Relationship between structural variation and spin transition of hcp-Fe under high pressures and high temperatures

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1 Introduction
The high-pressure spin state of Fe is key to the understanding of magnetic, electronic, and structural properties of 3d electrons and of the structure of the Earth’s or other planets’ interiors. It is known from experiments that the pressure-induced transition from body-centered cubic (bcc) to hexagonal close-packed (hcp) is accompanied by a simultaneous magnetic transition from the ferromagnetic to nonmagnetic states, because Mössbauer effect experiments have never detected the presence of a hyperfine magnetic field in the hcp structure. However, some experimental observations of the structural variation, x-ray emission spectroscopy, or Raman mode splitting indicated that hcp-Fe could have remnant magnetism. According to the structural variation, first-principles calculations predicted that the c/a ratio of the hcp structure in nonmagnetic Fe increases as the pressure increases. In contrast, recent experimental observations showed that the c/a ratio of hcp-Fe decreased with increasing pressure, indicating that hcp-Fe has the antiferromagnetic state. The magnetic transition from the antiferromagnetic to the nonmagnetic state occur, and is accompanied by spin collapse at ~60 GPa. This spin transition from the high- to the low-spin states was predicted by the first-principles calculations and was confirmed from the structural variation using the high-pressure experiments. In this study, we investigated the pressure-induced spin transition at high temperatures using the structural variation of hcp-Fe.

2 Experiment
The high-pressure and high-temperature X-ray diffraction experiments were performed using a laser-heated diamond anvil cell high-pressure apparatus. Fe powder was loaded into a 30-100 μm diameter holes drilled into a rhodium gasket, which was preindented to a thickness of 20-70 μm. The sample was sandwiched between pellets of NaCl powder to reduce any residual nonhydrostatic stresses. The sample was probed using angle-dispersive X-ray diffraction, employing the NE1A synchrotron beamline at KEK. The angle-dispersive X-ray diffraction patterns were obtained on an image plate system. The spectra were collected for about 5-10 min. The observed intensities on the imaging plates were integrated as a function of 2θ using the ESRF Fit2d software code to obtain conventional, one-dimensional diffraction profiles.

3 Results and Discussion
The structural variation in the c/a ratio of hcp-Fe was investigated up to 180 GPa and 2000 K. Prior to laser heating, we compressed the α-Fe starting material to the desired pressure at room temperature, and found that it transformed to the hcp structure. The room-temperature data were in general agreement with those reported in our previous study. The c/a ratio decreased from 1.61 to 1.60 as the pressure increased to 60 GPa, and remained approximately constant at 1.60 after that. At high temperatures, the c/a ratio decreased at 2000 K with increasing pressure. At pressures above 140 GPa, the ratio deviated noticeably from the decreasing trend. These results show that the spin transition of Fe occurred at ~140 GPa at 2000 K [1]. The gradient of dP/dT of the spin transition boundary was positive. The boundary shown in Fig. 1 is represented by the linear equation:

\[ P \text{ (GPa)} = 51 + 0.045 \times T \text{ (K)}. \]

Fig. 1: Schematic phase diagram of iron at high pressures and temperatures. The dashed line represents the boundary between the high-spin (HS) and low-spin (LS) states in hcp-Fe.

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References

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