

Structural changes in crystalline, glassy and liquid Phosphorus selenide materials under temperature and pressure using EXAFS.

The aim of this experiment was to undertake EXAFS measurements at the Se K edge of P_4Se_3 in various states. The room temperature, ambient pressure, crystalline form of this material is a periodic arrangement of P_4Se_3 molecular units. In this experiment we wished to investigate how this structure changed with pressure and temperature in both the liquid and solid phases. In particular we were looking for evidence of the break-up of these molecules and possible liquid-liquid phase transitions that may occur. All the measurements were made using a Paris-Edinburgh cell on the BM29 spectrometer. In our first measurement we investigated the EXAFS signal as a function of temperature at a pressure of just above ambient (~ 0.2 GPa). A clear change in the EXAFS signal was observed as the sample was heated. This corresponded well with its known melting temperature. On cooling to room temperature we did not recover the original EXAFS signal suggesting that we had recovered a different structural polymorph (possibly a glassy state). Figure 1 shows the EXAFS for the original material (red line), the molten material (green line) and the room temperature sample after heating and cooling to room temperature (blue line).

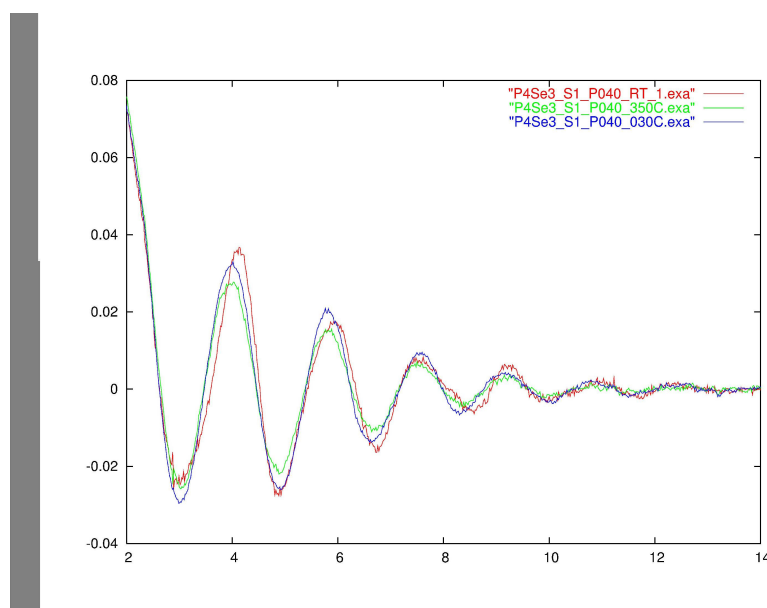


Figure 1.

When this room temperature phase was pressurised to 5 GPa there was little discernible change in the EXAFS signal suggesting there was little structure change taking place. Figure 2 shows the EXAFS signal as the sample at high pressure (4.5 GPa, red line) was heated above its melting point. The change in structure as the sample melts is clearly observable (green curve to blue curve). Again, when cooling the high temperature liquid sample (purple curve) to room temperature we saw no discernible change in the EXAFS signal (pale blue curve) suggesting we had probably produced an amorphous sample that was different to the original phase. The sample was then depressurised to near ambient pressure and cycled again through the solid – liquid – solid phases. Figure 3 shows a comparison of the original EXAFS of the re-solidified sample at room temperature and the re-solidified sample at room temperature after it had been through the high pressure cycles. It is evident that we have obtained the original phase despite the observation of the meta-stable phases at

high pressures. For the rest of the experiment we investigated this meta-stability for a wider range of pressures. In addition we investigated the high pressure changes of an as prepared sample (without melting it at ambient pressure). The EXAFS data is currently being properly analysed along with some high pressure diffraction data that we subsequently collected.

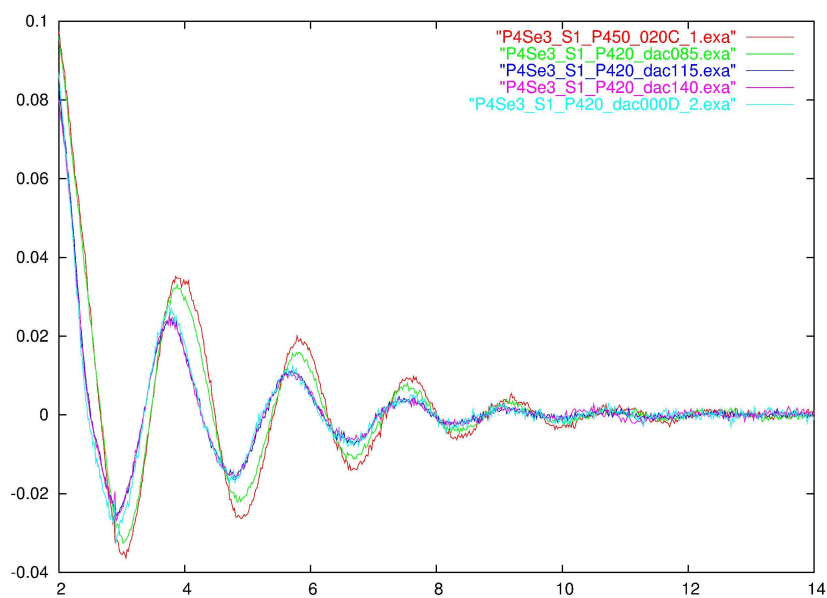


Figure 2.

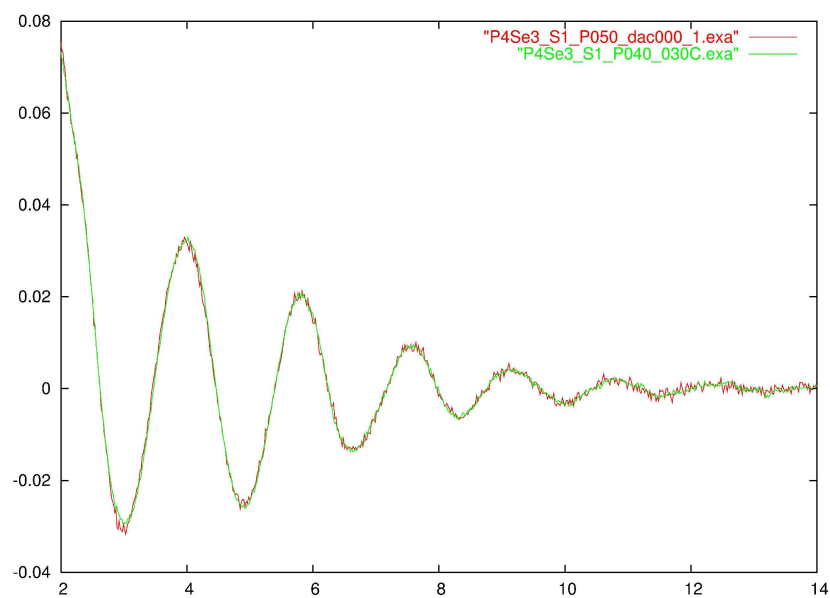


Figure 3