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Pressure-Induced Liquid-to-Liquid Crossover in GeI_4

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1 Introduction

We could confirm in SnI_4 the existence of the liquid—liquid critical point (LLCP) at around 1.5 GPa and 1000 K [1] and of the temperature of maximum density in the region between 1100 K and 1400 K just below 1 GPa [2]. SnI_4 thus allows us to enter the "no-man's land", which cannot be accessed for bulk water

It should be emphasized that a melting maximum [3] is not necessarily a condition for a liquid—liquid transition (LLT) to occur. The existence of a (seemingly) singular point on a melting curve may rather imply occurrence of an LLT [4]. Indeed, the melting curve of SnI_4 does not exhibit an apparent maximum but has a breakpoint at ~1.5 GPa [4], which may be the triple point among the two liquid phases and the crystalline phase (CP) [5].

The melting curve of a molecular crystalline GeI_4 exhibits quite a similar shape (see Figure 1, in which the melting points are marked by open circles). The breakpoint is shifted to ~3 GPa [6] reflecting a slight reduction of molecular size. The aspect suggests us to examine a possible LLT of liquid GeI_4 in a pressure—temperature region close to the breakpoint.

2 Experiment

To this end, the energy-dispersive synchrotron x-ray diffraction measurements were carried out employing MAX-80, a cubic-type multianvil press, installed in the beamline NE5C at KEK-AR. A new type of two-stage compression method that was described previously in full by [6] was employed. The compression was performed using a set of anvils with a truncation edge length of 6 mm to cover the relevant pressure range. NaCl was used as the pressure standard The distributions of scattered x-ray intensities at various scattering angles, 3 through 20°, were combined to construct a normalized structure factor, which was then converted to the reduced radial distribution function (RRDF) using the method by [7].

3 Results and Discussion

The characteristic feature of the RRDF was found to be completely shared with that found for SnI_4 [7]; the intramolecular I—I distance shrinks on compression whereas the intramolecular Ge—I distance *expands*. This latter unusual feature enables us to judge the occurrence of the LLT from the low-pressure liquid state (Liq-II) to the high-pressure liquid state (Liq-I). The distribution of structure measurements at which Liq-II (blue circles) and Liq-I (pink circles) were identified is depicted in Figure 1. Unlike the aspect observed for SnI_4, the transition between the two liquids is sluggish; transient states (purple circles) were indeed in the region near the breakpoint. The LLCP for GeI_4 might be located within the CP field below the melting curve, making the transition merely a crossover. The more complete discussion was given in [8].

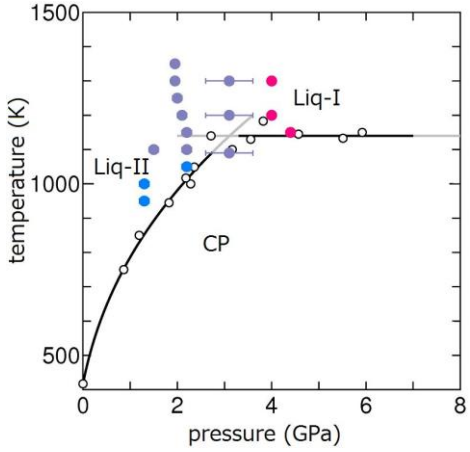

Fig. 1: Two liquid states of GeI_4 and their coexistence.

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