Magnetic States in Fe, Co, Ni hydrides under High Pressure Probed by X-ray Magnetic circular dichroism

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Abstract. Magnetic states of Fe, Co, and Ni hydrides under pressure have been investigated by X-ray magnetic circular dichroism (XMCD) at the K-edge. At room temperature, Fe, Co, and Ni metals are hydrogenated to ferromagnetic FeH, ferromagnetic CoH, and paramagnetic NiH, respectively. A sharp XMCD profile is observed after hydrogenation, which is attributed to the hydrogen-induced reconstruction of the electronic structure. The pressure dependence of XMCD demonstrates that the ferromagnetic state of FeH is less stable than that of CoH under pressure.

1. Introduction
Metal hydride systems have recently attracted considerable interest because of their potential applications as hydrogen storage materials and of hydrogen-induced modification to crystal- and electronic structures. 3d transition metal (TM) monohydrides can be synthesized by a direct reaction with H₂ fluid under gigapascal pressures [1]; hydrogen causes drastic changes in their magnetic properties. When ferromagnetic 3d TMs such as Fe, Co, and Ni undergo hydrogenation, they exhibit appearance or disappearance of the ferromagnetic states accompanied with large volume expansion and structural transition [2].

An investigation into the magnetic states of the TM hydrides and the pressure dependence of these states enables a fundamental understanding of the influence of hydrogen on the electronic structure of TM. For this purpose, we synthesized Fe, Co, and Ni monohydrides and measured the X-ray magnetic circular dichroism (XMCD) spectra at the K-edge. XMCD is a spectroscopic technique that probes the magnetic state with element- and orbital selectivities. Although the 1s→4p dipole transition is dominant at the K-edge, the XMCD spectrum is sensitive to the 3d magnetic states because of TM 4p-3d hybridization with neighbouring atoms [5,6]. In this paper, the magnetic states of these hydrides are discussed [3,4], and the stability of the ferromagnetic phase under pressure is also investigated.

2. Experimental Procedure
Polycrystalline metal foils 3–5 µm in thickness were prepared as the starting material. A tiny foil was set into a diamond anvil cell (DAC) with H₂ fluid that was initially pressurized to 0.18 GPa. We
employed a versatile gas-loading system to load H\textsubscript{2} fluid to the DAC [7]. The H\textsubscript{2} fluid functioned as a pressure-transmitting medium and as the source of hydrogen. X-ray absorption near edge structure (XANES) and XMCD were measured on the beamline 39XU at the SPring-8 facility [8]. The XMCD spectra were obtained using the helicity-modulation method. All the measurements were carried out at room temperature. A magnetic field of 0.6 T was applied perpendicular to the sample surface. The pressure applied to the sample was measured through the conventional ruby fluorescence method.

3. Results and Discussion

Figure 1 shows the XANES and XMCD profiles of the TMs and the TM hydrides. The XANES and XMCD spectra show significant change caused by hydrogenation. XANES spectra of the TMs are found to be different from each other, while those of the TM hydrides are almost the same, consisting of a suppressed shoulder a and a crest b. The characteristics of the XANES spectra mean that TM 4\textit{p} unoccupied density of states (DOS) is very similar among TM hydrides.

![Figure 1. XANES (lower part of the graph) and XMCD (upper part) spectra at selected pressures. The blue and red lines correspond to the spectra of TMs and TM monohydrides, respectively. The green lines represent the spectra of intermediate phases that correspond to the coexistence of TM and TM monohydride for Fe and Ni, and correspond to TM hydride with a small hydrogen content H/TM<1 for Co. The vertical lines indicate the absorption edge E\textsubscript{0}.](image)

The pressure ranges required to synthesize TM monohydrides were determined from the XMCD and X-ray diffraction measurements [4]. Hydrogenation of Fe to FeH was observed between 3.2 and 3.8 GPa. The hydrogenation of Co to CoH is gradual, in a wide pressure range of 2.7–5 GPa, while that of Ni was observed over a narrow and low pressure range of 0.67–0.84 GPa.

The XMCD spectrum of NiH completely vanishes after hydrogenation, revealing that NiH is paramagnetic [2]. In contrast to that, XMCD spectra of FeH and CoH do not disappear. The remaining XMCD shows that both hydrides are ferromagnetic.

In the XMCD spectra of FeH and CoH, the negative peak B shifts toward the absorption edge E\textsubscript{0}. In addition, the peak B exhibits sharp profiles with large amplitude as compared to those of Fe and Co. The XMCD profile near E\textsubscript{0} is interpreted as influence from the “orbital moment density” of the 3\textit{d} state via the 4\textit{p}-3\textit{d} hybridization [5,6]. Therefore, the sharp profile indicates that the orbital moment
density of the 3d state is concentrated just above $E_F$. According to the DOS calculated previously [9], this feature is probably attributed to the electronic structure of the unoccupied minority 3d DOS and the antibonding state between H and TM. We note that both the states are formed within an energy range of $-E_F + 6$ eV thorough the hydrogenation.

In the hydrogenation of Fe to FeH, it is observed that the positive peak A is significantly suppressed. The experimental result demonstrates that the electronic structure of FeH approaches to strong ferromagnetism from the weak ferromagnetism [5,6], as predicted from the theoretical calculation [9]. On the other hand, the absence of the positive peak A suggests that CoH maintains the electronic structure classified as strong ferromagnetism; strong ferromagnetism is similar to the electronic structure of Co. The present results show that the XMCD spectrum at the $K$-edge probes the reconstruction of the electronic structure, in particular the changes that occur in the 3d unoccupied DOS as a result of hydrogenation. The XMCD profile of FeH is similar to that of CoH except for the small positive peak A even though these hydrides have different crystal structure, i.e. dhcp for FeH, fcc for CoH [2]. This result indicates that the crystal structure has little effect on the XMCD profile.

Stability of the ferromagnetic state is investigated by the pressure dependence of XMCD. At the highest pressure, the XMCD amplitude of FeH becomes very small at 27.5 GPa, while the XMCD profile of CoH is almost unchanged at 28.4 GPa (figure 1). To clarify this trend, the pressure dependence of XMCD is summarized in figure 2, where the integrated intensity of XMCD is plotted. Because the XMCD profile changes largely by hydrogenation, marked variations occur at the corresponding pressure ranges. The intensity of FeH decreases linearly up to 20 GPa, after which the slope becomes steep with further increase in pressure. Extrapolating this decrease, we evaluate the critical pressure $p_c$ to be 29.5 GPa; $p_c$ is the pressure at which the XMCD spectrum vanishes. FeH is paramagnetic above $p_c$, and Curie temperature would be reduced below room temperature. In the case of CoH, the intensity of CoH linearly decreases up to 28.4 GPa; a sudden drop is absent. The slope of the CoH is two times smaller than that of the FeH below 20 GPa. We also note that the weak pressure dependence is comparable to the reported behavior of Co and Ni metals; the ferromagnetic states of Co and Ni are known to remain above 100 GPa [10,11]. The present result indicates the high stability of the ferromagnetic state in CoH under pressure.

![Figure 2. Integrated intensity of CoH (closed circles), FeH (closed diamonds), and NiH (closed triangles) as a function of pressure. $p_c$ denotes the estimated critical pressure of FeH.](image)

Appearance or disappearance of the ferromagnetic state can be explained by the 3d DOS around $E_F$. In the case of TM hydrides, hydrogenation causes remarkable volume expansion ($\Delta V \approx 2$ Å$^3$ per formula unit) [4,12,13], which leads to higher 3d DOS with a narrow width. The reduced overlap between TM 3d orbitals plays an important role in the electronic structure. Taking Stoner criterion into account [14], the electronic structure of FeH and CoH with higher densities around $E_F$ is suitable to stabilize ferromagnetic states. In contrast, most of the 3d DOS of NiH is occupied, and $E_F$ is, consequently, located above the upper threshold of the 3d DOS [15]. The electronic structure with low densities around $E_F$ results in the paramagnetic state of NiH.
Under higher pressure, broadening of the 3d DOS is introduced by the enhanced overlap between TM 3d orbitals due to the lattice contraction. This reduces the DOS around $E_F$, resulting in the instability of the ferromagnetic state. The high stability of the ferromagnetic state of CoH implies that its electronic structure is less influenced by the applied pressure, whereas the electronic structure of FeH is strongly modified. The marked contrast in the stability is probably attributed to the different profiles of the 3d DOS around $E_F$.

4. Conclusion
The magnetic states of Fe, Co, and Ni hydrides under pressure have been investigated by XANES and XMCD. The XMCD spectra reveal that Fe, Co, Ni metals are hydrogenated to ferromagnetic FeH, ferromagnetic CoH, and paramagnetic NiH, respectively. The sharp XMCD profiles near $E_0$ indicate that the orbital moment density of 3d states is concentrated just above $E_F$, which is probably attributed to the hydrogen-induced electronic structure around $E_F$, i.e. antibonding states, and the higher 3d DOS with a narrow width. The pressure dependence of XMCD shows that the ferromagnetic state of FeH is less stable than that of CoH under pressure. Our study demonstrates that the XMCD spectra at the K-edge sensitively probe the changes that occur in the electronic structure as a result of hydrogenation.

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