Melting Experiments on Fe_3C and FeH_x under High Pressures

The structure of the Earth is divided into three layers, i.e., hydrosphere, the silicate crust and mantle, and the metallic core. The metallic core is further divided into the liquid outer core (2900–5150 km depth corresponding to 136–330 GPa) and solid inner core (5150–6400 km depth corresponding to 330–364 GPa). The temperature of the core has been discussed on the basis of the melting temperature of the core constituent. Because the liquid outer core freezes to form a solid inner core at the inner-outer core boundary (ICB), the temperature at ICB must correspond to the liquidus temperature of the core building material. It is generally assumed that the Earth's core consists mainly of iron. Seismological and experimental studies show that the Earth's outer core is approximately 10% less dense than molten iron under corresponding pressure and temperature conditions, implying that some light elements exist in the core (e.g., Ref. [1]). In the past 50 years after Birch's report, hydrogen, carbon, oxygen, silicon and sulphur are recognized as possible candidates of such light elements. Therefore, the melting temperatures of the iron-light element systems will provide important information to understand the thermal structure of the core. However, most studies on the temperature of the core have been performed in the Fe-S-O system (e.g., Ref. [2]). In this study, in order to evaluate the effects of hydrogen and carbon on the melting temperature of the core, we performed melting experiments on Fe_3C and FeH_x under high pressures at the SPring-8 synchrotron facility [3,4].

In situ X-ray diffraction (XRD) experiments were conducted using a Kawai-type multianvil SPEED-Mk.II installed at beamline **BL04B1**. The starting specimen was a pre-synthesized Fe_3C, which was mixed with MgO powder in order to avoid grain growth during heating. In order to prevent the effect of crystal grain growth, the multianvil apparatus was oscillated during X-ray diffraction measurements.

High-pressure experiments on Fe_3C were performed at 20 and 29 GPa. A series of XRD patterns during heating at 29 GPa is shown in Fig. 1. In the XRD sequences during the heating experiments, the peaks of orthorhombic Fe_3C disappeared, and new peaks identified as those of hexagonal Fe_7C_3 were observed with increases of background due to the presence of a melt. Finally, the Fe_7C_3 peaks disappeared, and only the halo pattern was observed.

In the experiments on FeH_x, a mixture of sponge-like iron and MgO powder in 2:3 atomic ratio was used as a starting material. The sample material was packed into a NaCl container with $LiAlH_4$, which was separated from the sample by a thin MgO disk. Hydrogen was supplied by the thermal decomposition of $LiAlH_4$. The experimental pressure range was 10-20 GPa.

During heating under high pressures, the hydrogenation of iron was observed from the volume change. The hydrogen concentration of FeH_x was estimated from the excess volume compared with that of pure Fe. It was found that FeH_x in the present study at pressures between 10 and 20 GPa are nearly stoichiometric $FeH_{x=1.0}$. The melting temperature of γ-FeH_x was determined from the abrupt change in the XRD patterns of crystal to liquid. The typical change in the XRD pattern due to melting of the sample is

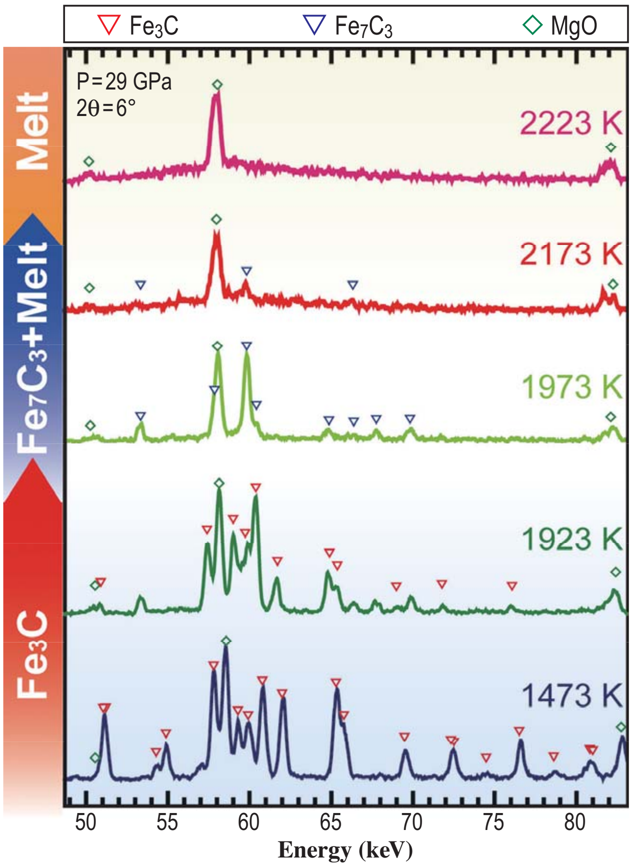

Fig. 1. Diffraction patterns of the Fe_3C during heating experiment at 29 GPa. Red inversed triangles, blue inversed triangles and green diamonds are the diffraction peaks of Fe_3C, Fe_7C_3 and MgO, respectively. During heating, Fe_3C melted incongruently to Fe_7C_3 plus melt between 1923 and 1973 K, and finally all the sample peaks except that of MgO disappeared at 2223 K.

shown in Fig. 2. At 11.5 GPa, the peaks of γ-FeH_x disappeared suddenly between 1423 and 1473 K. At the same time, the background increased due to the presence of a melt.

The phases observed in the Fe_3C and FeH_x experiments are shown in Fig. 3. Under the present experimental pressures, the melting temperatures of FeH_x and Fe_3C are significantly lower than that of pure Fe. The melting temperatures of FeH_x and Fe_3C are 1600 and 1850 K at 20 GPa, respectively, which are less than 2260 K at 20 GPa of Fe calculated by Anderson and Isaak [5] (Fig. 3). Our *in situ* XRD measurements show that hydrogen and carbon can lower the melting temperature of iron dramatically. Using the present observations and thermoelastic parameters for FeH_x [4] and Fe_3C [6], we extrapolated the melting curves for γ-FeH and Fe_3C obtained in our experiments to the core pressure. Those melting temperatures are estimated to be ~2600 and ~2800 K at the core-mantle boundary (CMB). In the present study, we have demonstrated that hydrogen and carbon have a profound effect in lowering the melting temperature of iron. The core temperature was previously proposed to be ~5000 K at ICB and ~4000 K at CMB on the basis of the melting experiments on the Fe-O-S system (e.g., Ref. [2]). If a large amount of hydrogen and/or carbon is present in the Earth's core, it is considered that the temperature of the outer core could be much lower than previous estimates.

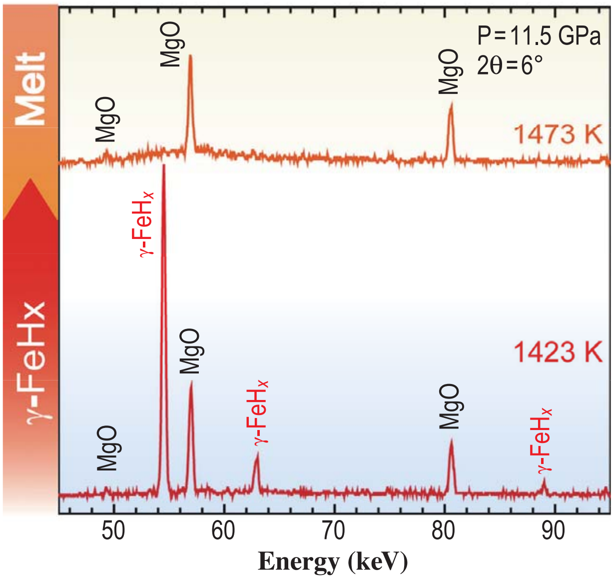

Fig. 2. Diffraction patterns of FeH_x during heating experiment at 11.5 GPa. The peaks of γ-FeH_x disappeared suddenly between 1423 and 1473 K, and a halo due to the presence of a melt was observed. At this pressure, the melting temperature of γ-FeH_x is located between 1423 and 1473 K.

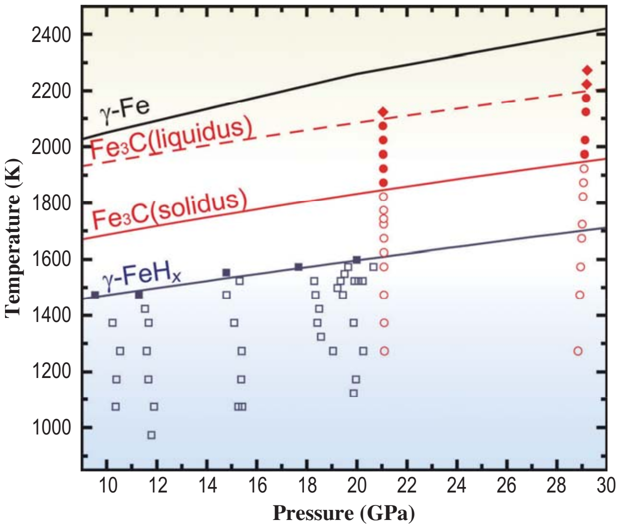

Fig. 3. Experimental results and melting curves for γ-FeH and Fe_3C. Open and solid squares are the γ-phase and melt of FeH, respectively. Open circles, solid circles and solid diamonds are solid Fe_3C, Fe_7C_3 + melt and melt, respectively. Melting curves for γ-FeH_x (blue line) and Fe_3C (red line) are determined in this study. The melting curve for γ-Fe (black line) is referred to Anderson and Isaak [5].

Yoichi Nakajima*, Koichi Sakamaki and Eiichi Takahashi

Department of Earth and Planetary Sciences,
Tokyo Institute of Technology

*E-mail: ynakajim@geo.titech.ac.jp

References

[1] F. Birch: J. Geophys. Res. **57** (1952) 227.
[2] R. Boehler: Annu. Rev. Earth Planet. Sci. **24** (1996) 15.
[3] *Y. Nakajima, E. Takahashi, T. Suzuki, K. Funakoshi: Phys. Earth Planet. Inter. **174** (2009) 202.*
[4] *K. Sakamaki, E. Takahashi, Y. Nakajima, Y. Nishihara, K. Funakoshi, Y. Fukai: Phys. Earth Planet. Inter. **174** (2009) 192.*
[5] O.L. Anderson and D.G. Isaak: Am. Miner. **85** (2000) 376.
[6] Y. Nakajima: Ph.D. thesis, Tokyo Inst. Technol., Tokyo (2009).