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Mössbauer studies of iron hydride at high pressure

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We have measured *in situ* Mössbauer spectra of iron hydride made in a diamond anvil cell at high pressure and room temperature. The spectra show a sudden change at 3.5 ± 0.5 GPa from a single hyperfine pattern to a superposition of three. The former pattern results from normal α-iron with negligible hydrogen content, and the latter from residual α-iron plus newly formed iron hydride. Between 3.5 and 10.4 GPa, the extra hydride pattern have hyperfine fields for one ranging from 276 to 263 kOe, and the other, from 317 to 309 kOe. Both have isomer shifts of about 0.4 mm/sec, and negligible quadrupole splittings. X-ray studies on quenched samples have shown that iron hydride is of double hexagonal close-packed structure, whose two nonequivalent iron sites may account for the observation of two different patterns. Even allowing for the effect of volume expansion, the observed isomer shifts for the hydride are considerably more positive than those of other metallic phases of iron. At the same time, the hyperfine fields are slightly smaller than that of α-iron. As a possible explanation, one may expect a bonding of hydrogen with iron, which would result in a small reduction of 4*s* electrons, possibly accompanied by a small increase of 3*d* electrons compared with the neutral atom in metallic iron. The difference between the hyperfine fields in the two spectra are presumably due to the different symmetry at the two iron sites.

Hydrogen solubility in iron under normal pressure is known to be extremely small. However, recent high-pressure studies have shown enormously enhanced solubility under high pressure. Since the first realization of the iron hydride (FeH) by Antonov *et al.* in 1980,[1] the FeH system has been studied extensively, especially by Russian and Japanese groups.[2,3] A recent x-ray study[4] has shown that the structure of FeH is double hcp (dhcp), and Mössbauer studies[5] have revealed two hyperfine field patterns. However, their experiments were on quenched samples at low temperature and atmospheric pressure, after synthesis of FeH at high pressure and high temperature. The thermal decomposition of other hydrides inside the same cell was used to supply pressurized hydrogen to iron, which inevitably involves heating of the sample. On the other hand, our experiment has been done at *in situ* conditions enabling the observation of the pressure dependence, and has shown a rapid hydride formation at room temperature.

A small piece of metallic iron sample (250 μm wide and 15 μm thick, cut from 98% ^{57}Fe enriched iron granules) with finely ground ruby powder was loaded into a diamond anvil cell containing a 125-μm-thick inconel gasket. Later, hydrogen was introduced into the sample chamber by putting the assembled cell into a hydrogen gas container initially pressurized to 0.3 GPa. Pressure measurement was done using standard ruby fluorescence technique.[6] In the pressure cell, hydrogen gas acts not only as hydrogen reservoir for an iron-hydrogen reaction, but also as hydrostatic pressure transmitting medium. Without any initial heating, we obtained *in situ* Mössbauer spectra at room temperature and pressures to 11 GPa, including the final one after pressure release. Since we did not employ any hydrogen sealing mechanism, the high mobility of hydrogen caused a pressure drop with time. After the somewhat rapid initial drop, however, the dropping rate slowed down substantially, enabling an amount of time required to measure spectra with good statistics.

A typical set of spectra is shown in Fig. 1. The spec-

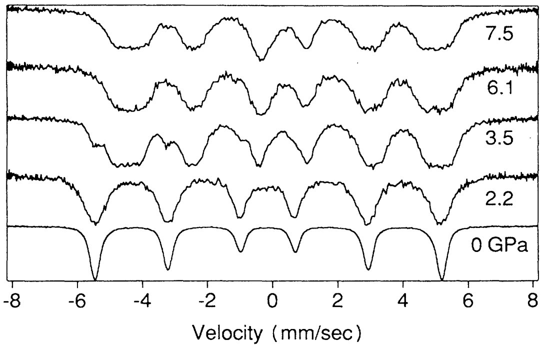

FIG. 1. Mössbauer spectra of the iron hydride at room temperature with respect to the applied pressure. The zero- (atmospheric) pressure spectrum is from α-iron foil outside the pressure cell. The sudden change of the spectral shape around 3.5 GPa signals the hydride formation.

trum at the bottom is for a thin (25 μm) natural α (bcc) iron foil at atmospheric pressure. At 2.2 GPa, there is little change in the spectral shape or hyperfine parameters. The only recognizable difference is the broadening of lines due to higher self-absorption of the enriched sample. This suggests no significant changes in the iron environment and in turn, the negligible hydrogen solubility in iron to 2.2 GPa. At 3.5 GPa, however, the spectrum shows a dramatic change. It has new intense peaks superimposed with a small amount of the residual α-iron sextet. This pressure is far below the usual α to ϵ (hcp) phase transition (about 12 GPa). This implies hydrogen has altered the iron environment substantially by forming the hydride. A further increase of pressure to 11 GPa has only a small effect on the spectral shape, accompanied by a reduction in the α-iron fraction (near zero, above 6.1 GPa) and a change of relative intensities between the new sextets. Such behavior is considered to be a full saturation of hydrogen in the iron lattice. The final spectrum after pressure release (not shown) is essentially identical to the initial atmospheric one, verifying the reversibility of the hydride formation. These observations lead us to the conclusion that a rapid and reversible hydride formation occurs at 3.5±0.5 GPa at room temperature.

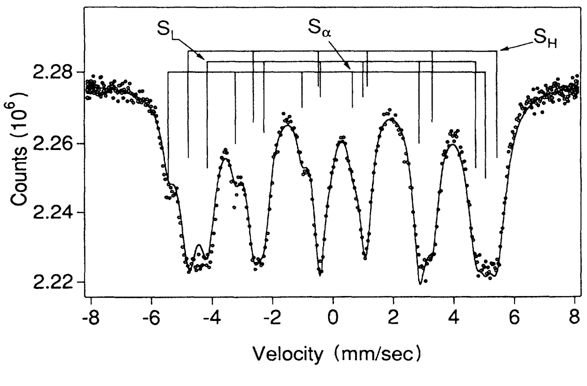

FIG. 2. Fit of the Mössbauer spectrum at 3.5 GPa showing three sextets: S_α from the unmodified α-iron, S_L and S_H from the iron hydride.

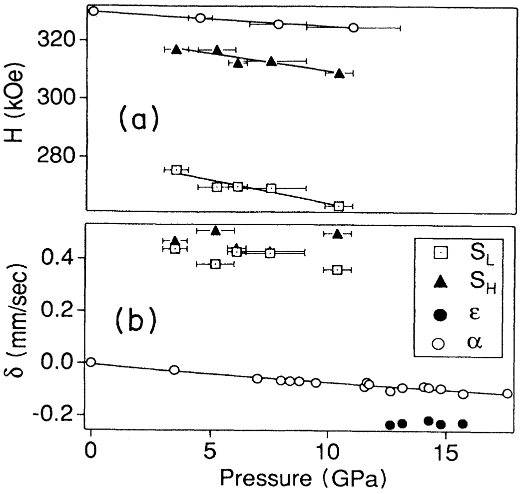

FIG. 3. Pressure dependence of the magnetic hyperfine fields (a) and isomer shifts (b). α and ϵ stand for normal iron phases. The hyperfine fields of the iron hydride have larger pressure dependence than those of α-iron.

The fit of the Mössbauer spectrum at 3.5 GPa is shown in Fig. 2. It is resolved into three subsextets labeled S_α, S_L, and S_H in the figure. S_α is from a small fraction of the sample with unmodified α iron, and the others from the iron hydride. Here "L" and "H" stand for the lower and higher magnetic field, respectively. The pressure and volume dependence of the hyperfine fields and isomer shifts are shown in Figs. 3 and 4, respectively. The volume of the FeH is derived from zero-pressure x-ray data by Antonov *et al.*[4] and P-V isotherm of ϵ-iron by

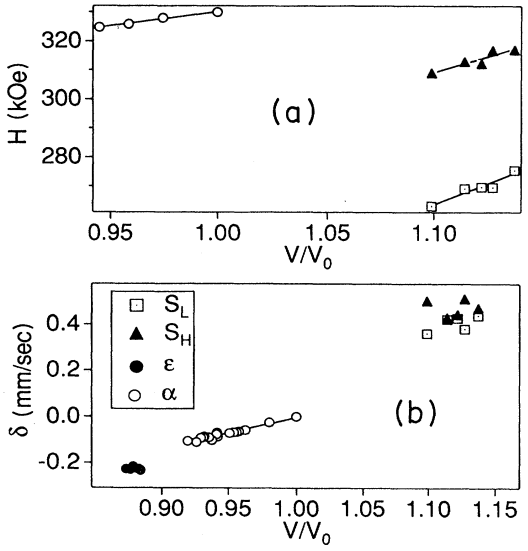

FIG. 4. Volume dependence of the magnetic hyperfine fields (a) and isomer shifts (b). An extrapolation in volume from metallic iron phases to the iron hydride is not sufficient to explain the isomer shift results.

Mao, Bassett, and Takahashi.[7] Some of the values for α- and ϵ-iron are quoted from the measurements by Williamson, Bukshpan, and Ingalls.[8]

The new sextets are well separated from each other and have similar relative intensities. This implies that FeH would likely be in a stoichiometric state on two different but equally populated lattice sites. The lattice structure of FeH has been shown as dhcp,[4] which is compatible with the above picture because dhcp has two nonequivalent lattice sites, one resembling hcp, and the other, fcc local configuration. Assuming the occupation of octahedral interstitial sites by hydrogen as in fcc nickel hydrides[9] or fcc palladium hydrides,[10] and 1:1 maximum hydrogen-to-iron ratio, both iron locations would be surrounded by six hydrogen nearest neighbors. The arrangements can be pictured as two equilateral triangles of hydrogen, one above the iron and one below. In one site the triangles have the same orientation, while in the other, they are rotated by 60° with respect to each other about the c axis.

The two spectra for the hydride have similar isomer shifts of about 0.4 mm/sec with respect to α-iron under standard condition. This is considerably more positive than in other metallic forms of iron. At the same time, the magnetic hyperfine fields associated with both spectra (276 and 317 kOe at 3.5 GPa) are somewhat smaller than in α-iron (328 kOe at 3.5 GPa), and differ from each other by about 40 kOe. The magnitude of the hyperfine field implies that FeH is ferromagnetic. Both isomer shifts and hyperfine fields decrease with pressure as in α-iron, while the pressure dependence of the hyperfine fields is larger than that of α-iron.

Since the contribution of the volume expansion to the isomer shifts of FeH is at most 0.2 mm/sec on the basis of an extrapolation from α- or ϵ-iron (see Fig. 4), or semiempirical calculation,[11] in order to explain the isomer shift results one should have either fewer $4s$ electrons, or more $3d$ electrons, or perhaps both. These changes would be on the order of several tenths of one electron. Because of the similarity of the two iron sites, the isomer shifts at both sites would be roughly the same.

More subtle effects can cause smaller hyperfine fields relative to α-iron. This could be a change of $4s$ contribution to the total field as well as a reduction in the magnetic moment due to $3d$ electrons themselves, or due to the modified coupling between moments caused by the hydrogen. Any added d electrons would reduce magnetic moments because they would likely go into the minority band which presumably has higher density of states at Fermi level. The electronic changes and the expanded volume may also account for the magnetic behavior which is different than in γ- (fcc) or ϵ-iron. These latter iron phases are not ferromagnetic, despite the fact that each has a local iron neighbor arrangement resembling one or another of the two sites in the dhcp FeH. Besides a simple d-band filling model,[3] which gives reasonable estimates on magnetic moments of several hydrides, in order to explain the magnetic (and electronic) behavior of FeH, more details of the bonding of hydrogen with iron[12] may have to be considered.

Because of our observed reduction in the hyperfine fields of FeH with decreasing volume, the ferromagnetism may tend to disappear at further reduced volume. Such an effect of course occurs in fcc iron-nickel alloys.[13]

The small difference in the hyperfine fields for two sites can be understood in terms of local conditions. Soon after the completion of the experiments reported here, we learned of new Mössbauer measurements on the quenched hydrides by Schneider *et al.*,[14] whose data are generally in agreement with ours. With better statistics available for the quenched sample at low temperature, their measurements have shown small quadrupole splittings, with electric-field gradients having opposite signs at the two sites. A finite quadrupole splitting is expected for the hexagonal symmetry. Similarly, a dipolar contribution to the hyperfine field is also then expected. Such behavior could account for the measured difference of 40 kOe, since the dipolar contribution to the hyperfine field is typically of this size,[15] and can be positive or negative, depending on the sign of deviation from cubic symmetry. Of course, we cannot completely rule out the effect of the different site symmetries on the local $3d$ electrons, which could also lead to slightly different hyperfine fields. A different hydrogen fraction at the two sites is another possible cause.

Finally, we report in Fig. 5 the pressure dependence of the intensity ratio of two hydride sextets for two different runs. Just after the hydride formation, the sextet S_H for both runs has a larger intensity than S_L. As pressure is increased, both runs show an intensity reduction of S_H relative to S_L. Although, as noted in other experiments,[14] the intensities characteristically depend upon sample preparation, in run B, we even observe a reversal of the intensity ratio at higher pressure, i.e., the intensity of S_L becomes larger than that of S_H. Considering the similarities between two sites (which would give similar Mössbauer fractions), this could be attributed to the change in the population of available sites corresponding to each sextet. A possible explanation would be a change in the stacking sequence (defects) relative to ideal dhcp. Recognizing the large uncertainties and limited data, we speculate that there may be a dominance of the S_L sites over S_H sites at much higher pressure. Since the hyperfine field of S_L decreases more rapidly with pressure

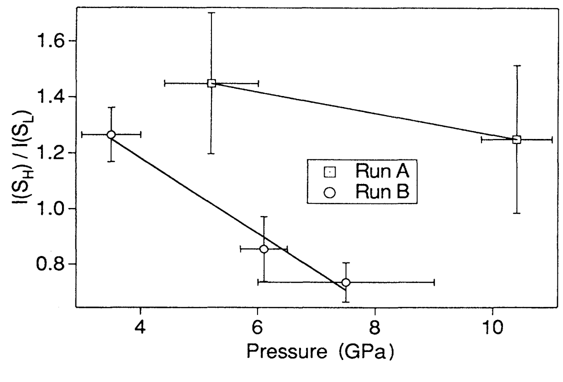

FIG. 5. Pressure dependence of the intensity ratio of two hydride sextets.

than that of S_H, and since ϵ-iron (hcp and reduced volume) is not ferromagnetic, one may then further expect the hcp type for the lower field site, and the fcc type for the higher field site.

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