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Journal of Alloys and Compounds 356–357 (2003) 84–86

Journal of ALLOYS AND COMPOUNDS

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Charge density measurement in MgH_2 by synchrotron X-ray diffraction

T. Noritake[a,*], S. Towata[a], M. Aoki[a], Y. Seno[a], Y. Hirose[a], E. Nishibori[b], M. Takata[b], M. Sakata[b]

[a]*Toyota Central R&D Labs., Inc., Nagakute, Aichi 480-1192, Japan*

[b]*Department of Applied Physics, Nagoya University, Nagoya 464-8603, Japan*

Received 10 June 2002; accepted 15 November 2002

Abstract

Magnesium and its alloys are considered one of the most promising materials for reversible hydrogen storage. However, their high thermodynamic stability is unfavorable for dehydrogenation processes. In order to improve their properties, understanding of the bonding nature of Mg and H is essential. In this study, we reveal the precise experimental charge density distribution in MgH_2. X-ray powder diffraction data were obtained using the synchrotron radiation. The charge density distribution was calculated by the MEM (maximum entropy method)/Rietveld analysis. 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. The number of electrons within the sphere around the Mg and the H atoms were estimated from the obtained distribution. As the result, Mg is almost fully ionized as Mg^{2+}, whereas hydrogen is very weakly ionized. The ionic charge of hydrogen is lower than the theoretical value.

Keywords: Hydrogen storage materials; Magnesium hydride; X-ray diffraction; Charge density; Synchrotron radiation

1. Introduction

Hydrogen is considered to be one of leading candidates for clean energy sources in the future. For the practical use of hydrogen, development of hydrogen storage technology is required. For safe and efficient hydrogen storage, developments of new hydrogen storage alloys are currently being researched. The hydrogen storage capacity per unit weight of typical metal alloys is very low and not sufficient for use in a fuel cell vehicle. Therefore, alloys containing light elements such as Li and Mg, are focused on as high performance storage materials. Magnesium especially has a high storage capacity. For this reason, magnesium and its alloys are considered to be one of the most important candidates for reversible hydrogen storage material.

Another important property of a hydrogen storage material is its hydrogen desorption temperature. Unfortunately, magnesium hydrides are thermodynamically stable. The dehydrogenation of magnesium hydrides requires high temperatures ($>$550 K). Studies of nanometer-scale structure and nano-composites for magnesium and its alloys were developed to lower the thermodynamic stability, thus increasing the dehydrogenation performance [1,2]. Furthermore, understanding the bonding nature of Mg and H is essential in order to improve its fundamental dehydrogenation performance. Several theoretical investigations on charge density distribution in MgH_2 have been reported [3–6]. But, the bonding nature and ionic state of MgH_2 have not been studied experimentally.

The position of hydrogen atoms in metal hydrides are usually determined by neutron diffraction analysis. Charge density distribution is typically investigated by X-ray diffraction analysis, but the diffraction intensity from hydrogen atoms in metal hydrides is very weak. So far, it has been difficult to determine the position and the charge density distribution of hydrogen by X-ray diffraction. In this study, we measured the precise X-ray diffraction intensity and analyzed the charge density distribution of hydrogen in metal hydrides using synchrotron radiation [7].

2. Experiment and analysis

The MgH_2 sample was prepared by hydrogen activation treatment of pure magnesium powder (purity: 99%). The activation treatment was performed by the repetition of

*Corresponding author. Tel.: +81-561-63-5360; fax: +81-561-63-6136.

E-mail address: e0553@mosk.tytlabs.co.jp (T. Noritake).

0925-8388/03/$ – see front matter
doi:10.1016/S0925-8388(03)00104-X

absorption under hydrogen pressure of 7 MPa and desorption by a rotary vacuum pump (5 Pa). These treatments were repeated five times at 573 K. The small size (submicron) powder was selected from the MgH_2 sample by precipitation. The obtained fine powder was inserted into a glass capillary (diameter: 0.1 mm) for X-ray diffraction measurement.

X-ray powder diffraction data were obtained using synchrotron radiation at the beam-line BL02B2 in SPring-8. The X-ray diffraction experiment was carried out by use of the large Debye–Scherrer camera with imaging plate as detectors. Further details of this apparatus are given in Ref. [7]. The X-ray powder diffraction pattern was measured at room temperature. To fully use the dynamic range of the imaging plate, the exposure time of 53 min was used for this sample. The wavelength of incident X-ray was 0.696 Å. The X-ray diffraction intensities were obtained with a 0.02° step from 5.0° to 73.0° in 2θ, which corresponds to 0.585 Å resolution.

The experimental data were analyzed by the Rietveld method using a computer program RIETAN [8]. At first, X-ray scattering factors of neutral atoms (Mg and H) were used in Rietveld analysis. MEM (maximum entropy method) 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 distribution in a crystal of MgH_2 was obtained by the MEM/Rietveld method. The MEM/Rietveld method, which is a combination of the MEM and the Rietveld refinement, is successfully employed in experimental investigations of charge density distribution in a crystal [9]. Details of the method are described in Ref. [10]. We applied this method to metal hydrides for the first time, and revealed experimentally, the bonding nature of MgH_2.

The MEM charge density analysis was carried out by use of 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 using the computer program ENIGMA [11].

3. Results and discussion

The X-ray powder diffraction sample was composed of three phases, MgH_2, Mg and MgO. By Rietveld analysis, the mass fractions for each phase were determined as 69.0, 27.0 and 4.0 wt% for MgH_2, Mg and MgO, respectively. The lattice parameter of MgH_2 is a=4.5180(6), c= 3.0211(4) Å, which is a little larger than that of MgD_2 [12,13]. 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. Fig. 2 illustrates the crystal structure of MgH_2 (rutile type). The charge density distribution of (001) plane in the crystal of MgH_2 is shown in Figs. 3 and 4. 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.

The number of electrons within the Mg atom region (within the sphere of 0.95 Å radius) was estimated as 10.09e 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

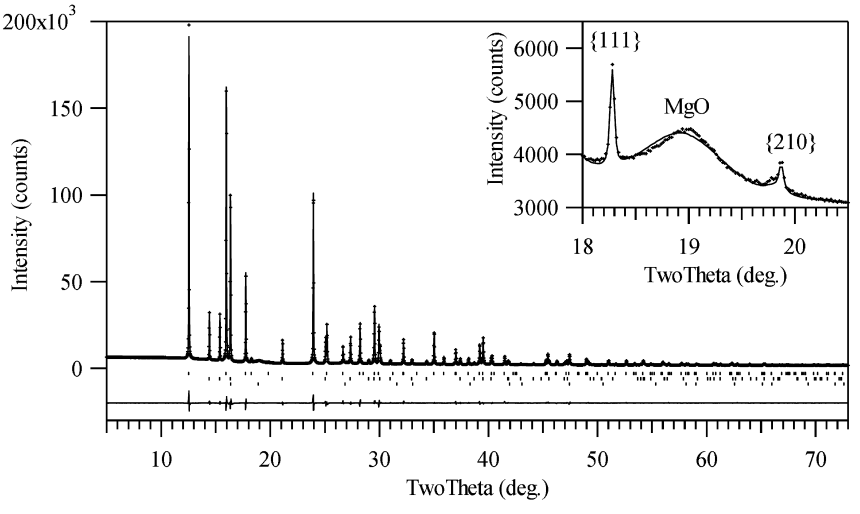

Fig. 1. Rietveld analysis pattern of the MgH_2 sample at room temperature. MgH_2, Mg and MgO are included in this sample. The enlargement pattern of the region from 18.0° to 20.5° is shown in the inset.

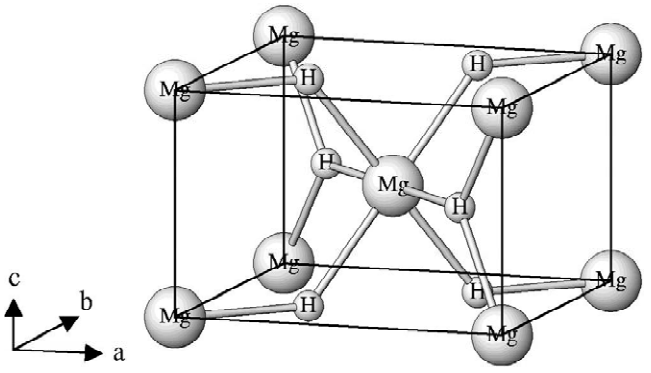

Fig. 2. The crystal structure of MgH_2 (rutile type).

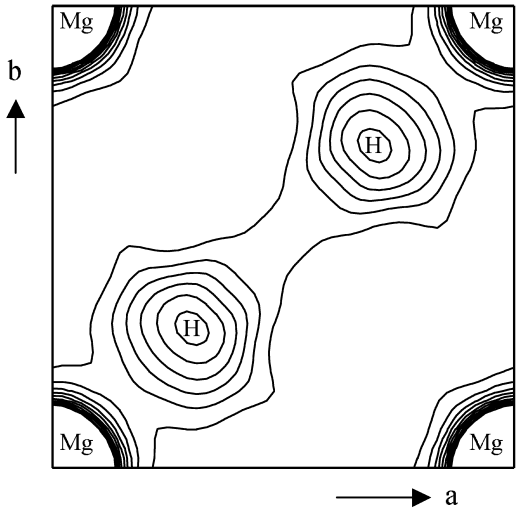

Fig. 3. The charge density distribution map in (001) plane of MgH_2 at room temperature by MEM. The contour lines are drawn from 0.0 to 1.5 at 0.15 e/Å^3 intervals.

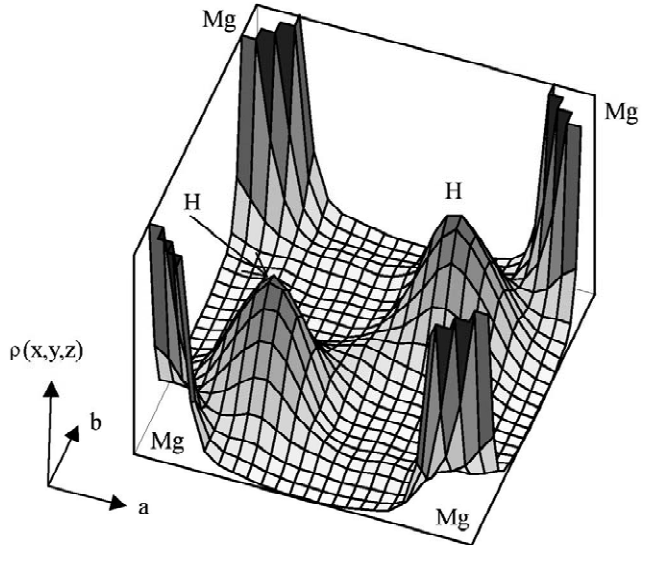

Fig. 4. The charge density distribution function in (001) plane of MgH_2 at room temperature.

as 1.26e. These values indicate that ionic charge of Mg and H are represented as $Mg^{1.91+}$ and $H^{0.26-}$. The results indicated that Mg is almost fully ionized as Mg^{2+}, whereas hydrogen is very weakly ionized. Experimentally, the ionic charge of hydrogen is lower than the theoretical values of $Mg^{1.97+}$ and $H^{0.48-}$ [4], $Mg^{1.95+}$ and $H^{0.60-}$ [5] or $Mg^{1.886+}$ and $H^{0.943-}$ [6]. More details about this experiment and further discussion are reported in Ref. [14].

4. Conclusion

X-ray powder diffraction data for MgH_2 were precisely obtained at room temperature using the synchrotron radiation. The electron density distribution in the crystal of MgH_2 was obtained by the MEM/Rietveld analysis. The charge density distribution around Mg atom is spherical. The lower charge density distribution around H atom is non-spherical slightly spreading in the direction of the nearest neighboring Mg and H atoms. The numbers of electrons within the sphere around Mg and H atoms were estimated as 10.09e and 1.26e, respectively, from the obtained distribution. This means that Mg in MgH_2 is fully ionized, but H atoms are in a weak ionic state. The ionic state and charge density distribution, which should be related to the stability of hydrogen in MgH_2, were revealed experimentally.

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