

High-Pressure Study of Iron Sulfide

The magnetic phase transition in iron sulfide, FeS, has been investigated using a high-pressure X-ray diffraction technique. The changes in cell parameters reveal that the spin state in iron atoms transforms from the high-spin to the low-spin state. According to our first-principles calculations, the change in the spin state observed in our experiments induces a magnetic transition from antiferromagnetic to non-magnetic state at high pressures. We propose a new phase diagram of iron sulfide including both structural and magnetic states.

The high-pressure behavior of iron sulfide, FeS, is of interest to planetary science because Fe-FeS alloy is thought to constitute the core of Mars based on geochemical arguments, because FeS has been found in many meteorites. In the case of the Earth, the density of the Earth's outer core is ~10% less than the density of pure iron, and there is also evidence that the Earth's inner core is less dense than pure iron. The difference in density indicates the possible presence of a low-atomic-weight component. As sulfur is one of the probable elements in the Earth's core, it is important to understand the phase stability and density of FeS at high pressures and high temperatures. The stable phase of FeS under ambient conditions is troilite (FeS I), a superstructure of the NiAs structure. Troilite transforms to an MnP-type structure (FeS II) at 3.4 GPa and to a monoclinic structure (FeS III) at 6.7 GPa as pressure increases at room temperature. At high temperatures, troilite transforms to a hexagonal NiAs-type structure (FeS IV) and to a simple NiAs-type structure (FeS V). In this study, we conducted laser-heated diamond anvil cell experiments combined with X-rays from a synchrotron radiation

source to acquire precise data on FeS phases at high pressures.

The starting material, FeS (purity >99%), was purchased from Kojundo Chemical Laboratory Corporation, Japan. X-ray diffraction analysis under ambient conditions revealed that the starting material had a troilite structure (FeS I, JCPDS 37-0477). The sample was ground to a fine powder and loaded into a diamond anvil cell with sodium chloride as the pressure transmitting medium. Sodium chloride was also used as an internal pressure calibrant [1]. Synchrotron X-ray diffraction experiments were performed at BL-13A [2]. The monochromatic X-ray beam was focused to less than 30 μm to minimize peak broadening caused by pressure gradients in the sample chamber. Angle-dispersive diffraction patterns were obtained on an imaging plate with exposure times of 10–20 min. The sample was heated using a multi-mode YAG laser to induce the observed phase transformation. After each change in pressure, the sample was heated to minimize the generation of pressure inhomogeneity in the sample.

In our experiments, the sample was gradually compressed to investigate the phase transition of FeS. At each pressure increment, the sample was heated to overcome transition kinetics. At 19 and 28 GPa, we observed FeS III with a monoclinic structure, which was in agreement with previous studies. When the pressure was increased to 43 GPa, however, the new high-pressure phase (FeS VI) appeared [3]. According to previous studies and our current findings, the phase boundary is likely to be at ~40 GPa. The diffraction peaks of FeS VI were reasonably indexed by the MnP-type structure, which is orthorhombic (*Pnma*) with $Z = 4$; the Fe atoms are coordinated by six S atoms arranged in an octahedron. This MnP-type structure is related to the NiAs-type cell, with hexagonal symmetry, and is a superstructure of the NiAs-type cell. Our first-principles calculations showed that the low-pressure MnP-type phase (FeS II) reported by previous studies had the antiferromagnetic state. In contrast, the newly discovered MnP-type phase (FeS VI) in our study had the non-magnetic state [4]. Figure 1 shows the effect of pressure on the unit cell parameters of both MnP-type phases. The value of the *b* axis of the antiferromagnetic phase

(FeS II) is almost identical to that of the non-magnetic phase (FeS VI). However, significant decreases in the *c* axis and, especially, in the *a* axis were observed between the two phases. Our first-principles calculations [4] showed that the spin transition from the high-spin to the low-spin state induced the magnetic transition observed in our study. The different magnetic configurations between the antiferromagnetic and the non-magnetic phases can reasonably explain these decreases of the *a* and the *c* axes.

REFERENCES

- [1] S. Ono, K. Kikegawa and Y. Ohishi, *Solid State Commun.* **137** (2006) 517.
- [2] S. Ono, K. Funakoshi, A. Nozawa and K. Kikegawa, *J. Appl. Phys.* **97** (2005) 073523.
- [3] S. Ono and T. Kikegawa, *Am. Mineral.* **91** (2006) 1941.
- [4] S. Ono, A.R. Oganov, J.P. Brodholt, L. Vošadlo, I.G. Wood, A. Lyakhov, C.W. Glass, A.S. Côté and G.D. Price, *Earth Planet. Sci. Lett.* **272** (2008) 481.

BEAMLINE

13A (This work was carried out at the former BL-13A.)

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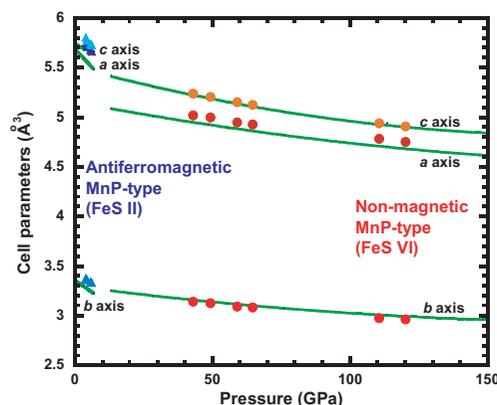


Figure 1
Unit-cell parameters of antiferromagnetic and non-magnetic MnP-type phases as a function of pressure. Abbreviations of symbols are as follows: triangles, antiferromagnetic MnP-type phase (FeS II); circles, non-magnetic MnP-type phase (FeS VI). The green lines are cell parameters estimated by first-principles calculations as a function of pressure.