Enthalpies of formation of magnesium compounds from first-principles calculations

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ABSTRACT

An energetics database of binary magnesium compounds has been developed from first-principles calculations. The systems investigated include Mg–X (X = As, Ba, Ca, Cd, Cu, Dy, Ga, Ge, La, Lu, Ni, Pb, Sb, Si, Sn and Y). The calculated lattice parameters and enthalpies of formation of binary compounds in these systems are compared with both experimental data and thermodynamic databases.

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1. Introduction

Magnesium alloys are of great importance to the industrial world. With a density of 1.741 g/cm^3 that is two-thirds of that of aluminum and one-quarter of that of steel, magnesium is the lightest structural metal. Magnesium alloys receive a substantial amount of interest for potential transportation applications such as automobile body materials for weight reduction and higher fuel efficiency. A greater understanding of the thermodynamics of magnesium alloys will allow better control in designing materials with desired properties. One type of critically important thermodynamic data is the enthalpy of formation of compounds, which can be reliably obtained through first-principles calculations as demonstrated in the literature [1–4]. By inputting only the crystal structure and composition of the phase, first-principles calculations can predict the total energy at 0 K of a compound, from which the enthalpy of formation can be derived. The predictive abilities of this approach has been verified in a recent study [5] on first-principles energetics of Al based systems. In our previous study, the thermodynamic database of the Mg–Zr [3] and the Mg–Ca [4] binary systems as well as the Mg–Ca–Sn [1] and the Mg–Ca–Sr [6] ternary systems were predicted using this method.

The present work further extends the calculations of the enthalpies of formation to a number of binary magnesium alloys.

We compute the energetics and structure of pure elements and ordered compounds observed for each system and provide structural information and enthalpies of formation for a large set of stable compounds. The X element in Mg–X systems investigated include: (1) Period III: Si, (2) Period IV: Ca, Cu, Ga, Ge, As, (3) Period V: Y, Pd, Cd, Sn, Sb, (4) Period VI: Ba, Pb, (5) Rare Earth: La, Dy, Lu. All the results are compared with available experimental data and thermodynamic databases.

2. Methodology

2.1. First-principles method

First-principles calculations, based on density functional theory (DFT), were performed using the projected augmented wave (PAW) pseudo-potentials as implemented in VASP (Vienna Ab-initio Simulation Package) [7,8] with the generalized gradient approximation refined by Perdew, Burke and Ernzerhof (PBE) [9]. All the structures were fully relaxed with respect to volume and the atomic coordinates. For calculations of elements involving magnetic properties, such as Dy and Lu, spin-polarized calculations were performed. For consistency, the 360 eV cutoff was used for all elements. The Monkhorst–Pack scheme was used for the Brillouin-zone integrations [10]. The settings of k-points correspond roughly to a 5000 k-point mesh per reciprocal atom. Some rare earth elements, such as Pr and Eu, were not included in this work due to the difficulty of calculating their energies accurately in DFT. This is due to the itinerant nature of the *f* electrons [8].

Table 1
Stable crystal structures of pure elements at room temperature [11].

Phase	Structure	Space group	Pearson symbol	Strukturbericht designation
As	α-As	$R\bar{3}m$	hR6	A7
Ba	bcc	$Im\bar{3}m$	cI2	A2
Ca	fcc	$Fm\bar{3}m$	cF4	A1
Cd	hcp	$P6_3/mmc$	hP2	A3
Cu	fcc	$Fm\bar{3}m$	cF4	A1
Dy	hcp	$P6_3/mmc$	hP2	A3
Ga	α-Ga	$Cmca$	oC8	A11
Ge	Diamond	$Fd\bar{3}m$	cF8	A4
La	hcp	$P6_3/mmc$	hP2	A3
Lu	hcp	$P6_3/mmc$	hP2	A3
Mg	hcp	$P6_3/mmc$	hP2	A3
Ni	fcc-FM	$Fm\bar{3}m$	cF4	A1
Pb	fcc	$Fm\bar{3}m$	cF4	A1
Sb	α-As	$R\bar{3}m$	hR2	A7
Si	Diamond	$Fd\bar{3}m$	cF8	A4
Sn	β-Sn	$I4_1/amd$	tI4	A5
Y	hcp	$P6_3/mmc$	hP2	A3

The enthalpy of formation of a compound can be defined as the difference in total energy of the compound and the energies of its constituent elements in their stable states:

$$\Delta_f E(\mathrm{Mg}_x \mathrm{X}_y) = E(\mathrm{Mg}_x \mathrm{X}_y) - \frac{x}{x+y}E(\mathrm{Mg}) - \frac{y}{x+y}E(\mathrm{X}) \qquad (1)$$

where $E(\mathrm{Mg}_x\mathrm{X}_y)$ is the total energy of the compound, and $E(\mathrm{Mg})$ and $E(X)$ are the total energies of pure elements in their stable structures. Since the influence of pressure on the condensed phases is ignored and the energies are calculated at 0 K without any entropic contributions, the energy of formation is taken to be the enthalpy of formation.

2.2. Crystal structures of pure elements and compounds

The Mg–X binary systems were chosen based on the availability of crystal structure data. The structure types range from relatively simple structures, such as MgX and Mg_3X_2 compounds with 2 and 5 atoms in the primitive cells, to complex phases, such as $Mg_{24}X_5$, $Mg_{38}X_9$ and $Mg_{23}X_6$, with 58, 94, and 116 atoms per primitive cell, respectively. The observed ground state structures for each pure element X are listed in Tables 1 and 2 summarize the crystal structures and k-point mesh of the intermetallic compounds in the Mg–X systems [11].

3. Results and discussion

3.1. Lattice parameters for elements and compounds

We begin the discussion of our results with the energies for the pure elements. One method to determine the accuracy of the calculations of the pure elements is to compare the calculated

Table 2
Stable crystal structures of compounds at room temperature considered in this paper [11].

System	Formula	Compound				k-point mesh
		Space group	Pearson symbol	Strukturbericht designation	Prototype	
Mg–As	α-Mg$_3$As$_2$	$P\bar{3}m1$	hP5	D5$_{19}$	La$_2$O$_3$	$6 \times 6 \times 6$
	β-Mg$_3$As$_2$	$Ia\bar{3}$	cI80		Mn$_2$O$_3$	$12 \times 12 \times 7$
	MgAs$_4$	$P4_12_12$	tP20		MgAs$_4$	$10 \times 10 \times 4$
Mg–Ba	Mg$_{17}$Ba$_2$	$R\bar{3}m$	hR57		Zn$_{17}$Th$_2$	$7 \times 7 \times 7$
	Mg$_{23}$Ba$_6$	$Fm\bar{3}m$	cF116	D8$_4$	Th$_6$Mn$_{23}$	$6 \times 6 \times 6$
	Mg$_2$Ba	$P6_3/mmc$	hP12	C14	MgZn$_2$	$9 \times 9 \times 6$
Mg–Ca	Mg$_2$Ca	$P6_3/mmc$	hP12	C14	MgZn$_2$	$9 \times 9 \times 6$
Mg–Cd	MgCd$_3$	$P6_3/mmc$	hP8	D0$_{19}$	Ni$_3$Sn	$8 \times 8 \times 10$
	MgCd	$Pmma$	oP4	B19	AuCd	$16 \times 10 \times 10$
	Mg$_3$Cd	$P6_3/mmc$	hP8	D0$_{19}$	Ni$_3$Sn	$8 \times 8 \times 10$
Mg–Cu	MgCu$_2$	$Fd\bar{3}m$	cF24	C15	MgCu$_2$	$10 \times 10 \times 10$
Mg–Dy	MgDy	$Pm\bar{3}m$	cP2	B2	CsCl	$14 \times 14 \times 14$
	Mg$_2$Dy	$P6_3/mmc$	hP12	C14	MgZn$_2$	$10 \times 10 \times 6$
	Mg$_3$Dy	$Fm\bar{3}m$	cF16	D0$_3$	BiFe$_3$	$12 \times 12 \times 12$
	Mg$_{24}$Dy$_5$	$I\bar{4}3m$	cI58	A12	Ti$_5$Re$_{24}$	$6 \times 6 \times 6$
Mg–Ga	Mg$_2$Ga$_5$	$I4/mmm$	tI28		Mg$_2$Ga$_5$	$8 \times 8 \times 8$
	Mg$_2$Ga	$P\bar{6}2c$	hP18			$7 \times 7 \times 7$
	MgGa	$I4_1/a$	tI32		MgGa	$7 \times 7 \times 7$
	MgGa$_2$	$Pbam$	oP24			$8 \times 4 \times 12$
	Mg$_5$Ga$_2$	$Ibam$	oI28	D8$_g$	Mg$_5$Ga$_2$	$8 \times 8 \times 8$
Mg–Ge	Mg$_2$Ge	$Fm\bar{3}m$	cF12	C1	CaF$_2$	$12 \times 12 \times 12$
Mg–La	MgLa	$Pm\bar{3}m$	cP2	B2	CsCl	$14 \times 14 \times 14$
	Mg$_2$La	$Fd\bar{3}m$	cF24	C15	MgCu$_2$	$10 \times 10 \times 10$
	Mg$_3$La	$Fm\bar{3}m$	cF16	DO$_3$	BiF$_3$	$12 \times 12 \times 12$
	Mg$_{17}$La$_2$	$P6_3/mmc$	hP38		Th$_2$Ni$_{17}$	$6 \times 6 \times 6$
	Mg$_{12}$La	$Immm$	oI338			$8 \times 8 \times 8$
Mg–Lu	MgLu	$Pm\bar{3}m$	cP2	B2	CsCl	$14 \times 14 \times 14$
	Mg$_2$Lu	$P6_3/mmc$	hP12	C14	MgZn$_2$	$10 \times 10 \times 6$
	Mg$_{24}$Lu$_5$	$I\bar{4}3m$	cI58	A12	Ti$_5$Re$_{24}$	$6 \times 6 \times 6$
Mg–Ni	Mg$_2$Ni	$P6_222$	hP18	C$_a$	Mg$_2$Ni	$9 \times 9 \times 4$
	MgNi$_2$	$P6_3/mmc$	hP24	C36	MgNi$_2$	$9 \times 9 \times 3$
Mg–Pb	Mg$_2$Pb	$Fm\bar{3}m$	cF12	C1	CaF$_2$	$12 \times 12 \times 12$
Mg–Sb	α-Mg$_3$Sb$_2$	$P\bar{3}m1$	hP5	D5$_{19}$	La$_2$O$_3$	$6 \times 6 \times 6$
Mg–Si	Mg$_2$Si	$Fm\bar{3}m$	cF12	C1	CaF$_2$	$12 \times 12 \times 12$
Mg–Sn	Mg$_2$Sn	$Fm\bar{3}m$	cF12	C1	CaF$_2$	$12 \times 12 \times 12$
Mg–Y	MgY	$Pm\bar{3}m$	cP2	B2	CsCl	$14 \times 14 \times 14$
	Mg$_2$Y	$P6_3/mmc$	hP12	C14	MgZn$_2$	$10 \times 10 \times 6$
	Mg$_{24}$Y$_5$	$I\bar{4}3m$	cI58	A12	Ti$_5$Re$_{24}$	$6 \times 6 \times 6$

Table 3
Calculated lattice parameters for elements in the Mg–X systems.

Element		Lattice parameters				
		Calc.	Exp. [11,12]	% Difference	Calc. [13]	% Difference
As	a	3.823	3.760	1.676		
	c	10.683	10.548	1.280		
Ba	a	5.025	5.025	0.000	5.006	0.380
Ca	a	5.537	5.599	−1.107	5.501	0.654
Cd	a	3.033	2.979	1.813	3.061	−0.915
	c	5.680	5.617	1.122	5.611	1.230
Cu	a	3.634	3.615	0.526	3.631	0.083
Dy	a	3.615	3.590	0.696	3.604	0.305
	c	5.639	5.640	−0.018	5.636	0.053
Ga	a	4.593	4.514	1.750		
	b	7.767	7.644	1.609		
	c	4.590	4.526	1.414		
Ge	a	5.724	5.658	1.166		
La	a	3.761	3.765	−0.106	3.753	0.213
	c	12.085	12.150	−0.535	12.212	−1.040
Lu	a	3.494	3.500	−0.171	3.511	−0.484
	c	5.473	5.505	−0.581	5.470	0.055
Mg	a	3.193	3.213	−0.622	3.189	0.125
	c	5.179	5.213	−0.652	5.169	0.193
Ni	a	3.514	3.524	−0.284	3.517	−0.085
Pb	a	5.024	4.950	1.489	5.049	−0.495
Sb	a	4.380	4.300	1.860		
	c	11.466	11.251	1.911		
Si	a	5.470	5.430	0.731		
Sn	a	5.930	5.830	1.715		
	c	3.230	3.180	1.572		
Y	a	3.655	3.655	0.000	3.654	0.027
	c	5.685	5.751	−1.148	5.649	0.637

lattice parameters with those determined experimentally. Table 3 lists the lattice parameters calculated in comparison with available experimental data [11,12] and previous calculations by Wang et al. [13]. It can be seen that the calculated data shows good agreement with experiments, with the difference being less than 2.0% for all results. Even though a different potential (GGA-PW91) and energy cutoff were used in Ref. [13], in general, we note quite similar results for the two sets of potentials. A similar assessment of lattice parameters for the binary compounds is listed in Table 4. The difference between experiments and calculations is less than 2.0%.

3.2. Enthalpies of formation of Mg–X compounds

The calculated enthalpies of formation of the binary compounds are compared with the available experimental data in Table 5 [14,15] and plotted in Fig. 1, in which the calculated and experimental values are plotted in the x- and y-axis, respectively. The top right corner of Fig. 1(a) is enlarged in Fig. 1(b). In both figures, the solid line represents perfect agreement between the calculated and experimental values, and two dashed lines are shown to define an error bar of ±5 kJ/mol. (Note: in this paper, the unit kJ/mol means kJ/mole of atoms.) The value of ±5 kJ/mol is set by the uncertainty in the latest experimental studies of enthalpies of formation of compounds [16,17]. The calculated enthalpies of formation compare favorably with experiment for most compounds, with differences often within about 10%. The largest discrepancies between first-principles and experimental data are found in the

Table 4
Calculated lattice parameters for binary compounds in the Mg–X systems compared with experiments [11,12].

System	Phase	a (Å)			b (Å)			c (Å)		
		Calc.	Exp.	% Difference	Calc.	Exp.	% Difference	Calc.	Exp.	% Difference
Mg–As	α-Mg₃As₂	4.294	4.264	0.704				6.768	6.738	0.445
	β-Mg₃As₂	12.455	12.355	0.809						
	MgAs₄	5.472	5.385	1.616				16.083	15.798	1.804
Mg–Ba	Mg₁₇Ba₂	10.625	10.650	−0.235				15.564	15.587	−0.148
	Mg₂₃Ba₆	15.220	15.263	−0.282						
	Mg₂Ba	6.665	6.636	0.437				10.577	10.655	−0.732
Mg–Ca	Mg₂Ca	6.234	6.230	0.064				10.093	10.120	−0.267
Mg–Cd	MgCd	5.049	5.005	0.869	3.213	3.222	−0.272	5.266	5.270	−0.067
	MgCd₃	6.353	6.234	1.917				4.949	5.045	−1.903
	Mg₃Cd	6.313	6.310	0.048				5.037	5.080	−0.846
Mg–Cu	MgCu₂	7.065	7.040	0.355						
Mg–Dy	MgDy	3.786	3.776	0.265						
	Mg₂Dy	6.049	6.020	0.482				9.788	9.760	0.287
	Mg₃Dy	10.300	10.33	−0.290				5.940	5.960	−0.336
	Mg₂₄Dy₅	11.255	11.246	0.080						
Mg–Ga	Mg₅Ga₂	7.036	7.017	0.271	13.747	13.708	0.285	6.028	6.020	0.133
	Mg₂Ga	7.805	7.794	0.141				6.941	6.893	0.696
	MgGa	10.690	10.530	1.519				5.555	5.530	0.452
	MgGa₂	6.868	6.802	0.970	16.457	16.346	0.679	4.139	4.111	0.681
	Mg₂Ga₅	8.725	8.627	1.136				7.178	7.111	0.942
Mg–Ge	Mg₂Ge	6.423	6.385	0.597						
Mg–La	MgLa	3.966	3.970	−0.101						
	Mg₂La	8.776	8.809	−0.375						
	Mg₃La	7.500	7.494	0.080						
	Mg₁₇La₂	10.351	10.36	−0.087				10.156	10.240	−0.820
	Mg₁₂La	10.337	10.34	−0.029				5.911	5.960	−0.822
Mg–Lu	MgLu	3.703	3.727	−0.644						
	Mg₂Lu	5.973	5.960	0.218				9.684	9.710	−0.268
	Mg₂₄Lu₅	11.162	11.185	−0.206						
Mg–Ni	Mg₂Ni	5.199	5.212	−0.244				13.188	13.254	−0.496
	MgNi₂	4.815	4.825	−0.207				15.821	15.790	0.196
Mg–Pb	Mg₂Pb	6.944	6.836	1.580						
Mg–Sb	α-Mg₃Sb₂	4.595	4.573	0.481				7.279	7.229	0.692
Mg–Si	Mg₂Si	6.358	6.351	0.110						
Mg–Sn	Mg₂Sn	6.825	6.759	0.971						
Mg–Y	MgY	3.803	3.797	0.158						
	Mg₂Y	6.049	6.037	0.199				9.831	9.752	0.810
	Mg₂₄Y₅	11.260	11.280	−0.177						

Table 5
Calculated enthalpies of formation of the binary compounds compared with the experimental data, COST507 database, and the Miedema's model.

System	Phase	Enthalpy of formation (kJ/mol atom)			
		Calc.	COST507 [24]	Exp. [14,15]	Miedema's Model [18,19]
Mg–As	β-Mg$_3$As$_2$	−59.51			
	α-Mg$_3$As$_2$	−61.26		−80.25	
	Mg As$_4$	−22.41		−24.57	
Mg–Ba	Mg$_{17}$Ba$_2$	−6.58			
	Mg$_{23}$Ba$_6$	−7.45			
	Mg$_2$Ba	−8.47			
Mg–Ca	Mg$_2$Ca	−12.14	−13.80	−12.23	
Mg–Cd	MgCd	−10.51		−8.04	
	MgCd$_3$	−6.44		−6.34	
	Mg$_3$Cd	−7.54		−7.43	
Mg–Dy	MgDy	−8.18	−12.40	−12.01	
	Mg$_2$Dy	−7.24	−16.35	−16.28	
	Mg$_3$Dy	−7.54	−16.26	−16.07	
	Mg$_{24}$Dy$_5$	−4.81	−13.80	−13.72	
Mg–Cu	MgCu$_2$	−4.75	−10.91	−4.28	
Mg–Ga	Mg$_5$Ga$_2$	−11.51		−10.90	
	Mg$_2$Ga	−12.59		−11.70	
	MgGa	−13.71		−13.00	
	Mg Ga$_2$	−11.58		−11.40	
	Mg$_2$Ga$_5$	−10.79		−9.90	
Mg–Ge	Mg$_2$Ge	−22.76		−38.52	
Mg–La	MgLa	−11.64	−16.70	−2.40	−12.74
	Mg$_2$La	−12.55	−8.94		−11.88
	Mg$_3$La	−13.44	−19.70	−3.20	−9.64
	Mg$_{17}$La$_2$	−7.70	−8.66		−4.14
	Mg$_{12}$La	−5.79	−6.40		−3.02
Mg–Lu	MgLu	−3.44			
	Mg$_2$Lu	−4.14			
	Mg$_{24}$Lu$_5$	−2.80			
Mg–Ni	Mg$_2$Ni	−19.87	−17.87	−20.10	−6.42
	MgNi$_2$	−25.85	−21.03	−25.96	−6.81
Mg–Pb	Mg$_2$Pb	−2.85		−6.84	
Mg–Sb	α-Mg$_3$Sb$_2$	−35.98	−98.00	−47.00	
Mg–Si	Mg$_2$Si	−17.70	−21.75	−21.20	
Mg–Sn	Mg$_2$Sn	−20.82	−26.30	−24.30	
Mg–Y	MgY	−10.64	−5.75	−12.60	−11.49
	Mg$_2$Y	−9.17	−13.03	−14.20	−10.37
	Mg$_{24}$Y$_5$	−5.84	−7.84	−7.40	−5.82

Fig. 1. Comparison of calculated enthalpies of formation for the binary compounds in the Mg–X systems with experimental measurements [14,15]. The solid line shows unity (y = x) while the dashed lines present an error range of ±5 kJ/mol. The region inside the dotted lines in (a) is enlarged in (b).

Mg–La system (Mg$_3$La and MgLa), the Mg–Dy system (Mg$_2$Dy, Mg$_3$Dy and Mg$_{24}$Dy$_5$), α-Mg$_3$As$_2$, α-Mg$_3$Sb$_2$, and Mg$_2$Ge. In the Mg–La system, the reason is not completely clear although it is likely that the acid solution method used to determine the enthalpies of formation was not reliable as reviewed in Ref. [15]. In the recent study of thermodynamic modeling of this system, the authors in Ref. [15] used the predicted enthalpies of formation of the compounds from the Miedema's model [18–20]. With regard to all the compounds in the Mg–La binary system, the first-principles calculated enthalpies of formation agree well with those from the empirical Miedema's approach [18] with differences less than 4 kJ/mol of atom. For α-Mg$_3$Sb$_2$, although the enthalpy of formation has been experimentally determined numerous times at high temperatures with values ranging from −64 to −48 kJ/mol [15], there is still no available experimental value at 298 K. And here we compare the experimental value at high temperatures with our first-principles calculations. One cause of discrepancy is likely that the emf measurement by Eremenko et al. [21] was done at 773 K and we expect the enthalpy of formation at 298 K will be slightly lower than the one at high temperatures. The error in the Mg–Dy system, on the other hand, is most probably due to errors in the first-principles calculations, where the use of an approximate exchange–correlation potential for the tightly bound ƒ electrons may exhibit strong correlations. This has also been mentioned in other calculations involving rare earth elements [22]. Furthermore, the
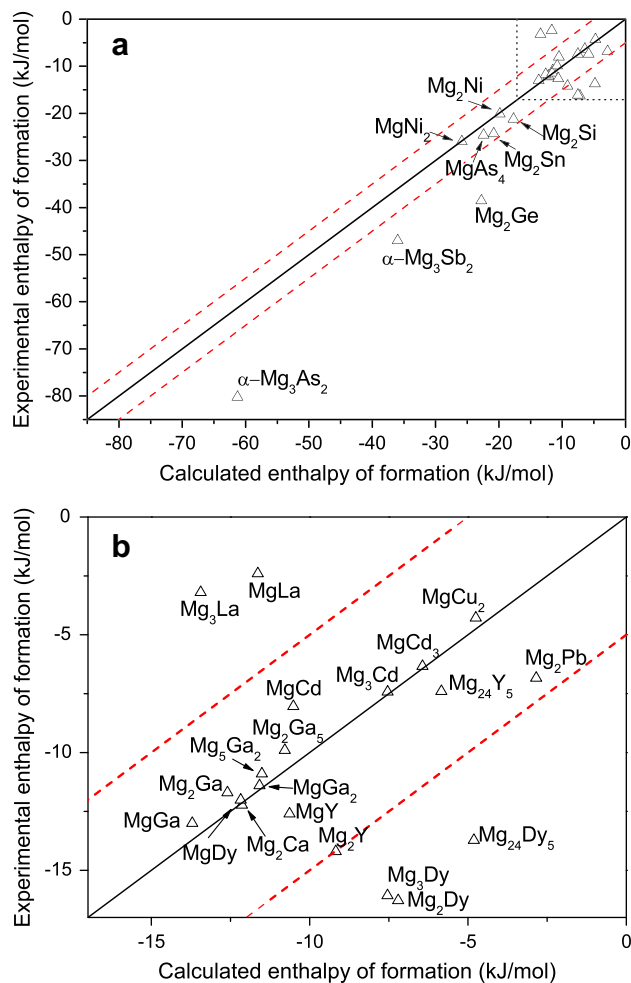
number of enthalpy of formation data is usually limited, so the uncertainty in a given experiment is hard to ascertain. For instance, there is only one experimental value of the enthalpy of formation of α-Mg$_3$As$_2$ [14], where both Mg and As are very volatile.

We also provide a comparison for the enthalpies of formation for the ordered compounds from first-principles calculations and the Miedema's approach. Miedema and coworkers [18,19] developed an extremely simple scheme for predicting the enthalpies of formation of compounds. As reviewed in a recent book [20], based on the Miedema's model, the predicted enthalpies of formation for compounds which consist of at least one transition metal agrees with experimental data in the great majority of cases. A comparison between our first-principles calculations and the Miedema's approach for the Mg–X systems is shown in Fig. 2 with an error bar set of ±5 kJ/mol. The first-principles enthalpies of formation for compounds in Mg–La and Mg–Y systems show excellent agreement with the values from the Miedema's model. In the case of the Mg–Ni system, the semi-empirical Miedema's values are in disagreement with both first-principles calculations and experiments, as it underestimates the stability of this phase by almost 14 kJ/mol and 17 kJ/mol, respectively. However, differences of this magnitude are within the uncertainty of this semi-empirical approach [23].

We next turn to a comparison of our first-principles enthalpies of formation with those from the COST507 [24] and other databases
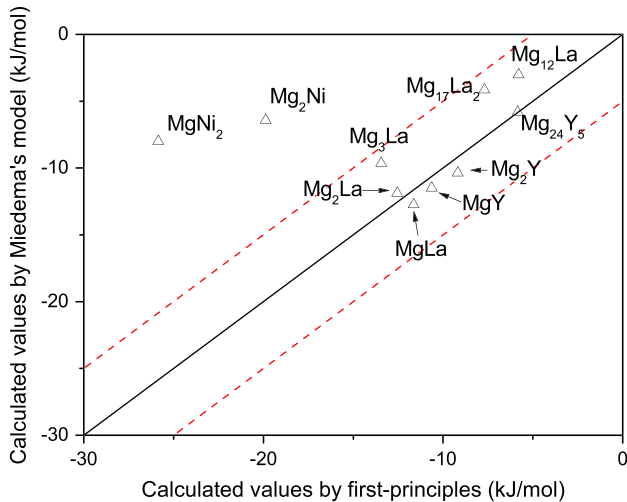
Fig. 2. Comparison of calculated enthalpies of formation for the Mg–X binary compounds with the values by the Miedema's approach [18,19]. The solid line shows unity (y = x) while the dashed lines present an error range of ±5 kJ/mol.

developed by the CALPHAD approach [25]. For most of the compounds, the differences are often within ±5 kJ/mol as shown in Fig. 3. The COST507 [24] database is developed based on all the available experimental data, and thus people usually believe that the thermodynamic description from this database is accurate for these phases. The largest discrepancies between our first-principles calculations and COST507 are the α-Mg$_3$Sb$_2$ and Mg–Dy compounds with possible sources of uncertainties discussed above.

3.3. Trends in binary systems

For several of the systems considered, more than one ordered compound are investigated in Mg–X (X = Ni, Ga, As, Y, Cd, Ba, La and Lu). The binary compounds in each system are listed in Table 2. All the intermetallic compounds are stable at 0 K except for Mg$_2$La and β-Mg$_3$As$_2$ which only exist at high temperatures. Fig. 4 shows the calculated ground state of these binary systems compared with experiment and COST507 data.

(1) Mg–Ni, Mg–Ga, Mg–Y, Mg–Cd, Mg–Ba and Mg–Lu

The experimental phase diagrams show all the intermetallic compounds in Mg–X (X = Ni, Ga, Y, Cd, Ba, Lu) to be stable at low temperature. Fig. 4 shows that our calculations of the energies of all these compounds indicate that they are all ground states, and therefore, their formation energies, when plotted as a function of composition, fall on the convex hull of ground states. We note that the intermetallic compounds in the Mg–Cd system have a relatively large solubility range as MgCd$_3$ (25–32 at. % Mg), MgCd (38–60 at. % Mg) and Mg$_3$Cd (63–82 at. % Mg). They are treated as stoichiometric compounds in this work and their enthalpies of formation lie on the convex hull, consistent with their 0 K stability.

(2) Mg–As, Mg–La

In the Mg–As system, three compounds are reported: α-Mg$_3$As$_2$, β-Mg$_3$As$_2$ and MgAs$_4$. α-Mg$_3$As$_2$ is confirmed stable at 0 K in our calculations while β-Mg$_3$As$_2$ lies above the convex hull by 1.75 kJ/mol, consistent with the experimental observation that β-Mg$_3$As$_2$ is stable at high temperatures. As the transition temperature between α-Mg$_3$As$_2$ and β-Mg$_3$As$_2$ is around 1273–1373 K [15] and hence, the change of entropy from α-Mg$_3$As$_2$ to β-Mg$_3$As$_2$ phase

transformation is estimated to be 1.27–1.37 J/K mol assuming that enthalpy of formation is independent of temperature. Our calculated enthalpies of formation of the Mg–La system show MgLa, Mg$_3$La, Mg$_{17}$La$_2$ and Mg$_{12}$La all lie on the convex hull, and Mg$_2$La lies above the convex hull by 0.3 kJ/mol as shown in red dotted line, in agreement with the experimentally observed phase, i.e., MgLa, Mg$_3$La, Mg$_{17}$La$_2$ and Mg$_{12}$La are stable phases at low temperatures and Mg$_2$La is known to be a high temperature phase.

We also compare the enthalpy of formation with the congruent melting point and bulk modulus of the compounds. For compounds that melt peritectically, we calculate the metastable congruent melting point from the thermodynamic database [24,26,27]. Fig. 5 shows the calculated enthalpies of formation compared with their congruent melting temperatures and bulk modulus [28]. It is interesting to note that for the transition metal systems, the enthalpy of formation of a stable compound at 0 K is more negative if it has a higher congruent melting temperature. This is to be expected since a more negative enthalpy of formation is an indicator of a greater stability and stronger interatomic bonding. Stronger bonding leads to higher congruent melting temperature. Such correlations between bulk modulus of solids and their melting temperatures have been observed experimentally [29]. It can also be seen that the compounds with more negative enthalpy of formation had in turn larger bulk modulus. For example, MgY has
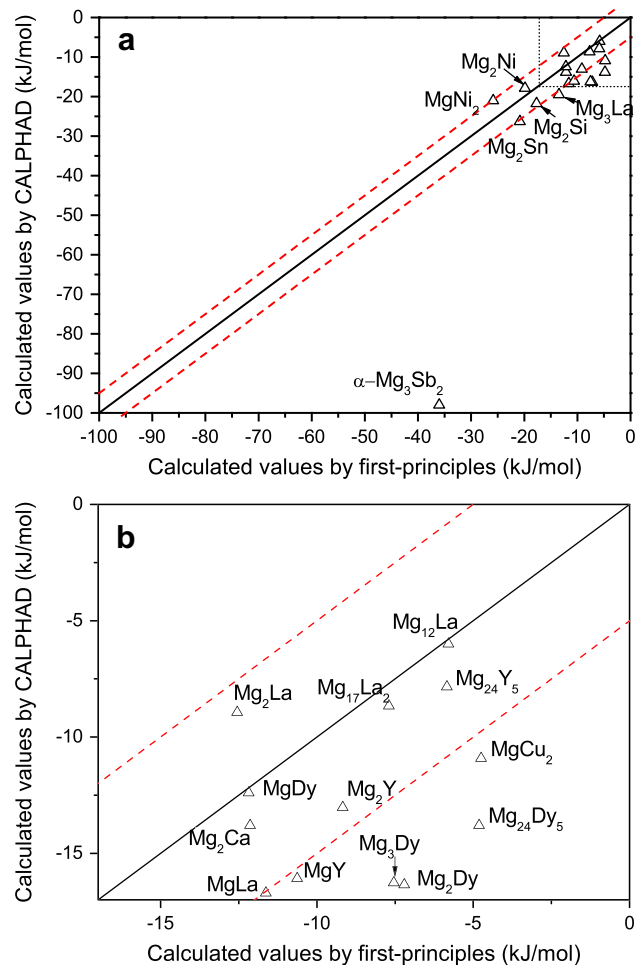

Fig. 3. Comparison of calculated enthalpies of formation for the binary compounds in the Mg–X systems with the values from COST507 [24]. The solid line shows unity (y = x) while the dashed lines present an error range of ±5 kJ/mol. The region inside the dotted lines in (a) is enlarged in (b).

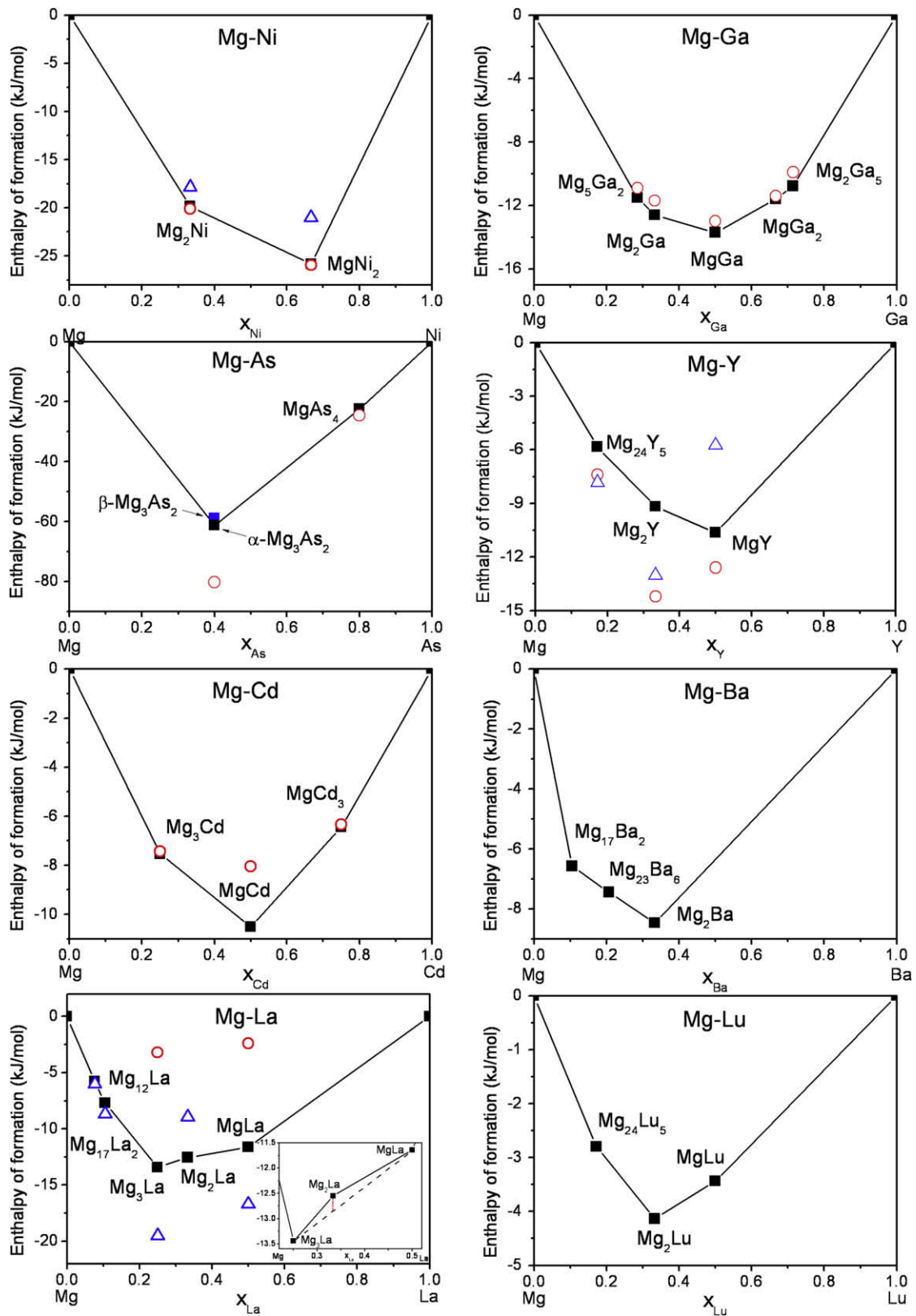**Fig. 4.** Calculated enthalpies of formation plotted as a function of composition for the Mg–X systems. Solid lines are tie-lines drawn between pure Mg and the stable Mg–X compounds. ■ calculated values from first-principles; ○ the experimental data; △ the COST507 data.
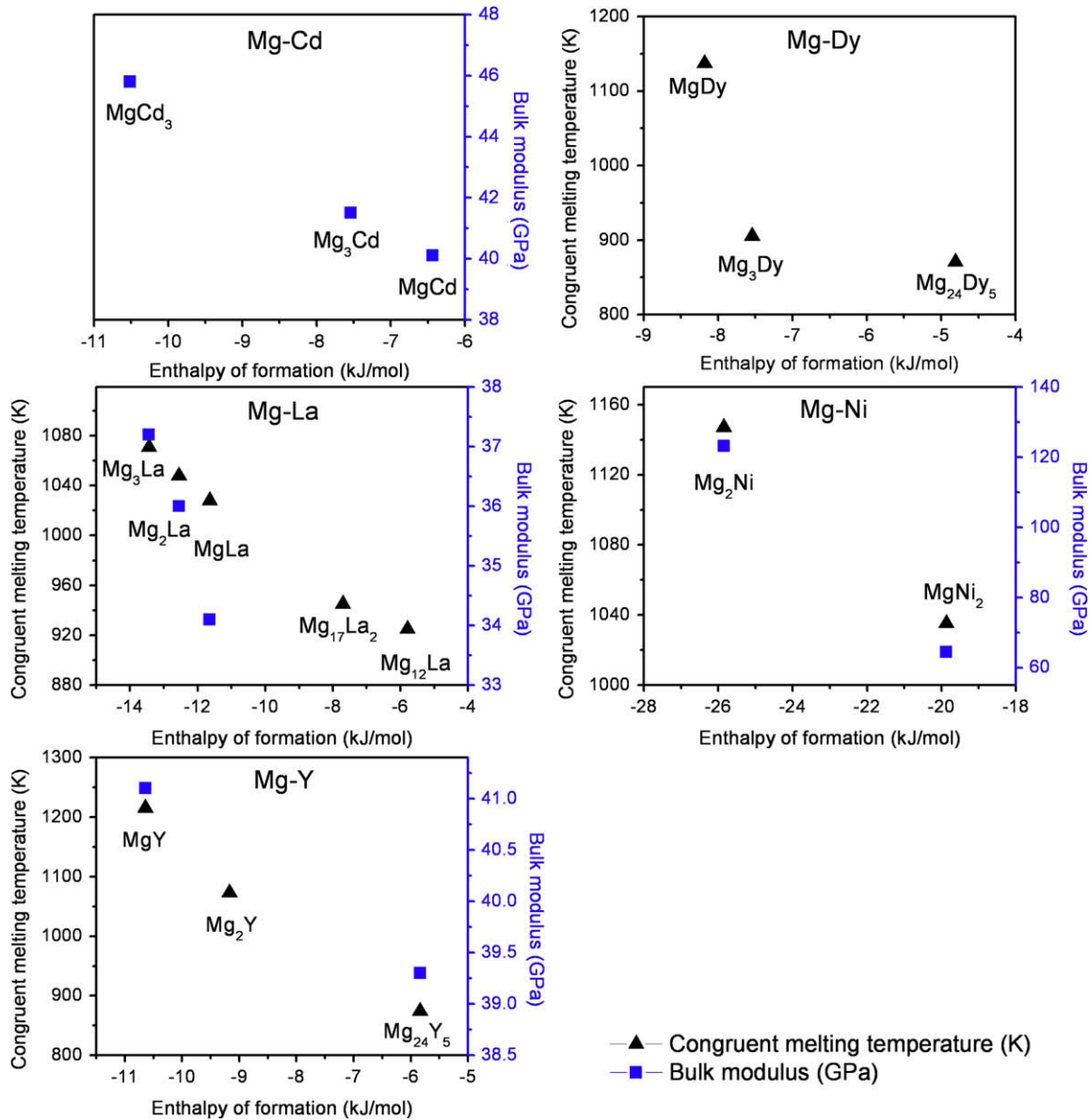
Fig. 5. Calculated enthalpies of formation of the Mg–X compounds compared with congruent melting temperatures [24,26,27] and bulk modulus [28].

a more negative enthalpy of formation than Mg₂₄Y₅, and, as predicted, it has a higher congruent melting temperature and larger bulk modulus.

4. Summary

We have applied density functional theory to calculate the energetic properties for 16 Mg–X systems. For each of these systems, the lattice parameter of the pure element in its equilibrium structure, as well as lattice parameters and enthalpies of formation of compounds are calculated and compared with available data. We conclude the following: (1) The lattice parameters at 0 K obtained by the first-principles calculations can be satisfactorily compared with experimental data. (2) The enthalpies of formation for Mg–X compounds agree with the available experiment and thermodynamic databases for the majority of systems. Possible sources of error include the uncertainty in the measurement of experimental data and errors in the calculation of rare earth elements. (3) The phase stabilities at 0 K obtained by the first-principles calculations

agree with the experimental data and thermodynamic databases. (4) It was observed that the compounds with a more negative enthalpy of formation have a higher congruent melting temperature and larger bulk modulus. In addition, the good agreement between the first-principles energetics and other thermodynamic data (e.g., experimental data, COST507 database, Miedema's model) provides confidence in the predictive abilities of this approach.

References:

[1] Arroyave R, Liu ZK. Phys Rev B 2006;74:174118.
[2] Curtarolo S, Morgan D, Ceder G. CALPHAD 2005;29:163–211.
[3] Arroyave R, Shin D, Liu ZK. CALPHAD 2005;29:230–8.
[4] Zhong Y, Ozturk K, Sofo JO, Liu ZK. J Alloy Compd 2006;420:98–106.
[5] Wolverton C, Ozolins V. Phys Rev B 2006;73:14410.
[6] Zhong Y, Sofo JO, Luo AA, Liu ZK. J Alloy Compd 2006;421:172–8.
[7] Kresse G, Furthmuller J. Phys Rev B 1996;54:11169–86.
[8] Kresse G, Furthmuller J. Comput Mater Sci 1996;6:15–50.
[9] Perdew J, Burke K, Ernzerhof M. Phys Rev Lett 1996;77:3865–8.
[10] Monkhorst HJ, Pack JD. Phys Rev B 1976;13:5188–92.
[11] Villars PP. Pearson's handbook of crystallographic data for intermetallic phases. American Society for Metals; 1985.
[12] Pauling file. or CD. Available on the web: https://crystdb.nims.go.jp/cgi-bin/lpf/W06-P01.pl; 2002.
[13] Wang Y, Curtarolo S, Jiang C, Arroyave R, Wang T, Ceder G, et al. CALPHAD 2004;28:79–90.
[14] Selected values of chemical thermodynamic properties. Washington: United States National Bureau of Standards; 1965.
[15] Nayeb-Hashemi AA, Clark JB. Phase diagrams of binary magnesium alloys. ASM International; 1988.
[16] Meschel SV, Kleppa OJ. J Alloy Compd 2005;388:91–7.
[17] Meschel SV, Kleppa OJ. J Alloy Compd 2006;415:143–9.
[18] Miedema AR, Dechatel PF, Deboer FR. Physica B & C 1980;100:1–28.
[19] Boer FRD, Boom R, Matten WCM, Miedema AR, Niessen AK. Cohesion in metals: transition metal alloys. Amsterdam: North-Holland; 1988.
[20] Bakker H. Enthalpies in alloys: Miedema's semi-empirical model. Zurich: Trans Tech Publications; 1998.
[21] Eremenko VN, Lukashenko GM. Zh. Neorg. Khim. 1964;9:1552–5.
[22] Gao MC, Rollett AD, Widom M. Phys Rev B 2007;75:174120.
[23] Chen XQ, Wolf W, Podloucky R, Rogl P. Intermetallics 2004;12:59–62.
[24] Ansara I, Dinsdale AT, Rand MH, editors. COST507: Thermodynamic database for light metal alloys, vol. 2. rue de la Loi 200 (SDME 1/44), B-1049 Brussels: European Commission; 1998.
[25] Liu ZK, Chen LQ. Integration of first-principles calculations, CALPHAD modeling, and phase-field simulations. In: Bozzolo G, editor. Applied computational materials modeling: theory, experiment and simulations. Springer; 2006.
[26] Guo CP, Du ZM. J Alloy Compd 2004;385:109–13.
[27] Du ZM, Yang XJ, Ling G, Liu HY. Z Metallkd 2004;95:1115–9.
[28] Ganeshan S, Shang SL, Zhang H, Wang Y, Mantina M, Liu ZK. Intermetallics 2009;17:313–8.
[29] Fine ME, Brown LD, Marcus HL. Scr Metall 1984;18:951–6.