NE5C/2014G012

Reexamination of the Structure of Liquid SnI_4 near the Expected Liquid-to-Liquid Phase Transition point

Kazuhiro Fuchizaki[1*], Takaki Hase[2], and Nozomu Hamaya[3]
[1]Department of Physics, Ehime University, Matsuyama 790-8577, Japan
[2]ANSYS, Tokyo 160-0023, Japan
[3]Graduate School of Humanities and Sciences, Ochanomizu University, Tokyo 112-8610, Japan

We confirmed the coexistence of the liquid phases, that manifests the first-order nature of the transition, at around 1.5 GPa in the liquid region close to the breakpoint of the melting curve.

1 Introduction

A molecular crystalline SnI_4 has been known to undergo pressure-induced amorphization [1]. The current project has started to unveil the physical origin of this novel feature. The first great strides were the finding of another amorphous state [2], which is a low-density amorphous state (LDA) consisting of randomly oriented tetrahedral molecules. We call the previously found high-density amorphous state (HDA) Am-I to distinguish it from the newly found one, Am-II.

Because amorphization is interpreted as melting in a solid-state field, we suspected that SnI_4 has an unusual melting curve as water does. This was indeed the case; although the melting curve exhibits not negative slope in the pressure—temperature phase diagram (as observed for water) but such an unusual shape as an abrupt change in its slope at around 1.5 GPa beyond which the melting curve becomes almost flat [3]. This feature of the melting curve strongly suggested the existence of two liquid states that correspond to Am-I and Am-II. The two liquid states with different microstructure were then identified using *in situ* synchrotron x-ray diffraction measurement [4]. We call the high-pressure and low-pressure liquid states Liq-I and Liq-II, respectively, in order for them to correspond to Am-I and Am-II.

The polyamorphic nature of SnI_4 is thus completely the same as that of water. The fact motivated us to explain the polyamorphism in view of a (second) critical-point scenario [5]. The observed polyamorphism of SnI_4 was thus successfully accounted by the pseudo-binary regular solution model [6] assuming that the second critical-point pressure is 1.3 GPa and that the breakpoint of the melting curve is the triple point among Liq-II, Liq-I, and the crystalline phase CP-I. We assumed the critical point at 1.3 GPa because no Liq-I was observed below ~1 GPa even at such a high-temperature as 1300 K [6]. The triple-point assumption was justified by reexaming the melting curve [7]. Surprisingly, the Son—Patashinski model [8], which supports the critical-point scenario as well, also gives the same critical-point temperature, 970 K, under the same assumption [6]. *In situ* Synchrotron x-ray absorption measurement under high temperatures and pressures could detect the slight but definite difference of ~0.4 g/cc in density between Liq-II and Liq-I [9]. The two liquid states, Liq-II and Liq-I, were thus finally identified as the low-density liquid (LDL) and high-density liquid (HDL) *phases*.

The only task that we have left to complete the critical-point scenario is to substantiate the remaining assumption, the existence of the critical point. According to the phase diagram [6] resulting from the scenario, the phase boundary separating Liq-II and Liq-I via the first-order phase transition is confined in a narrow region at around 1.5 GPa between the breakpoint (expected triple-point) temperature, 900 K, and the expected critical-point temperature 970 K. A sudden change in transmissivity of x rays is then expected upon isothermal compression between these temperatures whereas no unusual variation of transmissivity will be observed on isothermal compression along a path at a higher temperature beyond 1000 K.

This fascinating task was indeed achieved [10] in FY 2015 utilizing not only KEK but also SPring-8. In this report, we present another important result that supports the existence of the critical point at around 1.5 GPa and 1000 K in view of the structural change between Liq-II and Liq-I. The result was mainly achieved at KEK under proposal no. 2012G015. The reproducibility of the result was examined in 2015 under no. 2014G012.

2 Experiment

A series of experiments was conducted at KEK and the energy-dispersive x-ray diffraction experiments were performed using synchrotron radiation. MAX-80, a cubic-type multi-anvil press for high-pressure and high temperature experiments, installed in NE5C at AR, measured *in situ* x-ray diffraction at pressures and temperatures up to about 4 GPa and 1200 K, respectively. The high-pressure vessel consisted of six tungsten carbide anvils; a center flat of 27 mm of the anvil was employed to enclose a second set of inner anvils of a center flat of 6 mm. (Instead of this so-called 6—6 configuration, we occasionally adopted the normal configuration consisting of only the first set of six anvils with a center flat of 6 mm.)

The sample assembly used for high-pressure and high temperature experiments was explained in [11]. A graphite tube heater of 2.5-mm-o.d. and 2.05-mm-i.d., which contained the sample and NaCl, an internal pressure calibrant separated by a movable thin diamond disk (see Fig. 3 (b) of [11]), encapsulated by diamond container was embedded in a cubic pressure-transmitting medium made of a 4:1 (by weight) mixture of amorphous boron and epoxy resin. The cube with an edge length of a 9 mm was used. A chromel–alumel thermocouple was placed in the middle of the assembly and taken out through the gaps between the anvils. Heating was accomplished by passing a current through the graphite tube. The current was controlled by a PC, which collected electromotive force (emf) of the thermocouple as feedback. The pressure was determined from Decker's equation of state [12] using the lattice constant of NaCl in the pressure calibrant and the temperature measured through emf of the thermocouple as inputs.

Incident white x rays passed through a set of slits, which were in front of the press, to be collimated with a cross section of 0.1x0.2 mm^2 and impinged on the sample in the high pressure vessel. Diffracted x rays were detected by a solid state detector (pure Ge) after passing a collimator with a gap width of 0.1 mm placed behind the sample. The receiving slits had a cross section 0.2x0.5 mm^2. The diffraction angles were varied from three to 16 (or occasionally 20) degrees on measuring the diffracted x rays from the liquid sample. When measuring the diffraction from the pressure calibrant, the angle was fixed to eight degrees.

Initially, the load was applied at room temperature. Then, the sample was carefully heated, monitoring the diffraction pattern, until melting. The system was taken to a desired measuring point by controlling the load and emf applied. Typical exposure times to achieve a whole set of diffraction patterns with reasonable S/N ratio were 10 to 12 hours depending on the strength of incident x rays.

3 Results and Discussion

The reproducibility of the previous experimental results is presented first. The upper part of Fig. 1 shows the structure factor (black line) obtained at 2.3 GPa and 970 K in 2016 under proposal no. 2014G012, and is compared with the previous result (light blue line) measured at 2.7 GPa and 900 K. Considering a slight difference in the measuring condition, the two curves agree well, implying good reproducibility of the structure factor. Excluding a trace of the prepeak at ~1 Å^{-1}, four peaks are recognizable within the wavenumber range shown. Among those peaks, the fourth one is, though very broad, centered at around 7 Å^{-1}. This is the characteristic feature of Liq-I (HDL) appearing in the structure factor. The corresponding peak is positioned at ~7.5 Å^{-1} for Liq-II (LDL). The movement of the peak from the latter position to the former signals the transition. The displacement of a peak toward lower wavenumbers upon compression cannot be explained by simple contraction of the system. From the length scale represented by the peak position in question, we speculate that such a large deformation of the molecule occurs that causes polymerization at the transition.

The structure factors were then Fourier inverted to obtain the reduced radial distribution functions shown in the lower panel of Fig. 1. The radial distance is plotted in units of σ, the fundamental length scale of the system [13]. The two vertical dashed lines, positioned at $\tilde{r}_1^0 = r_1^0/\sigma = 0.710$ and $\tilde{r}_2^0 = r_2^0/\sigma = 1.159$, represent the intramolecular distances between Sn—I and I—I, respectively, for the unperturbed molecule at ambient conditions. (The peaks appearing below $\tilde{r}_1^0$ are spurious.) The two peaks located between the two lines thus represent the intramolecular correlations. The intramolecular I—I distance is shrunk whereas the intramolecular Sn—I distance is elongated upon compression. This latter behavior is again not explainable by simple contraction of the system. The phase diagram was constructed using the pseudo-binary regular solution model so that the measured points for Liq-II, Liq-I, Am-II and Am-I can be properly explained (see Fig. 1 of [4]). This phase diagram was then updated, as mentioned in Introduction, rechoosing 1.3 GPa as the critical-point pressure so as to be consistent with the observed region of Liq-II (see Fig. 1 of [6]).

The measurements carried out in 2012 through 2013 made us further update the phase diagram as shown in Fig. 2. During the measurements, we encountered a curious structure factor whose fourth peak is separated to form a double-peak structure. The lower-wavenumber peak corresponds to the peak characteristic to Liq-I (HDL) whereas the higher-wavenumber one corresponds to that of Liq-II (LDL). It is natural to consider that this situation represents the coexistence of the two phases. The double-peak was observed at the points (marked by purple dots in the phase diagram) close to the phase boundary predicted by the pseudo-binary regular solution model. Note that we expected the phase boundary with a negative slope. To confirm this anticipation, we tried to evaluate the phase boundary from the information regarding the structure obtained thus far.

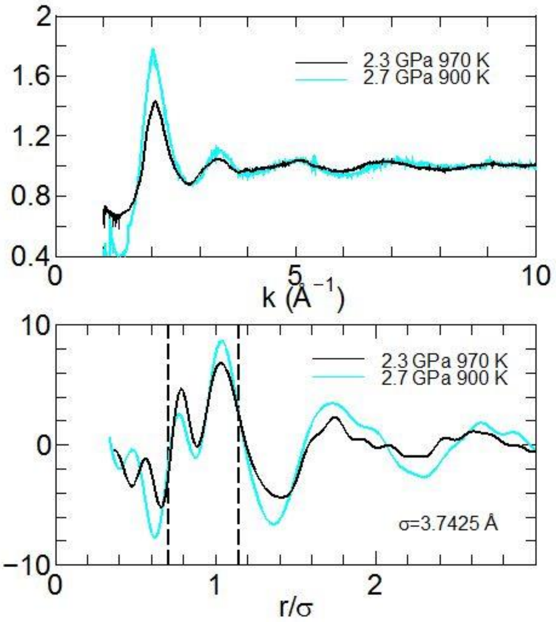

Fig. 1: The structure factors (upper panel) and the corresponding reduced radial distribution functions (lower panel) of SnI$_4$ measured at the thermodynamic conditions indicated.

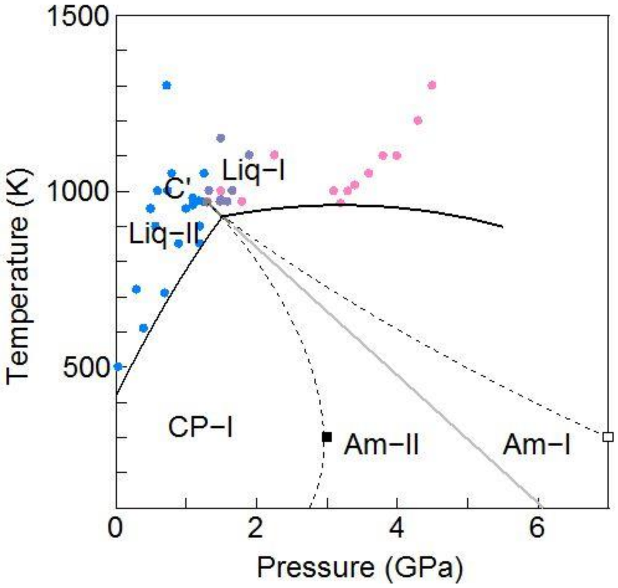

Fig. 2: The revised phase diagram showing polyamorphism in SnI_4. The melting curve of CP-I (delineated by a heavy line) and the points of structure measurements are plotted. The latter points include blue and pink circles at which Liq-II (LDL) and Liq-I (HDL) were identified, and squares representing the existence limits of Am-I (HDA) and Am-II (LDA) [2]. The coexistence of Liq-II and Liq-I were recognizable at the points marked by purple circles. The light straight line and the dashed curves emanating from the liquid—liquid critical point C' located at 1.3 GPa and 970 K are the phase boundary and the spinodal lines, respectively, obtained based on the peudo-binary regular solution model [6].

To this end, we define the following (local) order parameter ϕ representing the degree of deformation of the molecule as a function of $x = r_2 / r_1$, where r_2 and r_1 denote the intramolecular I—I and Sn—I distances, respectively: $\varphi(x) = (x - x_\mathrm{I})/(x_\mathrm{II} - x_\mathrm{I})$, where $x_\mathrm{II} = r_2^0 / r_1^0$ and $x_\mathrm{I} = 1.286$. The order parameter was evaluated for the measuring points, and is plotted as a function of pressure and temperature. This then forms a surface above the phase diagram. Approximating the surface by a quadratic surface, we could obtain the contour map of the surface as depicted in Fig. 3. The breakpoint in the melting curve is located at about 1.5 GPa and 900 K (see Fig. 2). The contour line emanating from the breakpoint, which is the expected triple point, would be the one close to the green line. The order parameter defined above takes ~0.4 at the expected phase boundary, which is almost vertical but has a *negative* slope as expected from the theory [4,6].

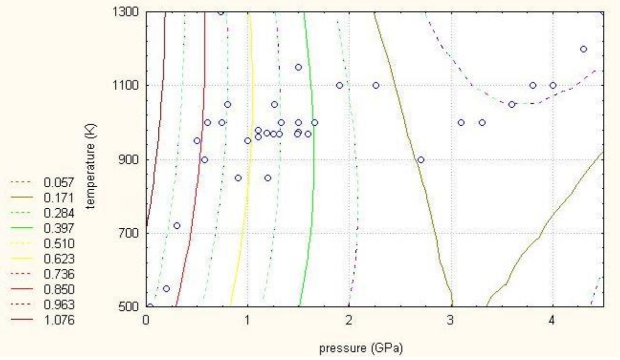

Fig. 3: The contour map showing the surface of the order parameter represented as a function of pressure and temperature.

Conclusions

The double-peak feature of the fourth peak in the structure factor of liquid SnI_4 observed near the breakpoint of the melting curve strongly suggests the coexistence of Liq-II (LDL) and Liq-I (HDL) separated by the phase boundary with a negative slope.

Acknowledgement

Thanks are due to Mr. H. Nishimura for his assistance at the experimental site. Preparations for the experiments were carried out using the facility at the Geodynamics Research Center, Ehime University. This work was supported by KAKENHI (Grant No. 26400398).

References

[1] Y. Fujii *et al.*, *J. Phys. C* **18**, 789 (1985).
[2] N. Hamaya *et al.*, *Phys. Rev. Lett.* **79**, 4597 (1997).
[3] K. Fuchizaki *et al.*, *J. Chem. Phys.* **120**, 11192 (2004).
[4] K. Fuchizaki *et al.*, *J. Chem. Phys.* **130**, 121101 (2009).
[5] K. Stokely *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **107**, 1301 (2010).
[6] K. Fuchizaki *et al.*, *J. Chem. Phys.* **135**, 091101 (2011).
[7] K. Fuchizaki, *J. Chem. Phys.* **139**, 244503 (2013).
[8] L. D. Son *et al.*, *Physica* A **324**, 634 (2003).
[9] K. Fuchizaki, *J. Phys. Soc. Jpn.* **82**, 033003 (2013).
[10] K. Fuchizaki *et al.*, presented as a talk at StatPhys26, July 18-22, 2016, Lyon, France; to be published.
[11] K. Fuchizaki and N. Hamaya, *Phys. Rev.* B **84**, 144105 (2011).
[12] D. L. Decker, *J. Appl. Phys.* **42**, 3239 (1971).
[13] K. Fuchizaki *et al.*, *J. Chem. Phys.* **112**, 10379 (2000).

Research Achievements

The existence of not only the second critical point but also the density maximum in liquid SnI_4 was confirmed by x-ray absorption experiments carried out under proposal no. 2014G012.

* fuchizak@phys.sci.ehime-u.ac.jp