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We performed an in-situ angle dispersive X-ray diffraction study of iron up to 2500 K between 30 and 100 GPa in a YAG laser-heated diamond-anvil cell at the ID30 beamline. In comparison with previous studies on iron at high-pressures, we significantly improved both resolution and reliability of the diffraction peak intensities due to the combination of monochromatic X-radiation and image-plate detector. It thus allowed the first full structural Rietveld-refinement under these extreme conditions of pressure and temperature. The space group was determined to be Pbcm, and the atomic topology is close to that of ε-hcp iron. The structure is also closely related to the lower pressure high-temperature polymorph y-iron (fcc). Orthorhombic cell parameters are strongly dependent on pressure and temperature. The high-temperature polymorph appears unquenchable at moderate pressures. However, the X-ray diffraction spectra of the back-transformed e-phase show some anomalies which explain ambiguities in previously reported structure determinations.

We used a DAC with large optical aperture mounted with diamond anvils with 0 300 μm culets. Rhenium gaskets were preindented to a thickness of 40 μm and drilled to a diameter of 80 μm. As samples we used a 5 μm thick iron foil mounted between two 15-20 μm thick pure Al_2O_3 (or SiO_2) polycrystalline discs. Samples were heated up to 2350 K using a multi-mode regulated YAG Laser. Corundum was observed to be chemically inert up to the maximum pressure achieved in this study. Since the iron samples in our experiments were always very thin (max. 5 pm), we assume the axial temperature gradient along the X-ray path to be negligible. This reasoning is supported by the experimental evidence of diffraction peak widths during laser-heating (ca. 0.07 deg 28) which are comparable to those of ambient condition Si-standard patterns (0.02 - 0.05 deg 28). Therefore, artifacts due to pressure or temperature gradient (spatial or temporal) are excluded.

Angle dispersive X-ray diffraction measurements were performed on the ID30 high-pressure beamline. The X-ray beam of wavelength 0.4245 Å was selected from an undulator using a channel cut Si(111) monochromator. The monochromatic beam was focused using two single-electrode bimorph mirrors to FWHM of about 15*8 μm². This is a convenient size to minimize the temperature gradient in the X-ray spot and avoid contamination of the recorded patterns with diffraction from gasket material. Full reciprocal angle data were collected during 5 to IO minutes using image plates located at 400 mm from the sample. 2-d patterns were then integrated after geometric corrections using the program Fit2d.

In a previous report (HS129). we have shown evidences for a new high-temperature iron polymorph at pressures between 30 and 60 GPa. During the laser heating, we observed significant modification of the diffraction pattern, with appearing of new lines and disappering of the 002 hcp-line. The new peaks also not compatible with either ε or y-iron. Reaction with the pressure transmitting medium or iron oxidation is also excluded since the new features are found unquenchable. All diffraction lines observed at high temperature can be explained by a doubling of the e-lattice in its basal (a,b) plane. It is one of the most common distortion observed for hcp lattices and produces an orthorhombic unit cell.

A spectrum which was recorded during laser heating at 2125 (70) K under a pressure of 44.6 GPa was chosen for a full structure refinement. To determine possible space groups, we checked the indexed pattern for systematic absences. Also, we deduced the symmetry elements for orthorhombic Fe using atomic positions compatible with the simple hcp-distortion described above. This analysis yielded unambiguously space group Pbcm, which therefore was used in LeBail and Rietveld refinements (using the program package GSAS). The Fe atom refined to a 12 coordinated site similar to the Fe environment in epsilon-Fe. However, unlike in the hcp structure of epsilon-Fe where we find a 2 x 6 surrounding, the environment in the new orthorhombic phase is distorted from a perfect hcp arrangement to give 6 x 2 bonds. The structure is thus very closely related to the hcp structure and can be described as a simple shift of the hcp-AB layers relative to each other parallel (1lO)-hex by roughly 0.3 Å. This very simple transformation mechanism, together with the quality of the Rietveld fit and the cell parameter refinement, leave little doubt about the correctness of the proposed model.

To avoid any artifact related to phase transformation in (or with) corundum, we checked the occurring of the orthorhombic lattice in a SiO_2 pressure transmitting medium. We present in figure 1 results obtained on iron loaded at about 100 GPa in a SiO_2 pressure transmitting medium. At this pressure, iron was not sufficiently insulated from the diamonds, and it was difficult to produce in-situ X-ray spectra during stable laser heating. The top spectrum is quenched after the laser heating up to about 2500 K. It clearly shows the doubling of the 100 and 101 lines of the hcp-lattice, which again evidences a phase transformation for iron at high pressure and temperature. All experimental lines are perfectly explained by an orthorhombic lattice similar to that previously observed. In contrast with results obtained at moderate pressures, the structure of the high-temperature polymorph is now preserved after the quench. At this pressure, the orthorhombic lattice is found about 1% denser than e-iron, with values of 10.76 and 10.85 10^3 kg/m^3 respectively.

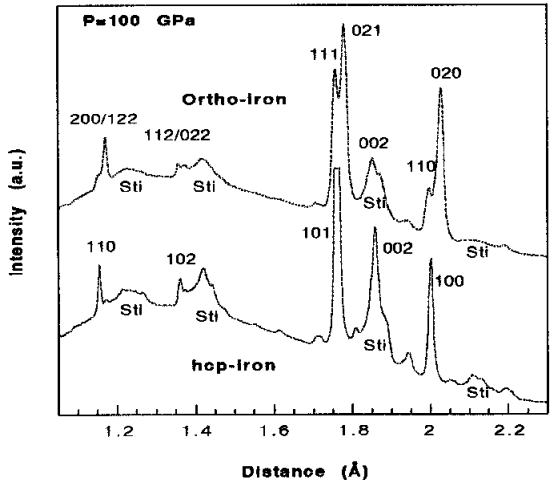

Figure 1: Diffraction spectra of hcp and orthorhombic-iron recorded at 100 GPa in a SiO2 pressure transmitting medium (quoted Sti). The 101 Bragg line of e-iron (bottom spectrum) was truncated for clarity reason (intensity up to 20000 cps). Top spectrum was recorded after laser heating at about 2500 K. It clearly shows doubling of the 100 and 101 peaks of e-iron, sign of phase transformation. All diffraction features are interpreted by the occurring of the orthorhombic lattice.

References:

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