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Structural information on ball milled magnesium hydride from vibrational spectroscopy and ab-initio calculations

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Abstract

Ball milled magnesium hydride with an average size of about 40 nm and bulk magnesium hydride have been studied with vibrational spectroscopy together with density functional computer calculations. Using this combination of techniques structural information can now be obtained on a nanometer scale, which is especially important for nanosized samples. Such samples exhibit very broad diffraction lines, from which limited information about the structure can be extracted. It was found that ball milling distorts the vibrational spectra due to distribution in stresses over the sample. Cycling of the hydrogen content of ball milled samples results in the spectrum of unmilled samples, while the particle size remains small and hydrogen storage characteristics continue to be better for ball milled samples. We conclude that improved performance for hydrogen storage applications of ball milled magnesium hydride has to be attributed to the reduction of the particle size, while defect densities inside the particles play less of a role.

Keywords: Hydrogen storage materials; Density functional calculations; Magnesium hydride; Neutron scattering

1. Introduction

Magnesium metal is an interesting material in connection with hydrogen storage. The metal being light in weight is capable of storing up to 7 wt.% of hydrogen. However, due to slow kinetics and thermodynamic characteristics, pure magnesium can only be hydrided at high temperatures and high hydrogen pressures. Several ways have been reported that speed up the hydriding and dehydriding processes. The addition of a catalyst to the surface of magnesium particle enhances the kinetics [1–3]. Ball milling breaks down the magnesium hydride particles and induces stresses and defects in the structure [4,5]. The ball milling treatment increases the hydriding kinetics by approximately a factor of 10. As ball milling breaks down the particles, a higher surface area is present for hydrogen to enter the particles. Ball milling introduces defects zones which may assist the diffusion of hydrogen to the MgH_2 nucleus, and defect clusters which may lower the barrier for nucleation of MgH_2. In order to reveal the most important factors in increasing hydrogen sorption, it is crucial to have a better understanding of the changes made by the ball milling treatment. Diffraction experiments are not suited for this purpose, because they rely on long range order in samples. The ball milled particles being small, show broad lines, and little information can be extracted from the diffraction spectra. Local changes and defects in the structure are only visible in the background. Vibrations on the other hand, are governed by forces between atoms which in general have a range less than 1 nm. By probing vibrations, together with a structural model and a method that predicts the vibrations, we can effectively probe the

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material on a nanometer scale and in this way become more sensitive to local defects [6]. As we reported before [7], we calculated and reproduced the vibrational spectrum of bulk MgH_2 (i.e. before ball milling). The present article reports further studies on ball milled magnesium hydride samples.

Magnesium hydride crystalizes in a rutile-type structure with spacegroup $P4_2/mmm$. MgH_2 transforms in an orthogonal γ-phase (α-PbO_2-type structure) at high temperatures and pressures [8]. In ball milled samples this phase is also present (according to X-ray diffraction results up to an amount of 25 wt.% [4]). This phase is meta-stable in the ball milled samples and is removed when the hydrogen content of the sample is cycled or when a sample is heated to 570 K [4,8].

2. Experimental

Bulk magnesium hydride (95 wt.% MgH_2 and 5 wt.% Mg) has been bought from Th. Goldschmidt AG. The hydride was mechanically milled under argon by using a Spex 8000 ball mill. A hardened steel crucible and three steel balls of 12.7 mm in diameter were used for milling. The ball to powder weight ratio was 10:1. All handlings were performed in a glove box under argon. X-ray diffraction was carried out using a Siemens D-5000 X-ray diffractometer with Cu Kα radiation. Hydrogen was removed from one ball milled sample by heating to 473 K under vacuum. When all hydrogen was removed from the hot cell, new hydrogen gas was introduced at a pressure of 5 bar, so that MgH_2 was formed again. Three samples of approximately 0.3 g were used in the experiments: a bulk sample, a ball milled and a ball milled rehydrided sample.

2.1. Vibrational spectroscopy

Vibrational spectroscopy is an ideal tool for studying materials with a nanostructure. For nanostructured materials, diffraction experiments cannot distinguish between the size of the particles in the sample and a distribution in unit cell parameters. Vibrational spectroscopy is sensitive for the immediate environment of atoms. The vibrational frequencies and intensities are the result of forces between atoms which generally have a range shorter than 1 nm. Using neutrons in a sample with a high hydrogen content as MgH_2 means that we only observe the vibrations of the hydrogen atoms (the cross-sections of Mg and H differ more than a factor 20). Neutrons are especially suited for vibrational analysis because they measure motions of nuclei, not of the electrons. The motions of nuclei are relatively easy to simulate using ab-initio calculations and the interaction between neutrons and nuclei is well known.

The inelastic neutron scattering spectrometer TOSCA is an instrument at the pulsed neutron spallation source at ISIS, UK. The instrument uses an inverted geometry, in which *scattered* neutrons with a final energy of about 3.5 meV are analyzed. Initial energies are calculated from the time-of-flights. TOSCA has an energy transfer range between 4 and 500 meV.

2.2. Calculations

Vibrations in adjacent unit cells of MgH_2 are coupled so that we actually measure a phonon spectrum. An accurate description of the measured spectrum requires a calculation of all phonons that exist in the Brillouin zone. The forces need to be mapped for all atoms within its range, about a nanometer. Therefore we chose a supercell with dimensions of $2a \times 2b \times 3c$ (that is optimized dimensions 9 Å × 9 Å × 9 Å) for the force calculations of MgH_2. All DFT calculations were performed with VASP [9,10] using Vanderbilt-type ultrasoft pseudopotentials [11]. A series of single point energy calculations, each of which give Hellmann–Feynmann (HF) forces acting on all atoms in the supercell, were then performed on the structures obtained by displacing, one at a time, each of the three inequivalent atoms by 0.05 Å in the inequivalent, positive and negative Cartesian directions. That gave 8 HF force calculations in all. More details of this procedure are given elsewhere [7].

The optimized supercell and HF forces were then given as input to the program PHONON [12–14], which, by implementing the direct method, generates and diagonalizes the dynamical matrix for any point in reciprocal space, using all the symmetry of the crystal structure. Force constants were checked and found to decay by three orders of magnitude in going from the supercell centre to the closest cell boundary. For the density of states (DOS), a large number of reciprocal space points were chosen at random. By repeatedly convoluting this one-phonon spectrum with itself, the multiphonon (upto 5) was obtained. The dynamical structure factor $S(\mathbf{Q}, \omega)$ was calculated for an isotropic polycrystalline sample, using the scattering configuration of the instrument. Finally the spectrum was convoluted with the instrumental resolution function.

Essentially the same procedure was used to simulate the vibrational spectrum of the γ-phase of MgH_2. We used a supercell with dimensions of $2a \times 2b \times 2c$ (giving 9 Å × 11 Å × 10 Å).

3. Results and discussion

The spectra that we measured for bulk MgH_2, ball milled MgH_2 and for MgH_2 that was ball milled and rehydrided is shown in Fig. 1 together with the calculations for respectively the β- and γ-phases. The sharp features in the spectrum result from parts of the phonon dispersion curves which are relatively flat so that they make up a peak or a sharp feature when summed up to form the experimental spectrum. These flat parts of the phonon dispersion curves can be found near the edges of the Brillouin zone as is clear from Fig. 2a together with the picture of the Brillouin zone of MgH_2 in Fig. 2b.

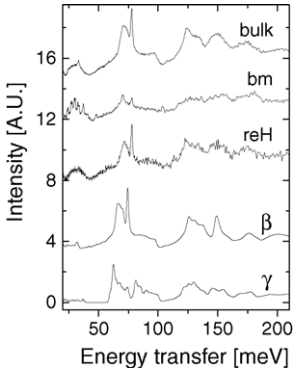

Fig. 1. Vibrational spectra (from top to bottom) of bulk MgH_2, ball milled MgH_2 and for MgH_2 that was ball milled and rehydrided. The calculations for β- and γ-MgH_2 are also shown.

The sharp peak in the spectrum disappears almost completely during the ball milling treatment. The whole spectrum seems to have rounder features. Take for example the shoulders around 60 and 120 meV. The edge is much sharper for both the bulk and the ball milled rehydrided sample, whereas it is rounded off in the spectrum of the ball milled sample. It is expected that small changes in unit cell parameters due to the ball milling treatment shift the positions of these features in the spectrum. A relatively small distribution in stresses can thereby cause the observed rounding of the spectrum.

In order to check the assumption that a distribution of stresses rounds the vibrational spectrum, we calculated the spectrum for magnesium hydride under an isotropic pressure of 10 kbar and for contractions of 2% of the *a* and *c* axes. Clear shifts of the features occur in these calculations. For the γ-phase we simulated a 2% contraction of all axes. A 'fit' of the experimental ball milled spectrum was constructed by taking the average of the different calculations for both the MgH_2 β- and γ-phases. Fig. 3 shows the measurement on the ball milled sample and a fit made from 25% of the averaged calculation for the γ-phase plus 75% of the averaged β-phase calculations together with an exponential background (the approximate phase fractions are taken from Ref. [4]).

The low-energy part of the specta (i.e. between 20 and 50 meV) are shown in Fig. 4. In this part the spectrum from the

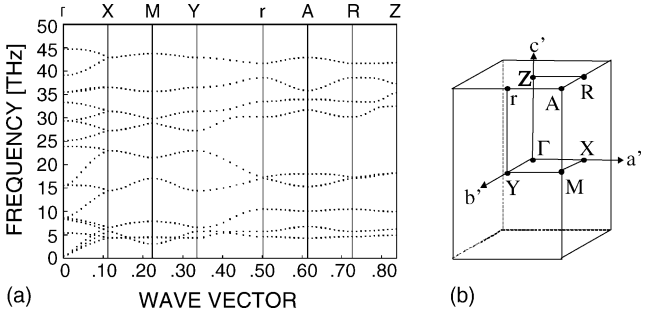

Fig. 2. The phonon dispersion curve as calculated by PHONON from force constants obtained from a density functional theory calculation using VASP (a) and the Brillouin zone of the tetragonal MgH_2 structure (b). Symmetry points used by the calculation are indicated.

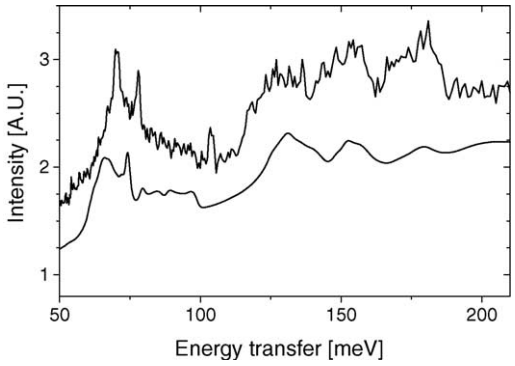

Fig. 3. The vibrational spectrum of ball milled magnesium hydride (top) with 'fit' (bottom). For both phase (β and γ) calculations have been performed on deformed structures. These calculations are averaged and used in the fit shown which consists of 75% of the calculated and averaged spectrum of β-MgH_2 plus 25% of γ-MgH_2 plus the background function $2.2 - 1.7\exp(-0.01E)$. However, as becomes clear from Fig. 4, the actual fraction of the γ-phase is much higher than 25% and a large portion of the background has to be attributed to γ particles.

ball milled sample shows much more structure than the bulk and annealed samples. A comparison with the calculations shows that this part resembles more the γ-phase calculation than the β-phase calculation. The phase fraction of γ-MgH_2 might be as high as 50%, as judged from the low-energy region. A possible explanation may be that the γ-phase is so much distorted that in the high energy part (fitted in Fig. 3) only a huge background is found. The calculations show that the low energy part is less affected by these stresses, so that the low energy part is a better source for the determination of the phase fractions. We conclude that the amount of γ-phase MgH_2 is much higher than 25%, likely as high as 50%. In the diffraction experiments [4] the excess amount of γ-MgH_2 apparently is invisible due to a very small particle size and possibly also strain effects, making the diffraction peaks too broad to be distinguishable from the background.

The extraction of hydrogen from the ball milled MgH_2, followed by a successive reloading gives a sample which has

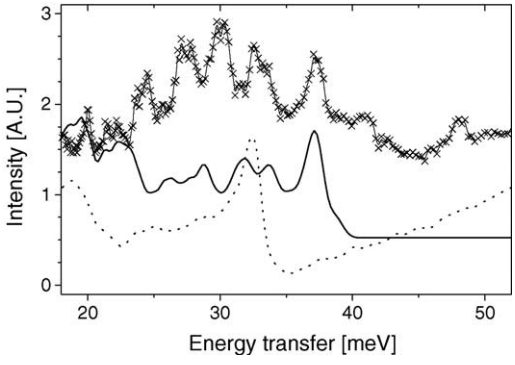

Fig. 4. The vibrational spectrum of ball milled magnesium hydride (top line with crosses) with calculated spectra for γ-MgH_2 (bottom solid line) and β-MgH_2 (bottom dotted line). The calculated spectra are enlarged by a factor 10 with respect to the scale used in Fig. 3. The ratio between β- and γ-phase in the ball milled sample samples might be as high as 50%.

a vibrational spectrum equivalent to that of the bulk, unmilled powder (see third spectrum from top of Fig. 1). The cycling of the hydrogen content thus reduces the stresses resulting from the ball milling treatment, removes the γ-phase and anneals defects because the whole of the sample undergoes a phase transition during the cycling of hydrogen. It is known that the kinetics of a ball milled sample remain fast after the sample has been cycled a few times [4]. This indicates that the improvements in the ball milled samples should be sought in the reduction of the particle size, rather than in side effects of the ball milling (i.e. defects and the presence of the high pressure γ-phase).

4. Conclusions

Ball milled and bulk magnesium hydride has been studied with vibrational spectroscopy. Using density functional computer calculations, it is now possible to reproduce the spectrum of bulk MgH_2 accurately. The spectrum which results after ball milling shows a distribution in stresses over the sample. Calculations where stresses were induced have been performed showing that key features in the spectrum are sensitive to a distribution of stresses in the sample. It was found that the high energy part of the vibrational spectrum is rather sensitive to stresses induced by for instance ball milling. Certain phases whose spectra exhibit large stress-dependence might be invisible in the high energy part (i.e. above 50 meV) of the inelastic spectrum. However, vibrational spectroscopy together with density functional frequency calculations provide answers to questions relating to structure not available with diffraction methods. Especially in the field of nanoscale-science, vibrational spectroscopy reveals information which is difficult or impossible to extract from broad diffraction lines. Cycling of the hydrogen content of the sample returns the vibrational spectrum of bulk magnesium hydride, while the particle size remains small. This shows that cycling of the hydrogen content anneals the structure. We conclude that the enhanced hydrogen sorption and desorption kinetics are mainly due to the reduction of the particle size and not due to stresses and defects. We predict that the same improvement will be found in nanosized magnesium samples prepared by other means.

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