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Report:

Phase transition studies of the large family of compounds AM_2O_7 are of a significant interest for two major reasons. The first is the very low or negative thermal expansion of the high temperature (HT) cubic modification. This phase has $Pa\bar{3}$ symmetry and unit cell parameter $a_c \sim 8.7$ Å. The second, is the existence of commensurate and incommensurate modulated cubic low temperature (LT) modifications with unit cell parameter $a'_c = 3 \times a_c$. Experimental evidence of an incommensurate-commensurate phase transition for the LT cubic modification were reported in ZrP_2O_7 using electron diffraction work. On the other hand, the structural investigation of ZrP_2O_7 based on neutron powder diffraction points to the existence of a cubic LT modification similar to that observed in ZrV_2O_7 over a wide range of temperature from 20°C to 290°C. All these data point to an elaborate system of phase transitions close to the LT modification. The most interesting phase transformations relate to ZrP_2O_7 and this has been the subject of our present study.

Taken into account our earlier powder diffraction results as well as the published data, we can expect at least three phase transitions for ZrP_2O_7 at different temperatures. The first transition from the HT (space group $Pa\bar{3}$, $a_c = 8.72$ Å) cubic modification is to an LT cubic modification with commensurate modulated structure (space group $Pa\bar{3}$, $a'_c = 3 \times a_c \sim 24.72$ Å). A second phase transition is presumed to take place from the LT cubic commensurate structure to an incommensurate one. The third one should take place between the LT cubic modification (with commensurate or incommensurate modulated structure) and the commensurate modulated orthorhombic modification observed at room temperature.

We have carried out a series of data collections with the MAR345 area detector above room temperature using high quality single crystals. Fig 1 shows images collected during a thermal cycle from room temperature to above the HT cubic modification and lowered again to room temperature. The images reveal the appearance of many additional reflection in the diffraction pattern, suggesting the presence of a modulated phase.

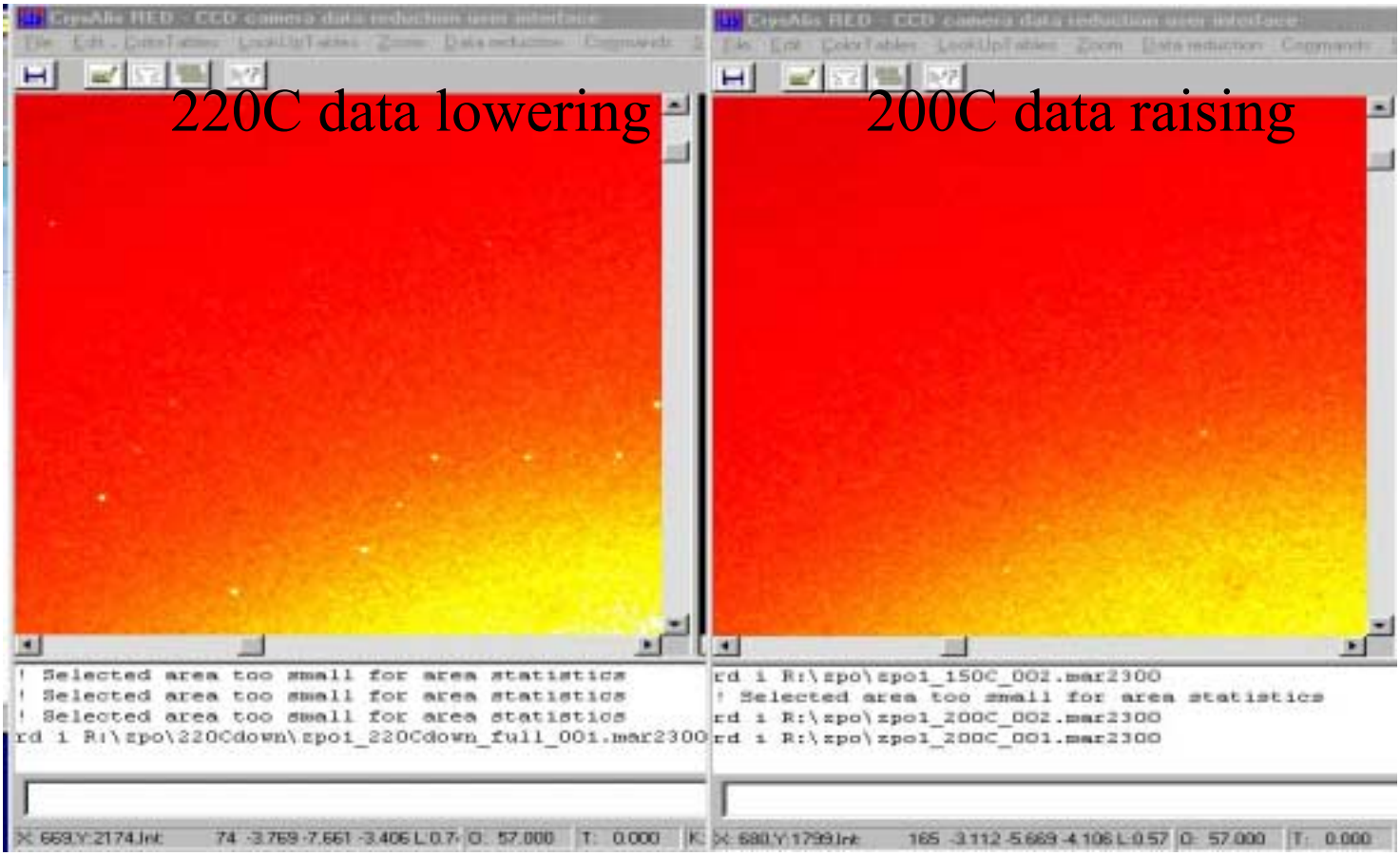

Fig 1 Rotation images of single crystal diffraction patterns of ZrP_2O_7 showing the effects of a thermal cycle through the high temperature phase transition

The room temperature diffraction pattern of ZrP_2O_7 can be indexed to a slighlty distorted orthorhombic cell with lattice constants of 24.739Å, 24.718Å and 24.743Å. After thermally cycling through the high temperature cubic phase, we were able to index the above diffraction pattern to a tetragonal cell with lattice a,b = 35.07Å and c = 24.805Å. The appearance of this type of supercell allows us to index all reflections without recourse to an incommensurate modulation, of the type observed with electron diffraction. Further analysis of the data is in progress.

In summary, it would seem that many different structural modifications can occur in ZrP_2O_7 close to the orthorhombic-to-cubic phase transition. Which of these subtle moldulation actally appears depends upon the thermal history of the sample. The crystals used in this experiment were prepared by hydrothermal synthesis below the transition temperature. This could account for their excellent crystalline quality, but may also explain some of the differences between our results and the behaviour reported elswhere in the literature. DSC and powder diffraction measurements carried out on our samples reveal that even the transition temperature itself is significantly lower (by about 20ºC) compared with the literature value of 290ºC. It is clear that this interesting family of compounds of type AM_2O_7 offer a complex and challenging materials problem, and that further measurements will probably be necessary before we can account for various structural modifications of ZrP_2O_7.