Absence of β-iron up to 44 GPa and 2100 K: *In situ* X-ray Observation of Iron using Kawai-type Apparatus Equipped with Sintered Diamond

The properties and states of iron at high-P/T have been extensively studied by Earth scientists, leading them to understand Earth's core that is composed of iron. By the 1970s, four polymorphs of iron, namely α (bcc), γ (fcc), ε (hcp) and δ (bcc), were known. In the 1990s, however, based on experiments using a diamond anvil cell (DAC), a fifth phase called β was claimed to be present under conditions typically higher than 35 GPa and 1500 K. If the β phase really does exist, we might replace ε-iron as the most likely phase to constitute Earth's inner core with β phase. However, both the existence and structure of β phase are controversial; two different crystal structures have been proposed for β (double-hcp (dhcp) [1] and orthorhombic [2]), while the absence of β up to 84 GPa and 3500 K has also been reported [3]. So far, exploration of β-iron has been impossible when using an eight cubic anvil system (Kawai-type apparatus) equipped with tungsten carbide, because the maximum attainable pressure was limited to less than 30 GPa. Nevertheless, by adopting sintered diamond (SD) as the anvil material [4], it has become possible to generate pressure exceeding 40 GPa by using the Kawai-type apparatus. Under these circumstances, we studied the phase relations of iron using a Kawai-type apparatus equipped with SD, whose geometry aids considerably in providing a quasi-hydrostatic environment for the sample.

The sample consisted of fine iron powder mixed with MgO in a 1:1 weight ratio to suppress grain growth of the iron at high temperature. The sample was put into a semi-sintered MgO sleeve (Fig. 1) that served as the pressure standard. High pressure was achieved by compressing the octahedral specimen assembly (Fig. 1) in a Kawai-type apparatus using "SPEED 1500" press installed at beamline **BL04B1** [5]. Energy dispersive X-ray diffraction profiles for both the sample and the MgO standard were collected along temperature cycling at fixed press loads of 660 and 800 tons at up to 1850 and 2100 K, respectively. Pressure was determined from the measured unit cell volume of the MgO pressure standard.

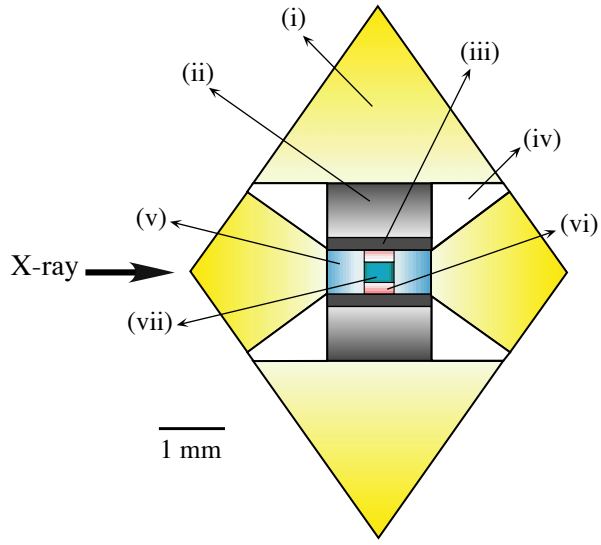

*Fig. 1. A cross-section of the octahedral specimen assembly. **(i)** Pressure medium ($MgO+5wt\%\ Cr_2O_3$), **(ii)** Thermal insulation sleeve ($LaCrO_3$), **(iii)** Cylindrical heater (Re), **(iv)** Wedge-shaped electrode (Cu), **(v)** Diamond powder, **(vi)** Sample sleeve (pressure standard) (MgO), **(vii)** Sample (MgO+Fe). A thermocouple (W97/Re3-W75/Re25, not shown) is placed perpendicular to the paper and in contact with the outer surface of the heater. The incident X-ray beam (arrow) was collimated to 0.05 mm horizontally and 0.1 mm vertically, which made it possible for us to acquire diffraction patterns from the sample and the pressure standard independently.*

Several diffraction profiles of the sample are reproduced in Fig. 2. In the first cycle at 660 tons, iron initially assumed the ε phase at 37 GPa and 300 K, and it persisted at 1370 K and 38.4 GPa (Fig. 2(a)) upon heating. Diffraction peaks of γ appeared at 1450 K and 38.4 GPa and intensified simultaneously with reduction of ε as the temperature increased to 1850 K and 39.2 GPa (Fig. 2(b)). A substantial amount of ε still survived at 1850 K due to the temperature gradient through the sample. Upon cooling, enhancement of peaks for ε was noticed with a simultaneous reduction of γ at 1350 K and 37.1 GPa, but a certain amount of the γ phase remained even after quenching to 300 K and 34 GPa (Fig. 2(c)). In the second cycle at 800 tons, no change was observed up to 1700 K. At 1750 K and 41.9 GPa, the growth of γ was recognized together with a reduction of ε, which was rapid with increasing temperature up to 2100 K and 44 GPa (Fig. 2(d)). The mutual growth relations of the γ and ε phases corresponding to heating and cooling completely deny the presence of any phase between the stability fields of γ and ε up to 44 GPa. Moreover, we could not find any characteristic

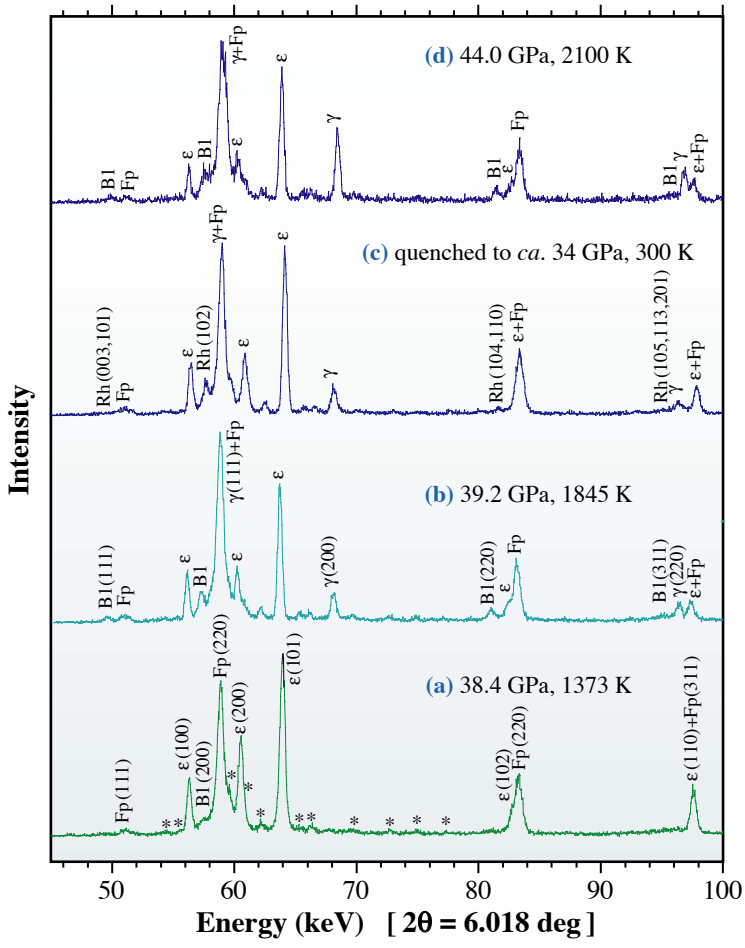

*Fig. 2. Examples of diffraction profiles of the sample. **(a)**, **(b)**, and **(c)** are on the first cycle at 660 tons and **(d)** is on the second cycle at 800 tons (see text). ε: ε-iron, γ: γ-iron, Fp: MgO mixed with the iron sample, B1; (Fe, Mg)O with the B1 structure, Rh: (Fe, Mg)O with the rhombohedral structure, asterisk: Fe_3C. Numbers in parentheses are Miller indices. In addition to iron, diffraction peaks of MgO (mixed with the iron) were also observed.*

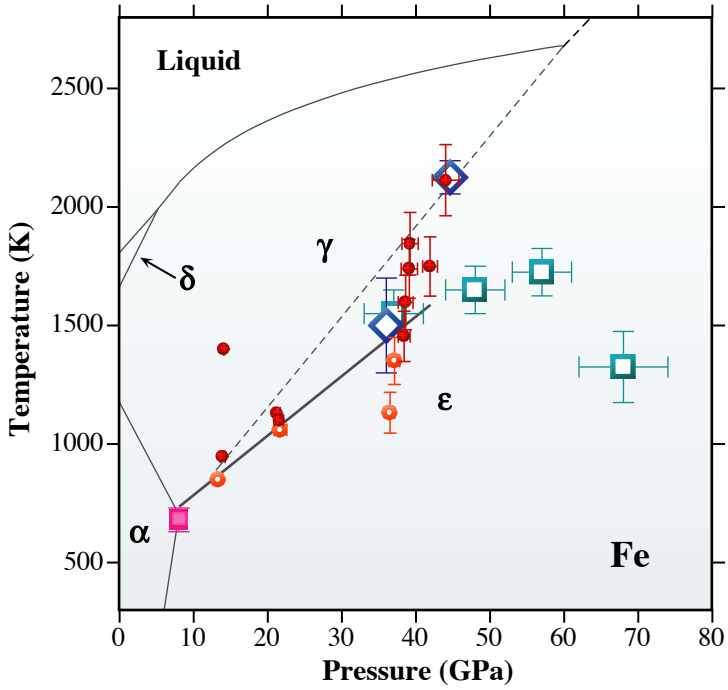

Fig. 3. Summary of the experimental results. The solid and open circles denote the conditions at which the growth of γ and ε phases were observed, respectively. The thick line shows the ε-γ boundary constrained in the present study. The open squares and diamonds are the conditions under which β phases of dhcp and orthorhombic structures were reported, respectively [1, 2]. The solid square indicates α-γ-ε triple point [6]. The dashed lines are the previously reported melting curve and ε-γ boundary of iron [3]. Bars indicate error in temperature and pressure. Note that we observed growth of the γ phase at the P/T conditions where β phase has been reported as a stable phase in previous studies [1, 2].

peaks of dhcp- and orthorhombic iron in any of the diffraction profiles. All the identified phases of iron are plotted on a P/T space along with selected previous results (Fig. 3). As the β phase(s) has been observed in DAC without using pressure medium [1] or using high-strength pressure media [2], strong uniaxial stress on the sample might cause an incomplete phase transition from ε to a "metastable" β phase.

Atsushi Kubo[a], Eiji Ito[a] and Kenichi Funakoshi[b]

(a) Okayama University
(b) SPring-8 / JASRI

E-mail: akubo@misasa.okayama-u.ac.jp

References

[1] S. K. Saxena and L. S. Dubrovinsky, Am. Mineral. **85** (2000) 372.
[2] D. Andrault *et al*., Am. Mineral. **85** (2000) 364.
[3] G. Shen *et al*., Geophys. Res. Lett. **25** (1998) 373.
[4] E. Ito *et al*., Geophys. Res. Lett. **25** (1998) 821.
[5] W. Utsumi *et al*., Spec. Issue Rev. High Press. Sci. Technol. **6** (1997) 512.
[6] T. Uchida *et al*., J. Geophys. Res. **106** (2001) 21799.
[7] Atsushi Kubo, Eiji Ito, Tomoo Katsura, Toru Shinmei, Hitoshi Yamada, Osamu Nishikawa, Maoshuang Song and Kenichi Funakoshi, Geophys. Res. Lett. **30** (2003) 1126.