

Nature of the First-Order Phase Transition in Fluid Phosphorus at High Temperature and Pressure

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An *in situ* x-ray diffraction experiment has been performed on phosphorus to characterize the liquid-liquid transition which occurs at high temperature and pressure. The transition line has been measured over an extended temperature range up to 2200 °C at 0.3 GPa. From the shape of this line, a thermodynamic characterization of the transition is obtained in terms of latent heat and internal energy change. Moreover, the addition of the high-pressure high-temperature data to the known phase diagram of phosphorus allows us to conclude that this is a first-order transition between a dense molecular fluid and a polymeric liquid.

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Liquid-liquid transitions, i.e., first-order transitions between two liquid states characterized by different local structures and thermodynamic properties, are common in multicomponent systems and in liquid crystals, where composition and molecular orientation are the respective order parameters. Recently, the possible occurrence of liquid-liquid transitions in pure, isotropic liquids has been suggested [1], thus stimulating the development of models [2,3] and computer simulations [4,5] that have discussed cases where these transitions are indeed possible. The suggestion of candidate systems to exhibit this kind of transitions is, however, difficult, as shown, for example, by the case of carbon, where a liquid-liquid transition discovered in a classical molecular dynamics simulation [4] no longer occurs in a first-principles one [6].

From the experimental side, the support for liquid-liquid transitions in pure, isotropic liquids is still rare [7–12] and even controversial [13,14], mainly as a consequence of the technical difficulties of the experiments reported so far. Those indeed refer to transitions in highly reactive systems [7,13], in metastable phases [8,9,14], or in challenging conditions of pressure (p) and temperature (T) [10–12]. However, a remarkably clear example of a pure, isotropic system displaying a liquid-liquid transition has recently been discovered in phosphorus [11,12]. There, an abrupt, pressure driven, reversible structural transformation between a low-pressure molecular-liquid and a high-pressure polymeric liquid has been reported at a temperature of 1050 °C and a pressure of about 1 GPa [11,12]. This transition has been interpreted as being first order for the two following reasons [11]: (i) It is very sharp, being completely achieved by a pressure change of only 0.02 GPa. (ii) The coexistence between the two different liquid structures has been directly observed. Computational studies on P [5,15] support the interpretation of the experimental data in terms of a first-order transition. Actually, phosphorus appears, to the moment,

as the only available example of a pure, isotropic system exhibiting a liquid-liquid transition between two stable liquid phases.

In this Letter, we report an *in situ* x-ray diffraction experiment performed on P in order to characterize this first-order transition. We have measured the transition line over an extended temperature range up to 2200 °C at 0.3 GPa. The addition of the high- p high- T data on the transition line to the known phase diagram of P [16] shows that this is a first-order transition between a dense molecular fluid and a polymeric liquid. Moreover, the knowledge of the shape of the transition line allows us to obtain a thermodynamic characterization of the transition in terms of latent heat and internal energy change.

The *in situ* high- T high- p x-ray diffraction experiment on phosphorus was performed using the Paris-Edinburgh large-volume apparatus installed at the high-pressure beam line ID30 at the European Synchrotron Radiation Facility. The wavelength of the x-ray beam was tuned to 0.4859 Å using an in-vacuum Si(111) monochromator. The starting P material was commercial amorphous red P. The sample container was a 0.8 mm internal diameter, 0.5 mm thick BN cylindrical cell. The thickness and shape of this container were optimized in order to keep the sample confined at high T and are critical parameters of the experiment. With these parameters, a limited diffusion of phosphorus into the BN cell was achieved up to the highest reached temperatures, and the samples recovered after the thermal and pressure cycles were found to be in good condition. Angle-dispersive diffraction data were collected using a recently developed multislit system [17], which allows sample diffraction patterns to be taken with the minimum of signal from the BN sample capsule, the surrounding graphite furnace, and the B-epoxy gasket. Subtraction of the background was made possible by displacing the cell and diffracting from an off-center position, thus revealing the relative extent of the B gasket, furnace, and BN contribution to the sample

scan. Pressure was determined from scans taken on the BN capsule [18] and temperature from furnace power curves calibrated by both an internal cross-calibration method [19] and against known fusion points. The estimated absolute error in the temperature and pressure determination is $\pm 75^\circ\text{C}$ and $\pm 0.1\text{ GPa}$, respectively, while relative errors are about 1%.

The experiment was conducted by first transforming amorphous red P into crystalline black P as previously described [20,21] and then melting the sample at pressures slightly higher than 1 GPa. Pressure was then decreased in steps and a diffraction pattern was collected at each step until the transformation to the molecular phase was encountered. As a starting point, a similar p - T region as in Refs. [11,12] was investigated, and our results confirm the most important observations reported there: we have observed a sharp, reversible structural transition between a molecular and a polymeric phase that takes place at 0.9 GPa and 1050°C [22], and we have found as well the coexistence point between the two different structural forms. Moreover, sharp transformations between the two phases and their coexistence have been directly observed at several p - T points along the transition line, as shown in the examples reported in Figs. 1 and 2.

In particular, in Fig. 1 the $S(q)$ patterns across the transition points at 1090°C (left panel) and at about 0.67 GPa (right panel) are reported and refer to the polymeric phase (upper spectra) and to the molecular phase (lower spectra), respectively. It is interesting to point out that Fig. 1 shows that the polymerization process can be driven not only by pressure, as already observed

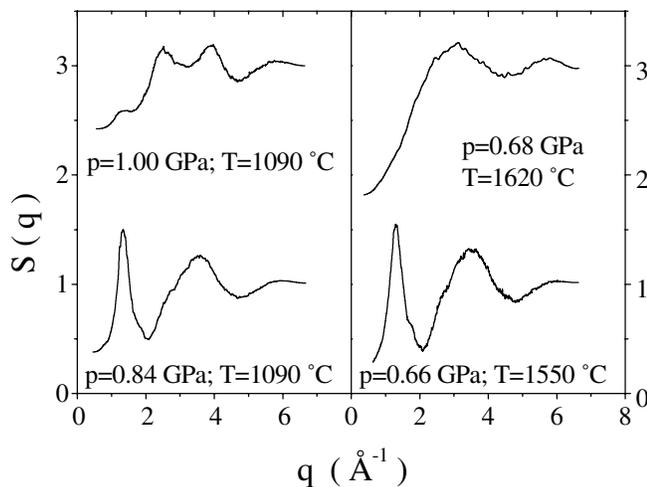


FIG. 1. Examples of spectra across the first-order transition encountered by varying pressure at constant temperature (left panel) or by varying temperature at (almost) constant pressure (right panel). The upper (lower) spectra refer to the polymeric (molecular) phase. The upper spectra have been vertically shifted by 2, for clarity.

[11,12], but by temperature as well. This implies that only the polymeric phase can stably exist at high temperature, thus confirming a previous first-principles molecular dynamics simulation result [5]. The patterns in the left panel of Fig. 1 look very similar to those already reported by Katayama *et al.* [11] and with similar peak positions. Upon increasing T and decreasing p , the features in the $S(q)$ patterns broaden, and this is particularly clear in the case of the polymeric phase where the diffraction peaks at 2.48 and 3.85 \AA^{-1} merge into a single broad peak (right panel, upper plot). For what concerns the coexistence of the two phases, an example is reported in Fig. 2 and refers to 0.72 GPa and 1450°C (middle plot, full line). The reported pattern compares well with a linear combination (middle plot, grey line) of the patterns obtained at the two sides of the transition (upper and lower plots for the polymeric and molecular phases, respectively).

Upon changing p and T in a zigzag path in several runs on different samples, the structural transformation has been followed over an extended T range up to about

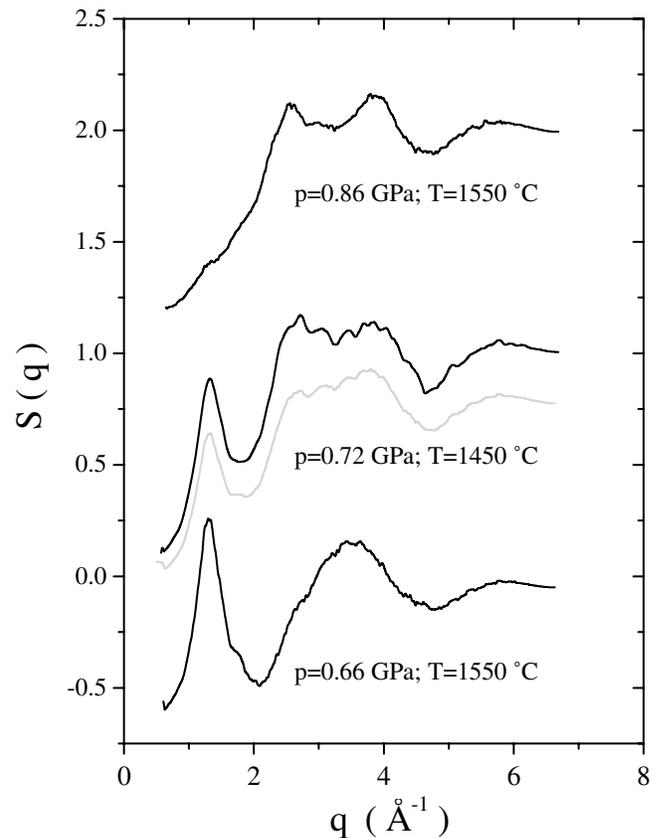


FIG. 2. The $S(q)$ pattern corresponding to the coexistence point on the transition line at 0.72 GPa and 1450°C (middle plot, full line) compared with a pattern in the molecular phase (lower plot, vertically displaced by -1) and one in the polymeric phase (upper plot, vertically displaced by 1). The pattern at coexistence compares well with a linear combination of 35% of the upper polymeric pattern and 65% of the lower molecular one (middle plot, grey line, vertically displaced by -0.2).

2200 °C at 0.3 GPa. The corresponding results are summarized in Fig. 3(a): solid circles and open squares correspond to data in the polymeric and in the molecular phase, respectively (only data close to the transition line are reported), and open stars correspond to thermodynamic points where the coexistence of the two different phases has been directly observed. This whole set of data describes a transition line which is well represented by a 2nd order polynomial (full line across the experimental points).

In order to better understand the results obtained on this first-order phase transition in P, it is important to consider them in the light of the entire phase diagram [11,12,16,20,23,24] that, in a simplified version, is reported in Fig. 3(b). It is known that, at ambient conditions, phosphorus can be essentially found in three allotropic forms: (i) black P, which is an orthorhombic crystal with a puckered layered structure; (ii) white P, which is a molecular crystal with P_4 tetrahedral units; and (iii) red P, which is usually amorphous and with polymeric structure. Among these different forms, black P is generally considered to be the stable phase [16]. It sublimates to a molecular P_4 gas at about 500 °C at ambient pressure [16], and the corresponding sublimation line, in the range where it has been measured, is reported in Fig. 3(b) (full line at low pressure). At high pressure, data on the melting line of black P are available in the literature [11,12] (grey line). However, no experimental data on the sublimation/melting line of black P are available, to our knowledge, in the pressure range between about 10 and 200 MPa.

Further insight into the phase diagram of phosphorus comes from the consideration of its metastable white form, and, in fact, in Fig. 3(b) we superimpose the (metastable) phase diagram of white P onto that of black P. White P melts at 44 °C at ambient pressure, and the melt is a molecular liquid with tetrahedral units as in the crystal [16]. The boiling line corresponding to this molecular liquid is also reported in Fig. 3(b) (dashed line). Such a boiling line is known up to 360 °C: above that temperature the liquid becomes unstable towards a solid amorphous red form [16]. This instability leads to a molecular-liquid to polymeric-solid transformation that, at the structural level, is strikingly similar to the transition found at high- p high- T conditions. At temperatures higher than 500 °C, the P_4 molecular liquid can be produced again, and the corresponding boiling line has been measured up to 630 °C. The critical point at the end of the P_4 liquid-vapor transition line is calculated to be at 695 °C and 8.2 MPa [16]. This means that the critical point at the end of the boiling line of the metastable white P form comes out to be in the stable phase diagram. This observation allows us to conclude that the high- p high- T transition studied here is a first-order transition between a dense molecular fluid and a polymeric liquid.

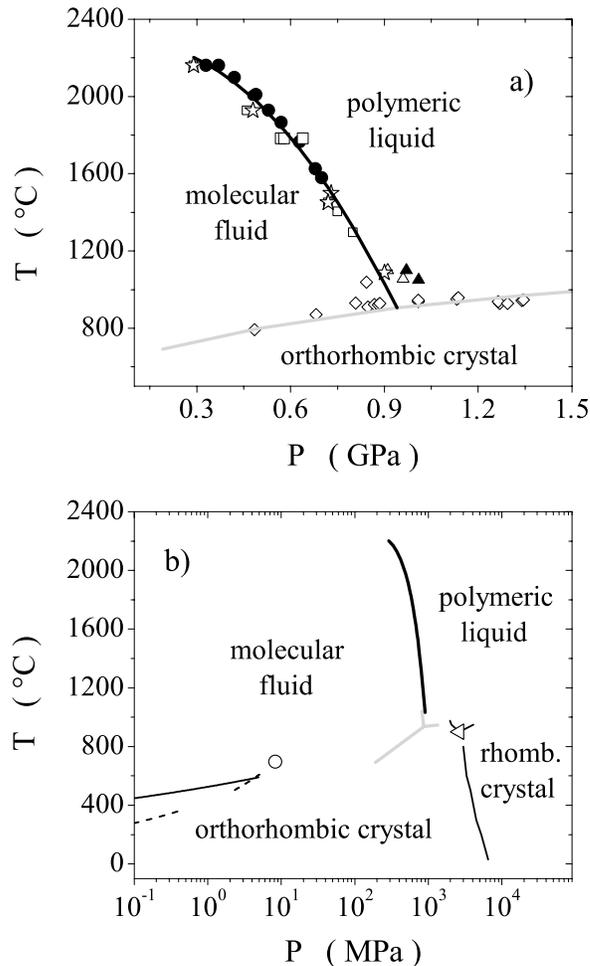


FIG. 3. (a) The high- p high- T portion of the phase diagram of phosphorus in the region where the first-order phase transition is located. Stars correspond to coexistence points; solid circles and open squares correspond to data in the polymeric and in the molecular phase, respectively (only data close to the transition line are reported). The black line is the 2nd order polynomial that best represents the transition line. Solid and open triangles correspond to literature data for the polymeric and the molecular phase, respectively [11]. Open diamonds and the grey line refer to the melting line of black phosphorus [12,23]. (b) A simplified version of the phase diagram of phosphorus in semilog scale in order to put the low and high pressure data in a unified picture. At room conditions the orthorhombic black crystal is the stable phase which, on increasing T , sublimates to the molecular P_4 gas [16] (solid line). At high pressure, together with our results on the high- T high- p phase transition (solid line), we sketch previous results on: the melting line and the high- T high- p phase transition (grey line) [11,12]; the orthorhombic to rhombohedral (rhomb.) crystal transition [24]; and the orthorhombic, rhombohedral, and liquid triple point (open triangle) [23]. At low p , the boiling line of the metastable molecular P_4 liquid is also reported (dashed line) [16]. The critical point at the end of this line is calculated to be at 695 °C and 8.2 MPa (open circle) [16]. The ensemble of these data allows us to conclude that the high- p high- T transition is a first-order transition between a dense molecular fluid and a polymeric liquid.

Figure 3 also shows that the slope (and the concavity) of the fluid-liquid transition line is negative in the whole p - T range considered here. Such a slope, being the transition first order [11], is related to the changes in volume, ΔV , and entropy, ΔS , between the two phases by the Clausius-Clapeyron relation: $dT/dp = \Delta V/\Delta S$. From the knowledge of the slope of the transition line, more quantitative results can as well be obtained exploiting the fact that values for the density of the molecular fluid (ρ_f) and of the polymeric liquid (ρ_l) are known at two p - T points [5,11], $\rho_f = 1.6 \text{ g cm}^{-3}$ and $\rho_l = 2.7 \text{ g cm}^{-3}$ at the transition point corresponding to 1130°C , and $\rho_f = 1.6 \text{ g cm}^{-3}$ and $\rho_l = 2.5 \text{ g cm}^{-3}$ at the transition point corresponding to 0.7 GPa . We can then derive the latent heat at the transition at those points, λ_{fl} , and, in particular, we find that $\lambda_{fl} = 3.6 \pm 1.3 \text{ kJ g-atom}^{-1}$ at 1130°C and 0.87 GPa , and $6 \pm 2 \text{ kJ g-atom}^{-1}$ at 1600°C and 0.7 GPa . These are quite large values for a latent heat—a consequence of the strong changes involved in the polymerization process in fluid P. Moreover, using the available values of ΔV and the slope of the transition line we can also calculate the change in the internal energy, ΔU , at the transition, $\Delta U = T\Delta S - P\Delta V$. The entropy and the volume contributions to ΔU come out to be comparable in size, and we obtain $\Delta U = 10 \pm 3 \text{ kJ g-atom}^{-1}$ both at 1130°C and 0.87 GPa and at 1600°C and 0.7 GPa . This value of ΔU is compatible with the energies of formation of P clusters of different structures and sizes [25], and it is consistent with the fact that the highly symmetric, tetrahedral form of P transforms into a low-symmetry, polymeric form.

Figure 3(a) also shows that the transition line in fluid P is very steep at $\approx 1000^\circ\text{C}$ and that it has a decreasing slope (likely implying decreasing ΔV) when T is increased. Actually, the slope tends to vanish at about 2200°C : this might indicate that we are actually approaching a fluid-liquid critical point, but no definite evidence of it has been found in the p - T range studied here.

In conclusion, we have presented an *in situ* x-ray diffraction experiment on phosphorus performed with the aim of characterizing the first-order liquid-liquid transition recently reported at high- p high- T conditions [11,12]. We have measured the transition line over an extended p - T range up to 2200°C at 0.3 GPa , finding that it has negative slope and concavity. We have shown that the transition can be temperature driven as well as pressure driven and that only the polymeric liquid form of P can stably exist at high temperature. From the slope of the transition line we have derived the latent heat and the

internal energy change at the transition. Moreover, the comparison of the transition line data at high- p high- T conditions with the known phase diagram of phosphorus [16] allows us to conclude that this is a first-order transition between a dense molecular fluid and a polymeric liquid.

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