Liquid-liquid transition in phosphorus: Temperature evolution of the density jump and search for a liquid-liquid critical point

Abstract of the proposal

Two or more liquid states may exist even for single-component substances, and the transition between these states is called a liquid-liquid transition (LLT). The LLT of phosphorus (P) has attracted considerable attention since the direct experimental observation of two fluid phases. However, several important questions remain, such as the variation of the density jump along the transition line, and whether the latter ends at a critical point (LLCP). Moreover, there are at present large discrepancies between different experimental measurements of the melting line, especially in the region of the LLT. The aim of this proposal is to explore the HP-HT phase diagram of P at pressure up to 4 GPa and temperature up to 3000 K, employing X-ray powder diffraction and absorption, to determine precisely the density change across the LLT and melting transitions, and extend the measurement of the LLT to higher T to check for the existence of a LLCP.

During the beamtime, the first part was focused on performing a dynamic experiment where black phosphorus is heated up at a very fast pace, at room pressure. Black phosphorus is known to spontaneously decompose starting from 700 K at room pressure due to mechanical instability. The objective here was to increase the temperature very quickly, while performing X-ray diffraction at a very rapid pace to try to catch the molten state of phosphorus before decomposition occurs. Melting at room pressure has never been experimentally observed in the literature but is estimated between 800 and 900 K. Two runs were performed, in Paris-Edinburgh press at ID27 at 33 keV and 20 keV respectively. The two runs were performed using the newly implemented pink beam at ID27, increasing the flux measured during the acquisition by several orders of magnitude. This mode was essential for obtaining good quality diffraction patterns during the dynamic experiment. Temperature was increased from 300 K to 1800 K in the span of 1 minute, and diffraction pattern were collected every 30 ms. Experiment was a success and the data are still being analyzed.

Second part of the beamtime was dedicated to the study of black phosphorus melt under high pressure and high temperature, still in the Paris-Edinburgh press, with the objective of studying the reversibility of the melt. Several runs were performed, where the melting curve of black phosphorus was crossed in the low-pressure regime, where the solid transits into a molecular liquid, and in the high-pressure where the solid transits into a polymeric liquid. These runs also enabled adding experimental point on the melting curve of black phosphorus.

Lastly, we used the remaining beamtime available to perform x-ray diffraction and x-ray absorption of liquid sulfur at high pressure and high temperature using the Paris-Edinburgh press. The objective was to measure the density of the liquid at several isotherms from 500 K to 1100 K. The density is a key parameter when one wants to obtain PDF from diffraction patterns of liquids. These runs were performed in prevision of the future beamtime HC 4875 by the same proposers. A great amount of density measurements where performed at 500 K, 650 K and 800 K using the same sample, but a contamination of the sample with NaCl was noticed during the 800 K isotherm, invalidating the measures for this specific isotherm. Another assembly was loaded and an additional isotherm was performed at 1050 K where a critical point has been evidenced in the liquid state in a previous work. During this run, the existence of the critical point in liquid sulfur has been reverified with the observation of several anomalies of the density and of the diffraction pattern of the liquid.