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Electronic origin of the anomalous solid solution hardening of Y and Gd in Mg: A first-principles study

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Y and Gd demonstrate anomalous solid solution hardening efficiency, which cannot be understood using the elastic impurity-dislocation interaction theory. We performed first-principles calculations to investigate the effect of different alloying elements such as Al, Zn, Y, and Gd on the chemical bonding of Mg solid solutions. The present calculations clearly show that the anomalous solid solution hardening of Y and Gd in Mg may be understood based on the increased bonding strength of both Mg-Y (Gd) and Mg-Mg.

magnesium alloys, solid solution hardening, first-principles, chemical bonding

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As the lightest metallic structural alloy with a good combination of castability, mechanical properties and ductility, magnesium alloys have attracted increasing attention in the automotive and aerospace industries [1]. It has been reported that the addition of rare-earth (RE) elements, such as Y, Gd, Ce, and Dy, significantly improves the mechanical properties of Mg alloys at ambient as well as at elevated temperatures [2,3]. The strengthening by the RE elements is more substantial than any other elements that have been added to Mg alloys [4,5]. One of the most effective strengthening mechanisms of RE in Mg is solid solution hardening, essentially of either elastic or electronic origin. The elastic origin has been quantitatively established based on the impurity-dislocation interaction theory by Fleischer [6] and Labusch [7], and is correlated with the atomic size factor (δ) and/or the modulus misfit parameter (η). For a number of alloying elements (Zn, Al, Pb, Li, Tl, Cd, In, etc.) in Mg the efficiency of solid solution hardening increases monotonically with the increase of $|\delta|$ or $|\eta|$, or a combined misfit parameter of them [8,9]. This relation has been verified for aluminium [10], iridium [11], copper [12], nickel [13], and stainless steel [14] solid solution alloys. However, recent experimental studies [4,5,15,16] have demonstrated that Y and Gd exhibit anomalously higher solid solution hardening efficiency than those of Al and Zn in terms of the misfit parameters, which cannot be understood using the elastic interaction model. Such anomalous solid solution hardening of other RE elements, such as Ce [17] and Dy [18], was also reported. A few experimental and theoretical studies have been carried out to explore the solid solution hardening of RE in Mg. However, the nature of this anomalous behavior has not yet been explained in the literature. Miura et al. [18] evaluated the elastic interaction based on isotropic or anisotropic distortion strains by solute atoms, and it was found that the elastic strain by Zn atoms is higher than those of Y and Dy, while the solid solution hardening of basal slip by Y or Dy addition is much higher than that by Zn addition. Ninomiya et al. [19] have proposed another solid solution hardening model based on a discrete variational-Xα molecular orbital calculation, but

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the details of the solid solution hardening mechanism of Mg-RE alloys have not been elucidated yet.

In this paper, we have studied the solid solution hardening from the view point of chemical bonding by means of first-principles calculations based on the density functional theory. The aim of this work is to explain the anomalous solid solution hardening of Y and Gd in Mg from the electronic origin. Our findings are important for the further understanding of the alloying behavior in a simple metal, and are useful for the design of commercial magnesium alloys.

1 Computational methods

Magnesium has a hexagonal close-packed (hcp) lattice of space group *P6₃/mmc* with two atoms in a unit cell. In the present work, $Mg_{53}X_1$ solid solutions corresponding to a doping concentration of 1.85 at.% were modeled by a 3×3×3 supercell of magnesium (Mg_{54}), in which one magnesium atom was substituted by a solute atom X (X = Al, Zn, Y, and Gd) at the center site of the supercell. Primary test calculations demonstrated that the results were independent of the doped position. The Vienna *Ab initio* Simulation Package (VASP) [20] based on the first-principles density functional theory (DFT) was used. The projector augmented-wave pseudo-potentials [21,22] were used to depict the interactions between the valence electrons and the core. The generalized gradient approximations (GGA) in Perdew-Wang-91 (PW91) scheme [23] was adopted for describing the exchange-correlation interactions. An energy cut-off of 1.25 times the maximum potential energy of either Mg or X (whichever element has the higher default cut-off energy) as given in their pseudo-potential files was performed. The relaxation convergence for ions and electrons was 1×10^{-6} eV. The integration in the Brillouin zone was made using Monkhorst-Pack [24] 5 × 5 × 5 *k*-points for the hcp supercell model. The convergence according to *k*-points has also been checked and the *k*-points of 5 × 5 × 5 are sufficient to give good results. The atomic arrangements were relaxed using the second-order Methfessel-Paxton technique [25] with a width of 0.2 eV. The tetrahedron method with Blöchl corrections [26] was used for the total energy calculation. The partial density of states (PDOS) and electron localization function (ELF) were obtained using the relaxed structure at the equilibrium volume.

2 Results and discussion

The calculated lattice parameters *a* and *c*/*a*, equilibrium volume V_0, and cohesive energy E_{coh} of pure Mg together with the available experimental data [27–29] and previous calculations [30–32] are shown in Table 1. It is clear that the present calculations agree well with the experimental values and previous calculations, with the difference being less than 3% for all the results. Figure 1 shows the theoretical equilibrium volume of Mg-X solid solutions as a function of solute composition. The values of the atomic size factor (δ) for each element can be determined from Figure 1 according to the method developed by King [28], as also shown in Table 1. The calculated atomic size factor of Al and Zn are –12.91% and –18.13%, respectively. Reasonable agreement between our calculations and the experimental data of King [28] (–13.73% and –20.00%, respectively) as well as with earlier calculations by Uesugi [30] on Al (–12.40%) is obtained. The calculated atomic size factor of Y and Gd are +15.63% and +17.29%, respectively. No experimental or theoretical data of δ for Y and Gd has been reported so far. Noting that the atomic size factor (absolute value) of Y and Gd are smaller than that of Zn, which cannot explain the prominent difference in strengthening efficiency between Mg-Y (Gd) and Mg-Al (Zn) alloys. Therefore, this anomalous solid solution hardening behavior may be due to the specific chemical bonding, as will be discussed in the following section using the $Mg_{53}X_1$ solid solutions as an example.

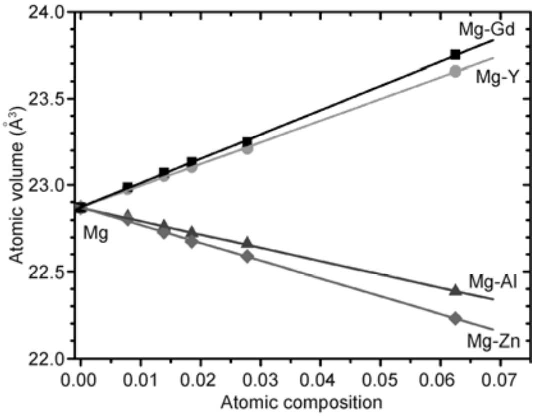

Figure 1 The theoretical equilibrium atomic volume of Mg-X (X = Al, Zn, Y, and Gd) solid solutions as a function of solute composition.

Table 1 The calculated and experimental lattice parameters *a* and *c*/*a*, equilibrium atomic volume V_0, and cohesive energy E_{coh} of pure Mg, as well as the atomic size factor δ for Al, Zn, Y, and Gd in Mg solid solutions, respectively

Mg	*a* (Å)	*c*/*a*	V_0 (Å³)	E_{coh} (eV/atom)	δ (%)			
					Al	Zn	Y	Gd
Calc. [this work]	3.191	1.627	22.88	–1.52	–12.91	–18.13	+15.63	+17.29
Exp. [27–29]	3.202	1.624	23.23	–1.51	–13.73	–20.00	–	–
Calc. [30–32]	3.193	1.622	22.86	–1.48	–12.40	–	–	–

In order to gain better understanding of the chemical bonding in $Mg_{53}X_1$, we have calculated the partial density of state (PDOS), which is shown in Figure 2. It is seen that the *s*- and *p*-electron states of alloying elements are spread in a relatively wide energy range. It is also interesting to note that the PDOS of $Mg_{53}X_1$ can be divided into two groups, one consisting of $Mg_{53}Al_1$ and $Mg_{53}Zn_1$, and the other consisting of $Mg_{53}Y_1$ and $Mg_{53}Gd_1$. For $Mg_{53}Al_1$ and $Mg_{53}Zn_1$ (Figure 2(a) and (b)), the valence states are dominated by the *p* states of Mg and Al (Zn), while for $Mg_{53}Y_1$ and $Mg_{53}Gd_1$ (Figure 2(c) and (d)), the states at the Fermi level as well as the valence bands are predominated by the *d*

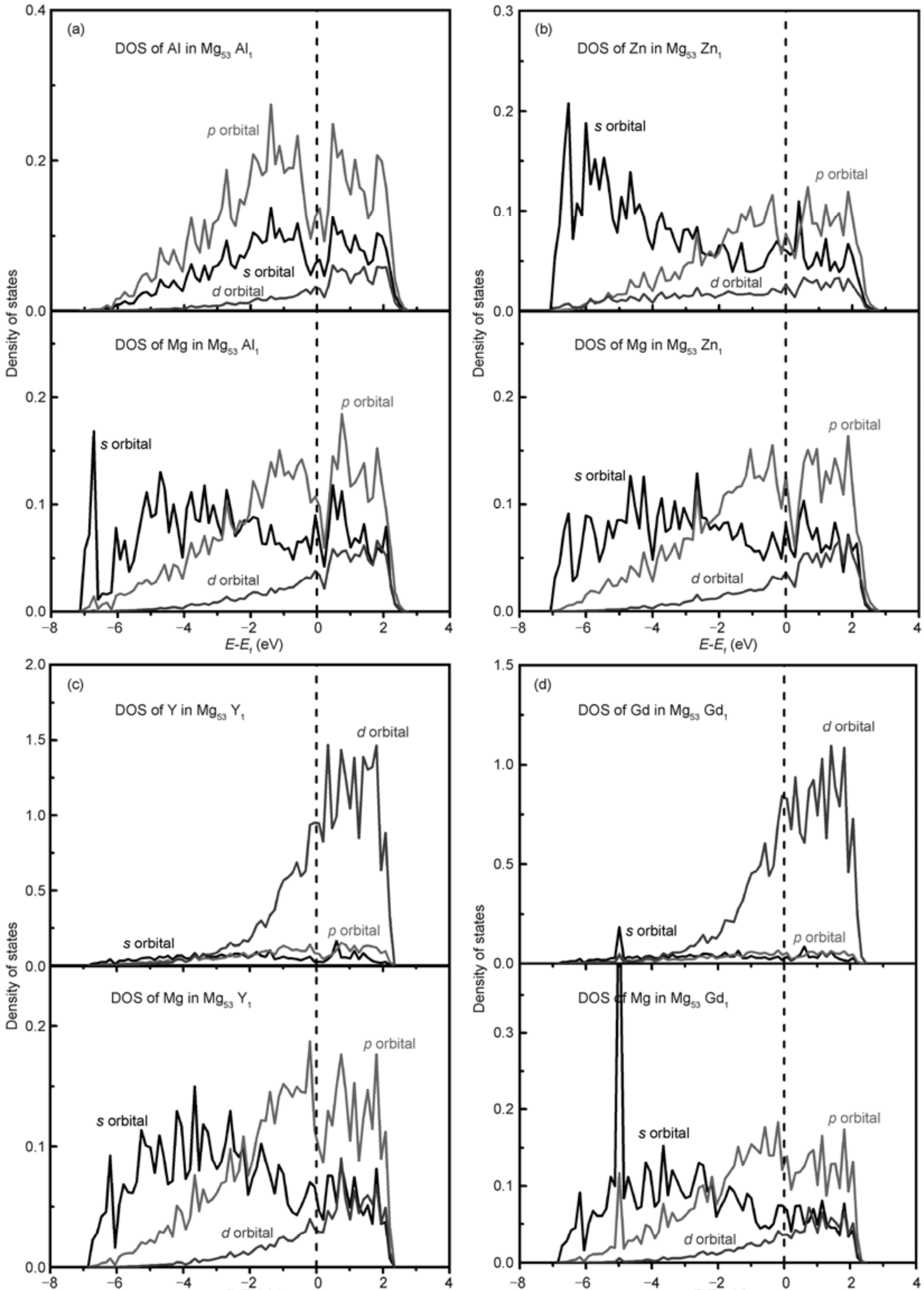

Figure 2 The calculated partial density of states (PDOS) for (a) $Mg_{53}Al_1$, (b) $Mg_{53}Zn_1$, (c) $Mg_{53}Y_1$, and (d) $Mg_{53}Gd_1$. The Fermi level (E_f) is set at zero and marked by a vertical dot line.

states of Y (Gd). Strong hybridization between the *p*-orbital of Mg and the *d*-orbital of Y (Gd) atoms is also observed. This hybridization presents covalent bonding characteristics identified by the electron localization function (ELF) as shown in Figure 3 and plays a major role in the solid solution hardening in Mg-Y (Gd) alloys. The results clearly show similar chemical bonding characters between $Mg_{53}Al_1$ and $Mg_{53}Zn_1$, and that between $Mg_{53}Y_1$ and $Mg_{53}Gd_1$.

A rather quantitative understanding on the chemical bonding of $Mg_{53}X_1$ solid solutions can be gained by analyzing the electron localization function (ELF). Figure 3 shows the ELF contours in the (0001) plane for $Mg_{53}X_1$, as well as that of Mg_{54} for comparison. For Mg_{54} (Figure 3(a)), a typical metallic bonding feature with ELF of 0.5 (green background) is observed together with weak covalent bonding (ELF = 0.7) between the adjacent Mg atoms. Significant difference in the chemical bonding caused by the introduction of a solute atom can be observed. Like the above analysis of PDOS, ELF of $Mg_{53}X_1$ can also be divided into two similar groups. For $Mg_{53}Al_1$ and $Mg_{53}Zn_1$ (Figure 3(b) and (c)), electrons at around Al (Zn) extend to two neighboring Mg atoms forming quite weak covalent bonds, for example, the Mg1-Al-Mg2 and Mg1-Zn-Mg2 covalent bonds, with the later bond being stronger than the former. Furthermore, the introduction of Al (Zn) results in the increased bonding strength between some neighboring Mg atoms, for example, between Mg2 and Mg3 in Figure 3(b) and (c), which is clearly seen by the large ELF values. For $Mg_{53}Y_1$ and $Mg_{53}Gd_1$ (Figure 3(d) and (e)), the covalent interaction among the Mg-Y(Gd)-Mg bonds is much stronger, suggesting the increased bonding strength. This enhanced bonding strength is attributed to the *p-d* covalent interactions, according to the PDOS analysis (Figure 2(c) and (d)). This further indicates that the hybridization of the valence electrons between the Mg and Y (Gd) atoms plays a decisive role in solid solution hardening in the Mg-Y (Gd) alloy. Furthermore, compared with Mg_{54}, the covalence bonding among some Mg atoms which are close to Y (Gd) is also increased, for example, between Mg3 and Mg4 in Figure 3(d) and (e), which is not the case in $Mg_{53}Al_1$ and

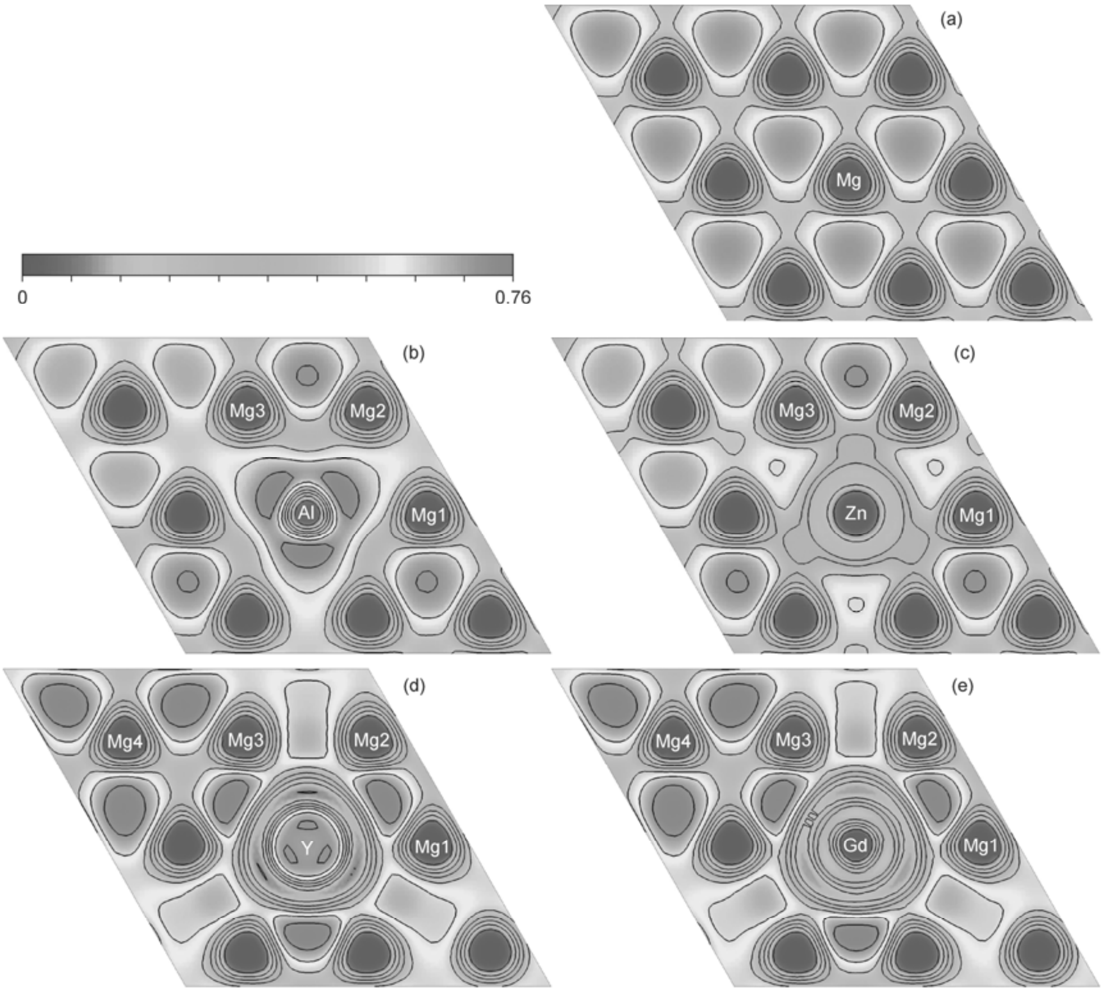

Figure 3 The plot of the electron localization function (ELF) in the (0001) plane of (a) Mg_{54}, (b) $Mg_{53}Al_1$, (c) $Mg_{53}Zn_1$, (b) $Mg_{53}Y_1$ (e) $Mg_{53}Gd_1$. The ELF contours range from 0 to 0.76 and increase in steps of 0.1.

$Mg_{53}Zn_1$. Therefore, the substitution of Y or Gd in Mg results in significant enhancement in the chemical bonding not only between the Y (Gd) and Mg atoms, but also between the Mg atoms. The covalent bond interactions in the Mg-Y (Gd) and Mg-Mg bonds are responsible for the anomalously higher solid solution hardening efficiency of RE elements in Mg.

3 Conclusions

In summary, we have studied the chemical bonding of $Mg_{53}X_1$ solid solutions, where X = Al, Zn, Y, and Gd, by means of first-principles calculations. Reasonable agreement between calculated and measured data is observed, thus validating the first-principles methodology employed. The addition of Y (Gd) to Mg affects the atomic binding states not only between Y (Gd) and Mg atoms, but also between Mg atoms. The mechanism of the anomalous solid solution hardening of RE elements in Mg may be understood based on the increased bonding strength of both Mg-Y (Gd) and Mg-Mg. This suggests the important role of the electronic origin of the solid solution hardening.

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1 Mordike B L, Ebert T. Magnesium: Properties-applications-potential. Mater Sci Eng A, 2001, 302: 37–45
2 Gao L, Chen R S, Han E H. Microstructure and strengthening mechanisms of a cast Mg-1.48Gd-1.13Y-0.16Zr (at.%) alloy. J Mater Sci, 2009, 44: 4443–4454
3 Mordike B L. Creep-resistant magnesium alloys. Mater Sci Eng A, 2002, 324: 103–112
4 Suzuki M, Sato H, Maruyama K, et al. Creep behavior and deformation microstructures of Mg-Y alloys at 550 K. Mater Sci Eng A, 1998, 252: 248–255
5 Maruyama K, Suzuki M, Sato H. Creep strength of magnesium-based alloys. Metall Mater Trans A, 2002, 33: 875–882
6 Fleischer R L. Solution hardening. Acta Metall, 1961, 9: 996–1000
7 Labusch R. A statistical theory of solid solution hardening. Phys Stat Sol A, 1970, 41: 659–664
8 Akhtar A, Teghtsoonian E. Substitutional solution hardening of magnesium single crystal. Philos Mag, 1972, 25: 897–916
9 Lukac P. Solid solution hardening in Mg-Cd single crystals. Phys Stat Sol A, 1963, 131: 377–390
10 Zander J, Sandstrom R, Vitos L. Modelling mechanical properties for non-hardenable aluminium alloys. Comp Mater Sci, 2007, 41: 86–95
11 Yamabe-Mitarai Y, Aoki H. Solid-solution hardening of Ir by Pt and Ni. Mater Lett, 2002, 56: 781–786
12 Čižek L, Kratochvíl P, Smola B. Solid solution hardening of copper crystals. J Mater Sci, 1974, 9: 1517–1520
13 Mishima Y, Ochiai S, Hamao N, et al. Solid solution hardening of nickel: role of transition metal and B-subgroup solute. Trans Jpn Institu Metals, 1986, 27: 656–664
14 Sieurin H, Zander J, Sandstrom R. Modelling solid solution hardening in stainless steels. Mater Sci Eng A, 2006, 415: 66–71
15 Gao L, Chen R S, Han E H. Effects of rare-earth elements Gd and Y on the solid solution strengthening of Mg alloys. J Alloys Compd, 2009, 481: 379–384
16 Gao L, Chen R S, Han E H. Solid solution strengthening behaviors in binary Mg-Y single phase alloys. J Alloys Compd, 2009, 472: 234–240
17 Chino Y, Kado M, Mabuchi M. Compressive deformation behavior at room temperature-773K in Mg-0.2mass%(0.035at.%)Ce alloy. Acta Mater, 2008, 56: 387–394
18 Miura S, Imagawa S, Toyoda T, et al. Effect of rare-earth elements Y and Dy on the deformation behavior of Mg alloy single crystals. Mater Trans, 2008, 49: 952–956
19 Ninomiya R, Yukawa H, Morinaga M, et al. An electronic approach to the prediction of the mechanical properties of magnesium alloys. J Alloys Compd, 1994, 215: 315–323
20 Kresse G, Furthmüller J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys Rev B, 1996, 54: 11169–11186
21 Blochl P E. Projector augmented-wave method. Phys Rev B, 1994, 50: 17953–17979
22 Kresse G, Joubert D. From ultrasoft pseudopotentials to the projector augmented-wave method. Phys Rev B, 1999, 59: 1758–1775
23 Perdew J P, Chevary J A, Vosko S H, et al. Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation. Phys Rev B, 1992, 46: 6671–6687
24 Monkhorst H J, Pack J D. Special points for Brillouin-zone integrations. Phys Rev B, 1976, 13: 5188
25 Methfessel M, Paxton A T. High-precision sampling for Brillouin-zone integration in metals. Phys Rev B, 1989, 40: 3616–3621
26 Blochl P E, Jepsen O, Andersen O K. Improved tetrahedron method for Brillouin-zone integrations. Phys Rev B, 1994, 49: 16223–16233
27 Busk R S. Lattice parameters of magnesium alloys. AIME Trans, 1950, 188: 1460–1464
28 King H W. Quantitative size-factors for metallic solid solutions. J Mater Sci, 1966, 1: 79–90
29 Kittel C. Introduction to Solid State Physics. New York: Wiley, 2005
30 Uesugi T, Kohyama M, Higashi K. Atomic size effects on Al, Ca, and Sc in Mg solid solutions from first-principles calculations. Mater Sci Forum, 2003, 426–432: 599–603
31 Wang Y, Curtarolo S, Jiang C, et al. *Ab initio* lattice stability in comparison with CALPHAD lattice stability. CALPHAD, 2004, 28: 79–90
32 Zhang H, Shang S, Saal J E, et al. Enthalpies of formation of magnesium compounds from first-principles calculations. Intermetallics, 2009, 17: 878–885