EARTH & PLANETARY SCIENCE

High-pressure B2 Phase of FeS: New High-pressure Polymorph under the Earth's Core Conditions

Properties of FeS under high pressure have been of great interest in both condensed matter physics and Earth and Planetary science. Since considerable amount of sulfur is possibly incorporated in iron-rich Earth's core (e.g. [1]), pressure-induced structural phase transitions in FeS have been extensively studied. Stoichiometric FeS has a NiAs-type (B8) related hexagonal structure (troilite, FeS I) at ambient condition. Previous experimental studies demonstrate a series of phase transitions with increasing pressure at room temperature; troilite transforms to a MnP-type structure (FeS II) above 3.4 GPa, and further to a monoclinic structure (FeS III) above 6.7 GPa. The structural change from FeS II to III involves magnetic disordering, spin transition of iron, and metal-semiconductor transition. FeS IV (hexagonal structure) and FeS V (NiAs-type structure) are also known to exist at high pressure and high temperature. Most recently, a phase transition to FeS VI was found to occur above 30 GPa and 1300 K. FeS thus exhibits a rich polymorphism, but all the known structures are closely related to the NiAs-type (B8) structure. Here we report the XRD measurements of FeS to 270 GPa and demonstrate the first experimental evidence for a structural phase transition to the B2 [2,3].

The synchrotron XRD experiments were conducted at high pressures using a diamond-anvil cell (DAC) at beamline **BL10XU**. We used synthesized polycrystalline sample of stoichiometric FeS (troilite) as the starting material. A rhenium gasket was pre-indented to 16-μm in thickness, and a hole (*ca.* 20-μm in diameter) was drilled in the center of the indentation as a sample chamber. A pelletized sample was placed between the pressure medium of MgO, which also served as thermal insulator and internal pressure standard. They were compressed by a pair of double-beveled 60-μm culet anvils up to 270 GPa. After each pressure increment, the sample was heated to less than 1300 K for *ca.* 30 minutes by a Nd:YLF laser. A monochromatic X-ray beam with a wavelength of *ca.* 0.4133 Å (30 keV) was collimated to 15- or 20-μm in diameter. Angle-dispersive X-ray diffraction (XRD) spectra were collected with an imaging plate (IP) detector or a charge coupled device (CCD) detector with a typical exposure time of 10 and 1 min, respectively. We obtained the XRD data only at room temperature.

We have collected the XRD data on FeS repeatedly with increasing pressure to 270 GPa. Below 215 GPa, the patterns were dominated by FeS VI. A new peak ($2\theta = 13.6°$) first appeared at 186 GPa

after heating approximately at 1300 K (Fig. 1). With further compression and heating at 198 and 215 GPa, the peak became more intense, although FeS VI was still dominant in these spectra. They further grew when the sample was re-pressurized at room temperature to 270 GPa. Upon subsequent heating, the pressure dropped to 233 GPa, and three other new peaks were found (Fig. 1), whereas the diffraction lines of FeS VI almost completely disappeared.

The four new peaks (Fig. 1) observed in the diffraction pattern obtained at 237 GPa can be indexed by a CsCl-type (B2) cubic unit-cell (a =
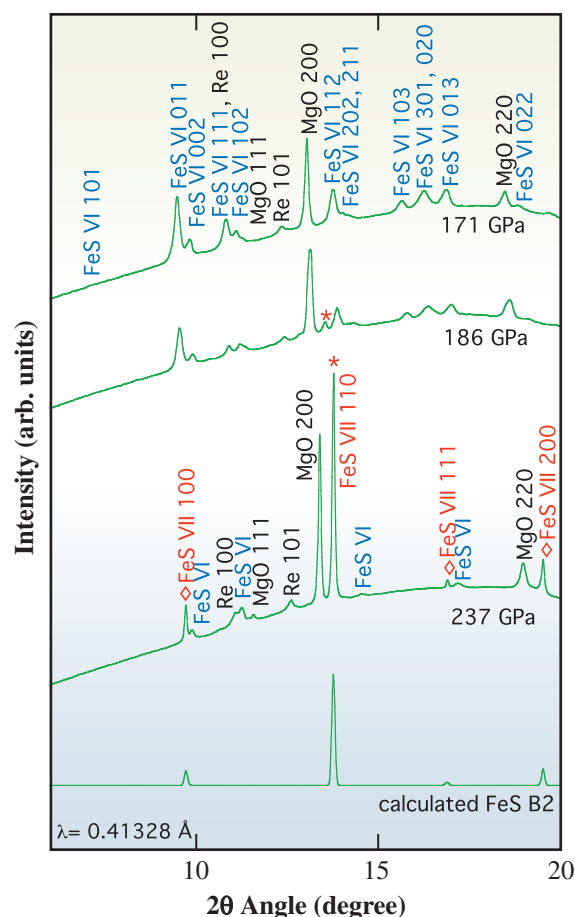

Fig. 1. XRD patterns of FeS at high pressure and room temperature. FeS VI was only observed with pressure medium (MgO) and gasket (Re) at 171 GPa. The most intense 110 peak of B2 phase first appeared at 186 GPa after heating at 1300 K. See text for details.

2.4339(3) Å). The peak intensities are also consistent with the CsCl-type structure (Fig. 1). Since the most intense 110 peak of B2 phase was not found below 171 GPa and first appeared at 186 GPa, the transition pressure from FeS VI to B2 phase (called FeS VII hereafter) was estimated to be around 180 GPa and 1300 K.

The phase transition from FeS VI to VII involves an increase in a coordination number from six to eight, and therefore a significant volume reduction is expected (Fig. 2). The volumes of FeS VII are remarkably smaller by 3.0% than those of FeS VI around 200 GPa. The Fe-S and Fe-Fe interatomic distances are 2.145 and 2.477 Å, respectively, in FeS VII at 186 GPa. These are even slightly longer than those in FeS VI; the Fe-S and Fe-Fe distances are 2.007 and 2.446 Å in average, respectively. On the other hand, the S-S distance is 2.477 Å in FeS VII, which is much shorter than that in FeS VI (2.819 Å).

Recently, a body-centered cubic (bcc) phase of $Fe_{0.9}Ni_{0.1}$ alloy was found at 225 GPa and 3400 K [4], suggesting that the Earth's inner core consists of the bcc phase. In addition, *ab initio* molecular dynamics calculations also demonstrated that the bcc phase is stabilized at the core conditions with Si or S impurity in iron. Since the bcc iron-rich Fe-Ni alloy and CsCl-type (B2) FeS adopt very similar structure, it is expected that sulfur is easily soluble in the Fe-rich bcc phase. The maximum solubility of sulfur in solid iron is limited to about 1 atomic % at 25 GPa [5] but would increase to more than 10 atomic % in bcc iron at inner core pressures (> 330 GPa), which is required to account for the seismologically observed density deficit from a pure iron at the inner core [1].
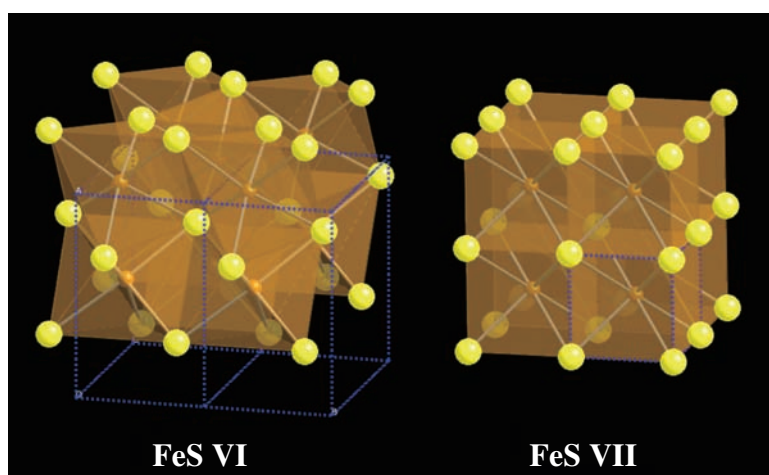

Fig. 2. Structure of FeS VI (left) and FeS VII (right). Yellow and orange spheres indicate sulfur (S) and iron (Fe), respectively. Blue dashed line indicates the unit cell. Coordination number of S to Fe increase from six in FeS VI to eight in FeS VII.

Nagayoshi Sata [a,*], Kei Hirose [b,a] and Hisao Kobayashi [c]

[a] Institute for Research on Earth Evolution,
  Japan Agency for Marine-Earth Science Technology
[b] Department of Earth and Planetary Sciences,
  Tokyo Institute of Technology
[c] Graduate School of Material Science, University of Hyogo

*E-mail: sata@jamstec.go.jp

References
[1] A. Jephcoat and P. Olson: Nature **325** (1987) 332.
[2] H. Ohfuji *et al.*: Phys. Chem. Minerals **34** (2007) 335.
[3] *N. Sata, H. Ohfuji, K. Hirose, H. Kobayashi, Y. Ohishi and N. Hirao: Am. Mineral. 93 (2008) 492.*
[4] L. Dubrovinsky *et al.*: Science **316** (2007) 1880.
[5] J. Li *et al.*: Earth Planet. Sci. Lett. **193** (2001) 509.