

## DIRECT OBSERVATION OF MACROSCOPIC SEPARATION OF DENSE FLUID PHASE AND LIQUID PHASE OF PHOSPHORUS

Many substances can exist in different crystalline structures. For example, graphite and diamond are both composed of carbon atoms. With a change in a parameter such as temperature or pressure, one crystalline structure transforms to another one. If the transformation is accompanied by a sudden change in density, it is called a first-order structural phase transition. While first-order phase transitions of crystalline solids are common, those in disordered states are extremely rare, with the exception of the liquid-gas transition [1]. The pressure- or temperature-induced structural change in the liquid state of a pure substance has been supposed to be gradual and continuous.

Phosphorus is an exceptional element that exhibits an abrupt structural change between two stable disordered states above its melting temperature when the pressure is changed to about 1 GPa at 1000°C [2]. From the structural features, the transformation is attributed to a conversion between a molecular form, comprising tetrahedral  $P_4$  molecules at low-pressures, and a polymerized networked form at high-pressures. An abrupt change in the slope of the melting curve indirectly indicates that the two forms have different densities [3]. The transformation was supposed to be a liquid-liquid phase transition, but a later study [4] pointed out that the low-pressure phase is a dense molecular fluid phase because the pressure-temperature range was higher than the liquid-gas critical point of the molecular liquid. We call the two forms low-density fluid phosphorus (LDFP) and high-density liquid phosphorus (HDLP).

To obtain further evidence for the first-order phase transition, we have carried out in situ X-ray radiography experiments under high pressure and high temperature using a cubic-type multi-anvil apparatus, SMAP2, at beamline BL14B1 [5]. Figure 1 shows a series of X-ray images. The dark area in Fig. 1(a) represents crystalline black P. The dark area became pale at 810°C as the sample was heated to 1000°C (Fig. 1(b)). X-ray diffraction measurements confirmed that LDFP was present. Then, the sample was gradually compressed. During compression, dark and round objects appeared in the radiograph. Figure 1(c) shows a large drop whose size is comparable to the diameter of the sample container. The diffraction pattern obtained for the drop was very different from

that of LDFP, whereas the pattern measured for the area above the large drop showed that the sample was LDFP. The drop grew and finally filled the

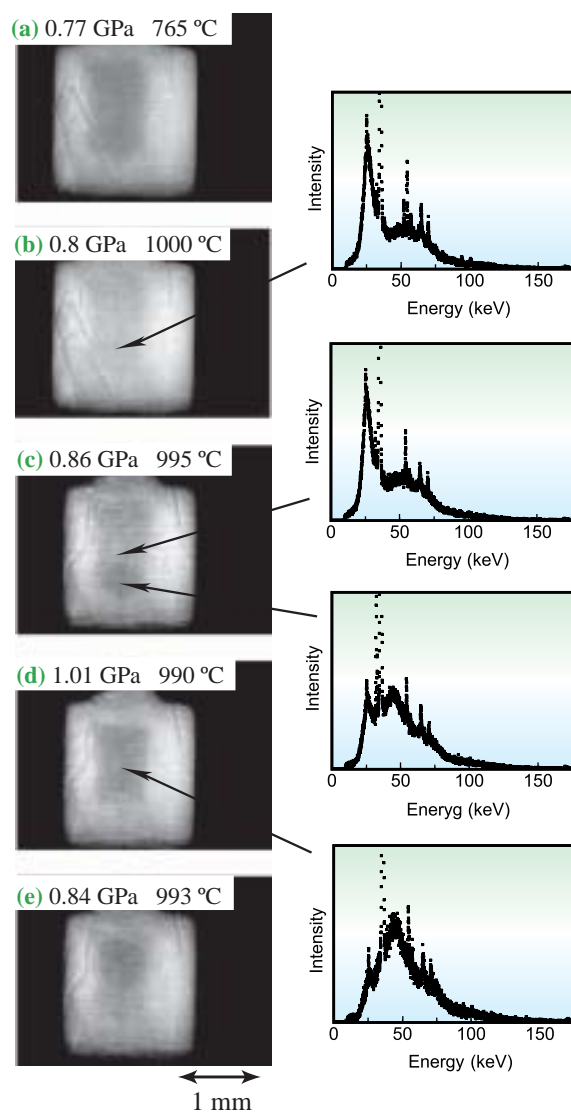


Fig. 1. Radiographs for phosphorus at various pressures and temperatures. Insets show X-ray diffraction patterns measured at the positions indicated by arrows. (a) Black P at 0.77 GPa and 765°C. (b) Low-density fluid phosphorus (LDFP) at 0.8 GPa and 1000°C. (c) A Drop of high-density liquid phosphorus (HDLP) in LDFP at 0.86 GPa and 995°C upon compressing. (d) The sample space filled with HDLP at 1.01 GPa and 990°C. (e) A drop of HDLP in LDFP at 0.84 GPa and 993°C upon decompressing. In the diffraction patterns, the broad peaks result from the liquid phase while sharp peaks mostly result from the high-pressure cell.

sample space (Fig. 1(d)) and the diffraction pattern at this stage was typical of that for HDLP. The diffraction pattern obtained for the drop shown in Fig. 1(c) was reproduced by the weighted sum of those of LDFP and HDLP in the ratio of 1:3. Hence, it was reasonable to suppose that the drop in shown Fig. 1(c) was HDLP. When the sample was decompressed, the dark area shrunk (Fig. 1(e)) and finally disappeared. The results demonstrate that LDFP and HDLP coexist and separate macroscopically. Moreover, the X-ray contrast between the two phases in the radiograph is direct evidence that the two phases have different densities.

To determine the densities of the two phases, we performed X-ray absorption experiments using a multi-anvil apparatus, SMAP180, and a monochromatic X-ray provided by beamline BL11XU [5]. The sample was placed in a sapphire ring with a 0.5 mm inner diameter, 1.0 mm outer diameter, and 1.0 mm height. The X-ray absorption of the sample was measured as

a function of sample position and the profile was fitted to obtain the density. Figure 2 shows the density of liquid phosphorus at about 1000°C as a function of pressure. The density drastically decreased between 1.02 GPa and 0.84 GPa. The change in density corresponds to about 40% of the density of HDLP and about 60% of that of LDFP.

The observed macroscopic phase separation supports the existence of a first-order phase transition between two stable disordered phases besides the liquid-gas transition. Diffraction, absorption, radiography, and simulation studies revealed that LDFP and HDLP have very different structures, densities, and properties. The large difference in density stabilizes one structure against thermally induced fluctuations in density. The difference in the cohesive mechanism and, thus, in the electronic property probably contributes to the immiscibility of the two phases. These differences play an important role in the first-order fluid-liquid transition.

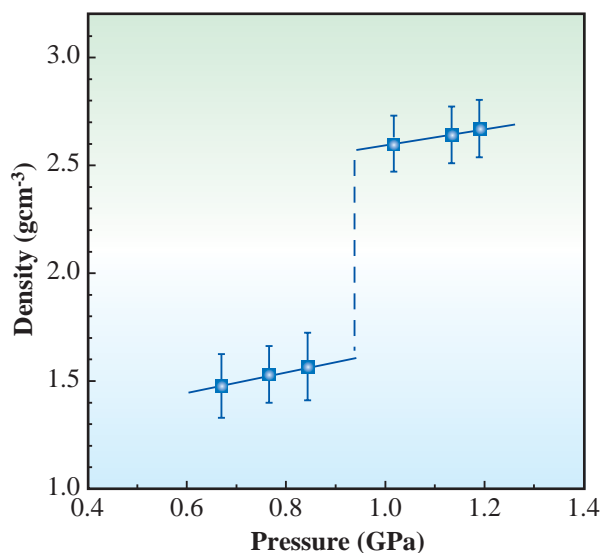


Fig. 2. Pressure dependence of density of liquid phosphorus at 1000°C. The solid and dashed lines are guides for eyes.

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