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Crystal structure of Mg_3Pd from first-principles calculations

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Abstract: Crystal structure of Mg_3Pd alloy was studied by first-principles calculations based on the density functional theory. The total energy, formation heat and cohesive energy of the two types of Mg_3Pd were calculated to assess the stability and the preferentiality. The results show that Mg_3Pd alloy with Cu_3P structure is more stable than Na_3As structure, and Mg_3Pd alloy is preferential to Cu_3P structure. The obtained densities of states and charge density distribution for the two types of crystal structure were analyzed and discussed in combination with experimental findings for further discussion of the Mg_3Pd structure.

Key words: crystal structure; Mg_3Pd; first-principles; formation heat; cohesive energy; density of states(DOS); charge distribution

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1 Introduction

During the past decades, the global greenhouse warming caused mainly by CO_2 emission is becoming more and more worrying. It is now well accepted that hydrogen is an ideal non-polluting vector of energy for the future. This means that we would go from a “petroleum economy” to a “hydrogen economy”. The widespread of hydrogen requires some progresses especially in the field of storage and mass production. Hydrogen-storage materials have attracted much attention in view of the development of hydrogen energy systems. Metal hydrides appear as a suitable route for storage compared with pressurized or liquefied mode. Among all materials, Mg is one metal hydrogen-storage material that can reach the highest mass capacity (i.e. 7.6%). According to its abundance on the earth’s crust and its low cost, it is often considered as the most promising material. However, the absorption and desorption of hydrogen molecule take place at high temperature and have very low-efficiency and low-rate. To solve these problem and increase its storage capacity, a considerable number of work aimed at improving the microstructure and researching for new hydrides or alloys has been reported[1−2]. HIGUCHI et al[3] and CHECCHETTO et al[4] investigated some advantageous hydrogen storage properties of magnesium-palladium intermetallic compounds or alloys. GAOTO et al[2] reported X-ray diffraction patterns of Mg-x%Pd(mole fraction) samples (x=10, 18, 22, 26, 33, 38, 50, 55) prepared by 4 h exposure to Ar gas at 1 073 K and 2 GPa, and their hydrogen storage properties. However, they did not give the structure information such as crystal lattice parameters of Mg-Pd systems except Mg_4Pd. In the recent study, FERRO[5], RANGE and HAFFNER[6] investigated the crystal structure of Mg_3Pd based on different crystal structure models, respectively. However, they still did not determine the structural stability and preferentiality.

The crystal structure with the first-principles plane-wave pseudopotential method was investigated based on the density functional theory(DFT). The total energies, formation heats, cohesive energies, electron

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density of states and charge distributions were studied and discussed for determination of the crystal structure of Mg_3Pd.

2 Model and method of calculation

The intermetallic compound of Mg_3Pd was firstly studied by FERRO[5] who assigned the Na_3As-type structure (Pearson symbol: hP8, space group: $P6_3/mmc$, number: 194, Z=2). However, the recent investigation of range showed that the Mg_3Pd was very likely to adopt the Cu_3P-type structure (Pearson symbol: hp24, space group: $P\overline{3}c1$, number: 165, Z=6)[6−7]. MOKONGO et al[8] thought that Cu_3P-type structure can be derived from the Na_3As-type structure by a slight deformation of the CN 11 polyhedra and the lattice constants follow the relationship $a'=\sqrt{3}a$ and $c'=c$ (a'=7.987 nm and c'=8.422 nm). In this work, we will provide further structural information of the Mg_3Pd intermetallic mainly based on the Cu_3P-type and Na_3As-type structural model.

The present work was based on density functional theory(DFT) at the level of the generalized gradient approximation(GGA) (using the PW-91 exchange-correlation functional). The method was implemented in the Vienna ab-initio simulation package(VASP) program. Ultrasoft pseudopotential was used to describe the election-ion interaction, and the energy cutoff(E_{cut}) of atomic wave functions was set at 340 eV, and the 4×4×4 and 6×6×6 k point meshes of the Monkhorst-Pack(MP) algorithm were used to sample the super cell of Cu_3P-type and Na_3As-type Mg_3Pd bulk respectively. These parameters are shown to give well-converged total-energies to less than 1.0 meV/atom (≈0.1 kJ/mol) [9]. Ionic relaxation and electronic energy minimization were performed using the conjugate gradient (CG) algorithm. Density of states(DOS) and charge distributions were calculated with finer k point meshes, and the tetrahedron method with Bloch corrections was used.

3 Results and discussion

3.1 Lattice parameters and electronic total energy

The lattice parameters of hcp Mg, fcc Pd, Mg_3Pd of Cu_3P-type and Na_3As-type structure were firstly calculated from the minimized total energy, and the obtained results are listed in Table 1. It can be found that the present lattice parameters a and c/a of hcp Mg are 0.319 5 nm and 1.624 1, which are in good agreement with the experimental values of 0.321 nm and 1.623[10] and other GGA calculations[11]. The lattice parameter a of fcc Pd is 0.395 1 nm, which is also in good agreement with the experimental value of 0.389 nm[12] and other GGA calculations[13], showing good accuracy of the present calculations. The present first-principles calculations show that the electronic total energy of Na_3As-type (there are 6 magnesium atoms and 2 atoms palladium atoms in the super cell) and Cu_3P-type (there are 18 magnesium atoms and 6 atoms palladium atoms in the super cell) structure Mg_3Pd are −69.390 0 eV and −22.956 6 eV, respectively. This results indicate that the Cu_3P-type structure is more stable than Na_3As-type structure, which is accordance with the suggestion of MAKONGO et al[8]. The calculated Mg_3Pd lattice parameters (a and c/a) of Cu_3P-type and Na_3As-type structure are 0.802 6 nm and 1.048 8, 0.465 1 nm and 1.805 7, respectively. It can also be found the Cu_3P-type and Na_3As-type structure lattice parameters have the following relationship, $a'=\sqrt{3}a$ and $c'\approx c$, which is in line with Ref.[8]. Based on the slight difference of the electronic total energy and the relationship between the lattice parameters, Cu_3P-type crystal structure is likely to derive from three same Na_3As-type crystal structure cells through a slight deformation.

3.2 Formation heat and cohesive energy

In order to assess the thermodynamic aspect of the two crystal structure types of Mg_3Pd, the formation heat is an important parameter. At the same time, the formation heat could also explain and deepen the understanding of the structural stability of alloys system[14]. The formation heat of Mg_3Pd alloy per atom can be calculated by[15]

$$\Delta\overline{H}=\frac{1}{x+y}[E_{\text{alloy}}-xE_{\text{Mg}}-yE_{\text{Pd}}] \tag{2}$$

Table 1 Contrast of VASP calculation and experiments or other GGA calculation

System	VASP calculation		Experiment result		Other GGA calculation	
	a/nm	c/a	a/nm	c/a	a/nm	c/a
Mg (solid)	0.319 5	1.624 1	0.321 0[10]	1.623 0[10]	0.319[11]	1.624[11]
Pd (solid)	0.395 1		0.389 0[12]		0.396[13]	
Mg_3Pd (Na_3As-type)	0.465 1	1.805 7	0.461 1[8]	1.826 4[8]		
Mg_3Pd (Cu_3P-type)	0.802 6	1.048 8	0.798 7[8]	1.054 5[8]		

where $\Delta\overline{H}$ is the average formation heat of Mg_3Pd alloy per atom; E_{alloy} is the electronic total energy of primitive cell of Mg_3Pd; E_{Mg} and E_{Pd} are the total energy of single magnesium and palladium atom at solid state, respectively; x and y are the number of magnesium and palladium atom in primitive cell of Mg-Pd alloy. The average formation heat of Mg_3Pd per atom for Na_3As-type and Cu_3P-type is expressed as $\Delta\overline{H}_{\text{Mg}_3\text{Pd(Na}_3\text{As-type)}}$ and $\Delta\overline{H}_{\text{Mg}_3\text{Pd(Cu}_3\text{P-type)}}$, respectively.

The obtained formation heats of Mg_3Pd per atom for Cu_3P-type and Na_3As-type are −0.440 1 eV and −0.418 4 eV, respectively. It is clearly shown that $\Delta\overline{H}_{\text{Mg}_3\text{Pd(Cu}_3\text{P-type)}}$ is lower than $\Delta\overline{H}_{\text{Mg}_3\text{Pd(Na}_3\text{As-type)}}$. Hence, the alloying ability of Mg_3Pd for Cu_3P-type crystal structure is thermodynamically stronger.

The stability of crystal structure is correlated to its cohesive energy[16], and the cohesive energy is often defined as energy needed when crystal is decomposed into the single atom. Hence, the lower the cohesive energy is, the more stable the crystal structure is[16]. In this work, average cohesive energy per atom for Mg-Pd binary alloy family was calculated using the following expression[15]:

$$E_{\text{coh}}=\frac{1}{x+y}(E_{\text{alloy}}-xE_{\text{atom}}^{\text{Mg}}-yE_{\text{atom}}^{\text{Pd}}) \tag{2}$$

where E_{alloy} is the electronic total energy of primitive cell of Mg_3Pd, x and y also are the number of magnesium and palladium atoms in primitive cell of Mg-Pd alloy; $E_{\text{atom}}^{\text{Mg}}$ and $E_{\text{atom}}^{\text{Pd}}$ are the electronic total energies of single Mg atom and Pd atom in freedom states. They are −0.045 8 eV and −1.478 4 eV for Mg and Pd free atoms, respectively. The obtained average cohesive energies of Mg_3Pd per atom for Cu_3P-type and Na_3As-type are −2.487 3 eV and −2.465 6 eV, respectively. It can be clearly found that the average cohesive energy of Cu_3P-type is also lower than that of Na_3As-type. Hence, Mg_3Pd of the Cu_3P-type crystal structure is slightly more stable than that of Na_3As-type.

From the above calculation results of formation heats and cohesive energies, it could be expected that the Cu_3P-type crystal is overall preferential to Na_3As-type.

3.3 Density of states(DOS)

For further understanding of the structural stability and microcosmic mechanism of the Mg_3Pd alloy, total and partial density of states(DOS) of Mg_3Pd for Cu_3P-type and Na_3As-type crystal structure are performed, and the results are shown in Fig.1. For comparison and analysis, the total and partial density of states(DOS) of hcp-Mg and fcc-Pd are also calculated, as shown in Fig.1. The partial DOS of pure hcp-Mg is much smaller than total density of states, and the s and p partial DOS of pure fcc-Pd crystal is also much less than d partial density of states. And the partial density of states of Mg(s), Mg(P), Pd(s) and Pd(p) of two types of Mg_3Pd is also more less than their total density of states and the Pd (d) partial density of states.

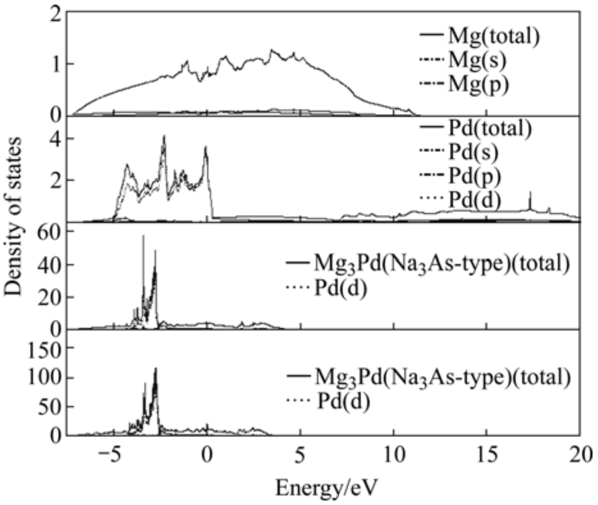

Fig.1 Total and partial density of states of hcp-Mg, fcc-Pd and Mg_3Pd for Cu_3P -type and Na_3As -type

From the total DOS in Fig.1, it can be seen that the main bonding peaks of both Mg_3Pd structure are in the energy range between about −3.4 and −2.6 eV under Fermi level, which are mainly dominated by the valence electron numbers of Pd(d) and Mg(p) orbits and also affected by part of Mg(s) and Pd(p) orbits. In this way, the dominant bonding possesses the characteristic of significant p-d hybridization, which leads to the relatively high formation heat and cohesive energy of Mg_3Pd. This feature is also found in other alloy of 3d transition metal and magnesium[17]. It should be noted that due to interaction of Mg and Pd in the Mg_3Pd, there are large variation in the valence electrons of Pd(d) orbits compared with partial density of states of fcc-Pd. The partial DOS of Pd(d) in the fcc-Pd reveals that the main bonding peaks are in the energy range between about −5.0 eV under Fermi level and 0.5 eV upon Fermi level. However the partial DOS of Pd(d) in the Mg_3Pd reveals that the main bonding peaks are in the energy range between about −3.4 eV and −2.6 eV under Fermi level. This shows that in the alloy, low energy end of Pd(d) DOS shifts up while high energy end of Pd(d) DOS shifts down, the width of main peak region is narrower and the density of states increases apparently, showing very strong interaction between Pd and Mg.

The electronic structures of two type crystal structures also can be further compared and analyzed as follows. Because the atom number of Mg_3Pd for

Cu_3P-type is triple of that for Na_3As-type, the electronic total and partial densities of states of Mg_3Pd for Cu_3P-type are also triple of those for Na_3As-type. From the total and partial densities of states for two type of crystal structures, the difference of the electronic structures can be further perceptible although it is very small. As shown in Fig.1, although two high peaks for both Mg_3Pd structure appear between −2.7 eV and −3.0 eV respectively, the two energy peaks (about −2.7 eV and −3.0 eV) in Na_3As-type structure is higher and sharper, showing that electron number of Na_3As-type is more than Cu_3P-type around the two energy positions. The other peaks of Cu_3P-type from about −3.4 eV to −2.6 eV under Fermi level are clearly higher than those of Na_3As-type, implying that the electron number of Cu_3P-type is more uniform in this energy region. This shows that density of states of Cu_3P-type is more helpful for alloy formation.

Further analysis reveals that in the energy range between −10 and 5 eV, the bonding electron numbers per atom for Cu_3P-type and Na_3As-type are 5.179 8 and 5.176 1, respectively. Because the electrons in low-energy region of Fermi level are the mainly bonding electron, when more electrons are in low-energy region, the bonding electron increases, and the interaction between valence electrons of crystal is intensified, so the stability of crystal structure is better[18]. From the density of states, it has a very good agreement with the formation heat and cohesive energy, hence, it could be also expected that the Cu_3P-type crystal is preferential to Na_3As-type.

3.4 Charge density

In order to further understand the microscopic mechanism of bonding in Mg_3Pd alloy, charge density distributions were investigated. The charge distributions calculated on (010) plane for Cu_3P-type and (100) plane for Na_3As-type are shown in Fig.2(a) and Fig.2(b), respectively. It is clear that the feature of covalent bond between Mg and Pd atoms exhibits apparently, and charge distributions between Mg and Pd atoms for two types of crystal structure are very similar. Nevertheless, according to the DOS and bonding electron number mentioned above, the charge density overlapping between Mg atom and Pd atom in the Cu_3P-type Mg_3Pd crystal should be enhanced very slightly compared with that in the Na_3As-type structure. So, the bond strength between Mg and Pd atoms Cu_3P-type structure should also be increased very slightly.

According the above discussion and analysis of the charge density distributions, it could be also expected that the Cu_3P-type crystal is preferential to Na_3As-type.

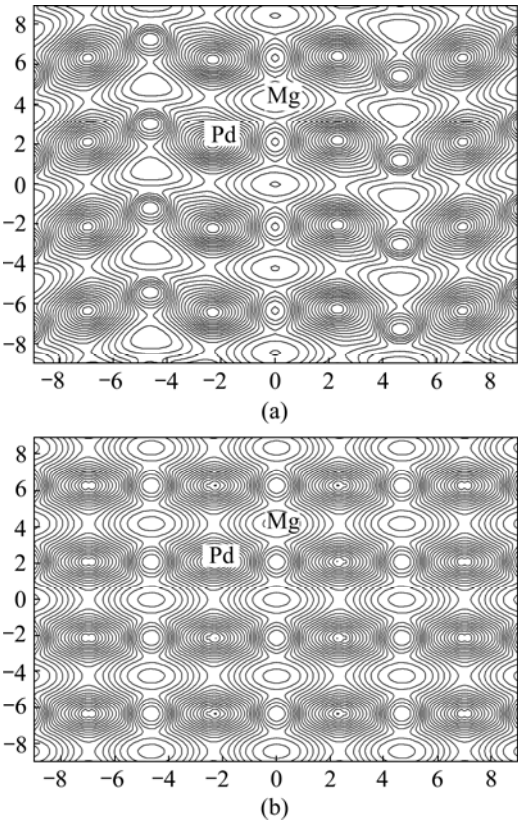

Fig.2 Charge distribution of Mg_3Pd on (100) plane for Cu_3P-type (a) and (010) plane for Na_3As-type (b)

4 Conclusions

1) The calculation results show that Cu_3P-type crystal structure is more stable, and the alloying ability of Cu_3P-type Mg_3Pd is also stronger.

2) The comparison and analysis of total and partial density of states(DOS) and charge distributions show that Cu_3P-type is more helpful for alloy formation. So Mg_3Pd alloy is overall preferential to Cu_3P-type structure.

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