Synchrotron Mössbauer spectroscopy measurements of Fe-Si alloys: Implication for planetary cores

Earth's core is divided into an outer liquid core and an inner solid core according to seismological observations. These cores are less dense than pure metallic iron under the high-pressure and -temperature conditions corresponding to the core conditions. This density deficit of the cores suggests the presence of one or more light elements in addition to Fe. Silicon has been proposed as a viable candidate for one of the light elements in the cores as it is one of the most abundant elements on Earth. Phase relationships in Fe and Fe-Si systems have been investigated and a hexagonal-close-packed (hcp) structure was revealed to be stable under the pressure and temperature conditions corresponding to Earth's cores. The compressional behavior [1] and sound velocities of hcp Fe-Si alloys [2] have been measured at high pressures and temperatures to evaluate the contribution of Si to the density deficit and seismic velocity in the inner core. In previous studies, the amount of Si in Earth's core was estimated to be at most 5 wt.%.

An electronic topological transition (ETT) in Fe and Fe-Ni alloy was reported by observations of the pressure dependences of the *c*/*a* axial ratio for the hcp structure, Mössbauer center shifts (CS), sound velocities, and theoretical calculations [3]. As the ETT affects elasticity, this transition could change the physical properties of the core. Therefore, the ETT must be investigated under conditions corresponding to terrestrial planetary cores. As the planetary cores have high temperatures, it is also important to consider this relationship at high temperatures. Ono [4] reported that a change in the pressure dependence of the *c*/*a* ratio of hcp Fe occurs at room temperature at around 50 GPa and at 2000 K at around 150 GPa. Thus, there is a possibility that the ETT and a change in *c*/*a* may occur in the Earth and planetary cores. Although the ETT in Fe and Fe-Ni alloys was previously reported to occur at high pressures and temperatures, the electronic properties and *c*/*a* ratios have not yet been investigated in Fe–light-element alloys under hydrostatic conditions. Since Si is a prime candidate for a light element in the core and substitutes Fe in the same way as Ni, we examined the structural, electronic, and compression properties of Fe-Si alloys with the hcp structure up to 60 GPa under quasi-hydrostatic conditions using a combination of XRD and synchrotron-based Mössbauer spectroscopy (SMS) [5].

The starting materials were Fe-2.8wt.%Si and Fe-6.1wt.%Si, which were 33% enriched with ^{57}Fe. Chips from the starting materials were used for energy-domain SMS at SPring-8 **BL10XU** (Fig. 1) and **BL11XU**, and for *in situ* XRD experiments at high pressures at BL10XU. A chip of Fe-2.8wt.%Si or Fe-6.1wt.%Si with a ruby chip as a pressure gauge was loaded into a sample chamber with helium gas as the pressure medium.

Mössbauer spectra and XRD patterns from hcp phases of Fe-2.8wt.%Si or Fe-6.1wt.%Si were obtained up to 60 GPa at room temperature. Typical SMS spectra are shown in Figs. 2(a,b) and a single peak was observed in each spectrum from Fe-2.8wt%Si or Fe-6.1wt%Si at all pressures, suggesting that they are nonmagnetic within the present experimental resolution. Only hcp-structured phases in Fe-2.8wt.%Si and Fe-6.1wt.%Si were observed above 21 GPa and 29 GPa, respectively. The relationships between the CS–pressure and *c*/*a*–pressure for the present Fe-Si alloys are shown in Figs. 2(c,d), together with those of pure Fe and $Fe_{0.9}Ni_{0.1}$ [3]. Both relationships showed changes in pressure dependence at high pressures. The pressures where the changes occurred increased with the amount of Si in Fe.

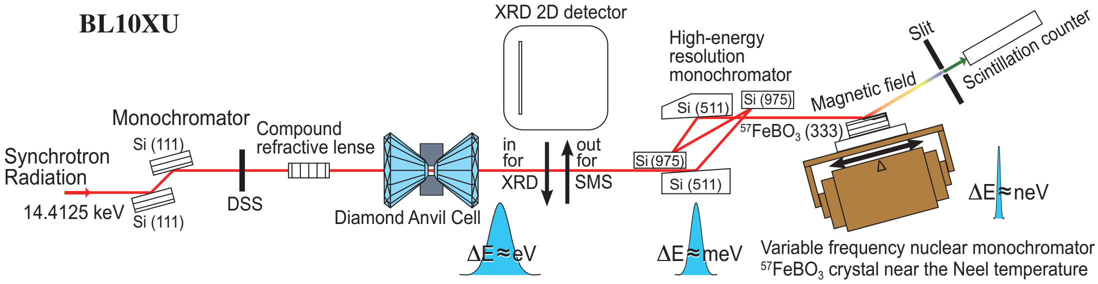

Fig. 1. Schematic view of Mössbauer spectroscopy system at BL10XU. Energy domain Mössbauer spectra and X-ray diffraction patterns can be taken with a typical collection time of 2 h.

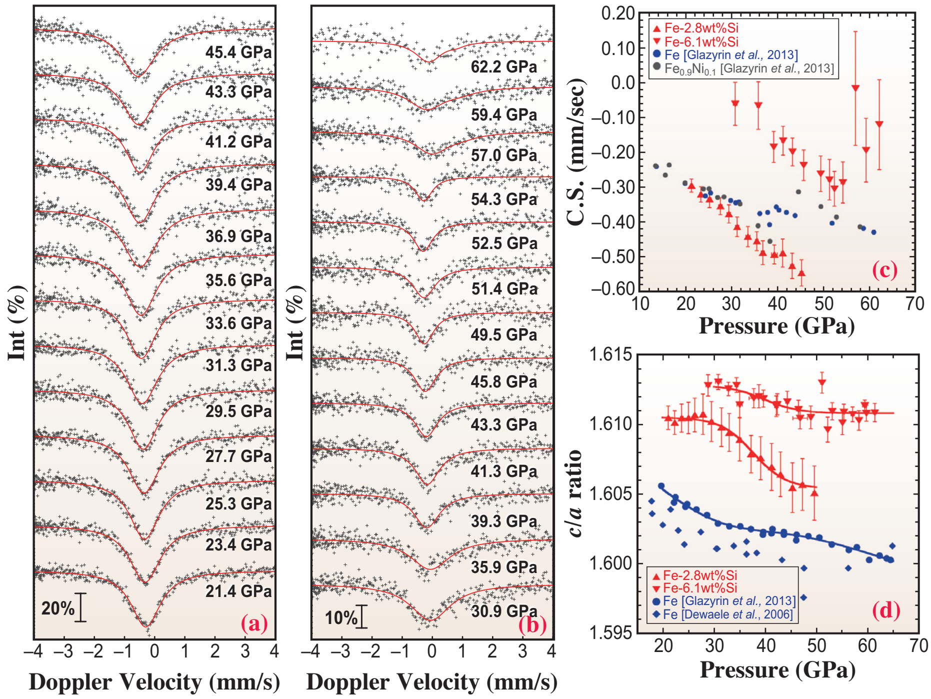

Fig. 2. **(a)** Obtained Mössbauer spectra from Fe–2.8wt%Si, **(b)** obtained Mössbauer spectra from Fe-6.1wt%Si. **(c)** C.S. of Fe–2.8wt%Si, Fe-6.1wt%Si, Fe, and Fe-10wt%Ni alloys are plotted against pressure. **(d)** *c*/*a* ratios as function of pressure.

Our results were used to estimate the effect of Si on the ETT and *c*/*a* evolution as a function of pressure in the interior of terrestrial cores [5]. The ETT pressure was regarded as a function of the amount of Si and temperature to discuss the interiors of terrestrial planets. The estimated pressure of the ETT is shown in Fig. 3 along with the Mercury, Venus, Earth, and Mars core conditions and the Fe phase relationship. Although we do not know exactly whether the terrestrial planets have solid inner cores owing to the lack of seismological data, our results indicate that only Venus's core could undergo a change in *c*/*a* ratio. If Venus has a solid inner core and the inner core intercepts the boundary of the *c*/*a* relationships as shown in Fig. 3, the inner core may have seismic wave velocities lower than those estimated under pressures lower than the ETT pressure [3].

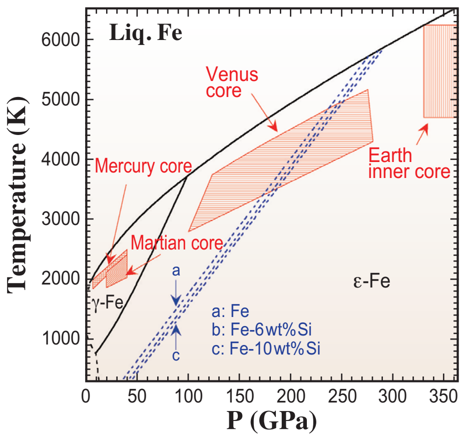

Fig. 3. Phase diagram of Fe with terrestrial planet core conditions and the transition boundary where *c*/*a* changes according to this study and previous studies. The ETT boundaries were estimated from the results for Fe, Fe-6wt%Si, and Fe-10wt%Si.

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References

[1] S. Tateno *et al.*: EPSL **418** (2015) 11.
[2] J. Badro *et al.*: EPSL **254** (2007) 233.
[3] K. Glazyrin *et al.*: Phys. Rev. Lett. **110** (2013) 117206.
[4] S. Ono: Solid State Commun. **203** (2015) 1.
[5] *S. Kamada, N. Suzuki, F. Maeda, N. Hirao, M. Hamada, E. Ohtani, R. Masuda, T. Mitsui, Y. Ohishi and S. Nakano: Am. Mineral.* ***103*** *(2018) 1959.*