Melting relation of FeS-H system under high pressure: Implications for the core of Ganymede

Ganymede is one of the Galilean satellites of Jupiter, and is the largest moon in our solar system. The observation data of the Galilean mission suggest that Ganymede has an intrinsic magnetic field and the interior is strongly differentiated into an outermost H_2O layer, a silicate rock mantle, and an iron-rich core [1]. The core is considered to consist of iron (Fe) and light elements. Sulfur (S) is one of the plausible light elements in the core because iron sulfide is found in many meteorites. Hydrogen (H) is also most probably present in the core. This is because, before the differentiation occurred in an early period, the silicate rock and the iron alloy mixed with and then may have reacted with H_2O in the interior of Ganymede. As a result, it may well be that the silicate rock layer contains a significant amount of water, and the iron alloy may contain hydrogen. It is known that hydrogen significantly lowers the melting temperature of metals. However, it has not been reported whether hydrogen affects the melting temperature of Fe–S alloy. If hydrogen lowers the melting temperature of Fe–S alloy, the previous models of Ganymede's core (e.g. [2]) may need to be revised. Therefore, in order to constrain the state and degree of melting of Ganymede's core, we first determined the melting temperatures of the FeS–H system ($FeSH_x$) at pressures up to 16.5 GPa [3].

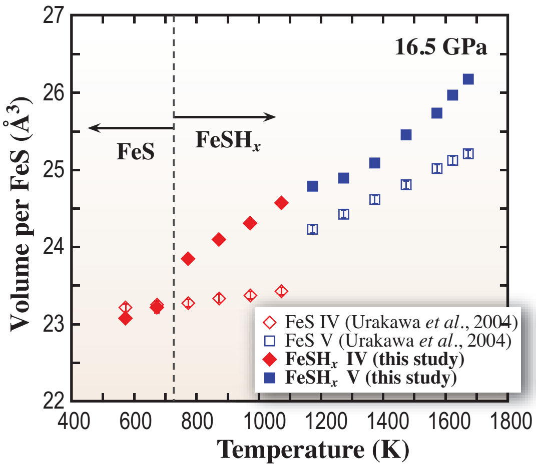

Fig. 1. Thermal expansion of FeS and $FeSH_x$ at 16.5 GPa. The volume per FeS is defined as V (unit cell volume) divided by Z (where $Z = 8$ for phase IV, and $Z = 2$ for phase V). The solid diamonds and squares correspond to $FeSH_x$ IV and $FeSH_x$ V, respectively. The open diamonds and squares correspond to FeS IV and FeS V, respectively, from Ref. [4].

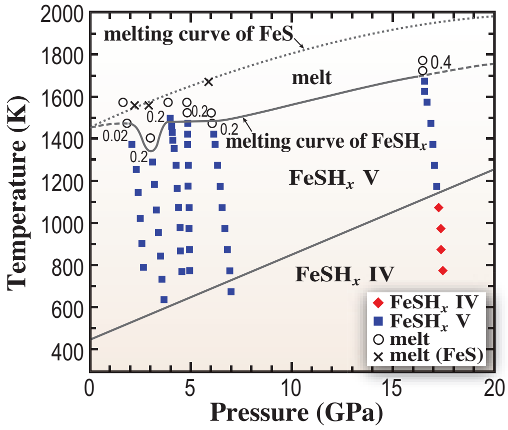

Fig. 2. Pressure-temperature phase diagram of $FeSH_x$, together with Boehler's melting curve of FeS [5]. The solid diamonds and squares correspond to $FeSH_x$ IV and $FeSH_x$ V, respectively, as determined in this study. The open circles correspond to the $FeSH_x$–melt. The crosses denote the observed melting temperatures of FeS. The numbers on the melting curve show the hydrogen concentration (x) just before the melting of $FeSH_x$, where x is defined as the number of hydrogen atoms per FeS in a unit cell.

Energy-dispersive X-ray diffraction experiments were carried out at high temperature and high pressure using a Kawai-type multianvil apparatus at **BL04B1**. The diffraction patterns were collected for a period of 120 or 300 s at each 50–100 K temperature step and at high pressure. In this study, melting of the sample was determined on the basis of observations of the disappearance of the diffraction peaks from the sample and the appearance of a broad halo peak. The FeS sample powder was packed into a NaCl container along with $LiAlH_4$, because NaCl is reported to effectively seal hydrogen at high pressures and temperatures. Hydrogen was supplied to the sample from the thermal decomposition of $LiAlH_4$.

The observed unit cell volumes of FeS and $FeSH_x$ with increasing temperature at 16.5 GPa are shown in Fig. 1. On the basis of the present X-ray diffraction measurements, the low-temperature phases of FeS and $FeSH_x$ have a hexagonal NiAs-type superstructure (Phase IV) and the high-temperature phase has a simple NiAs-type structure (Phase V). This is consistent with the previously reported phase relations of pure FeS [4]. However, above 800 K, the observed volume was clearly larger than that of pure FeS up to the melting point as shown in Fig. 1. This expansion in volume can be explained by hydrogenation, i.e., synthesis of $FeSH_x$. The drastic volume increase at high temperature was observed throughout the pressure range studied, except at 1.9 GPa. We considered that the structure of $FeSH_x$ is the same as that of FeS whereas the volume of $FeSH_x$ is larger than that of FeS owing to the dissolution of hydrogen in the interstitial sites of FeS.

The observed phase relationships of FeSH$_x$ are plotted on the pressure-temperature diagram shown in Fig. 2, together with the melting temperature of pure FeS [5]. The melting temperature of FeSH$_x$ was clearly decreased by 150–250 K compared with that of FeS between 3.0 and 16.5 GPa owing to hydrogenation. The melting temperature of FeSH$_x$ exhibited a minimum and the concentration of hydrogen increased at about 3 GPa ($x \approx 0.2$ at 3.0 GPa, whereas $x \approx 0.02$ at 1.9 GPa). This indicates that hydrogen starts to dissolve into the interstitial sites of FeS between 1.9 and 3.0 GPa. As a result, the depression of the melting temperature at about 3.0 GPa occurred.

Figure 3 shows the predicted phase diagram of the FeH$_x$–FeSH$_x$ system at 5 GPa with model temperatures equivalent to those of Ganymede's core. We assume that the FeH$_x$–FeSH$_x$ system has the same eutectic relation as the Fe–FeS system. Since the melting temperatures of Fe and FeS are depressed due to hydrogenation, the liquidus of the FeH$_x$–FeSH$_x$ binary system is lower than the core temperatures over a wide range of sulfur content in the core (Region I in Fig. 3). Then, Ganymede's core could be completely molten in Region I. If the core contains much sulfur (Region II in Fig. 3), it could be partially molten (solid FeSH$_x$ coexisting with liquid Fe–S–H) because the liquidus is higher than the core temperatures. Hauck *et al.* [2] showed that a completely molten core cannot sustain the Ganymede dynamo up to the present day by thermal convection. Thus, the partially molten core (Region II in Fig. 3) is more reasonable for sustaining the dynamo, suggesting that the core contains more than about 33 wt.% S.

The present study suggests that Ganymede's core could have a solid FeSH$_x$ inner core and liquid Fe–S–H outer core if the core consists of the Fe–S–H system (Fig. 4). The results of this study strongly indicate that hydrogen is certainly important for understanding the internal structures of planets and satellites outside the snow line, although additional experiments for the FeH$_x$–FeSH$_x$ system are needed in order to discuss the core in more detail.

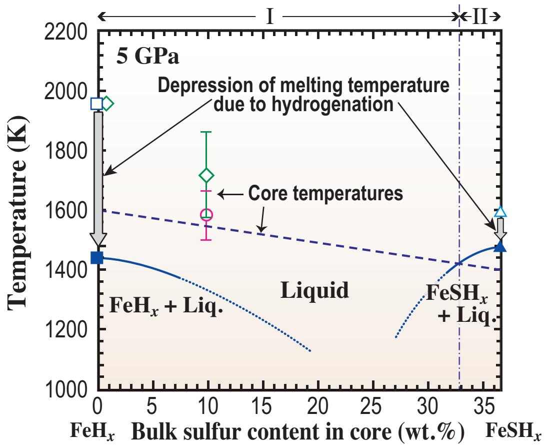

Fig. 3. Predicted phase diagram of the FeH$_x$–FeSH$_x$ system at 5 GPa, assuming it has the same eutectic relation as the Fe–FeS system. The open and solid squares denote the melting temperatures of Fe (Shen *et al.*, 1998) and FeH$_x$ (Fukai *et al.*, 2003), respectively. The open and solid triangles denote those of FeS (Boehler, 1992) and FeSH$_x$ (this study) [3], respectively. The solid and dotted lines denote the predicted liquidus. The broken line denotes Ganymede's core temperatures with various bulk sulfur contents in the core, taken from Kimura *et al.* (2009) (1030 km H$_2$O layer). The open circle and diamonds denote the core temperatures reported by Hauck *et al.* (2006) (S = 10 wt.%) and Bland *et al.* (2008) (S = 1 and 10 wt.%), respectively.

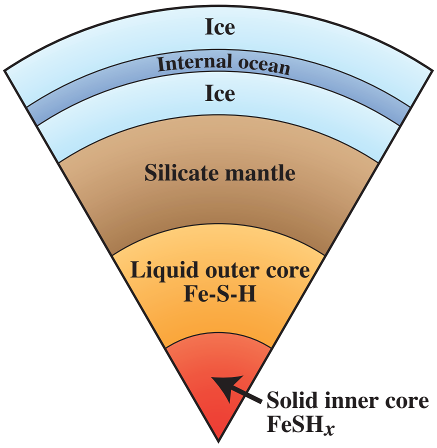

Fig. 4. Schematic figure of the internal structure of Ganymede with Fe–S–H core.

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