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Hydrogen diffusion in bulk MgB_2

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ABSTRACT

The diffusion of hydrogen in MgB_2 is crucial to the kinetics of rehydrogenation of $Mg(BH_4)_2$. We report a comprehensive combination of first-principles calculations and Kinetic Monte Carlo Simulations to examine the energetics of diffusion of hydrogen atoms through bulk MgB_2. From these calculations we find that diffusion is fast for the neutral interstitial hydrogen defect and that the overall migration barrier for hydrogen diffusion in MgB_2 is 0.22 eV, showing that rapid diffusion of hydrogen is possible even at moderate temperatures. The interstitial hydrogen defect formation energy is around 0.8 eV at 0 K, indicating a low hydrogen solubility at moderate temperatures.

1. Introduction

The design of reliable and efficient hydrogen storage materials remains a crucial barrier in the development of hydrogen fuel cell vehicles. A hydrogen storage candidate should possess high volumetric and gravimetric hydrogen densities, with thermodynamic properties that allow hydrogen release using the waste heat from the proton exchange membrane fuel cell at a pressure of a few bar [1,2]. In the last decade, a large effort has been devoted to developing hydrogen storage systems that meet the target range of de/re-hydrogenation temperatures and pressures (see e.g. [3–8]). In addition to the ideal thermodynamic properties, the hydrogen adsorption and desorption should occur rapidly. However, among the materials that possess ideal thermodynamic properties, none has been found to simultaneously meet the kinetic and storage density requirements for practical, on-board hydrogen storage. Therefore, an understanding of the kinetic mechanisms, especially the rate limiting steps, can guide experiments to promote the storage reaction rates by indicating, for example, which process(es) need to be catalyzed.

Significant effort has been invested in an attempt to understand the properties of $Mg(BH_4)_2$, because both the material-only hydrogen storage capacity and dehydrogenation thermodynamics are within the system-level targeted ranges set by DOE [9,10]. Unfortunately, due to kinetic constraints, $Mg(BH_4)_2$ suffers from low de/re-hydrogenation rates [11–14]. Many processes may potentially limit the de/re-hydrogenation of complex metal hydrides, such as defect diffusion, nucleation, and H_2 dissociation and recombination at the surfaces. In particular, there are many experimental and theoretical studies investigating defect diffusion and mass transport through bulk phases of various hydrogen storage materials and their reaction products. These previous studies suggest that these types of diffusive processes may be the rate-limiting steps in various hydrogen storage systems [15–27]. From this perspective, it is critical to understand the diffusion mechanisms for phases involved in the dehydrogenation of $Mg(BH_4)_2$.

MgB_2 is the fully dehydrogenated state of $Mg(BH_4)_2$ [12], and was observed to react with H_2 to yield $Mg(BH_4)_2$ at 673 K and 95 MPa H_2 pressure [13]. Subsequently, Li et al. [14] compared the rehydrogenation of pure MgB_2 and MgB_2 with grain boundary defects. Under moderate conditions (673 K, 40.0 MPa H_2 pressure, 24 h), Li et al. [14] found pure MgB_2 adsorbed no hydrogen, but MgB_2 with grain boundary defects adsorbed hydrogen and formed $Mg(BH_4)_2$. The authors [14] suggested that the grain boundary defects may promote the atomic diffusion (migration) in MgB_2. However, many aspects of hydrogen diffusion in MgB_2 are still unknown, such as the activation energy, diffusion pathway, migration barriers, and defect energies. These previous studies motivated us to study the defect energies and diffusion in bulk MgB_2.

A complete study of mass transport in $Mg(BH_4)_2$ reactions would require identifying all relevant point defects in all of the de/re-hydrogenated phases of $Mg(BH_4)_2$ system [18,24,28,17]. Those defects with small formation energies would be present in large concentrations and would therefore be prime candidates for mass transport. In this work, we have a more narrow candidate set, and are concerned only with the diffusion of hydrogen in MgB_2, which exists only as a neutral defect since MgB_2 does not contain a band gap. Therefore we limit all discussion in this work to neutral interstitial hydrogen atoms in bulk MgB_2. Density functional theory (DFT) has been used to obtain the defect formation energies, and the climbing image nudged elastic band method is applied to identify the transition states. DFT energies and transition states are further used in Kinetic Monte Carlo Simulation to extract diffusivities. We find that the formation energy of this particular defect is 0.8 eV at a temperature of 0 K and increases to approximately 1 eV in the range 300 to 500 K. Hence the equilibrium solubility of

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hydrogen in MgB_2 is relatively low. The calculated migration barrier for its diffusion is 0.22 eV, showing that rapid diffusion is possible once the defect has been created.

2. Methodology

Kinetic Monte Carlo Simulations require the following input: the locations of stable interstitial sites, formation energies of hydrogen atoms on these sites, and energetic barriers along all possible pathways between sites. Locations of possible interstitial sites were generated using the Materials Interface (MINT) package [17,29] (the MINT package is available on github https://github.com/materials/mint). All energies were calculated using density functional theory (DFT). Details of these calculations follow.

2.1. Generation of interstitial defect sites

The locations of possible interstitial sites in MgB_2 were predicted using a geometric method, which is described in reference [17]. Centered at each atomic site, a radially decaying exponential function was defined as

$$f_i(\mathbf{r}_i) = \exp(-|\mathbf{r}_i|/a) \tag{1}$$

where $\mathbf{r}_i$ is the Cartesian vector to a position in the crystal originating at a single atom, i. In Eq. (1), a controls the rate of decay and is taken as 0.5 Å in all cases. A sum over all atoms, including periodic images out to a set cutoff distance, defines an overall function for the crystal

$$F(\mathbf{r}) = \sum_{i\in\{atoms\}} f_i(\mathbf{r}_i). \tag{2}$$

Local minima in $F(\mathbf{r})$ are taken as possible interstitial sites and each is relaxed under the more physical DFT Hamiltonian (Section 2.3). From this process, two symmetrically-distinct interstitial sites were found (Fig. 2), and described in Section 3). This method of systematically finding interstitial sites in arbitrary crystal structures is coded in the MINT package [17,29].

2.2. Jump pathways and Kinetic Monte Carlo Simulations of point defects

The interstitial defect diffusivities were studied using Kinetic Monte Carlo Simulations (KMC). Two essential inputs to KMC simulations are jump paths and the corresponding jump rates along each path. Jumps were enumerated around each interstitial site to all others within a 2.5 Å cutoff distance under periodic boundary conditions, resulting in sixteen symmetrically-unique jumps. (Computing all the possible jumps is automated in the MINT package [17,29].) Such a choice of cutoff distance includes all of the nearest and second nearest neighbors for interstitial defects in MgB_2. Including jumps longer than this cutoff distance could possibly reduce the activation energy for diffusivity, but our calculations provide an upper bound (which is already low at 0.22 eV).

Once the jump pathways were identified, the jump rates were determined using transition-state theory (TST) [30–34]. In TST, the temperature dependent jump rate from state i to state j is defined as:

$$R_{ij} = v_{ij}\exp\left(-\frac{\Delta E_{ij}^{mig}}{k_B T}\right) \tag{3}$$

where ΔE_{ij}^{mig} is the barrier along the minimum energy path connecting state i and j at $T = 0$ K. v_{ij} is the jump attempt rate from state i to state j, and in this work, we simply take v_{ij} as $10^{13}\ s^{-1}$ in all cases. Since v_{ij} is independent of temperature in the classical limit [34], the choice of a constant v_{ij} does not affect the final diffusion migration energy. Consequently, the temperature dependence of R_{ij} only comes from the k_BT factor in the exponential. For each unique jump, (in the case of MgB_2, there are 16 unique jumps, see Section 3), the diffusion path and transition state energy were obtained using the climbing image nudged elastic band (NEB) [35–37] method. The energy difference between the transition state and initial state is taken as the migration barrier ($\Delta E_{i,j}^{mig}$), which will be used in Eq. (3).

Using the rates just described to perform the KMC simulation, the diagonal elements of the diffusivity tensor are determined by:

$$D_\gamma = \frac{\left\langle \sum \gamma_m^2 \right\rangle}{2\left\langle \sum \Delta t_m \right\rangle}, \tag{4}$$

where $\gamma\in\{x,y,z\}$ and (x_m,y_m,z_m) is the displacement vector of the mth jump and Δt_m is its corresponding jump time step. At a fixed temperature, many KMC simulations were performed, with 10^7 jumps performed for each simulation. The average was taken over all simulations at a fixed temperature, and for each temperature, the simulations were performed until the standard error of D_γ is below 1% (approximately 20,000 simulations at each temperature). Using isolated defects in an infinite crystal, the diffusivity was calculated at ten different temperatures in the range between 100 K and 1000 K to simulate dilute diffusion in the bulk of MgB_2. Again, we note that this entire procedure is automated in the MINT package [17,29]: finding interest sites, enumerating jumps, running DFT to get barriers, and performing KMC simulation of diffusivity.

2.3. DFT calculations

All total energies were obtained from density-functional theory (DFT) calculations as implemented in the Vienna ab initio simulation package [38]. For all calculations we used PW91 pseudopotentials with a cutoff energy of 450 eV and the generalized gradient approximation [39] for the electronic exchange-correlation functional. k-point sampling was performed on a $4 \times 4 \times 4$ Γ-centered mesh. A $3 \times 3 \times 3$ supercell of the conventional MgB_2 cell was used, which contained 81 atoms for the defect-free cell. With interstitial hydrogen defects, atomic positions were relaxed while lattice parameters and the cell shape were fixed to their values in the defect-free supercell. For each considered jump between stable interstitial sites, seven intermediate states were interpolated between the initial and final states and relaxed using NEB calculations. Once converged, climbing image NEB calculations [37] were performed to refine the transition state for each jump.

MgB_2 does not possess a band gap [40], so localized charged defects cannot exist in the bulk. Thus, only the neutral defects were considered in this system. For a charged neutral cell, the hydrogen interstitial formation energy is defined as:

$$E_{form}^{defect} = E_{MgB_2/H} - E_{MgB_2} - \mu_H \tag{5}$$

where $E_{MgB_2/H}$ is the total energy of $3 \times 3 \times 3$ MgB_2 supercell containing one hydrogen defect and E_{MgB_2} is the total energy of the same supercell without a defect. μ_H is the chemical potential of hydrogen, which, in this work, is half of the free energy of one hydrogen molecule. The free energy of hydrogen molecule is defined as [41]:

$$G_{H_2} = E_{H_2} + \frac{7}{2}k_BT - k_BT\left(\frac{7}{2}\ln(T) - \ln(p) - C_0\right), \tag{6}$$

where E_{H_2} is the total DFT energy of one hydrogen molecule in a $9 \times 10 \times 11$ Å^3 box. k_B is the Boltzmann constant. $\frac{7}{2}k_BT$ represents the temperature dependent part of the gas-phase H_2 enthalpy, which accounts for translational and rotational enthalpies and the pV term. k_B $(\frac{7}{2}\ln(T) - \ln(p) - C_0)$ is the gas-phase H_2 entropy, and the constant $C_0 = 4.222$ is fit to the experimental equation of state [42]. In this work, hydrogen pressure p is chosen as 1 bar, and temperature T is left as variable.