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# Pressure-induced local symmetry lowering on liquid–liquid transition of $GeI_4$ and $SnI_4$

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## 1 Introduction

$SnI_4$ undergoes pressure-induced liquid–liquid transition (LLT) from a low-density liquid (Liq-II) to a high-density liquid (Liq-I) phase at ~1.5 GPa [1] whereas an LLT of $GeI_4$ from Liq-II to Liq-I ends up as a crossover, which occurs at around 3 GPa [2]. Our next task is to identify the microscopic mechanism of the LLTs. To this end, we carried out *in situ* XAFS and X-ray diffraction (XRD) measurements for liquid $SnI_4$. We encountered the quite intriguing phenomenon of pressure-induced molecular symmetry lowering on a reverse Monte Carlo (RMC) analysis for the XRD data. We confirmed that the symmetry lowering is universally recognizable when liquid $GeI_4$ experiences the crossover from the analysis for the previous data. The phenomenon and the consequence inferred from the fact are reported. The full reports are now available [4]. The results for XAFS measurements are saved for another report.

## 2 Experiment and Analysis Method

We chose the beamline NE5C at KEK-AR, Japan because the beamline offers not only a cubic-type multianvil press, MAX80, for high-pressure and high-temperature measurements but also a superior environment in which switching between white and monochromatic mode is easily achieved. We employed the same sample assembly as that depicted in [5]. XRD measurements for the sample and a pressure standard made of NaCl were made with the energy-dispersive method using white X rays. We used entrance and receiving slits of cross sections $0.3 \times 0.1$ mm$^2$ and $0.1 \times 0.3$ mm$^2$, respectively. A collimator with width 0.1mm collimated diffracted X rays. We measured the sample and pressure standard with diffraction angles fixed at 4° and 8°, respectively. It took 5 min. to obtain diffraction patterns with a reasonable S/N ratio for both the sample and pressure standard. The method of EXAFS measurement is fully described in [6].

The number of molecules employed for the RMC analysis was 2744 for both $SnI_4$ and $GeI_4$. The molecular configuration to be used as input to the RMC analysis was prepared by conducting the isothermal–isobaric molecular dynamics simulation [7]. During the RMC run, the movements of the atoms were constrained so as not to approach unphysically close to each other. The minimum allowable distances adopted were 3.0, 0.5, and 2.0 Å for Sn–Sn (Ge–Ge), Sn–I (Ge–I), and I–I distances, respectively, throughout the analysis. For other details, see [4].

## 3 Results and Discussion

We found that a regular tetrahedral SnI4 molecule with Sn–I length of 2.66 Å at ambient pressure is “squashed” to a tetrahedral molecule with one short (2.25 Å) and three long (2.86 Å) Sn–I distances at 3.4 GPa. The curious behavior that the intramolecular Sn–I distance is elongated upon compression was detected in the reduced radial distribution function [2]. The present RMC analysis clarified that the shorter length correlation was buried in artifacts resulting from finite truncation upon the Fourier inversion.

The most intriguing fact that we found is that the local symmetry lowering from $T_d$ to $C_{3v}$ was also confirmed *prior* to the LLT (see the upper panel of the figure, in which the experimental structure factor is compared with the intramolecular structure factor derived assuming the molecular symmetry in question).

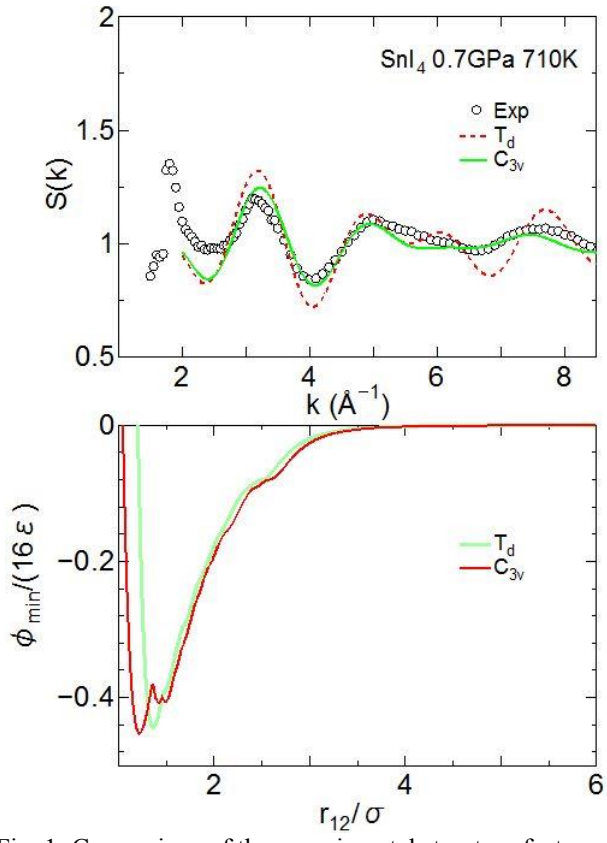


Fig. 1: Comparison of the experimental structure factor and the symmetry-adapted structure factors (upper panel) and the appearance of the two-length scales in the local potential on lowering symmetry from $T_d$ to $C_{3v}$ (lower).

We confirmed that the symmetry lowering from $T_d$ to $C_{3v}$ also occurs in liquid $GeI_4$ during the crossover from Liq-II to Liq-I [4].

Quite interestingly, this local symmetry breaking brings about a double-minimum character in the intermolecular interaction. (See a lower panel of the figure, in which $\min_{\omega_1,\omega_2} \phi(r_{12}, \omega_1, \omega_2)/(16\epsilon)$ is plotted against reduced intermolecular distance $r_{12}/\sigma$, the interaction $\phi$ being modeled by the 4-center Lennard-Jones potential characterized by $\epsilon$ and $\sigma$ [4]. The minimum over possible molecular orientations, $\omega_1$ and $\omega_2$, was taken.) The two length scales implemented in the Jagla potential [8] thus naturally appear.

## 4 Concluding Remarks

Pressure-induced LLT in liquid $SnI_4$ and $GeI_4$ is reflected in a shift of the broad peak at 7.5 $Å^{-1}$ of the structure factor toward lower wavenumbers. This feature has been used to judge the occurrence of the LLT. The structure factor can offer useful information, such as reduced radial distribution function when converted into real space. As far as inferred from the aspect of the radial distribution, the intramolecular Sn–I or Ge–I bond length seemed to be elongated upon compression. The RMC method offers an opportunity to address this curious finding. The elongation results from the lowering of molecular symmetry from $T_d$ to $C_{3v}$; four degenerated lengths are breaks into one long and three shorter lengths. The radial distribution function has suffered a loss of the peak corresponding to the shorter-length correlation upon Fourier transform with a finite wavenumber window.

Quantum chemical calculations for the electronic energy of a $SnI_4$ molecule could not explain such a type of symmetry lowering [4], leaving a new issue regarding the origin for the anisotropic deformation.

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