DOI https: //doi. org/10.1007/s11595-018-1806-z

First-Principles Calculations of Electronic, Elastic and Thermal Properties of Magnesium Doped with Alloying Elements

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Abstract: First-principles calculations have been carried out to investigate the effects of alloying elements (Zn, Li, Y and Sc) on the electronic structure, elastic and thermal properties of Mg solid solution. The calculated cohesive energies show that Mg-Sc has the highest structural stability. The calculations of the densities of states (DOS) and electronic charge density difference indicate that Mg-Y (Sc) alloys have very strong covalent bonding due to a very strong Mg *p*-Y(Sc) *d* hybridization. The bulk modulus *B*, shear modulus *G*, Young's modulus *E* and Poisson ratio *v* are derived using Voigt-Reuss-Hill (VRH) approximation. The results show that all the alloys can exhibit ductile properties at 2.77 at% *R*, and Mg-Zn(Li) alloys have the better ductility and plasticity. In the end, the Debye temperature and isochoric heat capacity are also calculated and discussed.

Key words: magnesium alloys; electronic structure; elastic properties; thermal properties; first-principles

1 Introduction

As the lightest of all structural metallic materials, magnesium alloys have been receiving a great deal of attention in the fields of automobile, microelectronics and aerospace industries because of their low density, high specific strength and excellent castability[1,2]. However, the application of magnesium alloys in modern industry is still limited because of the limited mechanical properties[3,4]. In general, the solid-solution strengthening is considered one of the most effective ways to improve the mechanical properties of the alloy. To date, there have been quite a few experiments[5,6] to explore the solid solution strengthening of solute atoms in magnesium alloys. Recently, in order to obtain deeper insight into the fundamental mechanisms of the solid solution, first-principles calculations have been considered to be an important method. Gao *et al*[7] focused on the solid solution strengthening behavior of Y and Gd in Mg from first-principles calculations. However, a theoretical study of cohesive energy, elastic and thermal property has not been reported. Ganeshan *et al*[8] studied the elastic properties of Mg by doping 12 alloying elements from first-principles calculations. Unfortunately, the details of cohesive energy, electronic and thermal properties have not been reported. Besides, Chen *et al*[9] studied that solid solution strengthening mechanisms associated with alloying additions of Al, Zn and Y (7.143 at%). Yang *et al*[10] studied the effects of Y and Zn on the elastic properties of Mg solid solution. To our knowledge, up to now, there is a lack of systematic research concerning the effects of alloying elements (Zn, Li, Y, Sc) on the electronic, elastic and thermal properties of Mg solid solution from first-principles calculations.

In this research, first-principles calculations based on the density functional theory are carried out to investigate the electronic structure, elastic and thermal properties of Mg-*R* (R=Zn, Li, Y and Sc) alloys. The results are discussed in comparison with the available theoretical and experimental values, which would give

(Received: Dec. 18, 2016; Accepted: Oct. 17, 2017)

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Funded by the National Natural Science Foundation of China (Nos.51574206, 51204147 and 51274175), International Cooperation Project Supported by Ministry of Science and Technology of China (No.2014DFA50320) and International Cooperation Project Supported by Shanxi Province(Nos.2013081017, 2012081013)

some essential guidance to the optimization and design of Mg alloys.

2 Method of computation

The calculations of the total energy, electronic structure and elastic properties were performed by the first-principles plane-wave pseudopotentials method based on density functional theory (DFT) implemented in Cambridge serial total energy package (CASTEP) code[11]. Ultrasoft pseudopotentials[12] were used to describe the ion-electron interaction. The generalized gradient approximation (GGA)[13] with the Perdew-Burke-Ernzerh (PBE)[14] was used to describe the exchange-correlation energy function, and the cutoff energy (E_{cut}) of the wave functions was set at 500 eV. The *k*-point meshes for Brillouin zone sampling were constructed using Monkhorst-Pack scheme[15] with 5×5×5 grids for Mg-R alloys. All lattice parameters and atomic positions in our model have been relaxed according to the total energy and force using the Broyden-Flecher-Goldfarb-Shanno (BFGS)[16] scheme. The total energy changes during the optimization finally converged to less than 5×10^{-6} eV, the force on every atom was less than 0.01 eV/Å and the displacement between cycles was below 5×10^{-4} Å.

3 Results and discussion

3.1 Crystal structure and stability

Magnesium has a hexagonal close-packed (hcp) lattice of space group *P*63/*mmc* with lattice parameters *a*=3.209 Å, *c*=5.211 Å[17]. In this study, a 3×3×2 supercell consisting of 36 atoms (35 Mg and 1R atom, corresponding to 2.77at% R) was constructed. At first, the lattice constants were calculated, and the results are listed in Table 1. It can be seen that the present calculations are in good agreement with the available theoret-

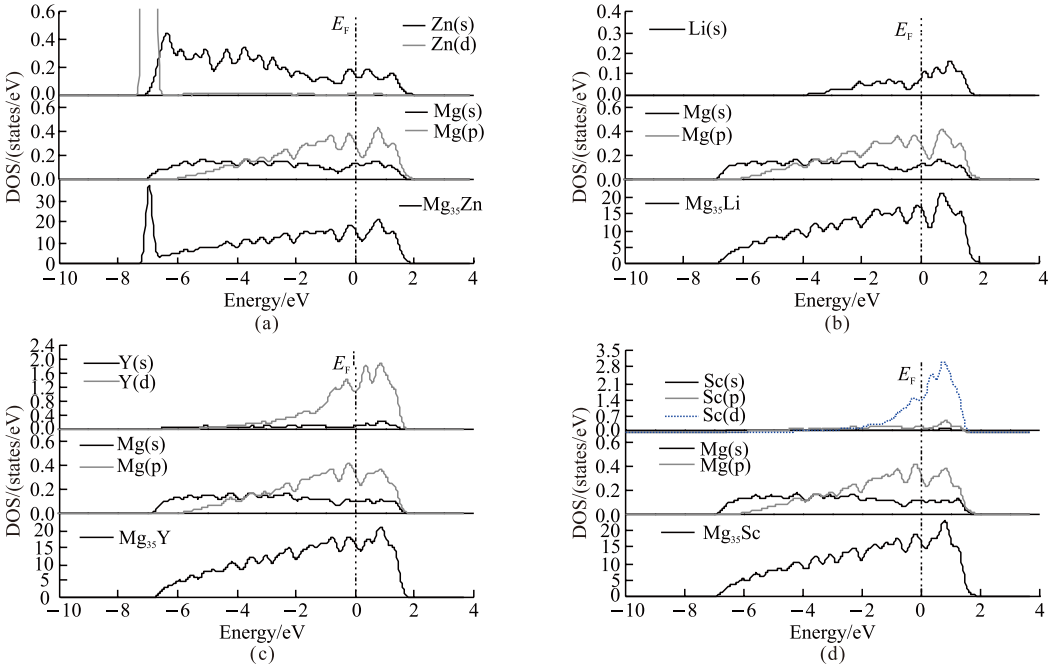

Fig.1 Density of states of Mg-R alloys

Table 1 Lattice constants and cohesive energy E_{coh} of Mg-R alloys

Phase	Present *a*/Å	Present *c*/Å	Cal. *a*/Å	Cal. *c*/Å	Exp. *a*/Å	Exp. *c*/Å	E_{coh}/(eV/atom)
Mg	3.206	5.224	3.195[8]	5.178[8]	3.209[17]	5.211[17]	−1.690
Mg-Zn	3.207	5.152	3.184[8]	5.148[8]	3.196[18]	5.188[18]	−1.666
			3.178[10]	5.208[10]			
Mg-Li	3.227	5.133	3.194[8]	5.150[8]	3.208[18]	5.203[18]	−1.681
Mg-Y	3.236	5.199	3.214[8]	5.205[8]			−1.756
			3.192[10]	5.214[10]			
Mg-Sc	3.223	5.177			3.211 8[19]	5.208 0[19]	−1.757

ical[8,10] and experimental values[17-19], confirming that the present calculations are highly reliable.

To analyze their structural stability, the cohesive energies (E_{coh}) are calculated as follows[20]:

$$E_{coh} = \frac{1}{x+y}(E_{tot} - xE^{A}_{atom} - yE^{B}_{atom}) \quad (1)$$

where E_{tot} is the total energy of the unit cell, x and y are the numbers of R atoms. E^{A}_{atom} and E^{B}_{atom} are the energies of the isolated atoms R in the free state, respectively. The calculated results are also listed in Table 1. The lower the cohesive energy, the better the structural stability[21]. Therefore, the structural stabilities of the Mg-R alloys increase in the following sequence: Mg-Zn, Mg-Li, pure Mg, Mg-Y, Mg-Sc.

3.2 Electronic structure

The electronic structures are calculated to provide further insight into the bonding of Mg-R and reveal the underlying structural stability mechanism. The total and partial densities of states (DOS) are presented in Fig.1. It can be found that the trends of Mg *p* and Y(Sc) *d* are very similar for Mg-Y(Sc) in the whole area, showing a very strong Mg *p*-Y(Sc) *d* hybrid phenomenon. But for Mg-Zn(Li), the weaker hybridization between the *s*-orbital of Zn(Li) and the *p*-orbital of Mg atoms is observed near the Fermi level. The hybridization presents covalent bonding characteristics. Therefore, Mg-Y(Sc) alloys have very strong covalent bonding, playing an important role in the solid solution strengthening.

The electronic charge density difference maps could reflect directly their chemical bonding nature and the results are displayed in Fig.2. From Fig.2, it can be seen that the solid solution atoms change the chemical bond characteristics of Mg in different degrees. The charge densities between the solute and solvent atoms are lower in the Mg-Zn (Li) (Fig.2(b,c)) compared with the pure Mg, indicating that electrons among Mg1-Zn(Li)-Mg2 form quite weak covalent bonds. But for Mg-Y and Mg-Sc (Fig.2(d,e)), the obvious overlap of electron densities among Mg1-(Y,Sc)-Mg2 indicates a strong covalent bonding which is consistent with the electronic DOS. In addition, the stabilities of Mg-Y and Mg-Sc are much higher from the perspective of covalent bond, which is accordant with the cohesive energy analysis.

3.3 Elastic properties

Elastic constants play an important role in the determination of the mechanical properties. The calculated elastic constants are summarized in Table 2. It can be seen that the calculated results are close to other available calculated and experimental values[8,10,22], and it is worth pointing out that the elastic constants C_{ij} of the Mg-R alloys satisfy the generalized elastic stability criteria of hexagonal crystal: $C_{11}>0$, $C_{44}>0$, $C_{11}-C_{12}>0$, $(C_{11}+C_{12})C_{33}-2C_{13}^2>0$. This implies that the solid solutions are elastically stable.

The bulk modulus B, shear modulus G and Young's modulus E are calculated by the Voigt-Reuss-Hill (VRH)[23], and the Voigt and Reuss bounds of B and G are:

$$B_V = \frac{2}{9}(C_{11}+C_{12}+2C_{13}+\frac{C_{33}}{2}) \quad (2)$$

$$G_V = (7C_{11}-5C_{12}+12C_{44}+2C_{33}-4C_{13})/30 \quad (3)$$

$$B_R = \frac{(C_{11}+C_{12})C_{33}-2C_{13}^2}{C_{11}+C_{12}+2C_{33}-4C_{13}} \quad (4)$$

$$G_R = \frac{5}{2}\left\{\frac{\left[(C_{11}+C_{12})C_{33}-2C_{13}^2\right]C_{44}C_{66}}{3B_VC_{44}C_{66}+\left[(C_{11}+C_{12})C_{33}-2C_{13}^2\right](C_{44}+C_{66})}\right\} \quad (5)$$

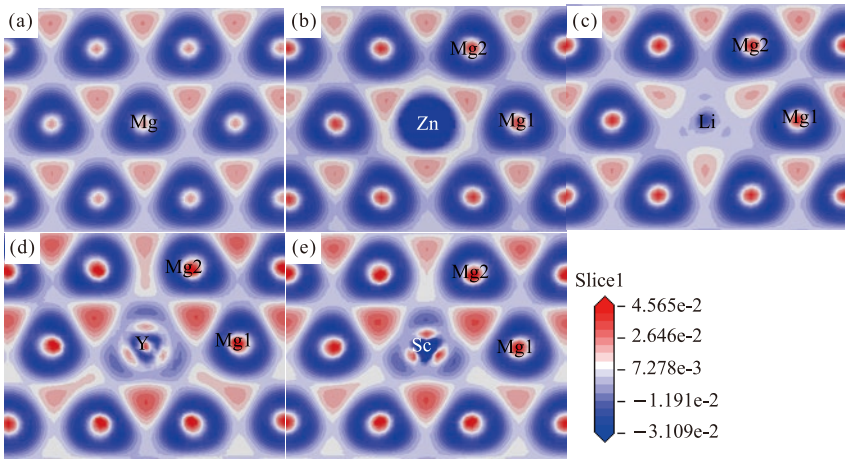

Fig.2 Electronic charge density difference contour plots on (0001) plane: (a)Mg; (b)Mg-Zn; (c)Mg-Li; (d)Mg-Y; (e)Mg-Sc

Table 2 Elastic constants C_{ij} of Mg-R alloys

Phase	Source	C_{11}/GPa	C_{12}/GPa	C_{13}/GPa	C_{33}/GPa	C_{44}/GPa
Mg	Present	65.68	21.27	23.03	63.28	13.94
	Cal. [8]	63.5	24.85	20.0	63.28	19.3
	Exp. [22]	59.5	25.9	21.8	61.6	16.4
Mg-Zn	Present	60.35	22.52	25.39	63.72	13.29
	Cal. [8]	62.3	25.5	23.1	66.2	14.1
	Cal. [10]	64.74	26.07	19.83	65.85	17.73
Mg-Li	Present	54.60	22.03	24.80	60.93	14.72
	Cal. [8]	58.9	24.5	23.2	54.0	15.0
	Exp. [22]	59.0	25.9	21.7	61.0	16.2
Mg-Y	Present	59.36	25.12	23.46	63.22	23.08
	Cal. [8]	59.5	27.3	21.6	64.5	19.0
	Cal. [10]	63.67	26.50	20.11	65.50	17.70
Mg-Sc	Present	61.72	24.04	24.47	65.04	22.99

The VRH mean values are obtained by

$$B=(B_V+B_R)/2,\quad G=(G_V+G_R)/2 \tag{6}$$

where the subscripts V and R designate the Voigt and the Reuss bounds $C_{66}=(C_{11}-C_{12})/2$. Further, the Poisson's ratio and Young's modulus can be obtained as:

$$\nu=(E-2G)/2G,\quad E=9BG/(3B+G) \tag{7}$$

The results are listed in Table 3, from which one can estimate and understand the influence of the alloying elements on the mechanical properties of Mg. As can be seen in Table 3, the calculated results are close to the available experimental and other theoretical values[8,10,22,24]. It is known that the hardness of materials is related to their Young's modulus E and shear modulus G. The general trend is that the larger the values of E and G, the harder the material[7]. Therefore, among the solid solutions, Mg-Sc is expected to be the hardest due to its largest modulus, while Mg-Li is the softest.

The ratio of the shear modulus to bulk modulus (G/B) of crystalline phases introduced by Pugh[25] can predict the brittle and ductile behavior of materials. If G/B<0.57, the material is ductile, otherwise, it is brittle. In the present work, G/B values of all the alloys are smaller than 0.57, implying that all the alloys can exhibit ductile properties at 2.77at% R. Further analysis finds that Mg-Zn and Mg-Li have relatively lower G/B, implying that they have the better ductility. The positive influence of Zn and Li on the ductility of Mg was reported earlier by the authors of Refs.[10]. On the other hand, the ductile-brittle nature of materials can also be discussed by their Cauchy pressure (C_{12}-C_{44}) [26]. If the value is positive, the material is expected to be ductile, otherwise, it is brittle. From Table 2, it can be found that the C_{12}-C_{44} values are all positive. Hence, Mg-R alloys are all ductile, which is in good agreement with the previous G/B results.

The Poisson's ratio could reflect the stability of a crystal against shear. The bigger the value of ν, the better the plasticity[12]. Besides, the plasticity is also estimated by the value of E. The smaller the value of E, the better the plasticity[27]. The results in Table 3 show that Mg-Zn and Mg-Li have relatively good plasticity, while Mg-Y and Mg-Sc have the poorer plasticity. All the results of the analysis indicate that adding Zn and Li to Mg can improve the ductility and plasticity.

3.4 Thermal properties

Debye temperature (Θ_D) is correlated with many physical properties of solids, such as specific heat, elastic constants and melting temperature. One of the standard methods to calculate the Debye temperature is from the elastic constants of the compound, since Θ_D may be estimated from the averaged sound velocity by the following equations[28]:

$$\Theta_D=\frac{h}{k_B}\left[\frac{3n}{4\pi}\left(\frac{N_A\rho}{M}\right)\right]^{1/3}\nu_m \tag{8}$$

$$\nu_m=\left[\frac{1}{3}\left(\frac{2}{\nu_s^3}+\frac{1}{\nu_l^3}\right)\right]^{-1/3} \tag{9}$$

$$\nu_l=\sqrt{\left(B+\frac{4}{3}G\right)\frac{1}{\rho}} \tag{10}$$

$$\nu_s=\sqrt{G/\rho} \tag{11}$$

where h is the Planck's constant, k_B is Boltzmann's constant, n is the number of atoms in the molecule, N_A

is the Avogadro number, M is the molecular weight, ρ is the density, v_m, v_l and v_s are the average, longitudinal and shear sound velocities, respectively. The calculated results are summarized in Table 4.

It is known that the Θ_D can be used to characterize the strength of covalent bonds in solids. From Table 4, we can conclude that the covalent bonds in Mg-Sc and Mg-Y are the stronger. Besides, the largest Θ_D is 397.00 K for Mg-Sc with the largest E and G, indicating that the mechanical stability of Mg-Sc is the best.

Additionally, the isochoric heat capacity (c_v) is a fundamental state property of matter. The heat capacity at low temperatures can be estimated from the electronic structure and elastic constants by the following equations[29]:

$$c_v(T)=\gamma T+\beta T^3 \tag{12}$$

$$\gamma=\frac{1}{3}\pi^2 k_B^2 D_f,\ \beta=\frac{12\pi^4 Rn}{5\Theta_D^3} \tag{13}$$

where γ and β are related to electron density of states and phonon excitations, respectively; D_f is the DOS value at the Fermi level; R is the molar gas constant and n is the total number of atoms per formula unit. We calculated γ and β values by using Eq.(13) and the results are also listed in Table 4. Note that Θ_D, as a rule, only describes the temperature dependence of c_v for $T<\Theta_D/10$[30]. Fig.3. shows the heat capacity of the alloys plotted in the range of 0-40 K. As can be seen from Fig.3, at very-low temperatures (near 0 K), the values of c_v have the following sequence: Mg-Li, Mg-Sc, Mg-Zn and Mg-Y, which are the same as the sequences of γ, indicating that the significant contribution to c_v is the excitation of electrons. From 2 to 40 K, the c_v values for Mg-R are the same as the sequences of β, indicating that phonon excitations dominate the heat capacity. Thus, we may conclude that the heat capacity is determined by the electron excitations at very-low temperatures (near 0 K) and the contributions from phonon

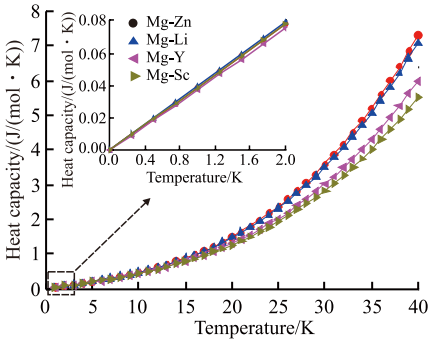

Fig.3 Heat capacity of Mg-R solid solution

Table 3 Calculated elastic modulus and Poisson's ratio using Voigt, Reuss and Hill's approximations

Phase	Source	B_V/GPa	B_R/GPa	B/GPa	G_V/GPa	G_R/GPa	G/GPa	E/GPa	G/B	v
Mg	Present	36.59	36.59	36.59	18.50	17.67	18.09	46.59	0.494	0.288
	Cal.[8]	35.83	-	-	18.5	-	-	47.4	0.518	0.28
	Exp.[22]	-	-	35.6	-	-	17.3	44.6	0.488	-
Mg-Zn	Present	36.78	36.70	36.74	16.51	16.05	16.28	42.55	0.443	0.312
	Cal.[8]	37.1	-	-	17.3	-	-	44.8	0.465	0.3
	Cal.[10]	36.31	36.27	36.29	19.60	18.98	19.29	49.16	0.532	0.274
	Exp.[24]	-	-	-	-	-	-	48.0	-	-
Mg-Li	Present	34.82	34.64	34.61	15.71	15.65	15.68	40.87	0.453	0.303
	Cal.[8]	34.84	-	-	16.17	-	-	42.00	0.465	0.30
	Exp.[22]	35.3	-	-	17.1	-	-	44.1	0.485	0.29
Mg-Y	Present	36.22	36.22	36.22	19.98	19.63	19.81	50.27	0.547	0.269
	Cal.[8]	36.1	-	-	18.3	-	-	47.1	0.508	0.28
	Cal.[10]	36.26	36.22	36.24	19.20	18.59	18.90	48.30	0.522	0.278
Mg-Sc	Present	37.16	37.13	37.15	20.66	20.49	20.58	52.12	0.554	0.266

Table 4 Calculated longitudinal, shear, average sound velocity v, Debye temperature Θ_D, the characteristic parameters of electron γ, and phonon specific heat β

Phase	v_l/(m/s)	v_s/(m/s)	v_m/(m/s)	Θ_D/K	γ/(J/(K^2·mol))	β/(J/(K^4·mol))
Mg-Zn	5 633.40	2 973.16	3 323.89	350.06	3.86	9.01
Mg-Li	5 700.05	3 029.28	3 385.02	355.46	3.91	8.64
Mg-Y	5 837.38	3 282.90	3 652.75	381.11	3.73	7.01
Mg-Sc	6 034.18	3 406.11	3 788.69	397.00	3.89	6.20

excitations are significant at higher temperatures.

4 Conclusions

First principles calculations based on the density functional theory have been applied to study the electronic structure, elastic and thermal properties of the Mg-R solid solutions. Cohesive energies show that Mg-Sc has the highest structural stability. The calculations of the density of states (DOS) and electronic charge density difference show that Mg-Y (Sc) alloys have very strong covalent bonding because Y(Sc) addition is associated with a hybridization between the *d*-orbital of Y(Sc) and the *p*-orbital of the Mg atoms. The calculated elastic constants, bulk modulus *B*, shear modulus *G*, Young's modulus *E* and Poisson ratio *v* show that all the alloy systems can exhibit ductile properties at 2.77 at% R, and Mg-Zn(Li) alloys have the better ductility and plasticity. The Debye temperatures of the solid solutions are estimated from the average sound velocity based on elastic constants evaluations. And the result shows that the mechanical stability of Mg-Sc is the best. The calculated isochoric heat capacity shows that electron excitations near 0 K are significant, while phonon excitations are significant at higher temperatures.

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