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Contribution of first-principles energetics to Al–Mg thermodynamic modeling

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Abstract

Despite numerous investigations, all previous efforts on thermodynamic modeling of Al–Mg have suffered from inaccurate energetics of solid phases. In the present work, the first-principles calculations were performed using VASP based on the pseudo-potentials and a plane wave basis set. The enthalpies of formation of the ε-$Al_{30}Mg_{23}$ phase, end-members of the γ-$Al_{12}Mg_{17}$ phase, and three laves phases at the Al_2Mg composition were calculated at 0 K. Special quasi-random structures (SQS's) were used to mimic random fcc and hcp solution phases, and their enthalpies of mixing were predicted by first-principles calculations. The Al occupancy in the γ-$Al_{12}Mg_{17}$ phase is also studied by first-principles calculations, and the sublattice model $(Mg)_5(Al, Mg)_{12}(Al, Mg)_{12}$ was verified as the proper model to describe the γ-$Al_{12}Mg_{17}$ phase. The complete thermodynamic description of the Al–Mg binary system was evaluated by this combined CALPHAD/first-principles calculations approach and was shown to be in a good agreement with experimental data with better defined energetics of solid phases than the previous modeling.

Keywords: Thermodynamic modeling; First principles; Al–Mg; Phase diagram; Mg alloys

1. Introduction

Al–Mg is the most important binary system for both Al and Mg alloys and it has been studied in numerous investigations. An extensive amount of experimental information has been reported on phase equilibria (liquidus, solidus, and solvus), crystal structures of solid phases, and thermodynamic properties as discussed in detail in previous work by Chartrand and Pelton [1]. However, there are no accurate measurements of solid-state energetics of Al–Mg compounds and no thermochemical data about fcc-Al and hcp-Mg solution phases.

There are three intermetallic phases in the Al–Mg binary system, i.e., β-$Al_{140}Mg_{89}$, ε-$Al_{30}Mg_{23}$, and γ-$Al_{12}Mg_{17}$, based on the most recent study [2]. The γ-$Al_{12}Mg_{17}$ phase was modeled as $(Mg)_5(Al, Mg)_{12}(Al, Mg)_{12}$ according to the Kasper Scheme [3,4]. The site occupations of Al and Mg were speculated by means of the Goldschmidt radii of Al and Mg atoms. In the present work, they are analyzed through first-principles calculations. The energetics of β and ε phases were also analyzed by calculating the enthalpy of formation of ε and three laves phases at the Al_2Mg composition in the present work.

Furthermore, the enthalpies of mixing of fcc and hcp are predicted by the first-principles calculations of special quasi-random structures (SQS's). The SQS concept was proposed by Zunger et al. [5] to mimic a random solution phase by reproducing the pair and multiple-body correlations using a small size supercell. The SQS's for fcc and hcp solutions were generated by Wei et al. [6] and Shin and Liu [7].

With these new data from first-principles calculations, the present work aims to improve the quality of thermodynamic modeling of the Al–Mg binary system.

2. Experimental data

The Al–Mg binary system has been studied by numerous authors. All experimental data about the liquidus, solidus and solvus data are in good agreement. However, there are discrepancies about phases involved and the related invariant reactions in various phase diagram compilations [1,2,8–13].

Prior to 1994, it was believed that there were four compounds in the Al–Mg binary system, i.e. β, ε, ζ, and γ. The

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existence of ζ was rejected in recent investigations [1,2]. For ε-$Al_{30}Mg_{23}$, the recent experiments by Czeppe et al. [14] and Benzio [15] show a good agreement with the lower temperature limit of the stability of the ε-$Al_{30}Mg_{23}$ phase proposed by Su et al. [16] and Liang et al. [2] while its upper temperature limit was determined between 663 and 683 K by several previous investigations [2,10,16,17] and 700 K by Czeppe et al. [14].

The enthalpy of mixing of the liquid phase was determined by Kawakami [18], Batalin et al. [19], and Agarwal and Sommer [20] using calorimetry. Bhatt and Garg [21] and Juneja et al. [22] derived the enthalpy of mixing from partial pressure measurements, while Belton and Rao [23], Tiwari [24], Agarwal and Sommer [20], and Moser et al. [25] obtained the enthalpy of mixing from electromotive force (EMF) measurements. The results from the experiments by Agarwal and Sommer [20] appear to be more reliable. Furthermore, the activity of Mg in the liquid phase was determined with EMF measurements [23,24,26,27] or derived from partial pressures of Mg [21,22,28,29].

The activity of Mg in solid phases at 660 and 710 K was determined by Brown and Pratt [30] using EMF measurements of reversible galvanic cells. However, the deduced phase boundaries do not agree well with very accurate solvus experimental data for fcc-Al and γ-$Al_{12}Mg_{17}$ phases at 660 and 710 K. Several experiments were done to measure the enthalpies of formation of Al–Mg binary compounds [31–33]. However, none of them were accepted by Hultgren et al. [34] and thus they cannot be used in the evaluation of model parameters.

3. Thermodynamic modeling

Six phases are modeled in the present work, i.e. liquid, fcc, hcp, β-$Al_{140}Mg_{89}$, ε-$Al_{30}Mg_{23}$, and γ-$Al_{12}Mg_{17}$ in the Al–Mg binary system. The liquid, fcc, and hcp phases are treated with one-sublattice models, (Al, Mg), with the molar Gibbs energy expressed as

$$G_m^{\Phi} = x_{\mathrm{Al}}\,{}^{o}G_{\mathrm{Al}}^{\Phi} + x_{\mathrm{Mg}}\,{}^{o}G_{\mathrm{Mg}}^{\Phi} + RT(x_{\mathrm{Al}}\ln x_{\mathrm{Al}} + x_{\mathrm{Mg}}\ln x_{\mathrm{Mg}}) + {}^{xs}G_m^{\Phi} \quad (1)$$

where ${}^{o}G_i^{\Phi}$ is the molar Gibbs energy of the pure element i with the structure Φ from Dinsdale [35] and ${}^{xs}G_m^{\Phi}$ the excess Gibbs energy, expressed in the Redlich–Kister polynomial [36] as

$${}^{xs}G_m^{\Phi} = x_{\mathrm{Al}}x_{\mathrm{Mg}}\sum_{j=0}^{n} {}^{j}L_{\mathrm{Al,Mg}}^{\Phi}(x_{\mathrm{Al}} - x_{\mathrm{Mg}})^j \quad (2)$$

where ${}^{j}L_{\mathrm{Al,Mg}}^{\Phi}$ is the jth binary interaction parameter expressed as ${}^{j}L_{\mathrm{Al,Mg}}^{\Phi} = {}^{j}A^{\Phi} + {}^{j}B^{\Phi}T$, and ${}^{j}A^{\Phi}$ and ${}^{j}B^{\Phi}$ are model parameters to be evaluated.

For γ-$Al_{12}Mg_{17}$, two different three-sublattice models, $(Mg)_5(Al, Mg)_{12}(Al, Mg)_{12}$ as suggested in [37] and the more general model, $(Al, Mg)_5(Al, Mg)_{12}(Al, Mg)_{12}$, are considered in the present investigation. Based on the first-principles calculations to be discussed later in this paper, the $(Mg)_5(Al, Mg)_{12}(Al, Mg)_{12}$ model is finally adopted in the present work for γ-$Al_{12}Mg_{17}$. The Gibbs energy of the compound can be expressed by the following formula:

$$G_{\mathrm{mf}}^{\gamma\text{-}\mathrm{Al_{12}Mg_{17}}} = {}^{\mathrm{ref}}G_{\mathrm{mf}} + {}^{\mathrm{mix}}G_{\mathrm{mf}} + {}^{\mathrm{ex}}G_{\mathrm{mf}}. \quad (3)$$

The reference Gibbs energy ${}^{\mathrm{ref}}G_{\mathrm{mf}}$ is defined by the end-members with only the one component in each sublattice, i.e. $Mg_5Al_{12}Mg_{12}$, $Mg_5Al_{12}Al_{12}$, $Mg_5Mg_{12}Mg_{12}$, and $Mg_5Mg_{12}Al_{12}$, respectively, with mf representing mole of formula. The three terms in Eq. (3) can be written as:

$$\begin{aligned}{}^{\mathrm{ref}}G_{\mathrm{mf}} &= y_{\mathrm{Al}}^{\mathrm{II}}y_{\mathrm{Al}}^{\mathrm{III}}\,{}^{o}G_{\mathrm{Mg:Al:Al}}^{\gamma\text{-}\mathrm{Al_{12}Mg_{17}}} + y_{\mathrm{Al}}^{\mathrm{II}}y_{\mathrm{Mg}}^{\mathrm{III}}\,{}^{o}G_{\mathrm{Mg:Al:Mg}}^{\gamma\text{-}\mathrm{Al_{12}Mg_{17}}} \\ &\quad + y_{\mathrm{Mg}}^{\mathrm{II}}y_{\mathrm{Al}}^{\mathrm{III}}\,{}^{o}G_{\mathrm{Mg:Mg:Al}}^{\gamma\text{-}\mathrm{Al_{12}Mg_{17}}} + y_{\mathrm{Mg}}^{\mathrm{II}}y_{\mathrm{Mg}}^{\mathrm{III}}\,{}^{o}G_{\mathrm{Mg:Mg:Mg}}^{\gamma\text{-}\mathrm{Al_{12}Mg_{17}}} \quad (4)\end{aligned}$$

$$\begin{aligned}{}^{\mathrm{mix}}G_{\mathrm{mf}} &= 12RT\left[\left(y_{\mathrm{Al}}^{\mathrm{II}}\ln y_{\mathrm{Al}}^{\mathrm{II}} + y_{\mathrm{Mg}}^{\mathrm{II}}\ln y_{\mathrm{Mg}}^{\mathrm{II}}\right)\right. \\ &\quad \left. + \left(y_{\mathrm{Al}}^{\mathrm{III}}\ln y_{\mathrm{Al}}^{\mathrm{III}} + y_{\mathrm{Mg}}^{\mathrm{III}}\ln y_{\mathrm{Mg}}^{\mathrm{III}}\right)\right] \quad (5)\end{aligned}$$

$$\begin{aligned}{}^{\mathrm{ex}}G_{\mathrm{mf}} &= y_{\mathrm{Al}}^{\mathrm{II}}y_{\mathrm{Mg}}^{\mathrm{II}}\left[y_{\mathrm{Al}}^{\mathrm{III}}\sum_{k=0}^{n} {}^{k}L_{\mathrm{Mg:Al,Mg:Al}}(y_{\mathrm{Al}}^{\mathrm{II}} - y_{\mathrm{Mg}}^{\mathrm{II}})^k\right. \\ &\quad \left. + y_{\mathrm{Mg}}^{\mathrm{III}}\sum_{k=0}^{n} {}^{k}L_{\mathrm{Mg:Al,Mg:Mg}}(y_{\mathrm{Al}}^{\mathrm{II}} - y_{\mathrm{Mg}}^{\mathrm{II}})^k\right] \\ &\quad + y_{\mathrm{Al}}^{\mathrm{III}}y_{\mathrm{Mg}}^{\mathrm{III}}\left[y_{\mathrm{Al}}^{\mathrm{II}}\sum_{k=0}^{n} {}^{k}L_{\mathrm{Mg:Al:Al,Mg}}(y_{\mathrm{Al}}^{\mathrm{III}} - y_{\mathrm{Mg}}^{\mathrm{III}})^k\right. \\ &\quad \left. + y_{\mathrm{Mg}}^{\mathrm{II}}\sum_{k=0}^{n} {}^{k}L_{\mathrm{Mg:Mg:Al,Mg}}(y_{\mathrm{Al}}^{\mathrm{III}} - y_{\mathrm{Mg}}^{\mathrm{III}})^k\right] \quad (6)\end{aligned}$$

where $y_{\mathrm{Al}}^{\mathrm{II}}$ and $y_{\mathrm{Mg}}^{\mathrm{II}}$ are the site fractions of Al and Mg in the second sublattice, $y_{\mathrm{Al}}^{\mathrm{III}}$ and $y_{\mathrm{Mg}}^{\mathrm{III}}$ are the site fractions of Al and Mg in the third sublattice, and ${}^{o}G_{\mathrm{Mg:Mg:Al}}^{\gamma\text{-}\mathrm{Al_{12}Mg_{17}}}$, ${}^{o}G_{\mathrm{Mg:Al:Al}}^{\gamma\text{-}\mathrm{Al_{12}Mg_{17}}}$, ${}^{o}G_{\mathrm{Mg:Al:Mg}}^{\gamma\text{-}\mathrm{Al_{12}Mg_{17}}}$, and ${}^{o}G_{\mathrm{Mg:Mg:Mg}}^{\gamma\text{-}\mathrm{Al_{12}Mg_{17}}}$ are the Gibbs energies of formation of the four end-members. ${}^{k}L_{\mathrm{Mg:Al,Mg:*}}$ (${}^{k}L_{\mathrm{Mg:*:Al,Mg}}$) is the interaction between Al and Mg in the second (third) sublattice. In the notation of the interaction parameters, a colon separates components occupying different sublattices, and a comma separates interacting components in the same sublattice.

Among the four end-members of the γ-$Al_{12}Mg_{17}$ phase, only $(Mg)_5(Mg)_{12}(Al)_{12}$ is stable. The Gibbs energies of these four end-members are given by the following equations:

$${}^{o}G_{\mathrm{Mg:Mg:Al}}^{\gamma\text{-}\mathrm{Al_{12}Mg_{17}}} = 12\,{}^{o}G_{\mathrm{Al}}^{\mathrm{fcc}} + 17\,{}^{o}G_{\mathrm{Mg}}^{\mathrm{hcp}} + \Delta_f G_{\mathrm{Mg:Mg:Al}}^{\gamma\text{-}\mathrm{Al_{12}Mg_{17}}} \quad (7)$$

$${}^{o}G_{\mathrm{Mg:Al:Al}}^{\gamma\text{-}\mathrm{Al_{12}Mg_{17}}} = 24\,{}^{o}G_{\mathrm{Al}}^{\mathrm{fcc}} + 5\,{}^{o}G_{\mathrm{Mg}}^{\mathrm{hcp}} + \Delta_f G_{\mathrm{Mg:Al:Al}}^{\gamma\text{-}\mathrm{Al_{12}Mg_{17}}} \quad (8)$$

$${}^{o}G_{\mathrm{Mg:Al:Mg}}^{\gamma\text{-}\mathrm{Al_{12}Mg_{17}}} = 12\,{}^{o}G_{\mathrm{Al}}^{\mathrm{fcc}} + 17\,{}^{o}G_{\mathrm{Mg}}^{\mathrm{hcp}} + \Delta_f G_{\mathrm{Mg:Al:Mg}}^{\gamma\text{-}\mathrm{Al_{12}Mg_{17}}} \quad (9)$$

$${}^{o}G_{\mathrm{Mg:Mg:Mg}}^{\gamma\text{-}\mathrm{Al_{12}Mg_{17}}} = 29\,{}^{o}G_{\mathrm{Mg}}^{\mathrm{hcp}} + \Delta_f G_{\mathrm{Mg:Mg:Mg}}^{\gamma\text{-}\mathrm{Al_{12}Mg_{17}}}. \quad (10)$$

In the present work, the Gibbs energies of formation of all four end-members are represented by the following equations:

$$\Delta_f G_{\mathrm{Mg}:i:j}^{\gamma\text{-}\mathrm{Al_{12}Mg_{17}}} = \Delta_f H_{\mathrm{Mg}:i:j}^{\gamma\text{-}\mathrm{Al_{12}Mg_{17}}} - \Delta_f S_{\mathrm{Mg}:i:j}^{\gamma\text{-}\mathrm{Al_{12}Mg_{17}}}T \quad (i, j = \mathrm{Al, Mg}) \quad (11)$$

Table 1
SQS calculation results for different compositions of fcc and hcp phases in the Al–Mg binary system

Structure	Composition	Total energy (eV/atom)	Enthalpies of mixing (kJ/mol atom)	Lattice constants (Å)	Method[a]
fcc	Al	−3.6892	0	$a = 4.041$	
	$Al_{0.75}Mg_{0.25}$	−3.1209	1.140	$a = 4.154$	1
		−3.1289	0.372	$a = 4.136$	2
	$Al_{0.5}Mg_{0.5}$	−2.5546	2.093	$a = 4.264$	1
		−2.5722	0.394	$a = 4.270$	2
	$Al_{0.25}Mg_{0.75}$	−2.0075	1.186	$a = 4.382$	1
		−2.0183	0.146	$a = 4.376$	2
	Mg	−1.4633	0	$a = 4.513$	
hcp	Al	−3.6570	0	$a = 2.844, c = 4.732$	
	$Al_{0.75}Mg_{0.25}$	−3.0996	1.399	$a = 2.938, c = 4.803$	1
		−3.1086	0.525	$a = 2.926, c = 4.831$	2
	$Al_{0.5}Mg_{0.5}$	−2.5453	2.489	$a = 3.018, c = 4.920$	1
		−2.5589	1.174	$a = 2.993, c = 4.952$	2
	$Al_{0.25}Mg_{0.75}$	−2.0078	1.959	$a = 3.103, c = 5.043$	1
		−2.0193	0.852	$a = 3.070, c = 5.081$	2
	Mg	−1.4852	0	$a = 3.177, c = 5.172$	

[a] 1: Symmetry preserved, 2: Fully relaxed.

where $\Delta_f H^{\gamma\text{-}Al_{12}Mg_{17}}_{Mg:i:j}$ and $\Delta_f S^{\gamma\text{-}Al_{12}Mg_{17}}_{Mg:i:j}$ are the enthalpy and entropy of formation of each end-member as model parameters to be evaluated or assigned.

The other two intermetallic compounds, i.e. ε-$Al_{30}Mg_{23}$ and β-$Al_{140}Mg_{89}$, were modeled as stoichiometric compounds, and their Gibbs energy functions are written as

$$G^{Al_aMg_b}_{mf} = a\,{}^oG^{fcc}_{Al} + b\,{}^oG^{hcp}_{Mg} + A^{Al_aMg_b} + B^{Al_aMg_b}T \qquad (12)$$

where $A^{Al_aMg_b}$ and $B^{Al_aMg_b}$ are the enthalpy and entropy of formation of the compound.

4. First-principles calculations: Energetics in Al–Mg

Total energies of all structures were calculated by means of the Vienna ab initio Simulation Package (VASP) [38,39] with ultrasoft pseudopotentials. Generalized gradient approximation (GGA) [40,41] calculations were employed. We use Vanderbilt ultrasoft pseudopotentials [38,39] with the energy cutoff of 365.887 eV for Mg and 129.208 eV for Al. Extensive tests of k-point sampling indicated that total energy differences were converged to within ~0.1 kJ/mol.

The first-principles calculations of fcc-Al were taken from our previous work [42] and of hcp-Mg from our work on the Ca–Mg binary system to be published. Also, hcp-Al and fcc-Mg were calculated to determine the enthalpies of mixing for fcc and hcp phases in Al–Mg.

SQS's of three different compositions ($x = 0.25$, 0.5, and 0.75) of $Al_{1-x}Mg_x$ random solutions were used for calculating the enthalpies of mixing of fcc and hcp phases in Al–Mg as shown in Table 1. Two calculations, one with the symmetry preserved, i.e. only volume relaxation for fcc (ISIF = 7 in VASP) and volume and c/a ratio relaxation for hcp (ISIF = 7 and ISIF = 6 in VASP), and another with full relaxation, were done for each composition (ISIF = 3 in VASP). The calculation results show that all the SQS results with both relaxations keep its initial symmetry by comparing simulated XRD diffraction patterns of fully relaxed structures with ideal fcc and hcp structures. The calculation results show the enthalpies of mixing from fully relaxed structures are much lower than those from symmetry-preserved structures. The results show that the enthalpies of mixing of fcc and hcp phases at each composition are slightly positive after full relaxation.

The crystal structures of intermetallic compounds in Al–Mg were taken from Refs. [43–45] for first-principles calculations as shown in Table 2. The total energies and enthalpies of formation ($\Delta_f H^{\gamma\text{-}Al_{12}Mg_{17}}$) of the eight end-members of the γ-$Al_{12}Mg_{17}$ phase defined by the general model $(Al, Mg)_5(Al, Mg)_{12}(Al, Mg)_{12}$ are given in Table 3. The enthalpies of formation of the four end-members with the first sublattice occupied by Al are much higher than those of the four end-members with the first sublattice occupied by Mg. The enthalpy of formation γ-$Mg_5Mg_{12}Mg_{12}$ shows an excellent agreement with the value from Dinsdale [35], being 4.602 kJ/mol atom. Comparing with the previous modeling [2], the enthalpy of formation of the stable end-member γ-$Mg_5Mg_{12}Al_{12}$ in the present work is much lower than the previous modeling, i.e. −3.599 versus −1.820 kJ/mol atom. The other two end-members γ-$Mg_5Al_{12}Al_{12}$ and γ-$Mg_5Al_{12}Mg_{12}$ are also different from the traditional settings [2], in which the enthalpy of formation of γ-$Mg_5Al_{12}Al_{12}$ was 3.375 kJ/mol atom and that of γ-$Mg_5Al_{12}Mg_{12}$ was determined by the reciprocal relation of the four end-members.

The site fraction of Al in the first sublattice of γ-$Al_{12}Mg_{17}$ is calculated as shown in Fig. 1 with very little amount of Al in the first sublattice within the stable composition range, i.e. 47 at.%–60 at.% Mg, of the γ-$Al_{12}Mg_{17}$ phase. With the increase of temperature, the first sublattice will be occupied with more Al atoms. The Gibbs energy difference between $(Mg)_5(Al, Mg)_{12}(Al, Mg)_{12}$ and $(Al, Mg)_5(Al, Mg)_{12}(Al, Mg)_{12}$ two models is almost zero within the composition range of the γ-$Al_{12}Mg_{17}$ phase (less than 50 J/mol atom). The simplified model $(Mg)_5(Al, Mg)_{12}(Al, Mg)_{12}$ is thus adopted in the present work.

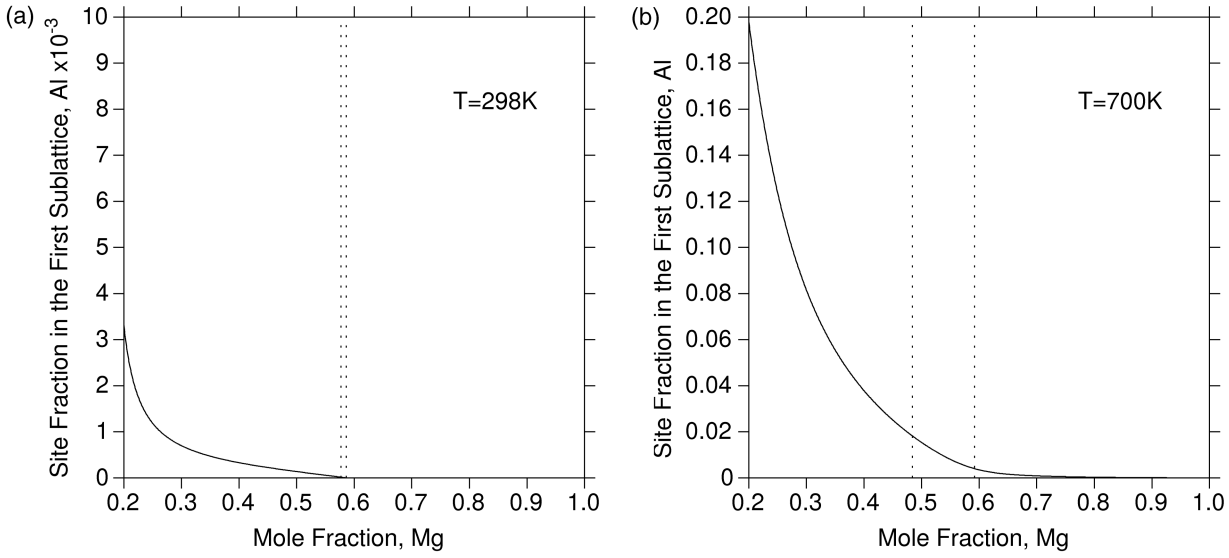

Fig. 1. Site fraction of Al in the first sublattice of γ-$Al_{12}Mg_{17}$ at 298 and 700 K in the Al–Mg binary system. Dotted lines are the solubility limits of γ-$Al_{12}Mg_{17}$ at corresponding temperatures.

Table 2
Crystal structures of stable Al–Mg phases

Phase	Strukturbericht designation	Space group	Prototype	Reference
fcc-Al	A1	$Fm\bar{3}m$	Cu	[70]
β-$Al_{140}Mg_{89}$	–	$Fd\bar{3}m$	Cd_2Na	[43]
ε-$Al_{30}Mg_{23}$	–	$R\bar{3}$	$Co_5Cr_2Mo_3$	[44]
γ-$Al_{12}Mg_{17}$	A12	$I\bar{4}3m$	α-Mn	[45]
Al_2Mg-C15	C15	$Fd\bar{3}m$	Cu_2Mg	[71]
Al_2Mg-C14	C14	$P6_3/mmc$	$MgZn_2$	[72]
Al_2Mg-C36	C36	$P6_3/mmc$	$MgNi_2$	[72]
hcp-Mg	A3	$P6_3/mmc$	Mg	[70]

Table 3
Structure properties and enthalpies of formation for the Al–Mg binary system in a variety of ordered structures by first-principles calculations

	Lattice constants (Å)	Total energy (eV/atom)	Enthalpies of formation (kJ/mol atom)
fcc-Al	$a = b = c = 4.041$	−3.6892	0
Al_2Mg-C15	$a = b = c = 7.667$	−2.9784	−2.301
Al_2Mg-C14	$a = b = 5.448$, $c = 8.742$	−2.9827	−2.713
Al_2Mg-C36	$a = b = 5.450$, $c = 17.514$	−2.9836	−2.802
β-$Al_{140}Mg_{89}$	–	–	–
ε-$Al_{30}Mg_{23}$	$a = b = 12.718$, $c = 21.848$	−2.7682	−3.423
γ-$Mg_5Mg_{12}Al_{12}$	$a = b = c = 10.514$	−2.4345	−3.599
γ-$Mg_5Al_{12}Al_{12}$	$a = b = c = 10.102$	−3.3062	0.288
γ-$Mg_5Mg_{12}Mg_{12}$	$a = b = c = 11.032$	−1.4354	4.806
γ-$Mg_5Al_{12}Mg_{12}$	$a = b = c = 10.584$	−2.3327	6.226
γ-$Al_5Mg_{12}Al_{12}$	$a = b = c = 10.419$	−2.7629	1.383
γ-$Al_5Al_{12}Al_{12}$	$a = b = c = 9.953$	−3.6299	5.721
γ-$Al_5Mg_{12}Mg_{12}$	$a = b = c = 10.903$	−1.7627	9.891
γ-$Al_5Al_{12}Mg_{12}$	$a = b = c = 10.424$	−2.6561	11.684
hcp-Mg	$a = b = 3.177$, $c = 5.172$	−1.4852	0

The crystal structure of β is very complicated, with more than 1000 atoms per unit cell. Due to the limit of computational power, its enthalpy of formation cannot be calculated directly from first-principles calculations. However, the enthalpy of formation of β-$Al_{140}Mg_{89}$ can be estimated indirectly by the first-principles calculations of other crystal structures close to the composition of β-$Al_{140}Mg_{89}$. The total energies of the three laves crystal structures, C14, C15, and C36, at the Al_2Mg composition were thus calculated as listed in Table 3. Their values vary from −2.301 kJ/mol atom to −2.802 kJ/mol atom. The calculation results show the structure with lowest enthalpy of formation is C36. Since laves phases are not stable in the

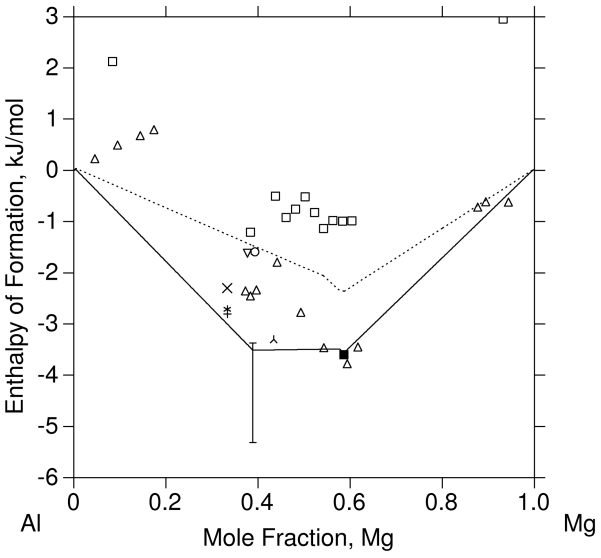

Fig. 2. Calculated enthalpy of formation at 298 K as a function of Mg concentration in comparison with experimental data (△) by Brown and Pratt [30], (□) by Predel and Hulse [73], (○) by Wittig and Piller [32,74], and (▽) by Sinvhal and Khanga [33], first-principles calculations (∗) C14, (×) C15, (+) C36, (⅄) ε-$Al_{30}Mg_{23}$, (■) γ-$Al_{12}Mg_{17}$, and previous modeling [2] (dotted line). The reference state is the fcc-Al and hcp-Mg at 298 K.

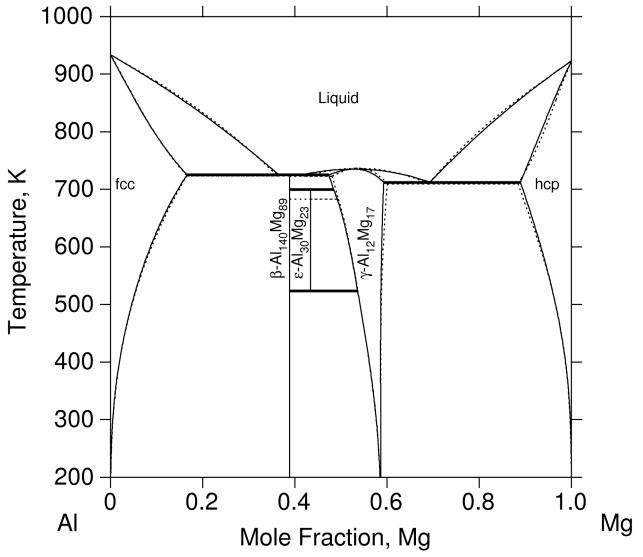

Fig. 3. Comparison between the calculated Al–Mg phase diagram in the present work (solid line) and the previous modeling [2] (dotted line).

Al–Mg binary system, the convex hull of enthalpy of formation should be lower than that of C36 at the Al_2Mg composition.

The enthalpy of formation of the ε-$Al_{30}Mg_{23}$ phase obtained from first-principles calculations in the present work is −3.423 kJ/mol atom, which is 2.431 kJ/mol atom lower than the previous modeling [2]. As a non-stable phase at low temperatures, it should be above the convex hull of stable states at room temperature.

Based on enthalpies of formation of ε-$Al_{30}Mg_{23}$, γ-$Al_{12}Mg_{17}$, and the three laves phases at the Al_2Mg composition, the upper and lower limits of the enthalpy of formation of the β-$Al_{140}Mg_{89}$ phase can be deduced between −3.370 and −5.318 kJ/mol atom, as the β-$Al_{140}Mg_{89}$ phase must lie on the convex hull of stable states with the error bar shown in Fig. 2. The calculations of the energetics of these structures in Al–Mg show that the enthalpy of formation is much lower than that from the previous modeling [2]. The remodeling of the thermodynamic description of the Al–Mg binary system is thus needed.

5. Evaluation of model parameters and discussion

All model parameters were evaluated using the Parrot module [46] in Thermo-Calc [47]. This program is able to take various kinds of experimental data in one operation. It works by minimizing an error of sum, with each of the selected data values given a certain weight. The weight is chosen and adjusted based upon the data uncertainties given in the original publications and upon the author's judgment by examining all experimental data simultaneously. The complete and self-consistent thermodynamic description for the Al–Mg binary system obtained is listed in Table 4. The reference state of the Gibbs energy of individual phases is the so-called Standard Element Reference (SER), i.e. the enthalpies of the pure elements in their stable states at 298 K.

The evaluation of model parameters procedure in the Al–Mg binary system started with the parameters from [2]. The model parameters of the solid phases were evaluated according to the enthalpies of formation of solid phases from first-principles calculations and the upper and lower temperature limits for the stability of ε-$Al_{30}Mg_{23}$. Many iterations were necessary to reproduce all experimental and first-principles data.

The standard deviations calculated by the formula below are included in figure captions to represent the agreement between the calculated values and experimental data:

$$\sigma = \sqrt{\frac{1}{n}\sum_{i}^{n}(A_i^{\mathrm{cal}} - A_i^{\mathrm{exp}})^2} \tag{13}$$

where σ is the standard deviation, A_i^{cal} the calculated result, A_i^{exp} the experimental datum, and n the number of experimental data.

Fig. 2 shows the enthalpy of formation at 298 K in the Al–Mg binary system calculated from the current thermodynamic description of the system (solid line). It shows a good agreement with first-principles calculation result for γ-$Al_{12}Mg_{17}$. It is observed that ε-$Al_{30}Mg_{23}$ is not stable at room temperature and the enthalpy of formation of β-$Al_{140}Mg_{89}$ is lower than those of laves phases.

Comparison between the calculated phase diagram using the present thermodynamic description of the Al–Mg binary system and previous modeling by Liang et al. [2] is shown in Fig. 3. An excellent agreement can be observed except the upper temperature limit for the stability of ε-$Al_{30}Mg_{23}$. The upper temperature limit given from the latest experiments by Czeppe [14] is adopted in the present work. The calculated invariant reaction temperatures and Mg contents in various

Table 4
Thermodynamic parameters of the Al–Mg binary system (all in S.I. units)

Phase	Sublattice model	Evaluated description	
Liquid	(Al, Mg)	${}^0L^{\text{liq}}_{\text{Al,Mg}} = -12\,000 + 8.566T$, ${}^1L^{\text{liq}}_{\text{Al,Mg}} = 1894 - 3.000T$, ${}^2L^{\text{liq}}_{\text{Al,Mg}} = 2000$	[2]
		${}^0L^{\text{liq}}_{\text{Al,Mg}} = -9019 + 4.794T$, ${}^1L^{\text{liq}}_{\text{Al,Mg}} = -1093 + 1.412T$, ${}^2L^{\text{liq}}_{\text{Al,Mg}} = 494$	Present work
fcc	(Al, Mg)	${}^0L^{\text{fcc}}_{\text{Al,Mg}} = 4971 - 3.500T$, ${}^1L^{\text{fcc}}_{\text{Al,Mg}} = 900 + 0.423T$, ${}^2L^{\text{fcc}}_{\text{Al,Mg}} = 950$	[2]
		${}^0L^{\text{fcc}}_{\text{Al,Mg}} = 1593 + 2.149T$, ${}^1L^{\text{fcc}}_{\text{Al,Mg}} = 1014 - 0.660T$, ${}^2L^{\text{fcc}}_{\text{Al,Mg}} = -673$	Present work
hcp	(Al, Mg)	${}^0L^{\text{hcp}}_{\text{Al,Mg}} = 1950 - 2.000T$, ${}^1L^{\text{hcp}}_{\text{Al,Mg}} = 1480 - 2.080T$, ${}^2L^{\text{hcp}}_{\text{Al,Mg}} = 3500$	[2]
		${}^0L^{\text{hcp}}_{\text{Al,Mg}} = 4336 - 2.863T$, ${}^1L^{\text{hcp}}_{\text{Al,Mg}} = -449 - 0.135T$, ${}^2L^{\text{hcp}}_{\text{Al,Mg}} = -1963$	Present work
β-$Al_{140}Mg_{89}$	$(Al)_{140}(Mg)_{89}$	${}^0G^{\beta\text{-Al}_{140}\text{Mg}_{89}}_{\text{Al:Mg}} = 140\,{}^0G^{\text{fcc}}_{\text{Al}} + 89\,{}^0G^{\text{hcp}}_{\text{Mg}} - 246\,175 - 675.550T$	[2]
		${}^0G^{\beta\text{-Al}_{140}\text{Mg}_{89}}_{\text{Al:Mg}} = 140\,{}^0G^{\text{fcc}}_{\text{Al}} + 89\,{}^0G^{\text{hcp}}_{\text{Mg}} - 803\,385 + 105.238T$	Present work
ε-$Al_{30}Mg_{23}$	$(Al)_{30}(Mg)_{23}$	${}^0G^{\varepsilon\text{-Al}_{30}\text{Mg}_{23}}_{\text{Al:Mg}} = 30\,{}^0G^{\text{fcc}}_{\text{Al}} + 23\,{}^0G^{\text{hcp}}_{\text{Mg}} - 52\,565.4 - 173.1775T$	[2]
		${}^0G^{\varepsilon\text{-Al}_{30}\text{Mg}_{23}}_{\text{Al:Mg}} = 30\,{}^0G^{\text{fcc}}_{\text{Al}} + 23\,{}^0G^{\text{hcp}}_{\text{Mg}} - 170\,832 - 8.047T$	Present work
γ-$Al_{12}Mg_{17}$	$(Mg)_5(Al, Mg)_{12}(Al, Mg)_{12}$	${}^0G^{\gamma\text{-Al}_{12}\text{Mg}_{17}}_{\text{Mg:Al:Al}} = 24\,{}^0G^{\text{fcc}}_{\text{Al}} + 5\,{}^0G^{\text{hcp}}_{\text{Mg}} + 97\,875 - 101.500T$ ${}^0G^{\gamma\text{-Al}_{12}\text{Mg}_{17}}_{\text{Mg:Mg:Al}} = 12\,{}^0G^{\text{fcc}}_{\text{Al}} + 17\,{}^0G^{\text{hcp}}_{\text{Mg}} - 52\,780 - 50.750T$ ${}^0G^{\gamma\text{-Al}_{12}\text{Mg}_{17}}_{\text{Mg:Al:Mg}} = 12\,{}^0G^{\text{fcc}}_{\text{Al}} + 17\,{}^0G^{\text{hcp}}_{\text{Mg}} + 284\,124.6 - 138.069T$ ${}^0G^{\gamma\text{-Al}_{12}\text{Mg}_{17}}_{\text{Mg:Mg:Mg}} = 29\,{}^0G^{\text{hcp}}_{\text{Mg}} + 133\,469.6 - 87.319T$ ${}^0L^{\gamma\text{-Al}_{12}\text{Mg}_{17}}_{\text{Mg:Al:Al,Mg}} = {}^0L^{\gamma\text{-Al}_{12}\text{Mg}_{17}}_{\text{Mg:Mg:Al,Mg}} = 113\,100 - 14.500T$	[2]
		${}^0G^{\gamma\text{-Al}_{12}\text{Mg}_{17}}_{\text{Mg:Al:Al}} = 24\,{}^0G^{\text{fcc}}_{\text{Al}} + 5\,{}^0G^{\text{hcp}}_{\text{Mg}} + 8360 + 20.339T$ ${}^0G^{\gamma\text{-Al}_{12}\text{Mg}_{17}}_{\text{Mg:Mg:Al}} = 12\,{}^0G^{\text{fcc}}_{\text{Al}} + 17\,{}^0G^{\text{hcp}}_{\text{Mg}} - 103\,596 + 22.121T$ ${}^0G^{\gamma\text{-Al}_{12}\text{Mg}_{17}}_{\text{Mg:Al:Mg}} = 12\,{}^0G^{\text{fcc}}_{\text{Al}} + 17\,{}^0G^{\text{hcp}}_{\text{Mg}} + 180\,556 - 138.069T$ ${}^0G^{\gamma\text{-Al}_{12}\text{Mg}_{17}}_{\text{Mg:Mg:Mg}} = 29\,{}^0G^{\text{hcp}}_{\text{Mg}} + 139\,371 - 87.319T$ ${}^0L^{\gamma\text{-Al}_{12}\text{Mg}_{17}}_{\text{Mg:Al:Al,Mg}} = {}^0L^{\gamma\text{-Al}_{12}\text{Mg}_{17}}_{\text{Mg:Mg:Al,Mg}} = 113\,100 - 14.500T$	Present work

Table 5
Calculated invariant reactions in the Al–Mg binary system

Reaction	Type	x^{Φ}_{Mg}	Temperature (K)
Liquid = fcc-A1 + β	Eutectic	36.6 16.6 38.9	725.1
Liquid = $\beta + \gamma$	Eutectic	41.3 38.9 47.3	725.0
$\beta + \gamma = \varepsilon$	Peritectoid	38.9 48.4 43.4	700.0
$\varepsilon = \beta + \gamma$	Eutectoid	43.4 38.9 53.6	523.2
Liquid = γ + hcp-A3	Eutectic	69.3 59.3 88.9	712.1
Liquid = β	Congruent	38.7 38.7 –	725.7
Liquid = γ	Congruent	52.8 52.8 –	735.0

phases are listed in Table 5, where x^{Φ}_{Mg} refers to the atomic percentage of Mg in the three phases in the order that they appear in the invariant reactions.

The calculated enthalpy of mixing in liquid at 973 K (solid line) is compared with experimental data [18–23,48] and values from previous modeling (dotted line) by Liang et al. [2] in Fig. 4. The standard deviation is evaluated with experimental data from [20], showing a good agreement.

First-principles calculation results of fully relaxed SQS's for fcc and hcp phases were adopted in the evaluation process of model parameters. Fig. 5 shows the calculated enthalpies of mixing of fcc and hcp phases and values from previous modeling (dotted line) by Liang et al. [2]. The calculation results show a good agreement for both phases with first-principles calculation results of fully relaxed SQS's.

Fig. 6 shows comparisons between the calculated activities of the liquid phase at 923 and 1073 K and the experimental values of [22–24,26–29,49] at temperatures between 917 and 1080 K. The calculated results from the present work and the previous modeling [2] are both within the experimental data uncertainties.

The calculated activities of Mg at 660 and 710 K are compared with experimental values of Brown and Pratt [30] in Fig. 7. The experimental data at 660 K do accurately show

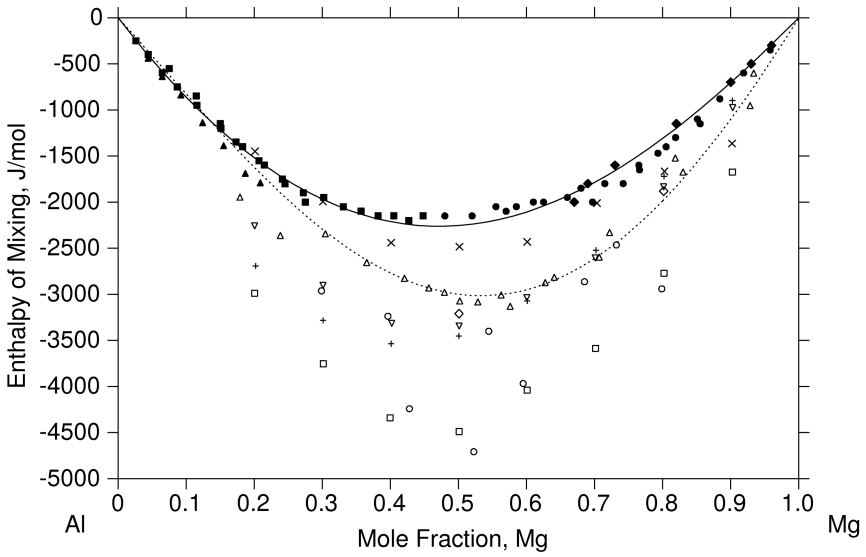

Fig. 4. Calculated enthalpy of mixing in liquid at 973 K as a function of Mg mole fraction in comparison with experimental data, (●▲■♦) by Agarwal and Sommer in temperature range between 943 and 973 K [20], (○) by Kawakami [18], (+) by Belton and Rao [23], (◇) by Batalin et al. [19], (×) by Bhatt and Grag [21], (▽) by Kazimov and Batalin [48], (□) by Juneja et al. [22], (△) and by Moser et al. [25] and previous modeling [2] (dotted line). The reference state is the liquid Al and Mg at 973 K. ($\sigma = 0.112$ kJ/mol atom.)

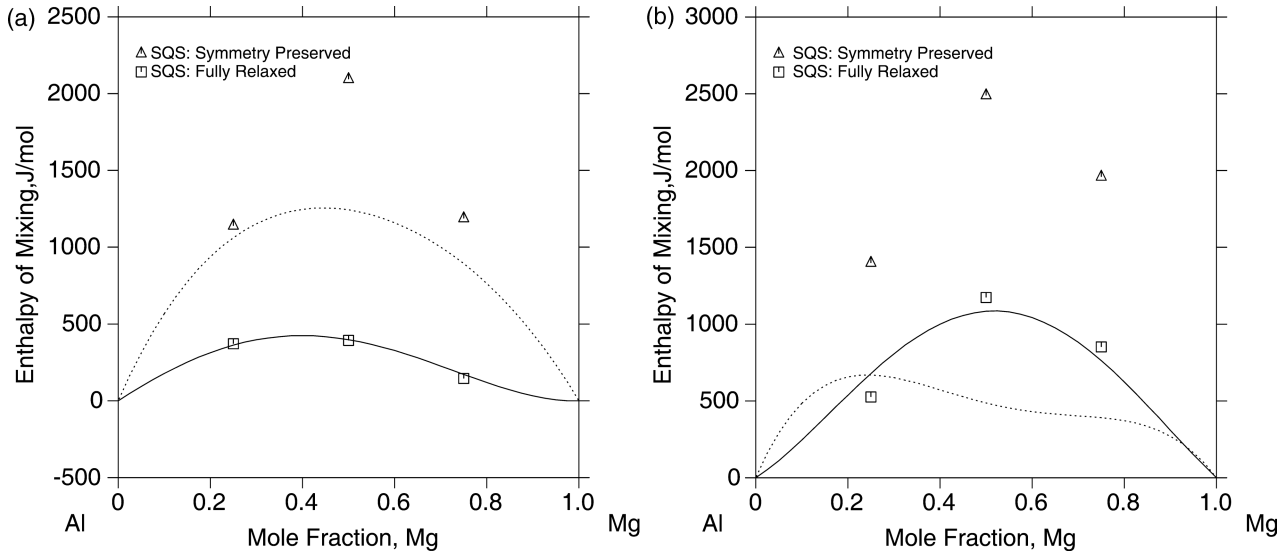

Fig. 5. Calculated enthalpy of mixing of the fcc phase (a) and hcp phase (b) in the Al–Mg binary system comparing with first-principles calculation results from SQS's. ($\sigma = 0.016$ kJ/mol atom for fcc and $\sigma = 0.115$ kJ/mol atom for hcp.)

the existence of ε-$Al_{30}Mg_{23}$, but the phase boundaries deduced from the activity data do not agree with well-established solubility ranges of γ-$Al_{12}Mg_{17}$ and fcc-Al [30,43,50–69].

6. Summary

Motivated by the lack of accurate solid energetics in previous Al–Mg thermodynamic modeling, the Al–Mg binary system was remodeled. Via a first-principles method, the enthalpies of formation of stable γ-$Al_{12}Mg_{17}$ and ε-$Al_{30}Mg_{23}$ compounds, and non-stable laves phases were calculated and found considerably lower than the values from the previous modeling. The range of the enthalpy of formation of the β-$Al_{140}Mg_{89}$ phase was consequently deduced. The enthalpies of mixing of fcc and hcp solution phases with the crystal structures generated by SQS's were predicted by first-principles calculations.

By combining these first-principles energetics with the available experimental thermochemical and phase diagram data, a new self-consistent CALPHAD thermodynamic description of Al–Mg was obtained. The current investigation linking first-principles calculations to CALPHAD thermodynamic modeling yields satisfactory results.

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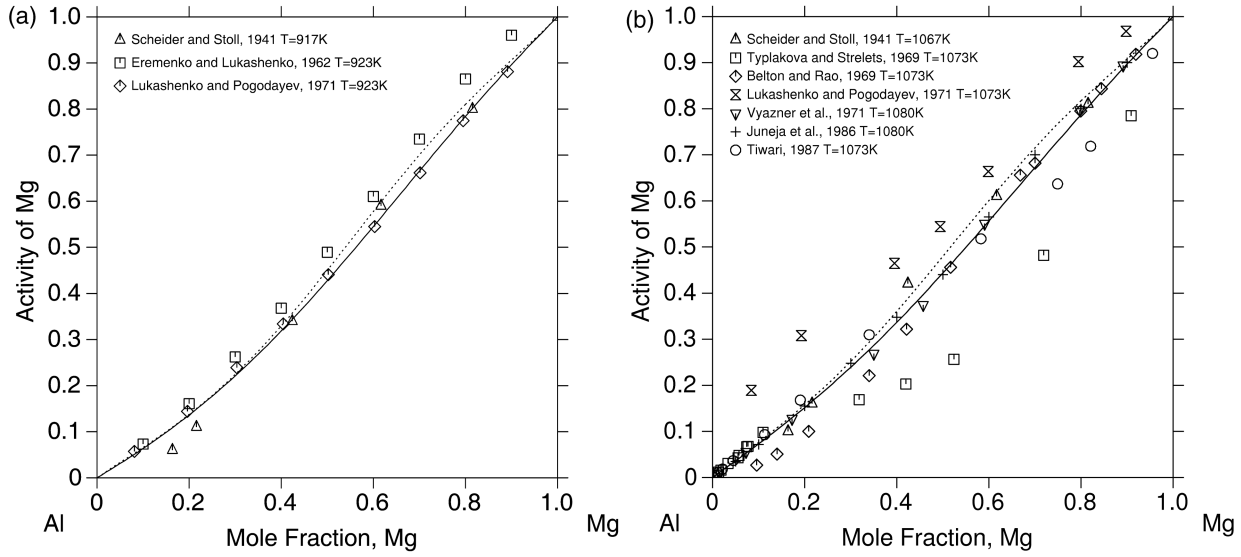

Fig. 6. Comparison between the calculated activity of Mg at 923 K (a) and 1073 K (b) with the experimental values from [22–24,26–29,49] in the Al–Mg binary system. The reference state is the liquid Al and Mg at corresponding temperatures. ($\sigma = 0.038$ for 923 K and $\sigma = 0.211$ for 1073 K.)

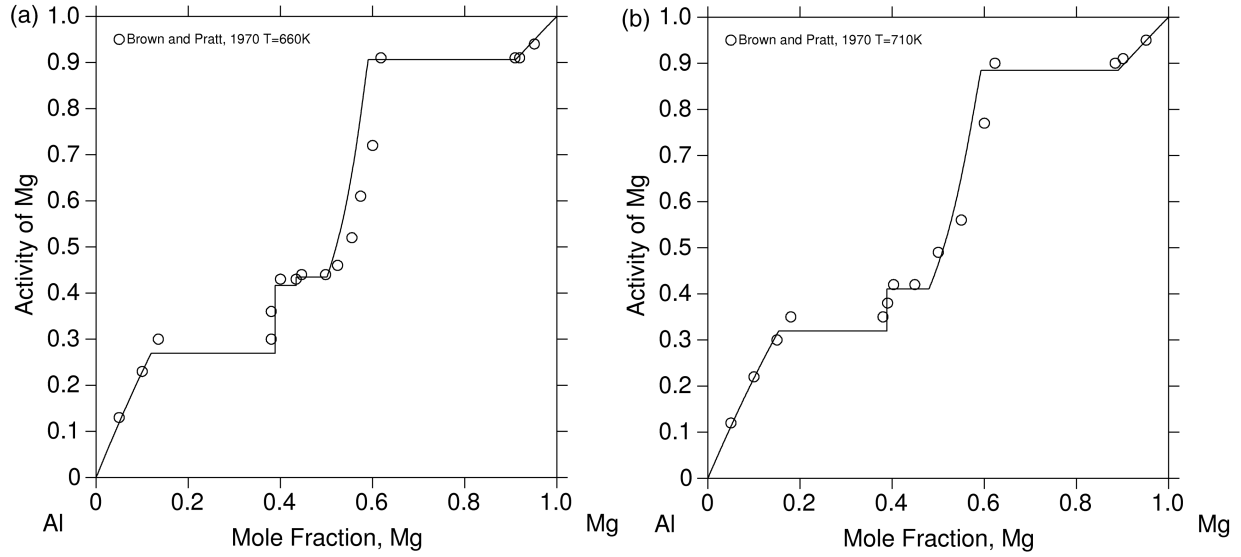

Fig. 7. Comparison between the calculated activity of Mg and the experimental values by Brown and Pratt [30] at 660 and 710 K in the Al–Mg binary system. The reference state is the fcc-Al and hcp-Mg at corresponding temperatures. ($\sigma = 0.069$ for 660 K and $\sigma = 0.039$ for 1073 K.)

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