

Liquid SnI₄ at 7 GPaKazuhiro FUCHIZAKI^{1,*}, Takuya NISHIOKA¹, Akio SUZUKI², and Takaki HASE³¹ Department of Physics, Ehime University, Matsuyama 790-8577, Japan² Department of Earth Science, Tohoku University, Sendai 980-8578, Japan³ ALPHA Corporation, Yokohama 236-0004, Japan

Using a multianvil press MAX80, we could measure *in situ* SnI₄ in its liquid state at about 7 GPa, the highest pressure ever attained. The close resemblance of the structure factor with that of its amorphous counterpart promises us to expect the percolation of metallic I₂ bonds.

1 Introduction

It is well recognized today that some intermediate-length scale orders are more developed in an amorphous state than in a thermodynamically stable liquid state. However, the relationship between the structures of amorphous and liquid states in SnI₄ exhibiting a water-type polyamorphism remains unrevealed.

SnI₄, a material of unique complexity, presents two stable liquid phases with a slightly different density of about 0.3 to 0.4 g/cc [1]. We refer to these as the low-density liquid (LDL) and high-density liquid (HDL), or Liq-II and Liq-I, respectively. These liquids exhibit characteristic structure factors; a broad peak at about 7.5 Å⁻¹ of LDL's structure factor is shifted toward lower wavenumbers in HDL's structure factor [2]. This shift has been used as a sign of the liquid-liquid transition (LLT) upon compression. Furthermore, the molecular symmetry is lowered from *T_d* to *C_{3v}* or *C_{2v}* upon the LLT [3]. We postulate that this local symmetry breaking, which introduces two different length scales, triggers the global transition [3]. Notably, the precise overall structure of Liq-I remains a mystery, adding to the intrigue of our research.

Surprisingly, the exact symmetry lowering occurs on a pressure-induced transition at 3 GPa and room temperature from the low-density amorphous (LDA) to high-density amorphous (HDA) state [4]. The LDA state (Am-II) consists of tetrahedral SnI₄ molecules, and so does Liq-II. The HDA state (Am-I) has metallic I₂ bonds percolated throughout [4]. The LDA-to-HDA transition is thus simultaneously a percolation transition.

In Am-I's structure factor, a bump at 4.4 Å⁻¹ develops with pressure [4]. The physical origin of the bump was revealed recently; it reflects the spatial correlation of iodine-atom distributions in a percolated cluster. Although the equivalent bump has not been recognized in Liq-I's structure factor up to 3.4 GPa, its appearance is highly expected as pressure increases. The present study is therefore devoted to whether the bump shows up in a structure factor of SnI₄ liquid measured at higher pressure.

2 Experiment

The X-ray scattering method of measuring liquid SnI₄ *in situ* under pressure has been established [2]. A diamond sleeve with an inner diameter of 0.5 mm has been used thus far as a sample container to avoid extra diffraction. However, such a hard material makes transferring pressure

from outside the container difficult. The maximum pressure attained by a multianvil press in this way was about 4 GPa, even using anvils with a truncation edge length of 4 mm. Hence, to go beyond this pressure limit, we had to replace the container with one made of a "soft" material. In the present experiment, we used a cup of hexagonal boron nitride (hBN) as a container, which was employed before a diamond sleeve. Then, the pressure-transfer ability was indeed improved on the one hand, but an area of an intense 002 diffraction peak of hBN (see Fig. 1 below) had to be removed by hand from the intensity profile on the other hand. Other hBN diffraction peaks were also contaminated, but their removal is relatively straightforward. The diffraction was mainly from an hBN lid on top of the cup, which worked as a piston transferring pressure to a sample inside. The inner diameter of the cup was extended to 1 mm to raise the sample quantity, thereby gaining scattered intensity from a sample. The lid had a cylindrical nub with a diameter of 1 mm to fit the cup. Such a small ingenuity could significantly improve the retaining ability of inviscid fluid such as liquid SnI₄. For other details of the experimental setup, see Ref. [5].

3 Results and Discussion

Figure 1 shows the X-ray scattering intensity profiles obtained at 6.970(9) GPa, 1050 K, and the indicated scattering angle. We confirmed the complete melting of SnI₄, and, as mentioned in the last section, the diffraction peaks still retained were ascribable to hBN. Before combining all profiles, these diffraction peaks should be removed to obtain the structure factor. Here, removal implies replacing the protruding part with a smooth background. Hence, removing such a peak (hBN 100) at 120 keV in the bottom panel, located on a relatively flat or a slowly varying background, would be untroubled. However, removing hBN 002 at 80 keV in the same panel is never straightforward, as it could be challenging to precisely imagine the background profile there. Therefore, some trials for the replacement are usually required to obtain a physically reasonable structure factor. A small "cliff" at 70 keV conspicuous in the intensity profiles measured with a scattering angle above 6 degrees is the *K* absorption edge of W contained in anvils. The sharp peak at 32.3 keV, the *K_β* emission line of an iodine atom, is removed upon the structure-factor construction. Note that the intensities shown in Fig. 1 are not normalized by the

exposure times; they were 354, 500, 900, 1500, 2000, 2000, 2600, 3000, and 6000 sec for the measurements at $2\theta=3, 4, 5, 6, 8, 10, 13, 16,$ and 20 degrees, respectively. The normalization was taken into consideration upon superimposing the profiles.

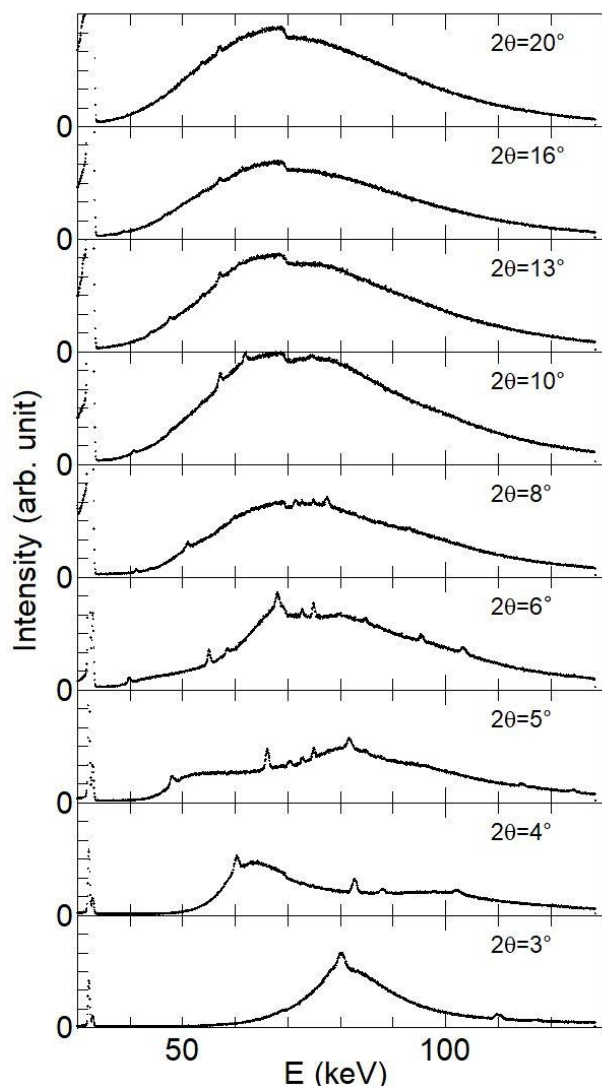


Fig. 1: The raw intensity profile taken at the indicated scattering angle is plotted against keV photon energy.

Following Ref. [6], the profiles were transformed into the structure factor, a significant step in our research, as shown in Fig. 2. A unique feature is soon noticeable—the appearance of a bump at 4.4 \AA^{-1} , which is absent in the structure factor of Liq-I at 3.4 GPa. This finding is a novel addition to the existing knowledge in the field.

The striking similarity of this aspect with that of Am-I above 3.3 GPa may lead us to a plausible scenario—the development of intermolecular I_2 bonds throughout the system at this pressure. This could lead to a percolation transition of I_2 bonds between 3.4 GPa and 6.9 GPa in Liq-I. However, based on the measurements conducted so far, no singularity exists in the melting curve of crystalline phases except at 1.5 and 5 GPa. The former(latter) singular point could be a triple point among CP-I, Liq-II, and Liq-I (CP-I, Liq-I, and CP-II). Therefore, predicting a

percolation transition boundary in Liq-I is challenging, highlighting the system's complexity under study.

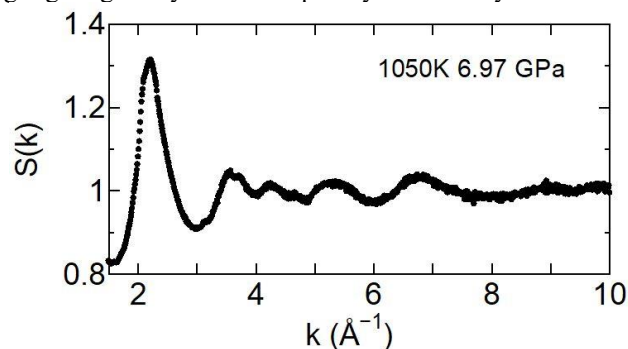


Fig. 2: The profiles shown in Fig.1 render the structure factor S given as a function of wavenumber k in \AA^{-1} .

There are two ways to avoid such a thermodynamic phase boundary in Liq-I, a single liquid phase. One is to envisage that such I_2 bonds are not chemically stable but physical bonds with a finite lifetime like hydrogen bonds. However, such physical bonds should be static in view from X-rays. The other possibility is that the boundary's terminal (critical) point would be located below the melting temperature, i.e., within either CP-I or CP-II phase fields. Then, the transition would be simply a crossover.

4 Conclusion

The strong resemblance of the structure factor at 7 GPa with Am-I's structure factor could imply the existence of percolated intermolecular I_2 bonds. This finding suggests that the HDL state of SnI_4 , Liq-I, may further be separated into two states. Thus far, we have encountered a lower-pressure state of Liq-I, where some molecules are linked to form supermolecules. Further compression takes this state to a denser state with percolated links. The transition from finite to infinite supermolecular state will not necessarily be thermodynamic if the links have finite lifetimes. In the amorphous states, a relatively high density makes the intermediate-state region shrink to the Am-II-to-Am-I transition point.

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References

- [1] K. Fuchizaki *et al.*, *J. Phys. Soc. Jpn.* **82**, 033003 (2013).
- [2] K. Fuchizaki *et al.*, *J. Chem. Phys.* **130**, 121101 (2009).
- [3] K. Fuchizaki *et al.*, *J. Chem. Phys.* **150**, 114501 (2019).
- [4] K. Fuchizaki *et al.*, *J. Phys: Condens. Matter* **33**, 365401 (2021).
- [5] K. Fuchizaki *et al.*, *J. Phys: Condens. Matter* **30**, 045401 (2018).
- [6] K. Tsuji *et al.*, *Rev. Sci. Instrum.* **60**, 2425 (1989).

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