Special Issue Materials Analysis Using Synchrotron Radiation

特集

Research Report

Charge Density Analysis in Magnesium Hydride

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水素化マグネシウムの電荷密度解析

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Abstract

Magnesium is considered one of the most promising materials for reversible hydrogen storage, because it has high storage capacity. However, the high thermodynamic stability of magnesium hydride is unfavorable for dehydrogenation processes. Understanding the bonding nature of Mg and H is essential for improving its dehydrogenation performance. Therefore, the charge density distribution in MgH_2 was measured. Charge density is typically investigated by X-ray diffraction, but the diffraction intensity from hydrogen atoms is very weak. So far, analyzing the hydrogen in metal hydrides by X-ray diffraction has been difficult. We have overcome this difficulty with precise powder diffraction measurement by synchrotron radiation, which is a highly-brilliant X-ray source. The charge density was analyzed by the MEM/Rietveld method from the measurement data. The results show weak covalent bonds between Mg and H as well as between H and H. The charge density in the interstitial region is extremely low, which denies the existence of metallic bonding. As a result of estimation of the number of electrons within the sphere around the Mg and the H atoms, the ionic charge in MgH_2 was represented as $Mg^{1.91+}H^{0.26-}$. We experimentally revealed that the crystal of MgH_2 is stabilized by ionic and weak covalent bonding. We consider that its ionic bonding must be made weaker in order to improve the dehydrogenation performance of MgH_2.

Keywords Synchrotron radiation, X-ray diffraction, Charge density, Hydrogen storage materials, Magnesium, Hydride, Rietveld analysis, Maximum entropy method

要　旨

マグネシウムは軽量で水素吸蔵量が多いことから，水素貯蔵材料として有望である。しかし，その水素化物MgH_2は熱力学的に非常に安定であるため，水素を放出しにくい特性を持っている。水素放出特性改善には，MgとHの結合状態の解明が重要である。そこで，MgH_2の電荷密度分布測定を行った。電荷密度分布はX線回折により解析できるが，水素からのX線回折強度は非常に弱く，これまでX線による金属水素化物中の水素の解析は困難であるとされてきた。そこで，強力なX線源である放射光を用いて精密な粉末X線回折測定を行い，MEM/Rietveld法により電荷密度を解析した。その結果，MgとH間およびHとH間に弱い共有性結合があること，格子間の電荷密度は非常に低く，金属性結合はないことが明らかになった。また，MgおよびH原子のまわりの球内の電子数を見積ることにより，MgH_2のイオン価数は$Mg^{1.91+}H^{0.26-}$と表されることがわかった。MgH_2結晶はイオン性結合と弱い共有性結合によって安定化していることが実験的に解明された。MgH_2の水素放出特性を改善するにはイオン結合性をさらに弱めることが必要と思われる。

キーワード 放射光，X線回折，電荷密度，水素吸蔵材料，マグネシウム，水素化物，
リートベルト解析，最大エントロピー法

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1. Introduction

Hydrogen is considered one of leading candidates for clean energy sources. New technology, such as fuel cells, hydrogen storage and so on, is developed to utilize hydrogen. Especially, hydrogen storage is a key technology. Currently, new hydrogen storage materials are being researched and developed.[1] Hydrogen storage alloys have suitable properties for safe and efficient hydrogen storage. However, typical metal alloys have very low hydrogen storage capacity per unit weight (about 2.0 mass % in Ti-V-Cr alloy), which is not sufficient for practical use in a fuel cell vehicle. Therefore, efforts to find high-performance storage materials focus on alloys containing light elements. Magnesium especially has a high storage capacity (7.6 mass %). For this reason, magnesium and its alloys are considered to be among the most important candidates for reversible hydrogen storage material. Unfortunately, magnesium hydrides are thermodynamically stable; the heat of formation ΔH in the following hydrogenation reaction is -74.8 kJ/mol H_2.[2]

$$Mg + H_2 \rightarrow MgH_2$$

Dehydrogenation of magnesium hydride requires high temperatures over 550 K under a hydrogen pressure of 0.1 MPa. According to the van't Hoff relation,

$$\ln (P/P_0) = \Delta H/(RT) - \Delta S/R,$$

heat of formation ΔH must be about -35 kJ/mol H_2 for dehydrogenation at room temperature under a hydrogen pressure of 0.1 MPa. The heat of formation for dehydrogenation is related to the bonding nature of hydrogen in metal. Therefore, understanding the bonding nature of magnesium and hydrogen is essential for improving its dehydrogenation performance.

In order to understand the bonding nature, charge density distribution is typically investigated by X-ray diffraction measurement, but the X-ray diffraction intensity from hydrogen atoms is very weak compared with metallic atoms. So far, analysis of hydrogen by the X-ray diffraction has been difficult. The structure of metal hydrides has usually been analyzed by only neutron diffraction. However, if it can be measured by use of the synchrotron radiation, weak X-ray intensity from hydrogen atoms will be detected precisely.

Recently, synchrotron radiation, which is a highly brilliant and highly directional X-ray source, has been utilized for the investigation of hydrogen storage materials. The following studies using the characteristic of the synchrotron radiation are reported.

(1) Measurement of crystal structure under high hydrogen pressure.[3]

(2) Analysis of the lattice strain induced by hydrogenation.[4]

(3) In-situ measurement of structure transition in the hydrogenation process.[5]

(4) Analysis of the complex crystal structure.[6]

This paper reports another study of hydrogen storage materials by synchrotron radiation.

(5) Hydrogen atom position and charge density distribution analysis.

Using the measured X-ray diffraction data, hydrogen atom position was analyzed by the Rietveld method and charge density distribution was analyzed by MEM (maximum entropy method). This MEM/Rietveld method has revealed the bonding nature of various materials.[7, 8] The bonding nature of hydrogen in MgH_2 was investigated experimentally by applying this method to metal hydrides.[9] Hydrogen atom positions can be analyzed in neutron diffraction. Whereas in X-ray diffraction, it is peculiarity that the charge density and bonding nature can be analyzed as well as the positions of hydrogen atoms.

2. Experiment and analysis

The MgH_2 sample was prepared by hydrogenation of pure Mg powder (purity: 99 %) under a hydrogen pressure of 7 MPa at 573 K. In order to avoid the effect of powder granularity on the in-homogeneity intensity of the Debye-Scherrer ring in the X-ray powder diffraction pattern, small size (sub-micron) powder was selected from the prepared sample, by means of the following process. The ground sample powder was dispersed in a less-reactive liquid suspension. The large particles were precipitated in liquid suspension, and only the top liquid in which the small particles were suspended was extracted and dried. The obtained fine powder was inserted into a glass capillary (diameter: 0.1 mm) for X-ray

diffraction measurement.

The synchrotron radiation X-ray powder experiment was carried out by use of a large Debye-Scherrer camera with imaging plates as detectors at the beam-line BL02B2 in SPring-8.[10] The X-ray powder diffraction pattern was measured at room temperature. The wavelength of incident X-rays was 0.696 Å. The X-ray diffraction intensities were obtained in steps of 0.02° from 5.0° to 73.0° in 2θ, which corresponds to 0.585 Å resolution.

The measurement data were analyzed by the Rietveld method by use of the computer program RIETAN.[11] In the Rietveld analysis, the crystal structure is refined by the least squares method from powder X-ray diffraction data. The reference data of MgH_2[12, 13] was used for the starting structure of the refinement. X-ray scattering factors of neutral atoms (Mg and H) were used in Rietveld analysis. MEM analysis revealed that Mg in MgH_2 was in an ionic state. Therefore, the scattering values of Mg^{2+} ion and H atom were used in the final refined analysis.

The charge density in MgH_2 was analyzed by MEM, using the observed structure factors of 103 reflections derived from the Rietveld analysis. The MEM calculation was carried out in 48 × 48 × 32 pixels per tetragonal lattice by use of the computer program ENIGMA.[14] Usually, charge density is obtained by Fourier transformation of structure factors. The result of Fourier transformation using structure factors of 103 reflections is shown in **Fig. 1**. The hydrogen atom position and charge density cannot be determined, because the number of structure factors is very low. Mathematically, an infinite number of structure factors must be used in Fourier transformation. The MEM analysis is a method of finding the most probable value by maximizing entropy, on the basis of information theory. The schematic diagram of the relation between the observed structure factor F_{obs} and charge density ρ is shown in **Fig. 2**.

The MEM calculation was begun from uniform charge density ρ_0 (ρ_0 = 0.454 e/Å^3 in MgH_2). The new charge density ρ was found in the direction in which the entropy S increases from preliminary charge density τ. Next, τ is replaced with ρ, and the calculation is carried out. These operations are iterated until the difference between F_{obs} and F_{cal} calculated from charge density ρ attain a similar level to measurement error σ (F_{obs}). In the case of MgH_2, the MEM calculation was iterated 12092 times and converged. The change in the found charge density in MgH_2 (110) plane during analysis is shown in **Fig. 3**.

3. Results and discussion

The Rietveld analysis pattern is partially shown in **Fig. 4**(a) (from 10.0° to 45.0°). In this pattern, the

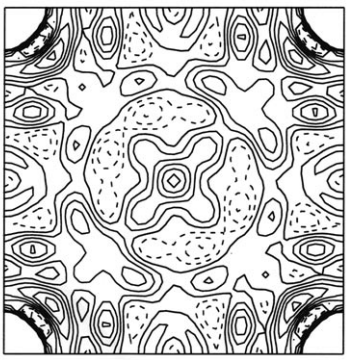

Fig. 1 The Fourier transformation in (001) plain of MgH_2.
Contour line interval: 0.3 e/Å^3,
Range: -1.2 ~1.8 e/Å^3

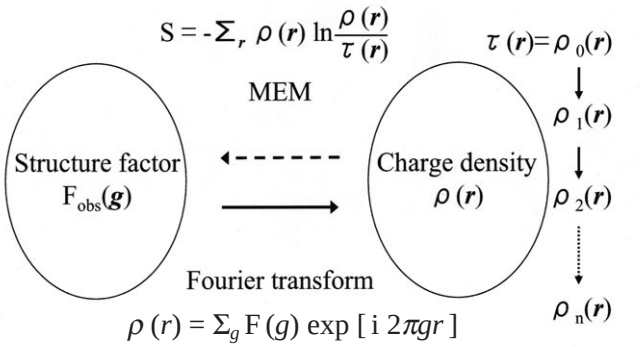

Fig. 2 The relation between structure factor $F_{obs}(g)$ and charge density $\rho(r)$.

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measurement data are shown by "+" marks, the calculation data are shown by a solid line, the peak positions are shown by a "|" mark and the difference between the measurement and the calculation data is shown by a solid line below the diffraction patterns. The powder sample was composed of three phases, MgH_2, Mg, and MgO. As a result of the Rietveld analysis, the mass fractions for each phase were estimated as 69.0, 27.0, and 4.0 % for MgH_2, Mg, and MgO, respectively. In Fig. 4(b), the pattern of the Rietveld analysis is enlarged in order to clearly show the {111} reflection and the {210} reflection, which are attributed to the sub-lattice of only H atoms. This indicates that the weak diffraction peaks from hydrogen atoms can be precisely measured by synchrotron radiation. The weighted profile reliability factor, R_{WP}, and the reliability factor based on integrated intensities, R_I, of the Rietveld analysis are 2.9 % and 1.7 %, respectively. The crystal data of MgH_2 which was obtained by the Rietveld analysis is shown in **Table 1**, along with the reference data from previous studies.[12, 13] So far, only the lattice parameter of MgH_2 was obtained by the usual X-ray diffraction. Furthermore, the atomic coordinates of hydrogen and the temperature factor of each atom have been determined by this study with synchrotron radiation. In comparison with MgH_2 and MgD_2, the lattice parameters of MgH_2 are larger than that of MgD_2, which seems to stem from the isotope effect.

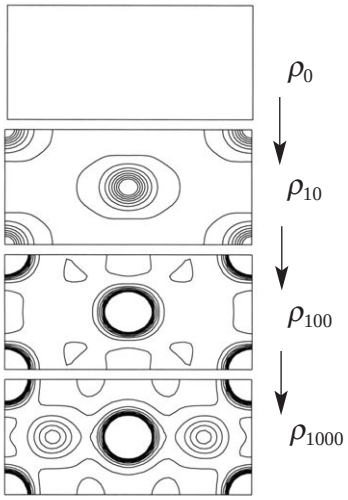
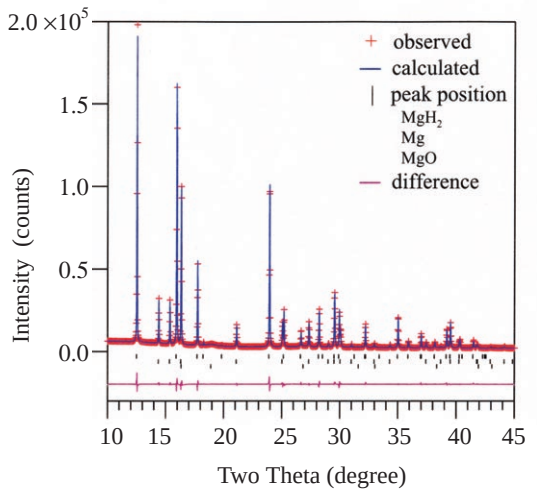
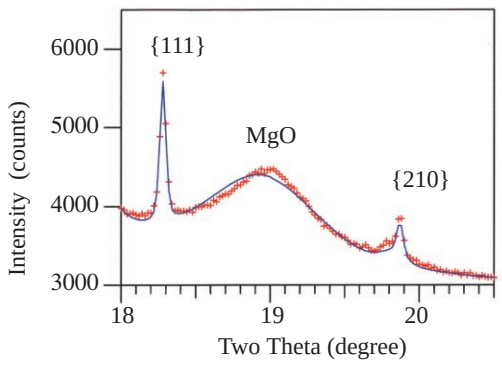


Fig. 3 The change of ρ_n in MgH_2 (110) plane during MEM calculation.
n: number of repetition,
Contour line interval: 0.15 e/Å^3,
Range: 0 ~1.5 e/Å^3



(a)



(b)

Fig. 4 (a) The Rietveld analysis pattern of the MgH_2 sample. MgH_2, Mg and MgO are included in this sample.
(b) The enlarged Rietveld analysis pattern of the MgH_2 sample.

In MEM analysis, the reliability factor R is 1.0 %, which is small enough to determine the charge densities of hydrogen and its bonding nature. The crystal structure of MgH_2 (Rutile type) is illustrated in **Fig. 5**. The charge density distributions of the (001) and (110) planes in the crystal of MgH_2 are shown in **Fig. 6**(a) and Fig. 6(b). In **Fig. 7**, the equal-charge density surface is drawn with a contour level of 0.15 e/Å^3.

At room temperature, the charge density distribution around Mg is spherical, whereas the lower charge density distribution around H is non-spherical and slightly spread in the direction of the nearest neighbor Mg and H atoms. At the bonding midpoint, the charge density is 0.26 e/Å^3 for the apical Mg-H bonds, 0.21 e/Å^3 for the equatorial Mg-H bonds, and 0.25 e/Å^3 for the H-H bonds. These values are much lower than 0.7 e/Å^3 for Si-Si bond [7] in silicon and 1.4 e/Å^3 for C-C bond[7] in diamond, which are typical covalent bonds. The results suggest that weak covalent bonds exist between Mg and H as well as between H and H. The minimum

Table 1 The crystal data of MgH_2.

Reference		This study	Ref.[12]	Ref.[13]
Sample		MgH_2	MgH_2	MgD_2
Temperature		R.T.	R.T.	260 K
Radiation		X-ray	X-ray	Neutron
Lattice	a	4.5180 (6)	4.5168	4.5010 (1)
constant (Å)	c	3.0211 (4)	3.0205	3.0100 (1)
H coordinate	x	0.303 (3)		0.3040 (2)
Temperature	B_{Mg}	0.79 (3)		0.56 (5)
factor (Å^2)	B_H	2.0 (7)		1.69 (4)
Inter-atomic	Mg-H	1.94 (2)		1.9351 (9)
distance (Å)	Mg-H	1.97 (2)		1.9549 (6)
	H-H	2.52 (4)		2.495 (1)

Space group : $P4_2/mnm$ No.136 (Rutile type)

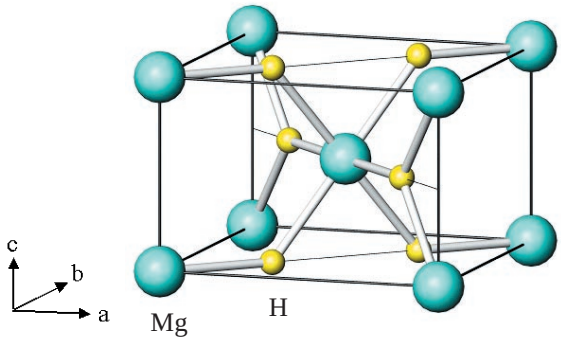
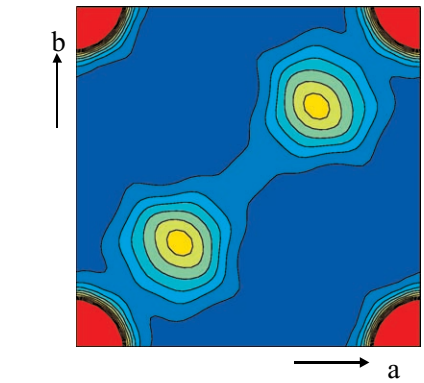
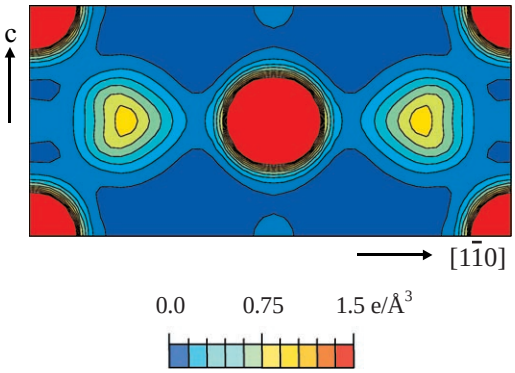


Fig. 5 The crystal structure of MgH_2 (Rutile type).



(a)



(b)

Fig. 6 (a) The charge density map of (001) plane in MgH_2.
(b) The charge density map of (110) plane in MgH_2.
Contour line interval: 0.15 e/Å^3,
Range: 0 ~1.5 e/Å^3

charge density in the interstitial region is 0.02 e/Å^3. This fact denies the significant existence of metallic bonding.

The Mg charge densities are localized within the sphere of the averaged radius, 0.95 Å, which is midway between the 6-coordinate octahedral type Mg^{2+} ion radius 0.86 Å and the 8-coordinate Mg^{2+} ion radius 1.03 Å. Most of the hydrogen charges are located in the region of 1.0 Å radius between the neutral atomic radius 0.53 Å (Bohr radius) and the H^{1-} ionic radius 2.08 Å. The number of electrons within the Mg atom region (within the sphere of 0.95 Å radius) was estimated as 10.09 e from the obtained charge density distribution. Similarly, the number of electrons within the H atom region (within the sphere of 1.00 Å radius) was estimated as 1.26 e. These values indicate that ionic charges of Mg and H are represented as $Mg^{1.91+}$ and $H^{0.26-}$. The electro-negativity is 1.2 for Mg and 2.1 for H. Therefore, in terms of electro-negativity coefficients Mg can be called a cation and H an anion in MgH_2. Furthermore, the results indicate that Mg is almost fully ionized as Mg^{2+}, whereas hydrogen is weakly ionized. The charges detached from Mg distribute in the interstitial region and contribute to the covalent bonding in Mg-H and H-H.

4. Conclusion

By the precise X-ray diffraction measurement and the MEM/Rietveld analysis, the hydrogen atom position and charge density distribution in MgH_2 were determined. As a result, we have experimentally revealed that the bonding nature of MgH_2 is a mixture of ionic and weak covalent bonding. Hydrogen in MgH_2 is in a weakly ionic state, expressed as $Mg^{1.91+}$ $H^{0.26-}$. The results also show weak covalent bonding between Mg and H. Consequently, hydrogen in MgH_2 is stabilized by the ionic and weak covalent bonding. We consider that its ionic bonding must be made weaker in order to improve the dehydrogenation performance of MgH_2. A problem for future study is to find an effective method to weaken the bonding strength by the selection of crystal structure, alloying elements, and so on. The electronic states and formation energy of metal hydrides can be calculated theoretically.[15] Then, the experimental and theoretical investigations of the bonding nature of hydrogen will be important in the development of superior hydrogen storage materials.

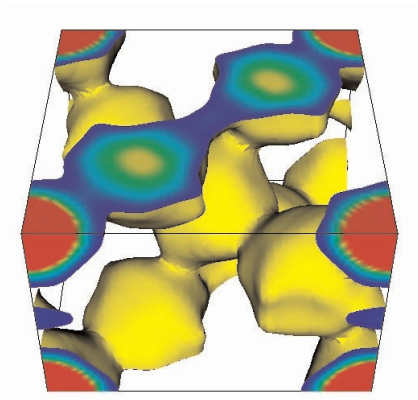


Fig. 7 The equal-charge density surface in MgH_2. Equal-charge density level : 0.15 e/Å^3

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References

1) Schlapbach, L., Züttel, A. : Nature, **414**(2001), 353
2) Fukai, Y., Tanaka, K., Uchida, H. : *Suiso to Kinzoku* (in Japanese), (1998), *Uchidaroukakuho*
3) Fukai, Y., Okuma, N. : Phys. Rev. Lett., **73**(1994), 1640
4) Cerny, R., et al. : J. Appl. Cryst., **33**(2000), 997
5) Pelletier, J. F., et al. : Phys. Rev. B, **63**(2001), 052103
6) Kohlmann, H., et al. : J. Alloys Comp., **322**(2001), 59
7) Takata, M., Nishibori, E., Sakata, M. : Z. Krystallogr., **216**(2001), 71
8) Takata, M., et al. : Nature, **377**(1995), 46
9) Noritake, T., et al. : Appl. Phys. Lett., **81**(2002), 2008
10) Nishibori, E., et al. : Nucl. Instr. and Meth. A, **467/468**(2001), 1045
11) Izumi, F. : Chap. 13, The Rietveld Method, (1993), 236, Oxford Univ. Press,

12) JCPDS 74-0934
13) Bortz, M., et al. : J. Alloys Comp., **287**(1999), L4
14) Tanaka, H., et al. : J. Appl. Crystallogr., **35**(2002), 282
15) Miwa, K., Fukumoto, A. : Phys. Rev. B, **65**(2002), 155114

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