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Influences of Al doping on the electronic structure of Mg(0001) and dissociation properties of H_2

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ABSTRACT

By using the density functional theory method, we systematically study the effects of the doping of an Al atom on the electronic structures of the Mg(0001) surface and on the dissociation behaviors of H_2 molecules. We find that for the Al-doped surfaces, the surface relaxation around the doping layer changes from expansion of a clean Mg(0001) surface to contraction, due to the redistribution of electrons. After doping, the work function is enlarged, and the electronic states around the Fermi energy have a major distribution around the doping layer. For the dissociation of H_2 molecules, we find that the energy barrier is enlarged for the doped surfaces. In particular, when the Al atom is doped at the first layer, the energy barrier is enlarged by 0.30 eV. For different doping lengths, however, the dissociation energy barrier decreases slowly to the value on a clean Mg(0001) surface when the doping layer is far away from the top surface. Our results well describe the electronic changes after Al doping for the Mg(0001) surface, and reveal some possible mechanisms for improving the resistance to corrosion of the Mg(0001) surface by doping of Al atoms.

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1. Introduction

Since hydrogen is one of the best clean fuels in the future, looking for an ideal storage material has become an important task for experimental and theoretical researchers. Among all the candidates, magnesium (Mg) based materials attract a lot of interest because they are relatively inexpensive and can hold a high weight percentage of hydrogen [1,2]. So the interaction between hydrogen and Mg has been extensively studied [3–11]. The main disadvantage that prevents the vast applications of Mg for hydrogen storage lies in that the corresponding hydrogenation and dehydrogenation temperatures are large [1,2]. In order to improve the performance of Mg in hydrogen storage, the adsorption of H_2 on decorated Mg surfaces are being considered. The decorating atoms include Ni [12], Ti [7,12,13], Pd [14,15], *etc.* Recently, it is experimentally found that the aluminum (Al) doped MgAl thin films have much lower hydrogenation temperatures than pure Mg films [1,16]. However, the specific reason for the improvement as well as the influence of Al doping on the electronic properties of Mg films, remains unclear. So, in order to advance the searches for ideal hydrogen storage materials and applications of hydrogen fuels, it is quite important to make clear the influence of Al doping on the electronic structure of Mg and how it influences the interaction between hydrogen and Mg.

Apart from the potential usages in hydrogen storage, Mg and its alloys are also important industrial materials used in aerospace and automotive applications [17,18]. The biggest restriction for their increasing applications is that Mg and its alloys are very susceptible to galvanic corrosion, which can result in severe pitting, particularly in wet and salty environments [19,20,18]. Through lots of experimental researches, it has been found that Al doping makes Mg more resistant to being corrupted [21,18]. Studying the interactions between small molecules and Al-doped Mg surfaces can give us critical information about the mechanisms for Al doping to improve the resistance of Mg to corruption, and thus are very meaningful and necessary. Based on this background and the requirements of hydrogen storage materials, we here perform first principles calculations to systematically study the influence of Al doping on the electronic properties of the Mg(0001) surface and the adsorption behavior of hydrogen molecules.

Previous studies have revealed that the Mg(0001) surface has both considerable *s* and *p* electronic states distributing around the Fermi energy, because of the *sp* hybridizations [22]. Here we further find that after doping of an Al atom, the electronic structures around the Fermi energy mainly distribute around the doping layer. For the dissociation of hydrogen molecules on the clean

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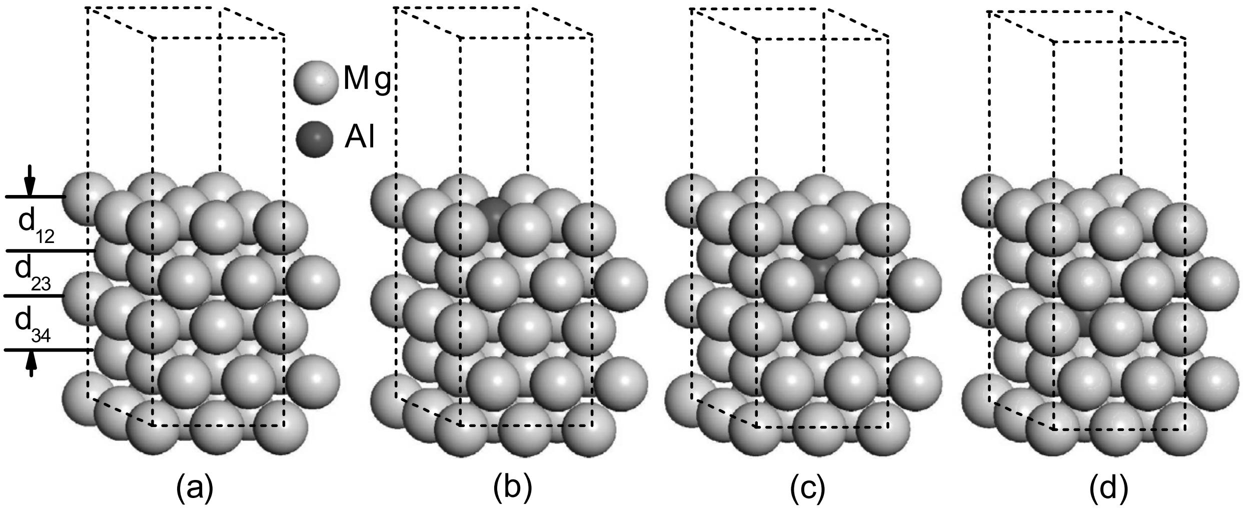

Fig. 1. Atomic configurations of the Mg(0001) (a), MgAl1 (b), MgAl2 (c), and MgAl3 (d) surfaces, with the corresponding supercells depicted in dashed lines. Mg and Al atoms are shown in grey and black balls.

Mg(0001) surface, it has been found that the most energetically favourable site is the surface bridge site [6–11], with the corresponding minimum energy barrier of 1.05–1.15 eV [6,7,9–11]. With our present first-principles calculations, we find that Al doping will not change the most energetically favourable dissociation channel. However, the minimum energy barrier for dissociation of hydrogen is critically dependent on the doping depth of Al, and the values are all larger than that on the clean Mg(0001) surface. The Letter is organized as follows. In Section 2, we describe our fist-principles calculation methods; in Section 3, we present in detail our calculated results, including the comparisons of the electronic structures of the Mg(0001) surface before and after Al doping, and the dissociation of hydrogen molecules on the Al-doped Mg(0001) surface; Finally, the conclusions are given in Section 4.

2. Calculation methods

Our calculations are performed within density functional theory (DFT) using the Vienna *ab-initio* simulation package (VASP) [23]. The PW91 [24] generalized gradient approximation and the projector-augmented wave potential [25] are employed to describe the exchange-correlation energy and the electron–ion interaction, respectively. The cutoff energy for the plane wave expansion is set to 250 eV, which is large enough to make the error from calculations of the adsorption energy below 0.01 eV. The clean and Al-doped Mg(0001) surface are modeled by a slab composed of five atomic layers and a vacuum region of 20 Å. The 2 × 2 supercell in which each monolayer contains four Mg atoms was used to study the H_2 adsorption. Our test calculations have shown that the 2 × 2 supercell is sufficiently large to avoid the interaction between adjacent hydrogen molecules. Integration over the Brillouin zone is done using the Monkhorst–Pack scheme [26] with 11 × 11 × 1 point grids. A Fermi broadening [27] of 0.1 eV is chosen to smear the occupation of the bands around the Fermi energy (E_f) by a finite-T Fermi function and extrapolating to $T = 0$ K. During geometry optimizations, the bottom layer of the clean and Al-doped Mg(0001) surface is fixed while other Mg and Al atoms are free to relax until the forces on them are less than 0.01 eV/Å. The calculation of the potential energy surface for molecular H_2 is interpolated to 209 points with different bond length ($d_{\mathrm{H-H}}$) and height (h_{H_2}) of H_2 at each surface site. The calculated lattice constants of bulk Mg (a, c) and the bond length of a free H_2 molecule are 3.21 Å, 5.15 Å and 0.75 Å, respectively, in good agreement with the experimental values of 3.21 Å, 5.20 Å [28,29] and 0.74 Å [30].

Table 1
Surface relaxations (Δd_{12}, Δd_{23}, and Δd_{34}) and work function (Φ) of the Mg(0001), MgAl1, MgAl2, and MgAl3 surfaces.

Surface	Surface relaxation			Φ (eV)
	Δd_{12} (%)	Δd_{23} (%)	Δd_{34} (%)	
Mg(0001)	+1.95	+0.55	+0.82	3.745
MgAl1	−3.00	−0.11	+0.10	3.767
MgAl2	−2.62	−2.60	+0.49	3.757
MgAl3	+0.28	−2.25	−2.12	3.757

3. Results and discussion

The clean Mg(0001) surface is firstly studied before our considerations for the effect of Al doping. The atomic structure for the relaxed Mg(0001) surface is shown in Fig. 1(a). After geometry optimizations, we find that the distances between the topmost three atomic layers of the clean Mg(0001) surface are expanded from their bulk values. Our results accord well with previous theoretical [31,32,9] and experimental reports [33]. The underling reason has already been revealed to be that due to its special surface charge redistribution, the topmost three layers of the Mg(0001) surface are negatively charged and hence repel each other [31]. Since most surface relaxations of metals show contraction characters [9], the surface expansion of the Mg(0001) surface is very interesting. Besides, other surfaces of Mg also show different surface relaxations [31]. The relaxation calculations for the clean Mg(0001) surface prove the preciseness of our methods. We then consider three different doping situations for Al in the Mg(0001) surface, with the Al atom respectively in the first (MgAl1), second (MgAl2) and third (MgAl3) atomic monolayer of the Mg surface.

The atomic structures for the relaxed MgAl1, MgAl2 and MgAl3 surfaces are shown respectively in Figs. 1(b), (c) and (d). During the geometry optimizations, we find that the surface structure is greatly changed after the doping of an Al atom. To describe more clearly the changes, here we define the surface relaxation as

$$\Delta d_{ij} = (d_{ij} - d_0)/d_0, \tag{1}$$

where d_{ij} and d_0 are respectively the depth between the ith and jth layer of the relaxed surface, and the lattice spacing along the (0001) direction of bulk Mg. Table 1 summarizes the calculated relaxations for the clean Mg(0001), MgAl1, MgAl2, and MgAl3 surfaces. We can easily see from Table 1 that the results critically depend on the doping length of the Al atom. If the Al atom is

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