ESRF	**Experiment title: X-ray powder investigation of the phase Bi-III**	**Experiment number**: HS-1413
Beamline: ID 9	**Date of experiment**: from: 25th of May 2001 to: 29th of May 2001	**Date of report**: 26th of August 2001
Shifts: 12	**Local contact(s)**: M Hanfland	*Received at ESRF:*

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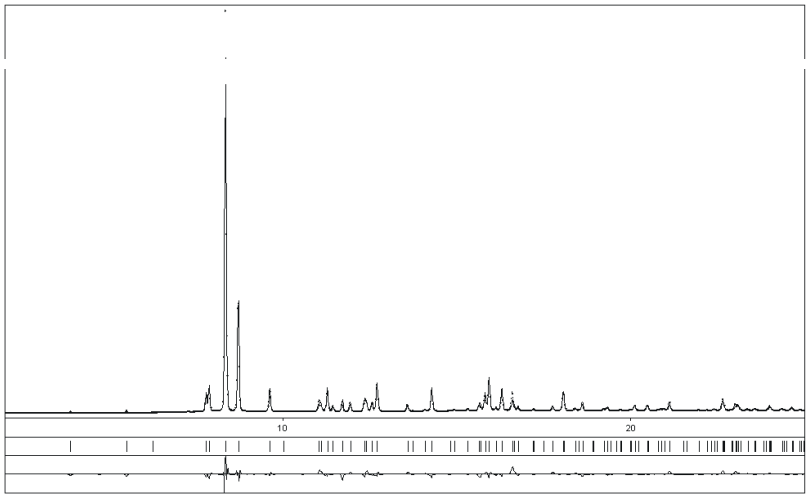
Report:

We have measured highly resolved x-ray powder diffraction data of the tetragonal high-pressure modification of Bi. Due a shortage of liquid He during our experiment we could measure for three out of four days diffraction data at ambient temperature only. At the last day, one set of low-temperature measurements on Bi was performed by means of a cryostat.



In accordance with a parallelly, but independently performed experimental work [1], our x-ray powder diffraction diagrams reveal that Bi realises a modulated element structure at pressures above 3 GPa. Since available Rietveld refinement packages could not properly treat modulated structures in more than three dimensions, an available program package was substantially expanded to allow full profile refinemets in four up to six dimensions to enable a physically correct description of modulated crystal structures in general and Bi in particular. On the basis of the ambient temperature high pressure data of the experiment, crystallographic models of the modulation have been developed and tested by full profile refinements. The results obtained for the best four dimensional model is shown in the

The symmetry of the crystal structure is assigned to the super group *I* 422:*I* 422 with the lattice parameters a_1 = 864.01(4) pm, c_1 = 422.74(4) pm and $a_2 = a_1$, c_2 = 322.45 pm with c_1/c_2 = 1.311. This means that two types of Bi-atoms build up crystal lattices which realize the same tetragonal lattice parameters *a*, but different indendity periods in direction of *c*. The first type of Bi-atoms on position *x/a* = 0.1551(1), *y/b* = *x* + 0.5, *z/c* = 0.25 *and t/d* = 0.25 (the fourth coordinate due the use of a four dimensional super group) builds up a framework, The resulting channels are occupied by a second type of Bi-atoms on position *x/a* = 0, *y/b* = 0, *z/c* = 0 *and t/d* = 0 (again four coordinates, see above). This means that the atoms within the channels have a shorter repeat unit than those of the framework. The non-commensurate character of the crstal structure results in a a non-integer number of atoms per “formula unit” (which needs to be defined on the basis of one of the two unit cells). Further refinements of data sets measured at different pressures and/or temperatures are in progress.

References

[1] M. I. McMahon et al., Phys. Rev. Lett. **85**, 4896 (2000).