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Hydrogen diffusion in magnesium metal (α phase) studied by ab initio computer simulations

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Abstract

Hydrogen diffusion through magnesium metal is one of the rate determining steps for sorption kinetics of magnesium. From known Gibbs free energies for the magnesium-hydrogen system we have calculated the concentration x of hydrogen in MgH_x in equilibrium with MgH_2: $x = 1.13 \times 10^{-3}$ at 673 K. From an ab initio dynamical simulation we obtained the position of hydrogen in magnesium metal (mostly in tetrahedral sites), the Debye–Waller factors (0.06 Å^2 for tetrahedral sites and 0.08 Å^2 for octahedral sites) and the diffusion constant $D = 6.6 \times 10^{-9}$ m^2/s at 673 K.

Keywords: Hydrogen storage materials; Density functional calculations; Ionic diffusion

1. Introduction

Hydrogen storage in light metals and alloys is interesting for mobile applications of hydrogen as an energy carrier. Until now the ideal metal alloy has not been found [1,2]. The search for new materials or new treatments for existing compounds is being undertaken by many scientists. Because of their low density, Mg and Mg_2Ni currently draw interest. However, the application of magnesium metal as a hydrogen storage compound is hampered by the slow dynamics at moderate temperatures so that operation temperatures above 350 °C are necessary for bulk materials. Magnesium may be loaded with hydrogen to form MgH_2, which possesses a reversible storage capacity by weight of about 7%. It has been shown that a ball milling treatment increases the dynamics of hydrogen sorption by about a factor of 10, and a further increase may be achieved by the addition of catalysts such as V and Nb [3] or metal oxides [4]. Measurements on ball milled MgH_2 + 5 at.% V indicate that the nucleation and growth process is important for this material, but long range diffusion also plays a role, especially when the driving force is small [5]. After the dissociation of hydrogen molecules into atoms, hydrogen atoms have to diffuse through magnesium metal to a magnesium hydride nucleus (the transport properties of MgH_2 are generally expected to be very poor). This paper focusses on the diffusion of hydrogen through Mg metal. New results on the location and dynamics of hydrogen in the magnesium metal (α phase) will be reported, based on ab initio simulations. First we calculate the amount of hydrogen in magnesium alpha using thermodynamical data. From the ab initio calculations we derive the positions of hydrogen, its Debye–Waller factor and the microscopic diffusion constants, which are in accordance with experiment.

2. Density functional calculations

Ab initio computer calculations were performed on a PC-cluster using density functional theory as implemented in the VASP code [6]. A supercell of 3 × 3 × 2 unit cells (space group 194, $a = 3.250$ Å, $c = 5.276$ Å), with one hydrogen atom per supercell was used, giving an effective hydrogen concentration of 2.8×10^{-2}. One k-point, an energy cutoff

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of 200 eV and LDA PAW-potentials were applied [7]. The energy difference between two typical confirmations was off by 10% with respect to a high precision calculation using a $4 \times 4 \times 4$ k-point-grid and a cutoff of 250 eV. The Methfessel–Paxton method with a SIGMA of 0.6 was used to model the occupation of bands around the Fermi level. With a timestep of 1 fs, a molecular dynamics simulation was run of 20 ps. Limited by the computing power, the concentration that we use in our calculations is much higher than the equilibrium value that we find below, 1.13×10^{-3}. Since we do a periodic calculation, the movements of the hydrogen atom in the adjacent unit cells are exactly the same and therefore no direct interaction effects (like Coulomb interactions between the hydrogen atoms) play a role in the calculations, apart from a constant bias in the energies. Furthermore, the fact that we use only one k-point, means that no interactions between adjacent unit cells are taken into account. So we regard these calculations to be representative for the low concentration limit.

3. Results and discussion

A precise thermodynamic modelling of the magnesium hydrogen system was performed by Zeng et al. [8] They calculated the Gibbs free energies for all phases of the Mg–H system as a function of temperature and gas pressure. The Mg-α phase is described with a sublattice model $(Mg)_1(H,Va)_{0.5}$. When there is equilibrium between the metal α-Mg phase and Mg+H_2, the Gibbs free energies per mole of MgH_x and Mg+H_2 are equal. Inserting the dependence of the equilibrium pressure of MgH_2 on temperature (which can be found in the same way), we can predict the concentration x of hydrogen in MgH_x in equilibrium with H_2 gas and MgH_2. A graph is shown in Fig. 1. We calculate $x = 1.13 \times 10^{-3}$ at 673 K. The calculated points can be approximated by $x = 20\ \exp(-54,800/RT)$.

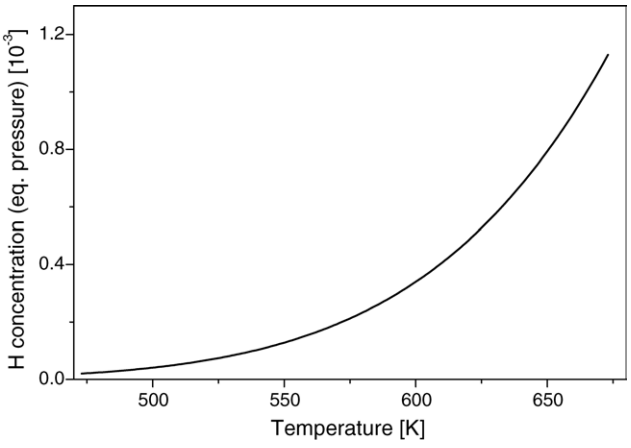

Fig. 1. The concentration of hydrogen in the α-phase of magnesium as a function of temperature in equilibrium with H_2 gas and MgH_2 at the same temperature.

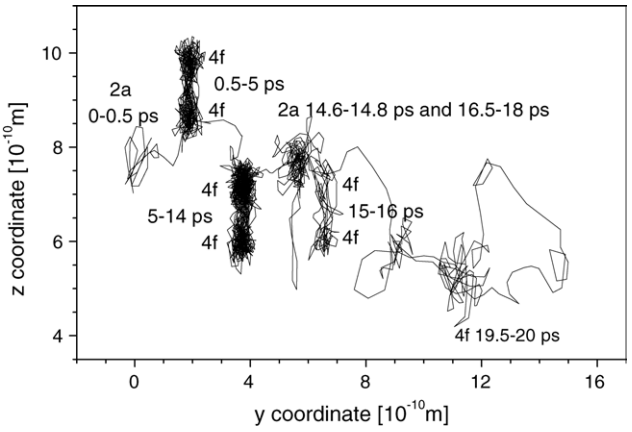

Fig. 2. During the 20 ps ab initio molecular simulation, the hydrogen atom followed this trajectory through the magnesium lattice, shown in a (cartesian) projection along the a-axis (i.e. along x). Hydrogen exchanges on a subpicosecond timescale between the two tetrahedral sites which are separated by 1.3 Å. Jumps between octahedral (2a) and tetrahedral (4f) sites occur on average every 2 ps. Some jumps over larger distances occur. The line is drawn between positions which are separated by 10 fs simulation time.

As for the dynamic part it is known that the diffusion coefficients of hydrogen in magnesium at 673 K may be as high as $2 \times 10^{-8}\ m^2/s$ ($D = 1.54 \times 10^{-6}\ \exp(-24,100/RT)$ [9]) or $3 \times 10^{-9}\ m^2/s$ ($D = 3.8 \times 10^{-6}\ \exp(-40,000/RT)$ [10]). Our ab initio computer calculations show that hydrogen diffuses through the metal by jumps between octahedral and/or tetrahedral sites. During the 20 ps of the simulation, the hydrogen atom spent roughly 5 ps on octahedral and intermediate positions and 15 ps on tetrahedral positions. Fig. 2 shows the path of the hydrogen atom in space during the simulation viewed along the crystallographic a-axis. The figure shows clearly that the hydrogen atom moves on a subpicosecond time-scale between the two adjacent tetrahedral sites (Wyckoff site 4f) which are separated by 1.3 Å in the z-direction (i.e. along the c-axis). Jumps from the set of tetrahedral sites towards neighboring octahedral sites (Wyckoff site 2a) at a distance of 2.0 Å occur as well. Furthermore direct jumps in the direction of the c-axis between two octahedral sites, which are 2.6 Å apart, are observed. From the animation of the motions, it becomes clear that once the hydrogen atom escapes from a site, it may travel over quite a distance before it settles down in a new site (i.e. the jumps may be correlated).

The Debye–Waller factor $U = \langle (u_q - \langle u \rangle)^2 \rangle$, where u_q is the inner product of the displacement u and the momentum transfer vector q, of magnesium is 0.05 $Å^2$, which agrees with the value of 0.047 $Å^2$ from recent experiments [11]. The mean square displacement of the hydrogen atom during the time that it stays in a certain site are about 0.06 $Å^2$ for the tetrahedral sites and 0.08 $Å^2$ for the octahedral sites.

When only one trajectory is available, an estimate for the diffusion coefficient D is [12]

$$D = \frac{\vec{r}^2}{2dt} \tag{1}$$

using the distance from the starting point r, simulation time t and the dimensionality of the system d ($d = 3$). From the trajectory that we calculated, we find a diffusion constant of $D = 6.6 \times 10^{-9}\,\mathrm{m^2/s}$, in agreement with the values quoted earlier.

Fick's first law states $J = -D\,\mathrm{d}c/\mathrm{d}x$, connecting the flux J, the diffusion constant D and the concentration gradient $\mathrm{d}c/\mathrm{d}x$. According to this law, it takes approximately 1.2 s to transport the amount of hydrogen in $1\,\mu\,\mathrm{m}^3$ MgH_2 via a magnesium metal cube of $1\,\mu\,\mathrm{m}^3$. The diffusion constant evaluated here and a concentration difference of 2.5×10^{-4} was used (which means that about 1.5 times the equilibrium pressure at 673 K has been applied). Under these conditions the diffusion is very fast, and other factors such as the dissociation and nucleation processes are rate limiting. The hydrogen flux is determined by the diffusion coefficient and the concentration gradient. When the pressure is kept constant, the concentration shows a weak dependence on temperature as the ratio between the applied and equilibrium pressures increases. The temperature dependence of the diffusion constant basically determines the flux of hydrogen atoms through magnesium at different temperatures and constant pressure. The diffusion path area may be much smaller than the particle size if hydrogen enters the particle via a small number of gateways: places where a catalyst particle is present on the surface. We note that for desorption the situation is different as the vacuum is a lower limit. For desorption we estimate a flux which scales as $\exp(-(87 \pm 8) \times 10^3/RT)$, meaning that it halves every 30 K around 650 K.

4. Conclusion

In this paper we show that the concentration of hydrogen in magnesium is about 0.1% for magnesium in equilibrium with hydrogen gas and magnesium hydride around 673 K. From ab initio computer simulations we calculate a diffusion constant in agreement with previously published values. For large particles at low temperatures the diffusion of hydrogen through the metal is normally not expected to be the limiting factor. However, when hydrogen enters the magnesium particle only via small catalyst particles, the cross section of the diffusion channels may be so low that the diffusion speed becomes rate-limiting.

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