ESRF	**Experiment title:** Structural phase transitions in Chevrel phase superconductors	**Experiment number**: 1-01-287
Beamline: BM1B	**Date of experiment**: from: 24.11.2002 to: 26.11.2002	**Date of report**: 25 March 2003
Shifts: 6	**Local contact(s)**: W van Beek	*Received at ESRF:*

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A structural transition from high temperature rhombohedral to triclinic in $PbMo_6S_8$ has been reported by Jorgensen and Hinks (1985) using neutron powder diffraction. Synchrotron data published by François *et al.* (1994) show a much smaller triclinic distortion, which suggests that sample preparation affects the low temperature transformation. Materials with the highest T_c are those metallic oxygen-free compounds adjacent to a structural instability. There may be in a mixed-phase region consisting both of a superconducting rhombohedral phase and an insulating triclinic phase. All structural observations point to the fact that high T_c's in the Chevrel phases are related in a systematic (but poorly understood) fashion to the lattice instability which drives the triclinic phase transition. Considerable effort has in the meanwhile gone into the preparation of high purity materials, which has also allowed the T_c to be pushed higher. Very careful exclusion of oxygen and water during material fabrication is essential to avoid oxygen substituting for sulphur in the Mo_6S_8 cluster. The $PbMo_6S_8$ powder samples used in our experiment have the highest reported superconducting transition temperature of 15.3K. We therefore undertook a remeasurement of the temperature-dependent powder diffraction patterns in order to provide some clarification of this complex behviour using samples of the best quality available today. We have carried out measurements of the powder patterns of a rotating capillary sample of $PbMo_6S_8$ contained in a Janos He-crystat on beamline BM1B of the Swiss-Norwegian Beamline. The results of a full-pattern Rietveld fit to the room temperature data measured at a wavelength of 0.48562Å is shown in Fig 1. Impurities of Mo (5.58 wt. %) and Pb (0.67 wt. %) were found, and these phases were included in the Rietveld fit. Low temperature powder data at 14K, 50K, 100K, 150K and 180K were then collected at a wavelength of 0.68957Å. Full pattern refinements were carried out at each temperature using the TOPAS Rietveld software package (Bruker AXS, 2000).

We found no evidence at any temperature of the appearance of the triclinic phase observed in earlier neutron and synchrotron powder diffraction measurements. We cannot exclude the possibility that the absence of the triclinic phase is due to the particular thermal path chosen in our data collection (ie we first measured at 14K, followed by an increase through the series of temperatures mentioned above). However, we believe that the more likely explanation is that the high degree of order in our $PbMo_6S_8$ phase has suppressed

the triclinic transformation at low temperature. Since it is known that it is the rhombohedral phase which is responsible for the superconducting behaviour in $PbMo_6S_8$, then our present results are consistent with the high Tc values observed with our samples.

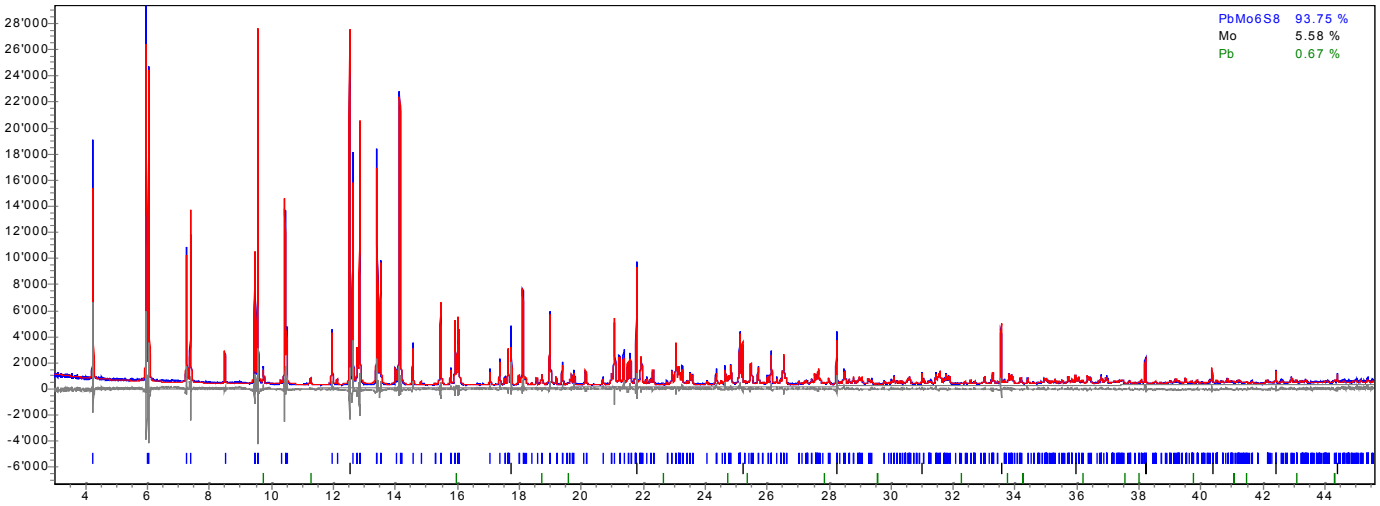

Fig 1 : Rietveld plot of $PbMo_6S_8$ at room temperature (R_{wp} = 12.8 % , χ^2 = 8.0).

The hexagonal lattice parameters (Fig. 2) vary smoothly with temperature, and the results for our single-phase sample are entirely consistent with the previous synchrotron results on the rhombohedral phase of the two-phase material. As the temperature decreases, c_{hex} goes through a shallow minimum as observed earlier. We also show in Fig 3 the displacement parameters for the Pb, Mo and S atoms. The large Pb displacement parameters at room temperature are not unusual in these Chevrel phase materials, and there is again a smooth and almost linear reduction down to 14K. It is interesting to note that our data do *not* show the dramatic increase in peak width on cooling observed in the previous synchrotron data, again indicating that structural instabilities and strain at low temperatures were more pronounced in the earlier samples.

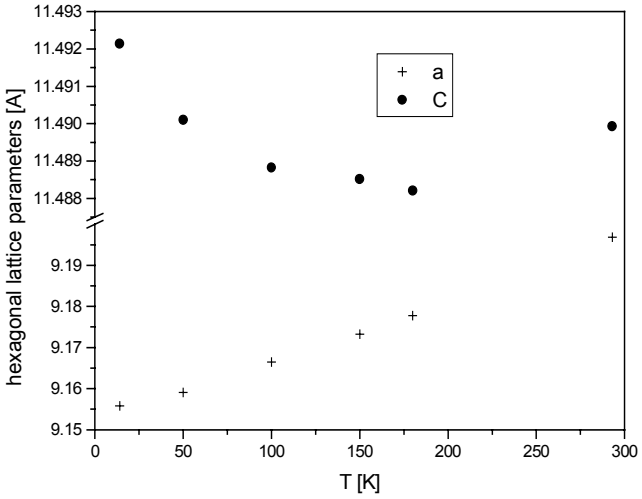

Fig 2 : Lattice parameters as a function of temperature.

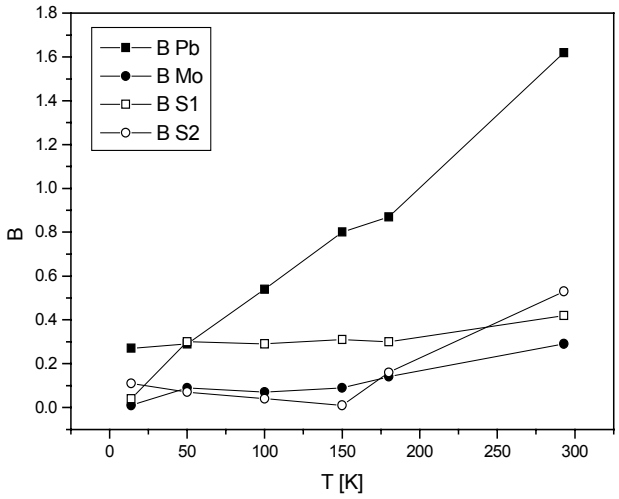

Fig 3 : Displacement parameters as a function of temperature.

The authors would like to thank W van Beek and H Emerich of the SNBL staff for their heroic efforts to repair the Janos cryostat, which allowed us to collect high quality data over the full temperature range.

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François, M., Yvon, K., Cattani, D., Decroux, M., Chevrel, R., Sergent, M., Boudjada, S. and Wroblewski, Th., *J. Appl. Phys.* **75**(1) (1994) 423.

TOPAS, *General profile and structure analysis software for powder diffraction data*, Version 3. beta, Bruker AXS, Karlsruhe 2000.