Structure of liquid iron hydrogen alloy under high pressure

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Abstract. In-situ x-ray diffraction measurement on liquid iron hydrogen alloy (FeH$_x$) was performed at 4 GPa and 1350°C. X-ray diffraction of pure liquid Fe was also measured at 3.5 GPa and 1700°C for comparison. The obtained structure factors for liquid FeH$_x$ and pure Fe are very similar though the second peak in the structure factor for liquid FeH$_x$ is more asymmetric. It suggests that hydrogen affects some local order in the liquid state. Slight elongation of the Fe-Fe nearest neighbour distance due to hydrogenation supports a notion that hydrogen and iron form interstitial alloy in the liquid state.

1. Introduction

Hydrogen reacts with many metals and form solid solutions and metal hydrides [1]. Metal hydrides are widely studied for hydrogen storage, which is one of the key challenges for realizing a hydrogen economy. In transition metals and rare-earth metals, hydrogen atoms usually occupy interstitial sites and the crystalline lattice expands. In many cases, the metal lattices undergo structural transition to accommodate a large number of H atoms at high hydrogen concentrations.

While there are many studies on crystalline metal hydrides, almost nothing is known about liquid metal-hydrogen systems. To study effect of hydrogen to the structure of liquid metals, we choose iron hydride as a sample. It is one of the most studied metal hydrides under high pressure because hydrogen is one of candidates for light elements in the earth’s iron core. A solubility of hydrogen in iron is small at ambient conditions but iron and hydrogen react under high pressure and form hydrides [2-10]. Hydrogen concentration in ε’-FeH$_x$ (high-pressure low-temperature phase with dhcp structure) is about $x=1.0$ [4,8,10]. That of γ-FeH$_x$ (high-temperature phase with fcc structure) increases with increasing pressure and reaches $x=1.0$ above 10GPa [3,7,8-10]. One of significant effects of hydrogen is lowering of the melting temperature. The melting temperature of γ-FeH$_x$ is lower than that of pure iron by about 500°C at 5GPa [5-9] and the difference in the melting temperature increases with increasing pressure [10]. The hydrogen concentrations of liquid FeH$_x$ at 7.5 GPa were estimated from textures of rapidly decompressed iron hydride grains [11]. It ranges from 0.4 to 0.7 depending on temperature.

We have performed in-situ x-ray diffraction measurements on liquid FeH$_x$ at about 4GPa and 1350°C. The x-ray diffraction measurements on liquid pure Fe at about 3.5GPa and 1700°C were also performed for comparison.

2. Experimental
In-situ energy-dispersive x-ray diffraction measurements at high pressures and high temperatures were conducted using a cubic-type multi-anvil press installed at beamline BL14B1 in SPring-8 synchrotron radiation facility [12]. The high-pressure cell assembly used in the present study was a modification of that used for metal hydrides experiments [8,9,13,14]. A cube made of pyrophyllite was used as pressure transmitting medium. A wire of 99.995% pure Fe, 1.0mm in diameter, was used as a starting material and LiAlH$_4$ was used as a hydrogen source. NaCl sample capsule was used to keep hydrogen inside. An Al$_2$O$_3$ ring and MgO plates were used as a sample container for the pure Fe measurement. Temperature was estimated from the power applied to the heater and pressure was estimated from the load applied to the press. The relations between temperature and the heater power, and that between pressure and the applied load were determined by separate experiments using the same high-pressure cell assembly with a thermocouple and a pressure marker. The diffraction data were measured at several two theta angles and structure factor $S(Q)$ was obtained using an empirical method [15, 16].

3. Results and discussion

By heating, the hydrogen source decomposed and hydrogen was released. X-ray measurements confirmed the hydrogenation of Fe through an increase of the lattice constant and the decrease of the melting temperature. Figure 1 shows structure factor, $S(Q)$, of FeH$_x$ at about 1350°C and 4 GPa together with that of pure Fe at about 1700°C and 3.5 GPa. In this analysis, x-ray scattering of hydrogen is neglected because hydrogen has very weak x-ray scattering power and because concentration of hydrogen is not known. Two structure factors are very similar though the second maximum for FeH$_x$ is more asymmetric than that for Fe. Such asymmetry was observed in a previous neutron scattering study on liquid Fe at ambient pressure [17]. The study showed that the asymmetry is a signature of some local orders such as icosahedral short-range order in the liquid state. The study also revealed that the height of the second maximum decreased and the dip between the first and the second peak became shallow as the temperature was increased [17]. Therefore the difference between Fe and FeH$_x$ is partly attributable to the difference in temperature. However the difference is larger than that observed in the temperature dependence of $S(Q)$ at ambient pressure. There is a possibility that hydrogen affects the local order.

Figure 1. Structure Factor, $S(Q)$, of liquid iron at 3.5 GPa and 1700°C (black line) and that of liquid iron hydrogen alloy at 4 GPa and 1350°C (red line).
The pair correlation functions, \( g(r) \), which are obtained by Fourier transformation of \( S(Q) \), is shown in Figure 2. Because densities of liquid Fe and liquid FeH\(_x\) are not known, the absolute value has uncertainty. Therefore we restrict our discussion to the peak positions. The difference between \( g(r) \) of liquid Fe and liquid FeH\(_x\) is very small. The first peak for liquid FeH\(_x\) is slightly shifted to higher-\( r \) in spite of lower temperature and higher pressure of the measurement. The elongation of Fe-Fe nearest neighbor distance supports a notion that hydrogen and iron form interstitial alloy in the liquid state. The position of the maximum of the first peak, \( r_1 \), is determined from a peak fitting using a Gaussian function. The fitting ranges are 2.43-2.61Å and 2.45-2.62Å for Fe and FeH\(_x\), respectively. It is 2.518Å for liquid Fe and 2.534Å for liquid FeH\(_x\). Because the maximum of the first peak in \( g(r) \) depends on several factors such as \( Q \) range of \( S(Q) \), choice of window function, fitting range in \( g(r) \), etc, the absolute value has large uncertainty. The position of the maximum does not represent exact average Fe-Fe nearest-neighbor distance but it is at least related to the Fe-Fe distance. In the present case, we use the same conditions in the analysis for both materials so that the difference in the maximum position, 0.016Å, is meaningful although small. The error in the difference is probably as large as ±0.005Å. In crystalline iron hydrides, hydrogen concentration is estimated from the observed increase \( \Delta \Omega \) of the atomic volume using the expression \( x=\Delta \Omega/\Omega_{H} \), where \( \Omega_{H}=1.9 \) Å\(^3\) is the increment of the atomic volume per unit concentration of hydrogen. This value is obtained for a fcc alloy Fe\(_{0.65}\)Mn\(_{0.29}\)Ni\(_{0.06}\)H\(_{0.95}\) [18] and used in previous studies on iron hydrides [9,10]. We roughly estimate the hydrogen concentration in the liquid FeH\(_x\) assuming that the atomic volume is proportional to \( r_1^3 \). To compensate temperature and pressure differences between the two measurements, results of previous compression data for \( \gamma \)-Fe were used [19,20]. The obtained hydrogen concentration, \( x=0.3±0.1 \), is in reasonable agreement with that for crystalline \( \gamma \)-FeH\(_x\) at 4 GPa and 900°C (\( x=0.3 \)) [9] and that for liquid FeH\(_x\) at 7.5 GPa (0.4<\( x <0.7 \)) [11]. This agreement also supports that hydrogen and iron form interstitial alloy in the liquid state. A previous study on crystalline \( \gamma \)-FeH\(_x\) reported a lattice contraction due to superabundant vacancy formation at high temperatures [8,9]. If similar phenomena occur in the liquid state, the hydrogen concentration is larger than the current estimation. Measurements of bulk density of liquid FeH\(_x\) is necessary for further discussion.

Figure 2. Pair correlation function, \( g(r) \), of liquid iron at 3.5 GPa and 1700°C (black line) and that of liquid iron hydrogen alloy at 4 GPa and 1350°C (red line).
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References
[1] Fukai Y 2005 The Metal-Hydrogen System (Berlin: Springer)
[2] Fukai Y 1984 Nature 308 174
[3] Antonov V E, Belash I T, Ponyatovsky E G 1982 Scr. Metal. 16 203
[4] Badding J V, Hemley R J, Mao H K, 1991 Science 258 421
[5] Suzuki T, Akimoto S, Fukai Y, 1984 Phys Earth Planet. Inter. 36 135
[6] Yagi T and Hishinuma T 1995 Geophys. Res. Lett. 22 1933
[7] Okuchi T 1998 J. Phys.: Condens. Matter, 10 11595
[8] Fukai Y, Mori K and Shinomiya H 2003 J. Alloys Comp. 348 105
[9] Hiroi T, Fukai Y and Mori K 2005 J. Alloys Comp. 404-406 252
[10] Sakamaki K, Takahashi E, Nakajima Y, Nishihara Y, Funakoshi K, Suzuki T and Fukai Y 2009 Phys Earth Planet. Inter. 174 192
[11] Okuchi T 1997 Science 278 1781
[12] Utsumi W, Funakoshi K, Katayama Y, Yamakata M, Okada T and Shimomura O 2002 J. Phys.: Condens. Matter 14 10497
[13] Saitoh H, Machida A, Katayama Y and Aoki K 2008 Appl. Phys. Lett. 93 151918
[14] Kamegawa A, Goto Y, Katoaka R, Takamura H and Okada M 2008 Renewable Energy 33 221
[15] Tsuji K, Yoaota K, Ima M, Shimomura O and Kikegawa T 1989 Rev. Sci. Instrum. 60 2425
[16] Funakoshi K 1997 Ph.D Thesis (Tokyo Institute of Technology)
[17] Schenk T, Holland-Moritz D, Simonet V, Bellisent R and Herlach D M 2002 Phys. Rev. Lett. 89 075507
[18] Antonov V E, Belash I T, Ponomarev B K, Ponyatovskii E G and Thiessen V G 1979 phys. stat. sol (a) 52 703.
[19] Boehler R, Besson J M, Nicol M, Nielsen M, Itie J P, Weil G, Johnson S and Grey F 1989 J. Appl. Phys. 65 953
[20] Boehler R, von Bargen N and Chopelas A 1990 J. Geophysical Res. 95 21731