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Polyamorphism in SnI_4

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Introduction

Polymorphism has been a research target in condensed matter physics and chemistry for a long time, and comprehensive knowledge regarding polymorphs has been accumulated. However, experimental researches on polyamorphism, which was triggered by a discovery of thermodynamically stable liquid-to-liquid phase transition in black phosphorus[1]. Other substances that can undergo a liquid-to-liquid transition have been searched, and finally, definitive evidence for the transition was obtained by *in situ* synchrotron x-ray measurements of liquid SnI_4 performed under high pressures[2]. To the best of our knowledge, this is the first example of thermodynamically stable polyamorphic transition found in general compounds.

A fundamental question arises then; is the density an only quantity that can distinguish one liquid state from another? To address this point the critical region of the liquids must be investigated. The purpose of this study is to identify the location of the critical point, if present, as well as the phase boundary of the liquids of SnI_4.

Experiment

The energy-dispersive x-ray diffraction experiments were performed using synchrotron radiation. MAX80, a cubic-type apparatus for high-pressure and high-temperature experiments, installed in BLNE5C at KEK-AR, measured *in situ* x-ray scattering at pressures and temperatures up to about 4GPa and 1300K, respectively. Tungsten carbide anvils with a center flat of 6mm were employed to generate high pressures. The sample assembly used for the experiments was rather specific and is explained in detail in Ref. [2]. The difference from the previous assembly is to use a Pt-Pt/Rh thermocouple when high-temperature region beyond 1100K is investigated. In those cases, MgO instead of NaCl was employed as an internal pressure calibrant. Two experimental opportunities were given in FY2006. The results obtained in each period are presented separately in the following.

Results

Mission in October, 2006

Four runs were performed. However, only in one run, a liquid sample could be held steadily during measurements. We could observe the liquid at 919K and 1018K. However, from a series of analyses using a new inversion method[3], an SnI_4 molecule was found to be dissociated into I_2 molecules during the holding. The dissociation was accelerated by some unexpected catalytic reaction between the sample and its surroundings.

Mission in February, 2007

The only but important improvement from the previous assembly is to employ pyrolytic boron nitride disks as a container top and a bottom of the sample. This is because the problem lay in holding a liquid sample in a stable form. Five runs were performed, among which we could succeed in taking a series of intensity patterns of the liquid at three different temperatures in one run. However, a thermocouple was broken on compression in other runs. Figure 1 shows structure factors obtained in the successful run. Since these structure factors are of low-pressure liquid phase (Liq-II), the phase field of Liq-II extends over at lease the temperatures and pressures indicated in Fig. 1.

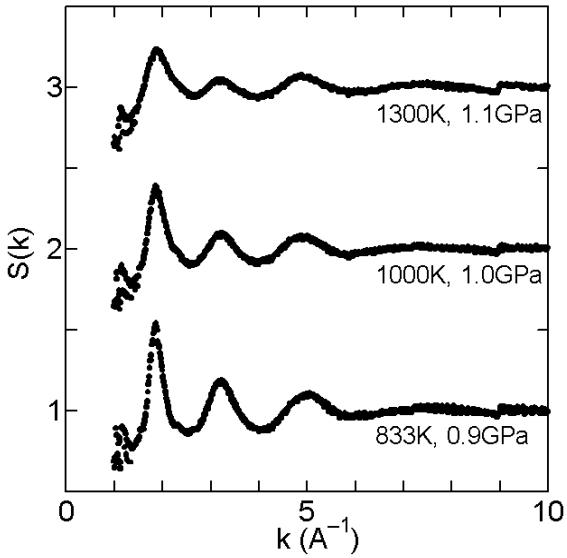

Fig. 1 Structure factors obtained at the condition indicated are plotted against wavenumber. Each plot is replaced upward by unity.

References

[1] Y. Katayama et al., Nature 103, 170 (2000).
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