Chemical Bonding of Hydrogen in MgH$_2$

Hydrogen is considered to be one of leading candidates for clean energy sources in the future. For safe and efficient hydrogen storage, developments of new hydrogen storage materials are currently being researched [1]. The hydrogen storage capacity per unit weight of typical metal alloys is very low (about 2.0 mass %) and not sufficient for use in a fuel cell vehicle. Therefore, alloys containing light elements are focused on as high-performance storage materials. Magnesium in particular has a high storage capacity (7.6 mass %). For this reason, magnesium and its alloys are considered to be some of the most important candidates for reversible hydrogen storage materials. Unfortunately, magnesium hydrides are thermodynamically stable, and the dehydrogenation of magnesium hydrides requires high temperatures (> 550 K). Understanding the bonding nature of magnesium and hydrogen is essential in order to improve its fundamental dehydrogenation performance.

To further understand the nature of bonding, charge density distribution is typically investigated by X-ray diffraction analysis. However, the diffraction intensity from hydrogen atoms in metal hydrides is very weak, although we have overcome that difficulty with the highly brilliant X-ray source of SPring-8. In our result, the diffraction intensities from hydrogen could be measured precisely and the positions of hydrogen in metal hydrides were determined by the analysis based only on the X-ray diffraction data. Furthermore, the MEM/Rietveld method, which is a combination of the MEM (maximum entropy method) and the Rietveld refinement [2], was applied to metal hydrides. By employing this method and precise X-ray diffraction data, the charge density distribution measurement, which has not so far succeeded, became possible for the first time, and the bonding nature of hydrogen in MgH$_2$ was revealed experimentally [3].

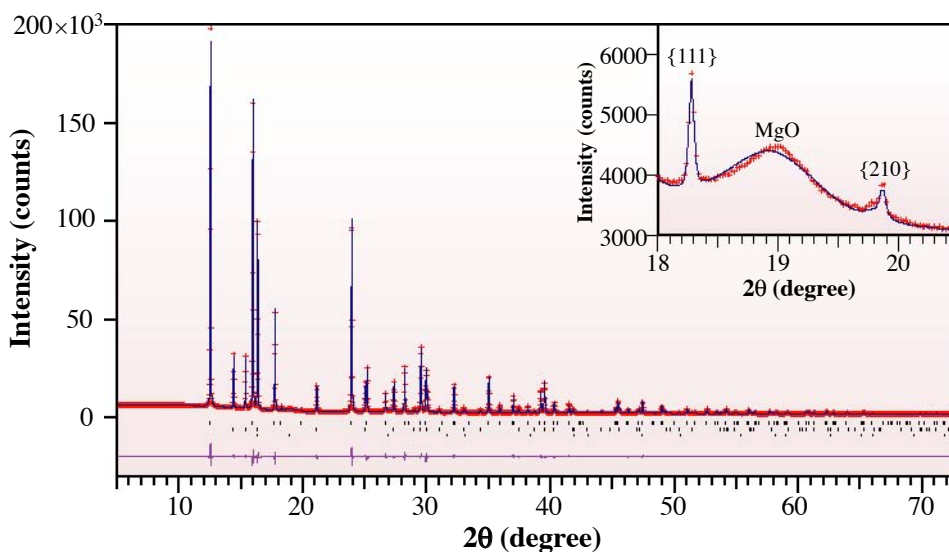The MgH$_2$ sample was prepared by hydrogen activation treatment of pure magnesium powder.

Fig. 1. Rietveld analysis pattern of the MgH$_2$ sample. Red + marks are measured intensity, the blue line is calculated intensity, black \ marks are peak positions, and the purple line is the deviation of measurement and calculated intensity. MgH$_2$, Mg and MgO are included in this sample. The enlarged pattern of the region from 18.0° to 20.5° is shown in the inset.

The obtained fine powder was inserted into a glass capillary (diameter: 0.1 mm) for measurement and the X-ray diffraction experiment was carried out using a large Debye-Scherrer camera with imaging plate as detector at beamline **BL02B2** [4]. The wavelength of the incident X-ray was 0.696 Å. The X-ray diffraction intensities were obtained with 0.02° steps from 5.0° to 73.0° in 2θ. The experimental data were analyzed by the MEM/Rietveld method using the computer programs ENIGMA [5] and RIETAN [6].

The powder sample was composed of three phases, MgH_2, Mg and MgO. By Rietveld analysis, the mass fractions for each phase were determined as 69, 27 and 4 mass%, respectively. The lattice parameter of MgH_2 is a = 4.5180(6) Å, c = 3.0211(4) Å, which is a little larger than that of MgD_2. The weighted profile reliability factor, R_{WP}, and the reliability factor based on integrated intensities, R_I, of the Rietveld analysis were 2.9% and 1.7%, respectively. The fitting result of the Rietveld analysis is shown in Fig. 1. The inserted figure clearly shows the {111} reflection at 18.2° and the {210} reflection at 19.8°, which are attributed to the sub-lattice of only H atoms.

In MEM analysis, the reliability factor R was 1.0%, which is small enough to determine the charge densities of hydrogen and its bond nature. Figure 2 illustrates the crystal structure of MgH_2 (rutile type). The charge density distribution of (001) and (110) plane in the crystal of MgH_2 is shown in Fig. 3(a) and Fig. 3(b). The charge density distribution around Mg is spherical, whereas the lower charge density distribution around H is non-spherical and spreads slightly in the direction of the nearest neighbor Mg and H atoms. At the bond midpoint, the charge density is 0.26, 0.21 and 0.25 $e/Å^3$ for the apical Mg–H, the equatorial Mg–H and the H–H bonds, respectively. These values are much lower than those of typical covalent bonds in diamond (1.4 $e/Å^3$) and Si (0.7 $e/Å^3$) [2]. The results suggest that there are weak but significant covalent bonds between Mg and H as well as between H and H. The charge density in the interstitial region is extremely low, 0.02 $e/Å^3$, which could deny the existence of the metallic bonding nature. The number of electrons within the spherical region was estimated as 10.09 e and 1.26 e for Mg (radius: 0.95 Å) and H (radius: 1.00 Å). These values indicate that ionic charge of Mg and
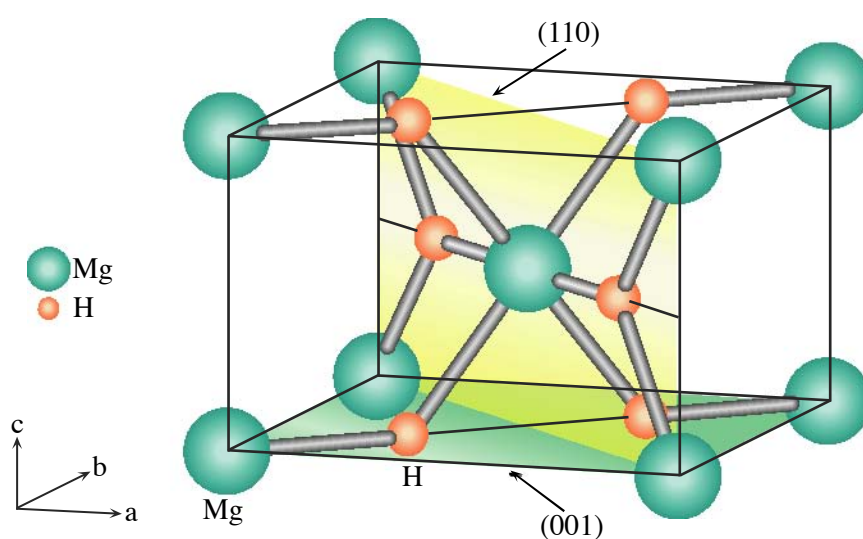

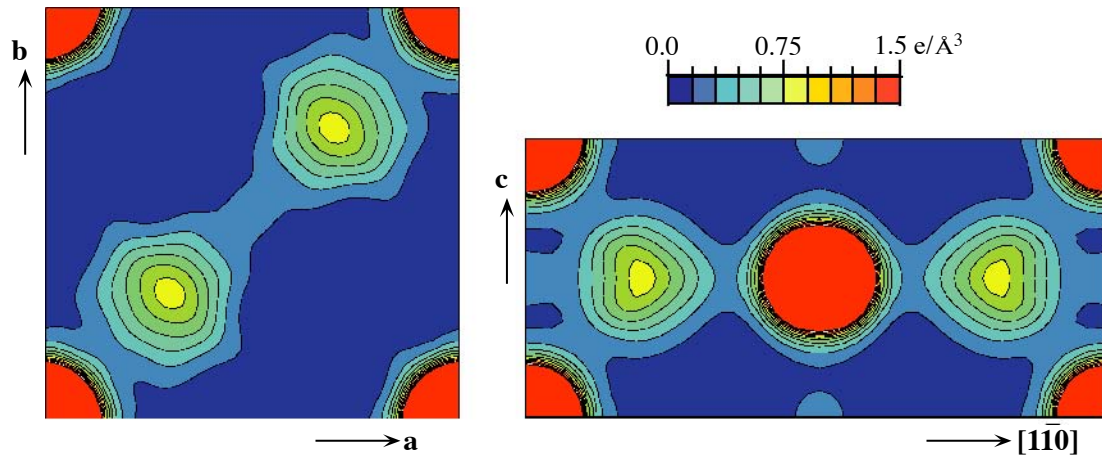*Fig. 2. The crystal structure of MgH₂ (rutile type).*

Fig. 3. MEM charge density maps of (001) and (110) plane in MgH₂. The contour lines are drawn from 0.0 to 1.5 at 0.15 e/Å³ intervals.

H are represented as $Mg^{1.91+}$ and $H^{0.26-}$. Hydrogen is far more weakly ionized than magnesium.

Experimentally, the bonding nature of MgH_2 has been revealed by the charge density distribution measurement. As a result, we consider that it is necessary to make its ionic bonding even weaker to improve the dehydrogenation performance of MgH_2. In the future, it will be necessary to find an effective method to weaken the bonding strength by the selection of a suitable crystal structure, adding elements and so on. The electronic states and formation energy of metal hydrides have been theoretically calculated [7]. The next step is to undertake experimental and theoretical investigations into the bonding nature of hydrogen to develop efficient hydrogen storage materials.

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References

[1] L. Schlapbach and A. Züttel, Nature **414** (2001) 353.
[2] M. Takata *et al.*, Z. Krystallogr. **216** (2001) 71.
[3] T. Noritake, M. Aoki, S. Towata, Y. Seno, Y. Hirose, E. Nishibori, M. Takata, M. Sakata, Appl. Phys. Lett. **81** (2002) 2008.
[4] E. Nishibori *et al.*, Nucl. Instrum. Meth. in Phys. Res. A **467-468** (2001) 1045.
[5] F. Izumi, The Rietveld Method, Ed. R. A. Young (Oxford Univ. Press, 1993) chap. **13**.
[6] H. Tanaka *et al.*, J. Appl. Crystallogr. **35** (2002) 282.
[7] K. Miwa and A. Fukumoto, Phys. Rev. B **65** (2002) 155114.