# Effect of hydrogen on the melting temperature of FeS at high pressure: Implications for the core of Ganymede

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## ARTICLE INFO

## ABSTRACT

We have carried out in situ X-ray diffraction experiments on the FeS–H system up to 16.5 GPa and 1723 K using a Kawai-type multianvil high-pressure apparatus employing synchrotron X-ray radiation. Hydrogen was supplied to FeS from the thermal decomposition of $LiAlH_4$, and $FeSH_x$ was formed at high pressures and temperatures. The melting temperature and phase relationships of $FeSH_x$ were determined based on in situ powder X-ray diffraction data. The melting temperature of $FeSH_x$ was reduced by 150–250 K comparing with that of pure FeS. The hydrogen concentration in $FeSH_x$ was determined to be $x = 0.2$–0.4 just before melting occurred between 3.0 and 16.5 GPa. It is considered that sulfur is the major light element in the core of Ganymede, one of the Galilean satellites of Jupiter. Although the interior of Ganymede is differentiated today, the silicate rock and the iron alloy mixed with $H_2O$, and the iron alloy could react with $H_2O$ (as ice or water) or the hydrous silicate before the differentiation occurred in an early period, resulting in a formation of iron hydride. Therefore, Ganymede's core may be composed of an Fe–S–H system. According to our results, hydrogen dissolved in Ganymede's core lowers the melting temperature of the core composition, and so today, the core could have solid $FeSH_x$ inner core and liquid $FeH_x$–$FeSH_x$ outer core and the present core temperature is considered to be relatively low.

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## 1. Introduction

Ganymede is one of the Galilean satellites of Jupiter, and is the largest moon in our solar system. The Galilean mission discovered that Ganymede has a small moment of inertia factor (0.3115) (Schubert et al., 2004) and an intrinsic magnetic field (Kivelson et al., 1996). These observation data suggest a strongly differentiated interior of Ganymede and the presence of a liquid metallic core. It is considered that sulfur is the major light element in Ganymede's core because iron sulfide is found in many meteorites (e.g. Krot et al., 2005). Hydrogen is also most probably present in the core. This is because Ganymede is located far from the Sun and outside the snow line, suggesting that it could have a large amount of volatile light elements. In addition, Ganymede's interior has been reported to consist of an outermost $H_2O$ layer, a silicate rock mantle, and an iron-rich core (e.g. Anderson et al., 1996). Although the interior of Ganymede is differentiated today, the silicate rock and the iron alloy mixed with $H_2O$, and silicate rock and iron alloy could have reacted with $H_2O$ (as ice or water) before the differentiation occurred in an early period. As a result, it may well be that the silicate rock layer contains a significant amount of water, and

the iron may contain hydrogen in the form of iron hydride which could have been formed via a reaction between this hydrous silicate and iron (e.g. Hishinuma et al., 1994; Okuchi, 1997; Shibazaki et al., 2009; Suzuki et al., 1984; Yagi and Hishinuma, 1995). The iron could also have reacted directly with $H_2O$, resulting in the synthesis of iron hydride (Ohtani et al., 2005). Therefore, hydrogen is possibly dissolved into the Fe–S core of Ganymede.

It is known that hydrogen significantly lowers the melting temperature of iron (by about 600 K) (e.g. Fukai et al., 2003; Sakamaki et al., 2009; Yagi and Hishinuma, 1995). However, it has not been reported whether hydrogen affects the melting temperature of FeS. Although it has been shown that there are several possible states of Ganymede's core depending on the amount of sulfur in the core and the temperature of the core (e.g. Bland et al., 2008; Hauck et al., 2006; Kimura et al., 2009), the previous models of the core may need revising if hydrogen lowers the melting temperature of FeS. In this study, we determined the melting temperatures of the FeS–H system to constrain the state and degree of melting of Ganymede's core.

## 2. Experimental methods

We carried out in situ X-ray experiments using a Kawai-type multianvil high-pressure apparatus employing synchrotron X-ray radiation at the BL04B1 beamline of the SPring-8 facility in Japan

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(Utsumi et al., 1998). The experimental pressure range was between 1.9 and 16.5 GPa at temperatures up to 1723 K. The 1500 ton multianvil apparatus (SPEED-Mk.II), installed at the BL04B1 beamline, could be oscillated at an angle from −7° to 13° during the X-ray diffraction measurements at high pressure and temperature, to reduce the effect of crystal grain growth on the diffraction patterns (Katsura et al., 2004). In this study, the typical oscillation angle range was from 0° to 4°.

The FeS sample powder was packed into a NaCl container along with LiAlH$_4$, which was separated from the sample using a thin MgO disk to avoid any adverse chemical reaction occurring. It is known that NaCl can effectively seal hydrogen at high pressures and temperatures (e.g. Fukai et al., 2003; Sakamaki et al., 2009; Yamakata et al., 1992). Hydrogen was supplied to the sample from the thermal decomposition of LiAlH$_4$ (e.g. Fukai et al., 2003; Sakamaki et al., 2009; Yamakata et al., 1992). The molar ratio of FeS to LiAlH$_4$ used was about 1:1. We used a set of WC cubic anvils with a 12 mm truncated edge length (TEL) for the experiments carried out between 1.9 and 6.1 GPa, and anvils with a TEL of 3.5 mm for the experiments carried out at 16.5 GPa. The high temperatures were generated using a cylindrical graphite heater or BN composite (TiB$_2$ + BN) heater. The temperature was measured using a W3%Re–W25%Re thermocouple, which was placed above the capsule inside the heater. A Ge solid state detector (SSD) was placed at a fixed angle of 4.5° or 5.5° from the incident X-ray beam, and the diffracted X-rays were energy-analyzed. The diffraction patterns were collected for a period of 120 or 300 s at each 50–100 K temperature step, and the sample was kept at a constant temperature of 773 and 1273 K for a period of about 15–20 min at each pressure point because hydrogenation of the metal was complete after a period of about 20 min (Shibazaki et al., 2009).

In general, in metal hydrides, the atomic volume of the host metal expands depending on the amount of hydrogen dissolved in the interstitial sites. Thus, the hydrogen concentration ($x$) in a metal hydride, MH$_x$, can be estimated using the following formula:

$$x = [V(MH_x) - V(M)] / \Delta V(H), \qquad (1)$$

where $V(MH_x)$, $V(M)$, and $\Delta V(H)$ denote the atomic volumes of the metal hydride and pure metal, and the increase in volume per hydrogen atom, respectively (e.g. Fukai, 1992). We assumed that this formula is applicable to FeS. We estimated $V(FeSH_x)$ from the diffraction data of FeSH$_x$ obtained in this study. The high pressure and high temperature phases of FeS in the pressure range studied (1.9–16.5 GPa) are Phase IV (a hexagonal NiAs-type superstructure) and Phase V (a simple NiAs-type structure) (e.g. Fei et al., 1995; Kusaba et al., 1998; Urakawa et al., 2004). Urakawa et al. (2004) showed that both FeS IV and FeS V were divided by a spin transition into two phases, i.e., a low-pressure phase (LPP) and a high-pressure phase (HPP). The LPP–HPP phase boundaries were located at a pressure around 7 GPa in both the FeS IV and FeS V phases. We used the equations of state of HPP-FeS IV and HPP-FeS V (Urakawa et al., 2004) for $V(FeS)$ at pressures above 7 GPa. However, the equations of state of LPP-FeS IV and LPP-FeS V have not been determined. Therefore, we determined the volume data of pure FeS at pressures of 1.9, 3.0, and 6.1 GPa and at elevated temperatures in separate experiments. Based on this volume data, we interpolated the volume of pure FeS at 3.9 and 4.8 GPa and at high temperature.

The values of $\Delta V(H)$ for FeS IV and FeS V are also unknown. The NiAs-type structure has alternating layers of Fe atoms (A layer) and S atoms (B and C layers), following the repeating ABAC pattern (Fig. 1A). In the case of an FeH, Badding et al. (1991) showed that hydrogen dissolved in the octahedral interstitial sites, and that the structure had an ABAC stacking sequence for double-hexagonal close-packed (dhcp)-FeH (Fig. 1B). Since the structure of FeSH$_x$ is similar to the dhcp structure if hydrogen dissolves in octahedral interstitial sites
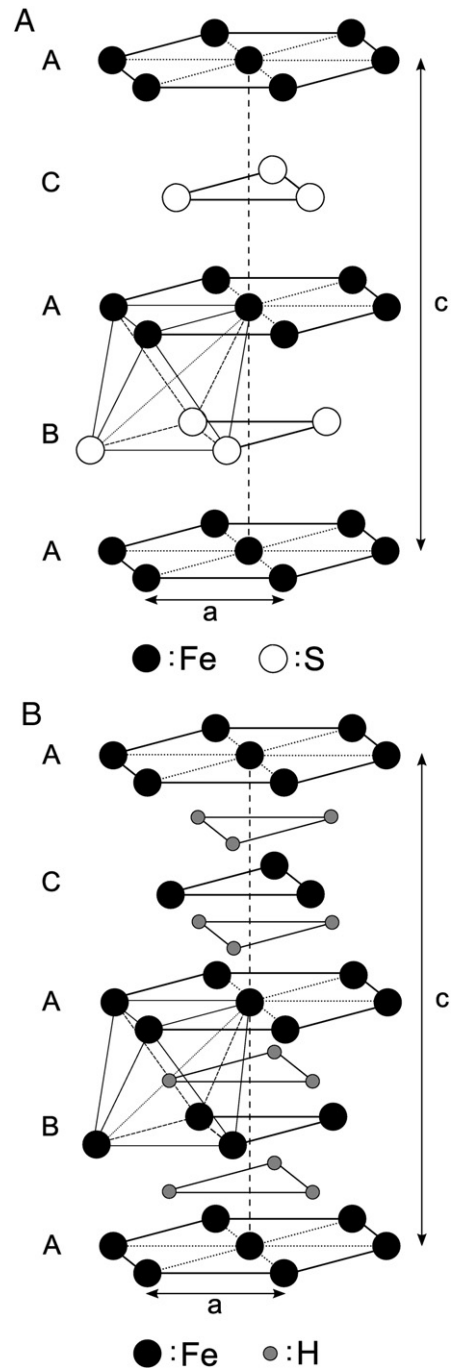


**Fig. 1.** The crystal structures of: (A) NiAs-type iron sulfide and (B) double-hexagonal close-packed (dhcp) iron hydride. The black circles show the positions of the Fe atoms, the open circles denote S atoms, and the small gray circles denote H atoms. The octahedron shows the octahedral interstitial site in the NiAs-type and dhcp structures. The hydrogen atoms are located in the octahedral interstitial sites. The length of the $c$-axis in these figures is represented as being longer than that in the actual $c$-axis to help the reader to understand the structures.

of FeS IV and FeS V, we assumed that the values of $\Delta V(H)$ for FeS IV and FeS V were the same as that for the dhcp-metal structure, and adopted the value for dhcp-FeH$_x$ by Badding et al. (1991) and Fukai (1992) ($V_0$ of 2.7 Å$^3$, $K_0$ of 99.2 GPa and $K_0'$ of 3.98 with Vinet equation of state). We estimated the value of $x$ for the number of hydrogen atoms per FeS in a unit cell. In a unit cell of the NiAs-type, the number of the octahedral interstitial sites is four, and the number of FeS is two ($Z = 2$) (Fig. 1A). Therefore, the maximum value of $x$ is estimated $x = 2.0$ for FeS IV and FeS V, whereas $x = 1.0$ for Fe.