Hydrogen diffusion in bulk MgB_2

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The diffusion of hydrogen in MgB_2 is crucial to the kinetics of rehydrogenation of $\text{Mg}(\text{BH}_4)_2$. 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 0K, indicating a low hydrogen solubility at moderate temperatures.

Key words: hydrogen storage, $\text{Mg}(\text{BH}_4)_2$ kinetics, atomic diffusion

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 $\text{Mg}(\text{BH}_4)_2$, 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, $\text{Mg}(\text{BH}_4)_2$ 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 $\text{Mg}(\text{BH}_4)_2$.

MgB_2 is the fully dehydrogenated state of $\text{Mg}(\text{BH}_4)_2$ [12], and was observed to react with H_2 to yield $\text{Mg}(\text{BH}_4)_2$ 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 hours), Li *et al.* [14] found pure MgB_2 adsorbed no hydrogen, but MgB_2 with grain boundary defects adsorbed hydrogen and formed $\text{Mg}(\text{BH}_4)_2$. 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 $\text{Mg}(\text{BH}_4)_2$ reactions would require identifying all relevant point defects in all of the de/re-hydrogenated phases of $\text{Mg}(\text{BH}_4)_2$ 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 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 requires 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 [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

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

where $\mathbf{r}_i$ is the cartesian vector to a position in the crystal originating at a single atom, i . In equation 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

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

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 (figure 2), and described in section 3). This method of systematically finding interstitial sites in arbitrary crystal structures is coded in the MINT package [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 [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:

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

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 $k_B T$ 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 (ΔE_{ij}^{mig}), which will be used in equation 3.

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

$$D_{\gamma} = \frac{\langle \sum \gamma_m^2 \rangle}{2 \langle \sum \Delta t_m \rangle}, \quad (4)$$

where $\gamma \in \{x, y, z\}$ and (x_m, y_m, z_m) is the displacement vector of the m th 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 [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 can not 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:

$$E_{\text{form}}^{\text{defect}} = E_{\text{MgB}_2/\text{H}} - E_{\text{MgB}_2} - \mu_{\text{H}} \quad (5)$$

where $E_{\text{MgB}_2/\text{H}}$ 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]:

$$G_{\text{H}_2} = E_{\text{H}_2} + \frac{7}{2} k_{\text{B}} T - k_{\text{B}} T \left(\frac{7}{2} \ln(T) - \ln(p) - C_0 \right), \quad (6)$$

where E_{H_2} is the total DFT energy of one hydrogen molecule in a $9 \times 10 \times 11 \text{ \AA}^3$ box. k_B is the Boltzmann constant. $\frac{7}{2}k_B T$ represents the temperature dependent part of the gas-phase H_2 enthalpy, which accounts for translational and rotational enthalpies and the pV term. $k_B \left(\frac{7}{2} \ln(T) - \ln(p) - C_0 \right)$ 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.

3 Results

Figure 1: Crystal structure of MgB_2 (top). The top view from [0001] direction (bottom left) and side view of (0001) plane of MgB_2 (bottom right). The primitive cell of MgB_2 has a hexagonal symmetry with lattice parameters $a = 3.07 \text{ \AA}$ and $c = 3.53 \text{ \AA}$ (DFT). The structure has alternating Mg and B layers with Mg-Mg, Mg-B, B-B bond length (DFT) as $3.08 \text{ \AA}$, $2.50 \text{ \AA}$, and $1.77 \text{ \AA}$ respectively. The bigger (orange) atoms represent Mg atoms, and the smaller (green) ones represent B atoms.

Figure 2: The top view from the [0001] direction and side view of the (0001) plane of the two unique interstitial sites. For both cases, a purple ball indicates the position of interstitial sites. Orange and greens balls represent the Mg and B atoms respectively. Figure 2a shows one interstitial site in the “hollow” of the Mg layer, and we denote it as the “Mg-int” site. On the other hand, the interstitial site in figure 2b is between the Mg and B layers and over the “bridge” of two B atoms and also the “bridge” of two Mg atoms, and it is marked as the “B-int” site. The B-int site is slightly closer to the B layer, $0.84 \text{ \AA}$ from the B layers, but $0.93 \text{ \AA}$ from the Mg layers. The Mg-int site is much closer to the Mg layer than the B layer — $0.46 \text{ \AA}$ above the Mg layers.

Table 1: Formation energies for the neutral hydrogen defect at the two unique interstitial sites. “Mg-int” and “B-int” represent the two unique interstitial sites in MgB_2 , and they are defined in figure 2. The defect formation energy E_{form}^{defect} is defined as equation 5.

Figure 3: Twelve jumps labeled in the MgB_2 structure. The MgB_2 conventional cell is shown in the volume enclosed by the solid lines. Mg and B are represented by yellow and black balls respectively. Faded atoms indicate that they are not inside the shown conventional cell. The radii of the balls do not have physical meaning. Blue and magenta balls represent the location of Mg-int and B-int sites respectively, where the definition of Mg-int and B-int sites can be found in figure 2. The dual color cylinders indicate the jumps allowed in the KMC simulations, with the direction of the jumps from green to red. The numbering of the jumps corresponds to table 2. The xyz labelings are orthogonal to each other, where the z direction is perpendicular to Mg and B layers, and the xy plane is in parallel with Mg and B layers.

The hexagonal structure (space group: $P6/mmm$) of MgB_2 [43] is formed by alternating hexagonal Mg layers and honeycomb B layers, stacked along the $[0001]$ direction. The DFT calculated Mg-Mg, Mg-B, and B-B bond lengths are 3.08 Å, 2.50 Å, 1.77 Å respectively, as shown in figure 1. The DFT relaxed MgB_2 conventional cell lattice parameters are 3.07 Å, 3.07 Å and 3.53 Å. As discussed in section 2.1, two unique interstitial sites were identified. The formation energy of hydrogen defects at these sites at 0 K are 0.83 eV and 0.71 eV (table 1), and their positions in the crystal structure are presented in figure 2. The site with a formation energy of 0.83 eV is illustrated in figure 2a; it is right above the “hollow” site of the Mg layer. The second site, which has a formation energy of 0.71 eV, is shown in figure 2b and is found over the “bridge” site of the B layer. In all the following discussion, the two unique sites are denoted as “Mg-int” and “B-int” sites respectively. The Mg-int hydrogen defect site has a coordination number of 3 Mg atoms and 1 B atom, with a distance of 1.83 Å to nearest Mg atom and 1.30 Å to nearest B atom. The B-int hydrogen defect site is coordinated by 2 Mg atoms and 2 B atoms. The nearest Mg atom and B atom to B-int site are 1.80 Å and 1.22 Å, respectively. B-int site is in the center of the tetrahedron formed by 2 B atoms and 2 Mg atoms. It has a relatively larger interstitial volume than the Mg-int sites (figure 2), which result in a lower formation energy of hydrogen defects at B-int sites.

Table 2: Migration barriers (eV) for sixteen jumps of H diffusion in MgB_2 . Among the sixteen jumps, four pairs have inequivalent initial and final states. For these paths the barrier depends on the direction of the jump (and the reverse direction jumps are indicated in parentheses). The transition states and energy barriers are obtained by climbing image NEB calculations. The third column indicates the jump routes. For example, Mg-B is for hydrogen defect jumping from a Mg-int site (initial state) to a B-int site (final state). The definition of the Mg-int site and the B-int site can be found in the section 3 and figure 2. The fourth column represents the jump distance between initial state and final state of each jump route. The migration barriers ΔE_{ij}^{mig} were calculated as the difference between the initial and transition state total energies, and were used in equation 3 for KMC simulations. The final row gives the migration barrier (eV) from a least squares fit to the diffusivities in figure 4 averaged over the x, y, and z directions.

Having identified the interstitial sites in the hexagonal structure of MgB_2 , we now turn to the discussion of jump pathways between them. The method to populate all the possible pathways is covered in section 2.1. Sixteen jumps were determined, and can be categorized into 3 groups. Geometrically, the first group (1 – 4 in table 2 and figure 3) represents paths along the Mg-B layers, while the other two groups (5 – 9 and 10 – 12 in table 2 and figure 3) describe paths through the Mg and B layers. The migration barriers were obtained for each jumps via NEB calculations and the results are tabulated in table 2. Comparing the migration barriers among the three jump groups, on average, the migration barriers for jumping along Mg-B layers are lower than penetrating Mg or B layer.

Figure 4: Diffusivity of interstitial hydrogen in MgB_2 at 10 different temperatures. Error bars are based on 1000 KMC simulations at each point. The KMC simulations are performed until the each of the diffusivities (along x, y, and z) are converged to within 1%. The xy plane is parallel to the Mg and B layers, and the z direction is perpendicular to the Mg-B layer.

Having determined the barrier energies for 16 possible jumps, we input these energies into KMC calculations. Using the migration energies shown in table 2 and an attempt jump frequency of 10^{13} s^{-1} , the calculated values of D_x, D_y, D_z at ten different temperatures ranging from 100K to 1000K are given in figure 4. According to the Arrhenius equation $D(T) = D_0 \exp(-\Delta E_{fit}^{mig}/k_B T)$, the slope of the linear fit in figure 4 is the diffusion barrier. From our calculations, ΔE_{fit}^{mig} for the x, y, and z directions are 0.22 eV, 0.22 eV, and 0.38 eV respectively, where the z direction is perpendicular to Mg and B layers, and the xy plane is in parallel with Mg and B layers. The migration barrier is much lower than the formation energies of hydrogen defects (0.71 and 0.83 eV). Once the hydrogen defects are formed, given the low migration barriers, they are expected to have fast diffusion in the bulk of MgB_2 .

4 Discussion

In principle, diffusion can occur through any of the de/re-hydrogenated phases in the $\text{Mg}(\text{BH}_4)_2$ system, and the diffusion process is dominated by the point defects that have small formation energies and large concentrations. In this work, only neutral hydrogen defects in MgB_2 are considered. Utilizing first principle calculations and KMC simulations, we calculate that the neutral hydrogen defect formation energy in MgB_2 bulk is around 0.8 eV at 0 K (table 1), and has a low migration barrier of 0.22 eV (figure 4). The hydrogen defect formation energy is relatively small even at 300 K to 500 K (around 1.0 eV, table 1), compared with defects in other de/re-hydrogenated phases of $\text{Mg}(\text{BH}_4)_2$ system. For example, Chao *et al.* found that the formation energies for interstitial H, H vacancies, Mg vacancies, and B vacancies are larger than 1 eV in $\text{Mg}(\text{BH}_4)_2$, $\text{MgB}_{12}\text{H}_{12}$, and MgH_2 [44]. In principle, the mass transport is determined by the combination of defect formation energy and migration barrier. The defect formation energy plus migration barrier for neutral hydrogen defect in MgB_2 is around 1 eV, which is similar to or lower than the value of defect formation energies in $\text{Mg}(\text{BH}_4)_2$, $\text{MgB}_{12}\text{H}_{12}$, and MgH_2 . Therefore, even if those defects have zero migration barriers, the total activation energies are still larger than that of neutral hydrogen defect in MgB_2 . However, we do not exclude the possibility that other defects, either in MgB_2 or in other de/re-hydrogenated states of $\text{Mg}(\text{BH}_4)_2$, may exist with lower activation energy. Nevertheless, our results provide an upper bound on the activation energy of hydrogen diffusion in $\text{Mg}(\text{BH}_4)_2$ system.

DFT+KMC calculations demonstrate that hydrogen defects diffuse fast on the plane parallel to Mg-B layers and have a smaller diffusivity perpendicular to the Mg-B layers. Such fast diffusion may contribute to fast reaction rates in the rehydrogenation of MgB_2 , but other kinetic processes should also be considered, such as hydrogen dissociation and diffusion on the surface. A prior study of MgB_2 rehydrogenation [45] reported that the activation barrier for hydrogen molecule dissociation and atomic diffusion of hydrogen on the MgB_2 (0001) surface are 0.89 eV and 0.17 eV, respectively. The diffusion barrier on the surface is similar to the migration barrier in MgB_2 bulk, but the dissociation barrier is much larger than both the diffusion barriers. Meanwhile, bulk MgB_2 also has a large neutral hydrogen defect formation energy. H_2 dissociation on the surface is a critical step in the rehydrogenation process, and fast diffusion on the surface and in the bulk will help hydrogen leave the surface adsorption site and penetrate into the bulk. Therefore, the low hydrogen diffusion barriers are in favor of MgB_2 rehydrogenation, however, the high dissociation barrier and large hydrogen defect formation energies may hinder the adsorption process. In previous work [45], transition metal as dopants on MgB_2 surface have been studied, and several viable catalysts (Ni, Cu, and Pd) have been proposed to reduce the dissociation barrier without simultaneously increasing the surface diffusion barrier. Since the dissociation barrier can be modified by catalysts, the large hydrogen defect formation energy must be reduced, if the reaction rate is to be improved.

In the experimental work of Li *et al.* [14], the authors compared the rehydrogenation of MgB_2 with and without mechanical milling. After mechanical milling, MgB_2 generates grain

boundary defects, and in the subsequent hydrogen adsorption process (673 K, 40.0 MPa H_2 pressure), nano-structured MgB_2 contains 3.6 wt% hydrogen with $Mg(BH_4)_2$ detected. Without mechanical milling, under the same rehydrogenation condition, the hydrogen concentration is essentially zero, and no trace of $Mg(BH_4)_2$ is observed. From the standpoint of reference [45] and this work, the H_2 dissociation rate is low on the pure layered MgB_2 surface, and it is also hard to form the hydrogen defects in the bulk of MgB_2 . Both of the two steps potentially prevent further rehydrogenation. MgB_2 with grain boundary defects may promote the hydrogen adsorption rate, in the sense that the grain boundaries can be the nuclei for the formation of hydrogen defects [46, 47], and the kinks and steps on the MgB_2 surface may also reduce the dissociation barrier. Therefore, combined with fast surface and bulk hydrogen diffusion, the nanostructured MgB_2 (with mechanical milling) is observed to have fast kinetic rehydrogenation rate compared to the layered MgB_2 (without mechanical milling). Despite the fact that we have not explicitly considered grain boundaries in our calculations, our theoretical model and calculated results support these experimental observations.

5 Summary and Conclusions

We have shown that interstitial hydrogen defects in MgB_2 have low migration barriers and large diffusivities. In the hexagonal layered MgB_2 structure, two unique interstitial sites are identified. One is next to the Mg layer with a hydrogen defect formation energy of 0.83 eV. The other is in the middle of Mg and B layers with a hydrogen defect formation energy of 0.71 eV. Sixteen unique jumps are used to simulate hydrogen diffusion, and the migration energies are calculated for each jump. Among the sixteen migration energies, three play a key role, which can be considered as jumping along Mg-B layers (0.09 eV), passing through the Mg layer (0.27 eV), and penetrating through the B layer (0.41 eV). The sixteen jumps can be combined into a 3-D network in MgB_2 , and KMC calculations are performed. The diagonal elements of the diffusivity tensor are obtained from KMC calculations for ten different temperature points from 100 K to 1000 K. A linear fit is applied to the calculated diffusivities on an Arrhenius plot, and the fitted migration barriers are 0.22 eV, 0.22 eV (both directions parallel with Mg and B layers), and 0.38 eV (the direction perpendicular to Mg and B layers). Our results thus suggest that if hydrogen defects form in the bulk of MgB_2 , then the subsequent diffusion of these defects will be rapid through the bulk of MgB_2 . It must be noted that rapid hydrogen diffusion is a necessary, but not sufficient, condition for fast de/re-hydrogenation kinetics. Other processes, such as nucleation or interfacial reaction, may also hinder the reaction rate.

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Table 1: Formation energies for the neutral hydrogen defect at the two unique interstitial sites. “Mg-int ” and “B-int ” represent the two unique interstitial sites in MgB_2 , and they are defined in figure 2. The defect formation energy E_{form}^{defect} is defined as equation 5.

T (K)	E_{form}^{defect} (eV)	
	“Mg-int”	“B-int”
0	0.83	0.71
300	0.99	0.87
400	1.06	0.94
500	1.14	1.01

Table 2: Migration barriers (eV) for sixteen jumps of H diffusion in MgB_2 . Among the sixteen jumps, four pairs have inequivalent initial and final states. For these paths the barrier depends on the direction of the jump (and the reverse direction jumps are indicated in parentheses). The transition states and energy barriers are obtained by climbing image NEB calculations. The third column indicates the jump routes. For example, Mg-B is for hydrogen defect jumping from a Mg-int site (initial state) to a B-int site (final state). The definition of the Mg-int site and the B-int site can be found in the section 3 and figure 2. The fourth column represents the jump distance between initial state and final state of each jump route. The migration barriers ΔE_{ij}^{mig} were calculated as the difference between the initial and transition state total energies, and were used in equation 3 for KMC simulations. The final row gives the migration barrier (eV) from a least squares fit to the diffusivities in figure 4 averaged over the x, y, and z directions.

Jump No. and route			Distance (Å)	ΔE_{ij}^{mig} (eV)
Diffuse along Mg-B layer	1 (13)	Mg-B	1.00	0.09 (0.21)
	2	Mg-Mg	1.77	0.09
	3 (14)	Mg-B	2.38	0.09
	4	B-B	1.54	0.22
Penetrate Mg layer	5	Mg-Mg	0.93	0.27
	6	Mg-Mg	2.00	0.26
	7 (15)	Mg-B	1.65	0.26 (0.38)
	8	B-B	2.41	0.38
	9	B-B	1.86	1.00
Penetrate B layer	10	B-B	1.67	0.41
	11 (16)	Mg-B	2.31	0.28 (0.40)
	12	B-B	2.27	0.64
				ΔE_{fit}^{mig}
				0.22

Figure1

Figure2a

Figure2b

Figure4