EUROPEAN SYNCHROTRON RADIATION FACILITY
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	Experiment title: Structure of liquid phosphorus across the liquid-liquid line transition at high temperature	**Experiment number**: HS1672
Beamline: ID30	**Date of experiment**: from: 09/11/2001 to: 13/11/2001	**Date of report**: 27/02/2002
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Report:

The study of structural transformations in liquids is mostly based on indirect measurements, e.g.on the observation of anomalies in the volt-amperometric characteristics [1,2]. Only few of these reported transformations have been characterized with diffraction measurements [3,4].

A breakthrough in this direction has recently been achieved with the direct observation in liquid P of a sudden structural change which has been interpreted as a first order phase transition between a low-pressure molecular P_4 liquid and a high-pressure polymeric liquid [3]. This interpretation is supported both by the abruptness of the transformation and by the observation of a coexistence region. This liquid-liquid phase transition in P has been studied at about P=1 GPa and T=1000 °C as shown in the phase diagram reported in fig. 1 (data from Ref. [3,5]).

These experimental results are also confirmed by Car-Parrinello numerical simulations [6].

The aim of the experiment that we have performed was to study the structure of liquid phosphorus across the liquid-liquid transition line and to determine the transition line at temperatures higher than those already reached by Katayama et al. [3].

We have performed angle-dispersive X-ray diffraction measurements on solid and liquid phosphorus at the Ag and Pt K-edge energies in order to get access to a broad q-range

comprised between 5 nm^{-1} and 100 nm^{-1}. We used a Paris-Edinburgh press in order to reach temperatures up to about 2000 °C and pressures in the range comprised between room pressure and 2 GPa.

We had two main difficulties during the measurements. The first one is due to the strong diffusion of liquid phosphorus in the boron nitride capsule that we used, a problem which becomes increasingly important at high temperatures. The second problem is the correct determination of temperatures and pressures at very high temperature. The first problem was solved by optimizing the ratio between the sample length and the thickness of the BN capsule and by choosing a thermodynamic path which minimizes mechanical stresses of the BN capsule. The second problem is much more difficult due to the high reactivity of phosphorus and the consequent difficulty of choosing a proper internal calibrant. Pressures and temperatures were then obtained using the diffraction pattern of the BN together with calibration curves determined for the electrical power used to heat up the sample.

On the basis of our measurements we confirm the results already obtained by Katayama et al. [3] at 1050 °C and 1 GPa. Examples of typical spectra in the two different liquid phases are reported in fig.2. From this kind of spectra we have determined additional points on the liquid-liquid transition line all the way up to 2000 °C and 0.3 GPa (see fig. 1) . In particular the slope of the transition line is negative, thus showing that the entropy of the high pressure polymeric phase is larger than that low pressure molecular phase .

References

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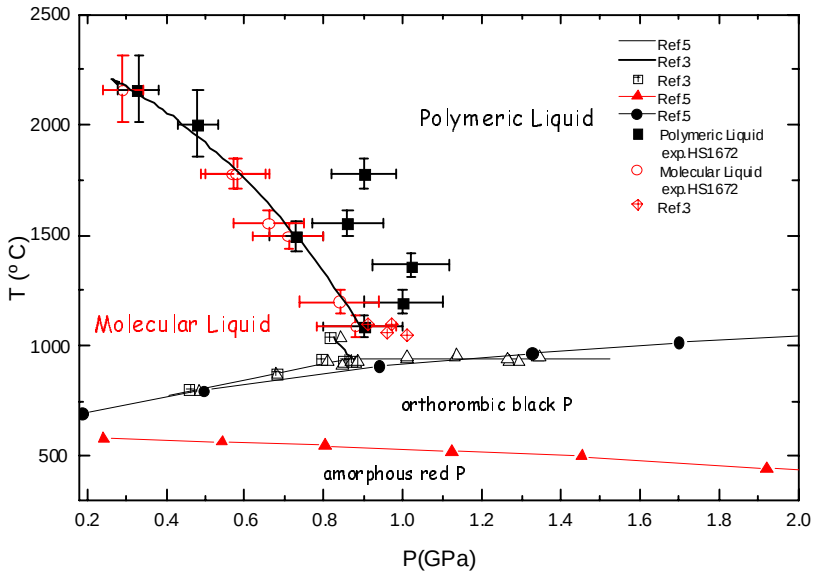

Figure.1: Phosphorus phase diagram; marks with errorbars are our esperimental data.

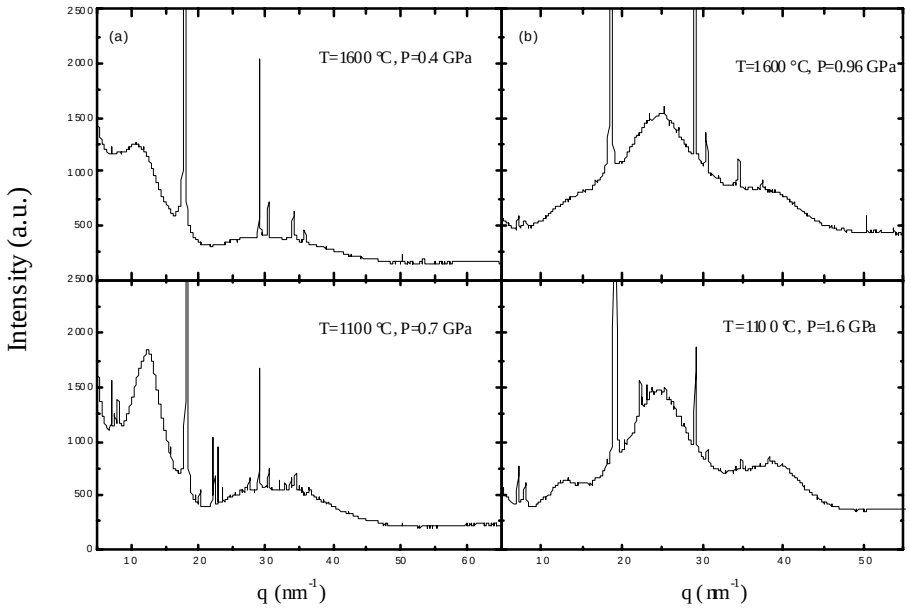

Figure 2: Temperature evolution of diffraction pattern of the molecular (a) and polymeric liquid (b).