A FIRST-ORDER LIQUID-LIQUID PHASE TRANSITION OBSERVED IN PHOSPHORUS

Although first-order structural phase transitions are common in crystalline solids, first-order liquid-liquid phase transitions, which occur between two liquid phases with different density and entropy, are exceedingly rare phenomena in pure substances. Recently, the possibility of such transitions has been proposed for several materials but their observation by structural methods have not been reported yet [1]. We have succeeded in the first direct observation of such a transition by *in situ* X-ray diffraction measurements on molten black phosphorus under high-pressure and high-temperature [2].

Phosphorus (P) has a number of allotropes in the solid state; white P consists of tetrahedral P_4 molecules, black P is a layered structure, and red P is usually amorphous. Each allotrope has a different melting temperature – white P melts at 44°C while black P melts at around 600°C. It is known that the melt of white P comprises P_4 molecules. However, no structural study on liquid P at high-temperatures has been performed other than an *ab initio* simulation study, which predicts a polymeric form at high temperature [3]. Recent developments in synchrotron radiation and large volume presses enable us to investigate the structures of liquids under high-pressure and high-temperature [4].

Energy-dispersive X-ray diffraction experiments were carried out using a cubic-type multi-anvil press, SMAP180, installed at beamline **BL14B1**. In addition to the known form of liquid P – a molecular liquid composed of tetrahedral P_4 molecules – we have observed a polymeric form at pressures above 1 GPa. Figure 1 shows the structure factor, S(Q), as a function of wave number Q, obtained from X-ray diffraction data. There is a large difference between S(Q) below and above 1 GPa. A prominent first peak around 1.4 $Å^{-1}$ disappears above 1 GPa, at which point a new maximum around 2.45 $Å^{-1}$ appears. On the other hand, S(Q) at 0.77 GPa is almost identical to that at 0.96 GPa and S(Q) at 1.01 GPa is similar to that at 1.38 GPa. These results indicate that there are two distinct forms of liquid P.

The low- and high-pressure forms are obtained by melting black P below and above 1.0 GPa, respectively. Alternatively, the forward and reverse transitions between the two forms can be directly induced simply by a change in pressure. Figure 2 shows the diffraction patterns taken at a diffraction angle of 6.0° across the transformation at 1 GPa. A broad peak around a photon energy of 25 keV in pattern (a) corresponds to the first maximum of S(Q) for the low-pressure form. The pressure was increased at the rate of about 0.01 GPa/min. During compression, the peak around 25 keV abruptly diminished. Pattern (b) was taken during the transformation. After 15 min, the diffraction pattern did not show any further change (pattern (c)). This increase in pressure by 0.02 GPa results in the generation of a completely different diffraction pattern. Alternatively, patterns (d) to (f) were taken with decreasing pressure. This reverse

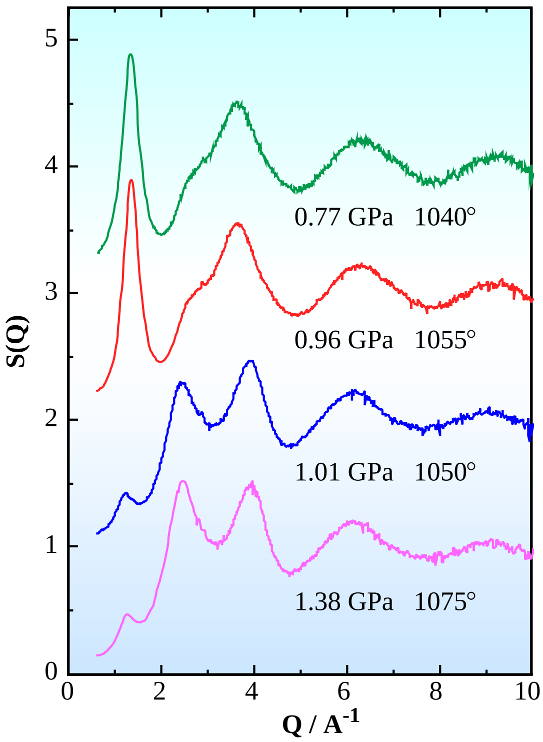

Fig. 1. Structure factor, S(Q), for liquid P at several pressures.

transformation was completed within a pressure range of less than 0.06 GPa and a time interval of 8 min.

The diffraction pattern taken during the transformation can be derived perfectly from the two diffraction patterns taken before and after the transformation. For example, adding patterns (a) and (c) with the ratio of 38:62 reproduces pattern (b). Pattern (e) can also be reproduced from patterns (d) and (f). This observation indicates that the two pressure forms coexist during the transformation, and that there no long-lived intermediate states contribute to the transitional X-ray diffraction pattern; that is, the low-pressure form is directly transformed into the high-pressure form.

The features of this transformation – the existence of two distinct forms of liquid, a sharp transformation between them and no detectable intermediate state – strongly support the view that it is a first-order liquid-liquid phase transition.

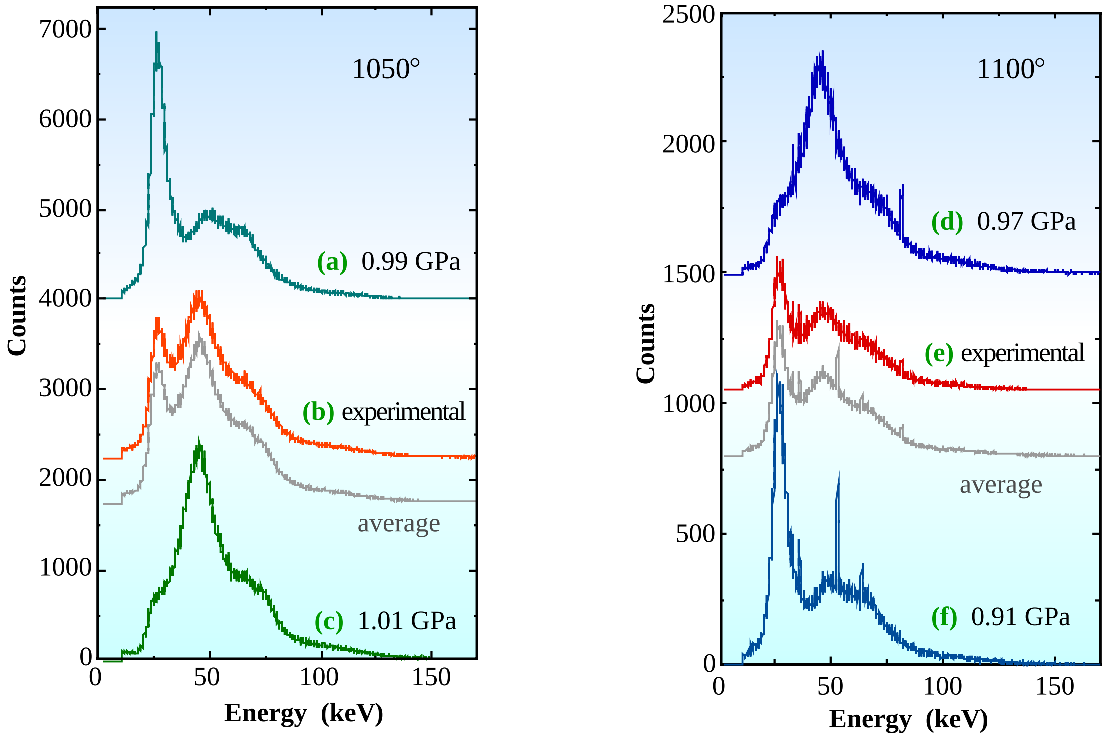

*Fig. 2. X-ray diffraction patterns that showing the transformation from the low-pressure form to the high-pressure form ((**a**) to (**c**)) and the reverse transformation ((**d**) to (**f**)). Pattern (**b**) and (**e**) were measured during the transformation. The data were taken at a diffraction angle of 6.0°. The grey line in patterns (**b**) and (**e**) indicate the weighted average of patterns (**a**) and (**c**), and patterns (**d**) and (**f**).*

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