order-disorder LL phase transition.

During the LL phase change in Pb-Sn melts, the old and new phases coexist, their quantity and the area of their interfaces change with the process. Thus,  $Q^{-1}$  is composed of three different parts: that of the old phase ( $Q_{op}^{-1}$ ), of the new phase ( $Q_{np}^{-1}$ ) and of the interfaces ( $Q_{if}^{-1}$ ). That is,  $Q^{-1}=Q_{op}^{-1}+Q_{np}^{-1}+Q_{if}^{-1}$ . As the LL transition proceeds,  $Q_{op}^{-1}$  decreases and  $Q_{np}^{-1}$  increases with their phase quantities. But the area of the interfaces rises at first and then declines, leading rise and then reduction to  $Q_{if}^{-1}$ , so that a peak appears in each  $Q^{-1}-T$  curve around the critical temperature.

In summary, the occurrence of a first-order LL phase tran-

sition in Pb-Sn melts was suggested by the results of internal friction experiments and verified by DTA, entropy driven as temperature was elevated up to hundreds of degrees above  $T_L$ , with an order-disorder changing mechanism. It differs from other already found LL phase transitions in its slow changing rate and moderate conditions, most importantly in that LL phase transitions have been quite rarely recognized in two-component systems to date and that there is no other defined phase line above  $T_L$  in the Pb-Sn phase diagram. Our work has shown that LL transitions may also occur in other binary systems, e.g., in Pb-Bi and In-Sn, the description of which is beyond the scope of this paper. The finding may throw useful light on understanding the nature of multiple

component liquid systems and explaining the common engineering phenomenon that the structures and properties of many materials are often dependent on the thermal history of the original liquids. Internal friction technique proved to be also suitable for studying liquids. Further work is needed to explore the concrete changes of structures and other physical properties during the transition.

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