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THERMODYNAMIC PROPERTIES OF MG BASED ALLOYS BY CALPHAD APPROACH COUPLED WITH FIRST-PRINCIPLES: APPLICATION TO MG-AL-CA-CE-SI SYSTEM

A Dissertation in

Materials Science and Engineering

by

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Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

December 2010
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**Abstract**

In the last few decades, first-principles quantum mechanics technique based on density functional theory has progressed significantly and demonstrated in many cases, e.g., the accurate predictions of thermodynamic properties. Within the similar time frame, computational thermodynamics based on CALPHAD (CALculation of PHAse Diagram) technique is emerging as a key technology, which is used to predict the phase equilibrium, phase stability, and phase transformation. In order to accelerate the understanding and design of magnesium alloys, an integrated first-principles calculations and CALPHAD modeling approach is used to study the elastic and thermodynamic properties of Mg-containing alloys.

The present project predicted the thermodynamic properties of Mg-based binary alloys from first-principles calculations. The obtained enthalpies of formation at 0 K were discussed for the Mg-X systems with X being the elements of As, Ba, Ca, Cd, Cu, Dy, Ga, Ge, La, Lu, Ni, Pb, Sb, Si, Sn and Y. By considering the phonon and thermal electronic contributions, first-principles are extended to predict the properties at finite temperatures. In the preset thesis, the phonon properties and the temperature dependent elastic and thermodynamic properties are also presented for the technically important $\gamma$-Al$_{12}$Mg$_{17}$ phase.

The thermodynamic description for the Ce-Mg binary system was updated using the CALPHAD approach by incorporating additional experimental data. The resulting thermodynamic description for the Mg-Ca-Ce system was then developed by combining
the derived databases of the Ca-Ce and Ce-Mg systems from the present work with that of the Ca-Mg system in the literature.

We obtained the equilibrium structural properties of Mg, Si, β-Mg₂Si, β’-Mg₁₈Si₁₀ and β’’-Mg₅Si₆ as well as the enthalpies of formation of β, β’ and β’’ in Al-Mg-Si ternary system. Using frozen-phonon calculations, we also ascertained the vibrational entropies of formation for each phase. The phase boundaries of β, β’ and β’’ were thus predicted for Al-Mg-Si ternary system.

To better understand the alloying behavior of Ca on Mg-Al alloys, the thermochemical properties of the Laves phases in the Mg-Al-Ca system are evaluated from both first-principles and CALPHAD modeling. First-principles provided insight into the understanding of phase stabilities of Laves phases, and herein developing self-consistent thermodynamic database of this ternary system by CALPHAD modeling.
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Acknowledgments

First of all, I deeply appreciate the unlimited support from my advisor, Dr. Zi-Kui Liu for providing me with the opportunity and means to grow under his guidance. He has an exceptional ability to inspire, and I have truly valued his advice and encouragement during the last few years. He showed me the way to be a good materials scientist via his famous TKC theory and ten pancake theory. His enthusiasm for science is always the hidden motivation for me. My sincere gratitude is also extended to my co-advisor, Dr. Long-Qing Chen for his personal and professional guidance during my research. I consider myself extremely fortunate for having had the chance to know and work with him for last few years.

I also wish to express my sincerest thanks to Dr. Jorge O. Sofo and Dr. Digby D. Macdonald for their willingness to serve on my thesis committee. Their generosity with their time, suggestion and encouragement are greatly appreciated.

We had the happy and productive cooperation with Dr. Lou Hector of General Motors Research and Development Center, and Dr. Chris Wolverton in Northwestern University. Their assistants in my thesis research are gratefully appreciated.

I would also take the opportunity to thank all the current and previous members of the Phases Research Lab, for their awesome training, discussion, help and cooperation during my stay. I express my deepest gratitude to Dr. Yi Wang and Dr. Shunli Shang for their patient guidance throughout my study. From them, I not only expanded my
knowledge about materials and computation techniques but also learned the methodical way to tackle problems in research.

I am exceptionally grateful to the National Science Foundation for the funding of this work.

I would like to acknowledge my parents and grandparents for their unconditional support and love even from the other side of the world. Their encouragement of being a scientist dates back to my childhood. Last but not least, I would like to thank my husband Guang Sheng. He makes the spare time in state college full of pleasure, and forms the backbone of my happiness. His support and love without any complaint has enabled me to complete this thesis.
Chapter 1 Introduction

1.1 Introduction

With a density of 1.741 g/cm$^3$ that is two-thirds that of aluminum, one quarter that of steel, Mg is the lightest structural metal. This makes magnesium alloys receive a substantial amount of interest for transportation applications such as the potential automobile body materials for weight reduction and higher fuel efficiency [1-3]. Among Mg-based alloys, Mg-Al is one group of the most important alloys that are widely used, e.g. the AM series (Mg-(2-6)%Al) show good performance at room temperature. Despite the high specific strength, these alloys have limited use as structural materials due to their poor creep resistance at high temperatures, mainly caused by the softening of the intermetallic phase Al$_{12}$Mg$_{17}$ [4-5]. Significant improvements can be achieved by adding the alloying elements, such as rare earth elements, Ca, Sr etc. Additions of mish metal (which is mixture of rare earth elements, e.g. 51.7% Cerium (Ce), 23.1% Lanthanum (La), 18.6% Neodymium (Nd), 6.5% Praseodymium (Pr) in mass% [6]), can improve mechanical properties caused by the formation of strengthening precipitates [7-8]. In particular, among all the rare earth elements, Ce is believed to be the good starting point since it has fascinating chemical and physical properties and precipitates containing Ce have been identified in Mg alloys [9]. Another alloying element toward the development of new Mg alloys is adding Ca [10]. As a lower cost element, the addition of Ca can improve the creep resistance of Mg-Al base alloys through the replacement of the Al$_{12}$Mg$_{17}$ phase by more stable Laves phases [11-12]. Therefore, this thesis on
computational thermodynamic properties of Mg alloys focuses on Mg-Al-Ca based and Mg-Ce based multicomponent systems.

To understand the effects of other elements on the phase stability and phase transition of magnesium alloys, a complete thermodynamic description of the Mg-Al-Ca-Ce-Si system is desirable. However, the conventional development of thermodynamic description of materials by “trial and error” method would be too costly and time-consuming, in searching for best combinations of chemical composition and processing procedures. Thus, it is inevitable to take advantage of computational methods for efficient and understanding materials behaviors in a multicomponent system.

Computational thermodynamics is the core component of computational materials science, since the thermodynamic properties are the most fundamental properties and could greatly affect kinetic properties and materials processing. In computational thermodynamics, CALPHAD (CALculation of PHAse Diagram) method is emerging as a key technology to accelerate the understanding and design of magnesium alloys. This technology can predict phase equilibrium, phase stability, and phase transformation, which are the main manifestations of thermodynamics. Starting from pure elements, CALPHAD provides a scheme to build thermodynamic databases for binary, ternary, and high-order systems. And in turn, link the properties of multi-phase materials to those of the individual phases.

In CALPHAD method, the fundamental thermodynamic properties of individual phases can typically be described with Gibbs energy functions: $G = H - TS$. The model parameters are evaluated from both thermochemical data of individual phases and phase equilibrium data between phases. These two kinds of data are complementary to each
other. However, in most cases, it is impossible to have enough thermochemical data of individual phases. Alternatively, those thermodynamic data, such as $H$ and $S$, can be obtained from first-principles calculations when experimental data are scarce.

### 1.2 Statement of goals

The objective of the project is to study the fundamental elastic, phonon, and thermodynamic properties in the Mg based alloys, such as $\text{Al}_{12}\text{Mg}_{17}$, Mg-Ca-Ce, Al-Mg-Si, and Mg-Ca-Ce alloys. And herein, provide understanding and guidance of design of Mg-Al-Ca-Ce-Si system through the CALPHAD approach coupled with first-principles calculations.

The following thesis is organized as:

Chapter 2 discusses the computational methodology for both first-principles and CALPHAD approaches in detail. And also explain how first-principles can be correlated with CALPHAD modeling.

Chapter 3 presents the development of an energetics database of binary magnesium alloys from first-principles calculations. The systems investigated include:

1. Period III: Si
2. Period IV: Ca, Cu, Zn, Ga, Ge, As
3. Period V: Sr, Y, Pd, Cd, Sn, Sb
4. Period VI: Ba, Pb
5. Rare Earth: La, Ce, Dy, Lu
Chapter 4 describes the elastic, phonon and thermodynamic properties of Al$_{12}$Mg$_{17}$ from first-principles calculations. All those properties are at finite temperature. In addition, the theoretical finding of brittleness behavior of Al$_{12}$Mg$_{17}$ is predicted, showing consistence with experimental observations, instead of the previous calculation showing ductile behavior.

Chapter 5 shows thermodynamic modeling of the Ca-Ce and Ce-Mg binary systems by means of the CALPHAD approach complemented by first-principles calculations. The thermodynamic description for the Mg-Ca-Ce system is herein obtained by combining the databases of the Ca-Ce and Ce-Mg systems with that for the Ca-Mg system from the literature.

Chapter 6 presents the thermodynamic properties for three phases ($\beta$-Mg$_2$Si, $\beta'$-Mg$_{18}$Si$_{10}$ and $\beta''$-Mg$_5$Si$_6$) in the Al-Mg-Si system using first-principles total energies and frozen phonon calculations. Phase boundaries in Al-rich corner are predicted and compared with available phase stability measurements.

Chapter 7 and Chapter 8 present the thermodynamic modeling of Mg-Al-Ca system by combining first-principles and CALPHAD methods. First-principles calculations are employed to investigate the structural and thermodynamic properties of all binary Laves phases (C14, C15 and C16 structures), both at 0 K and room temperature. Those results are employed to update the thermodynamic database of Mg-Al-Ca system.

Chapter 9 summarizes the contribution of the current work and discusses future work.
Chapter 2 Methodology

Computational thermodynamics using the CALPHAD method describes the Gibbs energy of individual phases using mathematically formulated models based on crystal structures. These model parameters are optimized using two types of data. One is thermochemical data and the other one is phase equilibrium data, with the former one typically for a single phase and the latter one indicating the relationship between the phases in that equilibrium. In principle, if there are enough precise thermochemical data of individual phases, the thermodynamic database of this system can be developed and herein the phase diagram can be calculated. However, under current experimental capability, thermochemical data are difficult to obtain and are not accurate enough. Therefore, it is almost impossible to build the thermodynamic database purely from the thermochemical data. On the other hand, phase equilibrium data are more accurate than thermochemical data, however, only phase diagram data cannot determine the Gibbs energy of phases precisely, since the experimental phase diagram cannot tell the exactly Gibbs energy of each phase. For example, the same experimental phase diagram can be achieved with completely different thermochemical properties for each phase. Therefore, both thermochemical data and phase equilibrium data are necessary in order to construct thermodynamic descriptions of a system.

However, it is not always feasible to have enough experimental thermochemical data. Alternatively, first-principles calculations can calculate the total energies directly
from crystal structure. Therefore, an integration of first-principles and CALPHAD approaches will allow one to develop the thermodynamic database for a multicomponent system. Figure 2.1 illustrates the flowchart of the CALPHAD approach for development of thermodynamic databases.

### 2.1 First-principles Approach

First-principles calculations are based on the Density Functional Theory (DFT) [14] and the projected augmented wave (PAW) pseudo-potentials as implemented in Vienna Ab-initio Simulation Package (VASP) [15-16] with the generalized gradient approximation refined by Perdew, Burke and Ernzerhof (PBE) [17]. The configuration of solid phase with an ideal crystal structure is defined by the repeated unit cells via translational symmetry. Even with these periodic boundary conditions, the multi-electron Schrödinger equation still cannot be solved with modern computing resources.

Equation 2.1

\[
\hat{H}(R_1,\ldots,R_N)\Psi(r_1,\ldots,r_n) = E_{TOT}\Psi(r_1,\ldots,r_n)
\]

where \( R_j \)'s are the ion coordinates, \( r_i \)'s the electron coordinates, \( \hat{H} \) the Hamiltonian operator, and \( E_{TOT} \) the total energy of the electrons. Hohenberg and Kohn [14, 18] have shown that the total energy of the electrons in an external potential can be described as a function of the charge density \( \rho(r) \).

Equation 2.2

\[
E_{TOT} = E[\rho(r)]
\]

According to DFT, the total energy of a system is uniquely defined by the charge
density \( (\rho) \). Given the symmetry with ionic coordinates, the density functional has the following form: \( E[\rho](R_1, R_2, R_3,...) \).

The Vienna Ab initio Simulation Package (VASP) processes the \( E[\rho](R_1, R_2, R_3,...) \) to obtain the charge density that minimizes the total energy. This minimized value is the ground state total energy, \( E_a[\{R_i\}] \), where \( R_i \) represents the equilibrium atomic positions. This total energy can be further minimized with respect to the atomic positions to obtain the stable structures of the system. Under the quasiharmonic approximation, the Helmholtz free energy, \( F \), of a system at temperature \( T \) and volume \( V \) is given by [19-23]:

Equation 2.3 \( F(V,T)=E_0(V)+F_{\text{vib}}(V,T)+F_{\text{el}}(V,T) \)

where \( E_0(V) \) is the first-principles static energy at 0 K and volume \( V \), \( F_{\text{vib}}(V,T) \) the lattice vibrational contributions to the free energy, and \( F_{\text{el}}(V,T) \) the thermal electronic contributions.

### 2.1.1 Static energy at 0 K

**2.1.1.1 Ordered phase**

As long as the crystal structure of a phase is defined, DFT codes can calculate its total energy. 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 state:

Equation 2.4 \( \Delta_f H(Mg_aX_b) = E(Mg_aX_b) - \frac{a}{a+b} E(Mg) - \frac{b}{a+b} E(X) \)
where the $E$’s are the total energies of compound Mg$_x$X$_{1-x}$ and pure elements Mg and X in their stable states. Since the influences of pressure on the condensed phases are ignored, the value of enthalpy is approximated to be the same as the value of internal energy.

2.1.1.2 Disordered phase

As discussed, the first-principles calculations of perfectly ordered periodic structures are somewhat straightforward. However, random solid solution phases could not be treated precisely with the implementation of the first-principles method developed for ordered structures [15-16]. In this thesis, the random structure is mimicked by a so-called Special Quasirandom Structure (SQS) method. The concept of SQS was first proposed by Zunger et al. [24-25] for the calculation of the fcc solutions. Within the given interaction ranges, the SQS possesses the local pair and multi-site correlation functions of the corresponding random alloys. Jiang et al. and Shin et al. extended this approach to the bcc [26] and hcp [27] structures, respectively. The total energies can be used to extract the enthalpies of mixing at $T=0$ K using:

\begin{equation}
\Delta_f H(A_xB_{1-x}) = E^\Phi(A_xB_{1-x}) - xE^\Phi(A) - (1-x)E^\Phi(B)
\end{equation}

where the $E$’s are the total energies of solution phase $A_xB_{1-x}$ and pure elements A and B in $\Phi$ structure.
2.1.2 Lattice vibrational and thermal electronic contributions to Helmholtz free energy

To calculate the temperature dependence of all the thermodynamic quantities, the phonon approach has been employed to calculate the lattice vibrational contribution to the free energy [19-21], $F_{ph}(T)$, as:

Equation 2.6 \[ F_{ph}(V,T) = k_B T \ln \left\{ 2 \sinh \left[ \frac{\hbar \omega}{2k_B T} \right] \right\} D(\omega) d\omega \]

where $D(\omega)$ represents the phonon density of states (PDOS) as a function of phonon frequency $\omega$. The Other thermodynamic functions can be obtained in the usual way from $F_{ph}(V)$; for example, entropy $S = -\left( \frac{\partial F}{\partial T} \right)_V$ and internal energy $E = F + TS$.

The free energy due to thermal electronic excitations is given by $F_{el} = E_{el} - TS_{el}$, with the $E_{el}$ calculated by [19]

Equation 2.7 \[ E_{el}(V,T) = \int n(\varepsilon,V) f\varepsilon \, d\varepsilon - \int_{\varepsilon_F}^{\varepsilon_F} n(\varepsilon,V) \varepsilon \, d\varepsilon \]

where $n(\varepsilon)$ is the electronic density of states, $\varepsilon$ the energy eigenvalues, $f$ the Fermi-Dirac (FD) distribution, and $\varepsilon_F$ the energy at the Fermi level. The thermal electronic entropy in the mean field approximation is written by [19-21]:

Equation 2.8 \[ S_{el}(V,T) = -k_B \int n(\varepsilon,V)[f \ln f + (1-f) \ln(1-f)] \, d\varepsilon \]
2.1.3 Elastic stiffness

In the present work, the elastic stiffness \( C_{ij} \)'s are calculated based on the stress-strain method [28]. This methodology involves a set of strains \( \varepsilon = (\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4, \varepsilon_5, \varepsilon_6) \) where \( \varepsilon_1, \varepsilon_2, \) and \( \varepsilon_3 \) refer to the normal strains, and \( \varepsilon_4, \varepsilon_5, \varepsilon_6 \) the shear strains. Set of strains are imposed on a crystal with lattice vectors \( \mathbf{R} \) specified in the Cartesian coordinates. After the strains are applied, the deformed lattice vectors \( \bar{\mathbf{R}} \) are obtained as follow:

Equation 2.9

\[
\bar{\mathbf{R}} = \mathbf{R} \begin{pmatrix} 1 + \varepsilon_1 & \varepsilon_6 / 2 & \varepsilon_5 / 2 \\ \varepsilon_6 / 2 & 1 + \varepsilon_2 & \varepsilon_4 / 2 \\ \varepsilon_5 / 2 & \varepsilon_4 / 2 & 1 + \varepsilon_3 \end{pmatrix}
\]

Using the matrix notation for elasticity and the general Hooke law, the stresses \( \sigma \) cased by the application of strains \( \varepsilon \) are related by the following:

Equation 2.10

\[ \sigma = \varepsilon \mathbf{C} \]

where \( \mathbf{C} \) is the \( 6 \times 6 \) elastic stiffness matrix with elements \( C_{ij} \)'s in Voigt’s notation. \( \sigma \) can be obtained by first-principles calculations. From \( n \) sets of strains and the resulting stresses, the elastic constants \( \mathbf{C} \) can be calculated by:

Equation 2.11

\[
\begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{pmatrix} \begin{pmatrix} \varepsilon_{1,1} & \varepsilon_{1,2} & \varepsilon_{1,3} & \varepsilon_{1,4} & \varepsilon_{1,5} & \varepsilon_{1,6} \\ \varepsilon_{2,1} & \varepsilon_{2,2} & \varepsilon_{2,3} & \varepsilon_{2,4} & \varepsilon_{2,5} & \varepsilon_{2,6} \\ \varepsilon_{3,1} & \varepsilon_{3,2} & \varepsilon_{3,3} & \varepsilon_{3,4} & \varepsilon_{3,5} & \varepsilon_{3,6} \\ \varepsilon_{4,1} & \varepsilon_{4,2} & \varepsilon_{4,3} & \varepsilon_{4,4} & \varepsilon_{4,5} & \varepsilon_{4,6} \\ \varepsilon_{5,1} & \varepsilon_{5,2} & \varepsilon_{5,3} & \varepsilon_{5,4} & \varepsilon_{5,5} & \varepsilon_{5,6} \\ \varepsilon_{6,1} & \varepsilon_{6,2} & \varepsilon_{6,3} & \varepsilon_{6,4} & \varepsilon_{6,5} & \varepsilon_{6,6} \end{pmatrix} = \begin{pmatrix} \sigma_{1,1} & \sigma_{1,2} & \sigma_{1,3} & \sigma_{1,4} & \sigma_{1,5} & \sigma_{1,6} \\ \sigma_{2,1} & \sigma_{2,2} & \sigma_{2,3} & \sigma_{2,4} & \sigma_{2,5} & \sigma_{2,6} \\ \sigma_{3,1} & \sigma_{3,2} & \sigma_{3,3} & \sigma_{3,4} & \sigma_{3,5} & \sigma_{3,6} \\ \sigma_{4,1} & \sigma_{4,2} & \sigma_{4,3} & \sigma_{4,4} & \sigma_{4,5} & \sigma_{4,6} \\ \sigma_{5,1} & \sigma_{5,2} & \sigma_{5,3} & \sigma_{5,4} & \sigma_{5,5} & \sigma_{5,6} \\ \sigma_{6,1} & \sigma_{6,2} & \sigma_{6,3} & \sigma_{6,4} & \sigma_{6,5} & \sigma_{6,6} \end{pmatrix}^{-1} \]
The minimum independent sets of strains are related to the symmetry of crystals. i.e. two for cubic structures and three for hexagonal structures. The following independent set of strains is applied in the present work:

Equation 2.12

\[
\begin{pmatrix}
  x & 0 & 0 & 0 & 0 & 0 \\
  0 & x & 0 & 0 & 0 & 0 \\
  0 & 0 & x & 0 & 0 & 0 \\
  0 & 0 & 0 & x & 0 & 0 \\
  0 & 0 & 0 & 0 & x & 0 \\
  0 & 0 & 0 & 0 & 0 & x \\
\end{pmatrix}
\]

with \( x = \pm 0.01 \) and \( \pm 0.013 \) in the present work.

### 2.2 CALPHAD approach

The thermodynamic description of the Mg-Al-Ca-Ce-Cu-Si-Sr-Zn system will be developed by using the CALPHAD approach based on the data from phase diagrams and thermochemistry [29-30]. Modeling of a multicomponent system is based on the evaluation of the thermodynamic descriptions of unary, binary, ternary, and higher-order systems. In this approach, the model for individual phases can be applied to the whole composition and temperature ranges, even if the regions untouched by experiments. The core component of developing an explicit thermodynamic database of a system is the modeling of the Gibbs energy of individual phases. The models used in the CALPHAD approach are based on the crystal structures of the phases. In this section, pure element and stoichiometric compound, multicomponent solution phase will be discussed accordingly.
2.2.1 Pure elements and stoichiometric compounds

Gibbs energies of pure elements in various crystal structures are taken from the Scientific Group Thermodata Europe (SGTE) database with the following form:

Equation 2.13  \[ G_m - H_m^{SER} = a + bT + cT \ln T + \sum d_n T^n \]

\( G_m - H_m^{SER} \) is the Gibbs energy relative to a standard element reference state (SER) where \( H_m^{SER} \) is the enthalpy of the element in its stable state at 298.15 K. \( a, b, c \) and \( d_n \) are coefficients, and \( n \) represents a set of integers.

For binary stoichiometric compounds, their Gibbs energies are directly referred to the SER in the form similar to Equation 2.13 as:

Equation 2.14  \[ G_m^{A_{\ldots}B_x} - (1 - x)H_A^{SER} - xH_B^{SER} = a + bT + cT \ln T + \sum d_n T^n \]

For compounds without heat capacity data, the Neumann-Kopp rule is used and their Gibbs energy functions are expressed as:

Equation 2.15  \[ G_m^{A_{\ldots}B_x} = (1 - x)G_A^{\Phi_A} + xG_B^{\Phi_B} + a + bT \]

where \( G_A^{\Phi_A} \) and \( G_B^{\Phi_B} \) are the molar Gibbs energies of the pure element \( A \) and \( B \) in their structures \( \Phi_A \) and \( \Phi_B \), respectively. \( a \) and \( b \) are the enthalpy and entropy of formation of the compound with respect to elements \( A \) and \( B \) in their structures \( \Phi_A \) and \( \Phi_B \).
2.2.2 Multicomponent solution phase

For multi-component solution phases, the Gibbs energy has the following general formula:

Equation 2.16  \[ G_m^\phi = G_0^m + \text{ideal} G_m^m + x_s G_m^m \]

where \( G^0 \) is the energy contribution from pure elements, so-called mechanical mixing, \( \text{ideal} G_m \) the energy contribution from ideal mixing and \( x_s G_m^m \) the excess Gibbs energy contribution from mixing. \( G^0 \) is taken from the SGTE pure element database. \( x_s G_m^m \) is the term that needs to be modeled.

Sublattice models are used to describe solution phases [31-32]. A disordered solution phase, such as liquids, fcc, bcc and hcp phases, can be described with a one sublattice model as \((A, B)\). The molar Gibbs energy in Equation 2.16 can be expressed as the following:

Equation 2.17  \[ G_m^\phi = \sum_{n} x_i 0 G_i^\phi + RT \sum_{n} x_i \ln x_i + x_s G_m^m \]

where \( 0 G_i^\phi \) is the molar Gibbs energy of the pure element \( i \) with the structure \( \phi \). \( x_s G_m^m \) is the excess Gibbs energy. \( k L_{i,j}^\phi \) is the \( k^{th} \) binary interaction parameter between \( i \) and \( j \) and may depend on temperature as \( a + bT \) [29]. \( I^\phi \) is the ternary interaction parameter.

For compounds with appreciable homogeneity ranges, two or more sublattice models are used. For example, intermetallic phases (e.g. Laves_C14, Laves_C15 and Laves_C36) in A-B system can be described using two sublattice model, \((A, B)_{A}(A, B)_{B}\),...
where subscripts a and b denote the number of sites of each sublattice. The molar Gibbs energy can be described as:

**Equation 2.18**  
\[ G^\circ = y_A^I y_B^I G_{A:B}^\circ + y_A^I y_B^I G_{B:A}^\circ + y_A^I y_B^I G_{A:B}^\circ + y_A^I y_B^I G_{B:A}^\circ \]


\[ \text{ideal} G_m = aRT \left( y_A^I \ln y_A^I + y_B^I \ln y_B^I \right) + bRT \left( y_A^I \ln y_A^I + y_B^I \ln y_B^I \right) \]

\[ G^s_m = y_A^I y_B^I \left( y_A^I \sum_{k=0}^{\infty} L_{A:A,B} (y_A^I - y_B^I)^k + y_B^I \sum_{k=0}^{\infty} L_{B:B,A} (y_A^I - y_B^I)^k \right) + y_A^I y_B^I \left( y_A^I \sum_{k=0}^{\infty} L_{A:A,B} (y_A^I - y_B^I)^k + y_B^I \sum_{k=0}^{\infty} L_{B:B,A} (y_A^I - y_B^I)^k \right) \]

where \( y^I \) and \( y^s \) are the site fraction of elements A and B in the first and second sublattices, respectively. \( G^\circ_{A:B} \) the Gibbs energy of the end-member of \( A_b B_a \). \( L_{A:A,B}^k \) (\( L_{A:B}^k \)) is the interaction parameter between component A and B in the first (second) sublattice.
Figure 2.1 A schematic diagram of the CALPHAD approach
Chapter 3 Enthalpies of formation of magnesium compounds from first-principles calculations

3.1 Introduction

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 [33-36]. 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 [37] on first-principles energetics of Al based systems. In our previous study, the thermodynamic database of the Mg-Zr [35] and the Mg-Ca [36] binary systems as well as the Mg-Ca-Sn [33] and the Mg-Ca-Sr [38] 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.

3.2 Methodology

3.2.1 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) [39-40] with the generalized gradient approximation refined by Perdew, Burke and Ernzerhof (PBE) [41]. 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 [42]. The settings of \( k \)-points correspond roughly to a 5,000 \( k \)-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 [40].

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:
Equation 3.1 \[ \Delta_f E(Mg, X, \gamma) = E(Mg, X, \gamma) - \frac{x}{x+y} E(Mg) - \frac{y}{x+y} E(X) \]

where \( E(Mg, X, \gamma) \) is the total energy of the compound, and \( E(Mg) \) 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.

### 3.2.2 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 Mg3X2 compounds with 2 and 5 atoms in the primitive cells, to complex phases, such as Mg24X5, Mg38X9 and Mg23X6, with 58, 94, and 116 atoms per primitive cell, respectively. The observed ground state structures for each pure element X are listed in Table 3.1, and Table 3.2 summarizes the crystal structures and k-point mesh of the intermetallic compounds in the Mg-X systems [43].

### 3.3 Results and Discussion

#### 3.3.1 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 lattice parameters with those determined experimentally. Table 3.3 lists the
lattice parameters calculated in comparison with available experimental data [43-44] and previous calculations by Wang et al. [45]. 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. [45], 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 3.4. The difference between experiments and calculations is less than 2.0%.

3.3.2 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 3.5 [46-47] and plotted in Figure 3.1, in which the calculated and experimental values are plotted in the x- and y-axis, respectively. The top right corner of Figure 3.1(a) is enlarged in Figure 3.1(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 [48-49]. 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 Mg-La system (Mg₃La and MgLa), the Mg-Dy system (Mg₂Dy, Mg₃Dy and Mg₂₄Dy₃), α-Mg₃As₂, α-Mg₃Sb₂, and Mg₂Ge. 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. [47]. In the recent study of thermodynamic modeling of this system, the previous work used the predicted enthalpies of formation of the compounds from the Miedema’s model [50-52]. 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 [50] with differences less than 4 kJ/mol-atom. For $\alpha$-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 [47], 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. [53] 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 $f$ electrons may exhibit strong correlations. This has also been mentioned in other calculations involving rare earth elements [54]. 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 $\alpha$-Mg$_3$As$_2$ [46], 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 [50-51] developed an extremely simple scheme for predicting the enthalpies of
formation of compounds. As reviewed in a recent book [52], 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 Figure 3.2 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 [55].

We next turn to a comparison of our first-principles enthalpies of formation with those from the COST507 [56] and other databases developed by the CALPHAD approach [57]. For most of the compounds, the differences are often within ±5 kJ/mol as shown in Figure 3.3. The COST507 [56] 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-Mg₃Sb₂ and Mg-Dy compounds with possible sources of uncertainties discussed above.
3.3.3 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 3.2. All the intermetallic compounds are stable at 0 K except for Mg\textsubscript{2}La and β-Mg\textsubscript{3}As\textsubscript{2} which only exist at high temperatures. Figure 3.4 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. Figure 3.4 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\textsubscript{3} (25~32 at. % Mg), MgCd (38~60 at. % Mg) and Mg\textsubscript{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\textsubscript{3}As\textsubscript{2}, β-Mg\textsubscript{3}As\textsubscript{2} and MgAs\textsubscript{4}. α-Mg\textsubscript{3}As\textsubscript{2} is confirmed stable at 0 K in our calculations while β-Mg\textsubscript{3}As\textsubscript{2} lies above the convex hull by 1.75 kJ/mol, consistent with the experimental observation that β-Mg\textsubscript{3}As\textsubscript{2} is stable at high temperatures. As the transition temperature between α-Mg\textsubscript{3}As\textsubscript{2}
and β-Mg₃As₂ is around 1273K ~ 1373K [47] and hence, the change of entropy from α-Mg₃As₂ to β-Mg₃As₂ 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, Mg₃La, Mg₁₇La₂ and Mg₁₂La all lie on the convex hull, and Mg₂La 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, Mg₃La, Mg₁₇La₂ and Mg₁₂La are stable phases at low temperatures and Mg₂La 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 [56, 58-59]. Figure 3.5 shows the calculated enthalpies of formation compared with their congruent melting temperatures and bulk modulus [60]. 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 [61]. It can also be seen that the compounds with more negative enthalpy of formation had in turn larger bulk modulus. For example, MgY has a more negative enthalpy of formation than Mg₂₄Y₅, and, as predicted, it has a higher congruent melting temperature and larger bulk modulus.
3.4 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.
Table 3.1: Stable crystal structures of pure elements at room temperature [43]

<table>
<thead>
<tr>
<th>Phase</th>
<th>Structure</th>
<th>Space Group</th>
<th>Pearson Symbol</th>
<th>Strukturbericht Designation</th>
</tr>
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<tr>
<td>As</td>
<td>α-As</td>
<td>$R\bar{3}m$</td>
<td>$hR6$</td>
<td>A7</td>
</tr>
<tr>
<td>Ba</td>
<td>bcc</td>
<td>$Im\bar{3}m$</td>
<td>$cI2$</td>
<td>A2</td>
</tr>
<tr>
<td>Ca</td>
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<td>$Fm\bar{3}m$</td>
<td>$cF4$</td>
<td>A1</td>
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<tr>
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<td>$hP2$</td>
<td>A3</td>
</tr>
<tr>
<td>Cu</td>
<td>fcc</td>
<td>$Fm\bar{3}m$</td>
<td>$cF4$</td>
<td>A1</td>
</tr>
<tr>
<td>Dy</td>
<td>hcp</td>
<td>$P6_3/mmc$</td>
<td>$hP2$</td>
<td>A3</td>
</tr>
<tr>
<td>Ga</td>
<td>α-Ga</td>
<td>$Cmca$</td>
<td>$oC8$</td>
<td>A11</td>
</tr>
<tr>
<td>Ge</td>
<td>diamond</td>
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<td>$cF8$</td>
<td>A4</td>
</tr>
<tr>
<td>La</td>
<td>hcp</td>
<td>$P6_3/mmc$</td>
<td>$hP2$</td>
<td>A3</td>
</tr>
<tr>
<td>Lu</td>
<td>hcp</td>
<td>$P6_3/mmc$</td>
<td>$hP2$</td>
<td>A3</td>
</tr>
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Table 3.2: Stable crystal structures of compounds at room temperature considered in this paper [43]

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Table 3.3: Calculated lattice parameters for elements in the Mg-X systems

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Table 3.4: Calculated lattice parameters for binary compounds in the Mg-X systems compared with experiments [43-44]

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<th>c (Å)</th>
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Table 3.5: Calculated enthalpies of formation of the binary compounds compared with the experimental data, COST507 database, and the Miedema’s model

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Figure 3.1 Comparison of calculated enthalpies of formation for the binary compounds in the Mg-X systems with experimental measurements [46-47]. 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).
Figure 3.2 Comparison of calculated enthalpies of formation for the Mg-X binary compounds with the values by the Miedema’s approach [50-51]. The solid line shows unity (y=x) while the dashed lines present an error range of ±5 kJ/mol.
Figure 3.3 Comparison of calculated enthalpies of formation for the binary compounds in the Mg-X systems with the values from COST507 [56]. 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).
Figure 3.4 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.
Figure 3.5 Calculated enthalpies of formation of the Mg-X compounds compared with congruent melting temperatures [56, 58-59] and bulk modulus [60].
Chapter 4 First-principles calculations of elastic, phonon and thermodynamic properties of $\text{Al}_{12}\text{Mg}_{17}$

4.1 Introduction

As lightweight structural materials with a good combination of cast ability and mechanical properties, Al-Mg based alloys have been applied extensively in the field of automotive and aerospace industries [3, 62-63]. For example, the (Mg-(2-6)$\%$Al) alloy and the AZ91 alloy (Mg-9$\%$Al-1$\%$Zn) show good performance at room temperature [3]. In those alloys, the $\gamma$-$\text{Al}_{12}\text{Mg}_{17}$ phase is the essential intermetallic phase and plays an important role in the strengthening of the alloys at room temperature. However, the existence or creep-induced precipitation of the $\gamma$-$\text{Al}_{12}\text{Mg}_{17}$ phase greatly damages the creep property of Al-Mg based alloys at elevated temperatures and hence limits their applications [64]. Although there are many experimental studies on crystal structure and precipitation of $\text{Al}_{12}\text{Mg}_{17}$ in the Al-Mg system in the past decades [65-67], the thermodynamic and mechanical properties of this phase are still incomplete.

The present work aims to investigate in detail the structure, mechanical, phonon, and thermodynamic properties of $\text{Al}_{12}\text{Mg}_{17}$ as well as compare with the reference elements fcc-Al and hcp-Mg from the first-principles calculations within the density functional theory [14]. We first systematically investigate the structural properties of $\text{Al}_{12}\text{Mg}_{17}$. By using the supercell method [68], the first-principles phonon calculations of those phases are carried out. The phonon density of states (DOS’s) are subsequently used to calculate
the vibrational contributions to the total free energy and the finite temperature thermodynamic properties. As indicated by Wang et al. [19], the thermal electronic contributions are important for metals, and we thus include it in the present work. The thermodynamic properties of Al, Mg and Al$_{12}$Mg$_{17}$, such as heat capacity, and thermal expansion are then predicted and compared with available experimental data in the literature. Furthermore, the temperature dependency of single crystal elastic constants and correspondingly bulk modulus, shear modulus, Young’s modulus, and Poisson’s ratio are predicted and compared with the available experiments. It is expected this study will provide useful guidance for both analysis and design of the Al-Mg based alloys containing Al$_{12}$Mg$_{17}$.

The rest of the paper is organized as follows. In Sec. 2, the theories of the calculations of elastic, phonon, and thermodynamic properties are introduced. The computational framework and simulation details are described in Sec 3. In Sec. 4, we discuss the obtained thermal, physical, and mechanical properties of Al, Mg and Al$_{12}$Mg$_{17}$ and finally lead to the conclusion of the present work.

4.2 Theory

The Helmholtz free energy of a system, $F$, at temperature $T$ and volume $V$ is given by [19-21]:

Equation 4.1 $\quad F(V,T)=E_0(V)+F_{\text{vib}}(V,T)+F_{\text{el}}(V,T)$
where \( E_0(V) \) is the first-principles static energy at 0 K and volume \( V \), \( F_{\text{vd}}(V,T) \) the lattice vibrational contributions to the free energy, and \( F_{\text{el}}(V,T) \) the thermal electronic contributions. Within the quasiharmonic approximation, the anharmonic effect is accounted by the harmonic approximation at several volumes. From the phonon density of states, the lattice vibrational free energy can be calculated [19-21].

In the present work, the elastic stiffness \( c_{ij} \)'s are calculated based on the stress-strain method [28]. This methodology involves a set of strains \( \varepsilon = (\varepsilon_1 \varepsilon_2 \varepsilon_3 \varepsilon_4 \varepsilon_5 \varepsilon_6) \) where \( \varepsilon_1, \varepsilon_2, \) and \( \varepsilon_3 \) refer to the normal strains, and \( \varepsilon_4, \varepsilon_5, \varepsilon_6 \) the shear strains. Set of strains are imposed on a crystal with lattice vectors \( \mathbf{R} \) specified in the Cartesian coordinates. After the strains are applied, the deformed lattice vectors \( \mathbf{R}' \) are obtained. Using the matrix notation for elasticity and the general Hooke law, the stresses \( (\sigma) \) cased by the application of strains \( (\varepsilon) \) are related by the following:

\[
\text{Equation 4.2} \quad \sigma = \varepsilon C
\]

where \( C \) is the \( 6 \times 6 \) elastic stiffness matrix with elements \( c_{ij} \)'s in Voigt's notation. \( \sigma \) can be obtained by first-principles calculations. From \( n \) sets of strains and the resulting stresses, the elastic constants \( C \) can be calculated by:

\[
\text{Equation 4.3} \quad C = \varepsilon^{-1} \sigma
\]

where ‘-1’ represents the pseudo-inverse, which can be solved by the singular value decomposition method. The minimum independent sets of strains are related to the symmetry of crystals. i.e. two for cubic structures (Al and Al\(_{12}\)Mg\(_{17}\)) and three for
hexagonal (Mg) structures. The following independent set of strains is applied in the present work:

\[
\begin{pmatrix}
  x & 0 & 0 & 0 & 0 \\
  0 & x & 0 & 0 & 0 \\
  0 & 0 & x & 0 & 0 \\
  0 & 0 & 0 & x & 0 \\
  0 & 0 & 0 & 0 & x
\end{pmatrix}
\]

Equation 4.4

For accuracy test purpose, elastic constants with the 0 K equilibrium volume were performed under additional sets of strains with \( x = \pm 0.007, \pm 0.01 \) and \( \pm 0.013 \) to evaluate the numerical error. For calculations at other volumes, two strains with \( x = \pm 0.01 \) are chosen. More details about the stress vs. strain method and its applications to determine \( c_{ij} \)'s can be found in: e.g., Al\(_2\)O\(_3\) [28], Mg-based alloys [69-70], Ni [71], BiFeO\(_3\) [72] and Fe\(_3\)C [73].

The temperature dependence of elastic stiffness is obtained by combination of the volume dependence of elastic stiffness and the temperature dependence of volume from the minimization of Helmholtz free energy (Equation 4.1) at given temperatures. First, we calculate \( c_{ij}(V) \) at different volumes. Second, the equilibrium volume at various temperatures is determined from Helmholtz free energy as described in Equation 4.1, with both lattice vibrational and thermal electronic contributions included. The combination of \( c_{ij}(V) \) and \( V(T) \) leads to the temperature dependence of elastic constants \( c_{ij}(T) \).
In the above procedure, the elastic stiffness coefficients are obtained under isothermal conditions \( c_{ij}^T \). However, most of the experimental elastic stiffness coefficients are measured by resonant vibrations under isentropic conditions \( c_{ij}^S \). To make them comparable, \( c_{ij}^T \) could be converted to \( c_{ij}^S \) according to the relations discussed by Davies [74] as follows:

\[
Equation\ 4.5\quad c_{ij}^S = c_{ij}^T + \frac{T \lambda_i \lambda_j}{\rho C_e} \quad c_{ij}^T
\]

\[
Equation\ 4.6\quad \lambda_i = -\sum_j \alpha_j c_{ij}^T
\]

where \( \rho \) is the density, \( C_e C_e \) the heat capacity under constant strain, and \( \alpha_j \) the thermal expansion. The conversion from \( c_{ij}^T \) to \( c_{ij}^S \) has been applied to both pure metallic elements and binary alloys like Mg-3wt.%Al, Mg-9wt.%Al [75], fcc-Cu, Al, NiAl [76], and bcc-Ta [77].

### 4.3 Computational details

The electronic structure and total energies of Al, Mg and Al\(_{12}\)Mg\(_{17}\) are calculated by using the projector-augmented wave (PAW) method as implemented in VASP [78-79]. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [80] is used for the exchange-correlation functional. The electronic configurations considered are \( 3s^23p^1 \) for Al, and \( 3s^2 \) for Mg, respectively. The crystal structure data of fcc-Al, hcp-Mg, and Al\(_{12}\)Mg\(_{17}\) are summarized in Table 4.1 [43]. We use the energy cutoff of 350 eV,
i.e., 1.3 times the highest energy cutoff between Al and Mg suggested by VASP. The Monkhorst-Pack scheme is used for the Brillouin-zone integrations [42] of Al and Al\textsubscript{12}Mg\textsubscript{17}, while Γ centered \( k \)-mesh is used for Mg. The phonon calculations are carried out by the supercell method [68, 81] as implemented in the ATAT code [68]. More detailed settings for first-principles calculations are shown in Table 4.1, including (i) Pearson’s symbol and the space group; (ii) the size of \( k \)-mesh for electronic structure calculations; (iii) the number of atoms in the supercell for phonon calculations; (iv) the size of \( k \)-mesh in the perturbed supercell for phonon calculations; (v) the setting of displacement from the equilibrium atomic position; and (vi) the cutoff distance used to fit the force constants. We carried out systematic tests in terms of the above first-principles calculations parameters and found out that the calculated elastic stiffness constants are well converged.

4.4 Results and discussion

4.4.1 Structure and vibrational properties

The total energy as a function of volume is calculated and fitted by the four parameters modified Birch-Murnaghan Equation of state [82-85]:

Equation 4.7 \[ E(V) = a + bV^{-1/3} + cV^{-2/3} + dV^{-1} \]
where $a$, $b$, $c$, and $d$ are fitting parameters. Herein the equilibrium volume, bulk modulus and its pressure derivative for Al$_{12}$Mg$_{17}$ at 0 K are derived and listed in Table 4.2. All predicted properties are in good agreements with experimental measurements.

To validate the first-principles phonon calculations, one of the most important steps is to calculate the phonon dispersions. The calculated phonon dispersions of Al and Mg agree with experimental measurements well. For Al$_{12}$Mg$_{17}$, no experimental data is available. Figure 4.1 shows the phonon dispersion relations for Al$_{12}$Mg$_{17}$ at their experimental equilibrium volumes at 298 K.

### 4.4.2 Thermodynamic properties

Starting from both the electronic and phonon DOS’s at several different volumes, the free energies ($F$) can be predicted based on the quasiharmonic approximation, i.e., Equation 4.1. In this work, the first-principles calculations are carried out at $P=0$ and hence $PV=0$, as a result, the Helmholtz free energy is equal to the Gibbs energy. The lattice vibrational entropy and thermal electronic entropy can be calculated accordingly, and the summation of these two parts gives the total entropy.

Figure 4.2 shows the predicted $S$ and $G$, where the reference state for $H$ is the commonly used setting in the thermochemistry community, i.e., at 298.15 K and 1 bar for the stable structure of pure elements. It is shown that there is only slight difference between the calculated values with and without the thermal electronic contribution, and
the value of S taken into thermal electronic contribution is slightly higher. Using the results shown in Figure 4.2, the enthalpy of formation for Al₁₂Mg₁₇ at 298 K can be predicted as shown in Table 4.2. Experimentally determined values by Brown and Pratt [86] and by Predel and Hulse [87] do not agree with each other. Our calculated value falls between these two sets of data and has a reasonable agreement with the value obtained by Zhong et al. [88] with the difference about 0.9 kJ/mol-atom. Table 4.2 also presents the calculated structure parameters at 298K compared with available experiments [43, 86-88].

Once the phonon spectrum over the entire Brillouin zone is available, the vibrational heat capacity (\(C^{\text{vib}}_V\)) and the thermal electronic contribution to heat capacity (\(C^{\text{el}}_V\)), both at constant volumes, can be obtained. Consequently, the heat capacity at constant pressure, \(C_p\), can be computed as

\[
C_p = C^{\text{vib}}_V + C^{\text{el}}_V + \alpha_v \times BVT
\]

where \(\alpha_v\) is the volume thermal expansion coefficient, and \(B\) the bulk modulus. Table 4.2 shows the predicted heat capacities of Al, Mg and Al₁₂Mg₁₇ at 298 K in comparison with experiments [43, 86-88], \(C_p\) of Al, Mg and Al₁₂Mg₁₇ with and without the thermal electronic contributions are plotted in Figure 4.3 where we can find a good agreement between the calculated results and the experimental data for both Al and Mg. Considering the contributions to the heat capacity from the terms in Equation 4.8, \(C^{\text{vib}}_V\) tends to the classical constant 3\(R\) while \(C^{\text{el}}_V\) keeps increasing with increasing temperature. It could be seen that the contribution from \(C^{\text{el}}_V\) increases with increasing temperature. At 700 K,
there are 2.65%, 2.75% and 1.81% differences of $C_p$ with and without $C_{el}^{v}$ for Al, Mg and Al$_{12}$Mg$_{17}$, respectively.

The linear thermal expansion coefficient $\alpha_L$ at a fixed pressure ($P=0$ in the present work) is given by:

$$\alpha_L = \frac{1}{3} \alpha_v = \frac{1}{3V} \left( \frac{\partial V}{\partial T} \right)_P$$

The calculated linear thermal expansion coefficients with both vibrational and thermal electronic contributions are shown in Table 4.2 at 298 K, and plotted in Figure 4.4 along with the experiments [89-90]. The thermal electronic contribution to the thermal expansion coefficient is relatively small, with which the difference is about 1.18%, 1.51%, and 0.89% for Al, Mg and Al$_{12}$Mg$_{17}$ at 700 K, respectively. The calculated thermal expansions of both Al and Mg are higher than those of experimental measurements, which was also noticed in the previous calculations [19], and the disparity is larger at higher temperatures probably due to the limitations of the current quasiharmonic approximation. Grabowski et al. [91] recently concluded that the anharmonic contribution to the free energy has a significant influence on thermal expansion coefficient at high temperatures, and quantitatively predicted anharmonic contribution to $\alpha$ is shifted downward by -6% at 700K for Al. Another reason of this disparity at high temperatures is that the GGA calculation underestimates bulk modulus and hence overestimates thermal expansion.

The isothermal bulk modulus can be calculated as a function of temperature as:
\[ B^T(V, T) = \frac{1}{V} \left( \frac{\partial^2 F(V, T)}{\partial V^2} \right)_T \]

Denoting \( \frac{C_p}{C_v} \) by \( \gamma \), we have \( \gamma B^T = B^S \), and the ratio of \( C_p \) to \( C_v \) is the ratio of the isentropic bulk modulus \( (B^S) \) to the isothermal bulk modulus \( (B^T) \). From this, we can conclude that \( B^S \) is always greater than \( B^T \), and they are equal at 0 K. The temperature dependence of both \( B^T \) and \( B^S \) for Al, Mg and Al\(_{12}\)Mg\(_{17}\) are shown in Figure 4.5, and the calculated results at 298 K are listed in Table 4.2. The calculated bulk modulus with and without thermal electronic contribution is almost identical (less than 0.2% for all the three phases at 700K) so the latter case is excluded in Figure 4.5, different from previous figures (Figs. 4.3~4.4) where both cases are presented. We note that the ratio of the bulk modulus \( B/B_0 \) of Al\(_{12}\)Mg\(_{17}\) decreases the least with temperature, which is consistent with the fact that Al\(_{12}\)Mg\(_{17}\) has the smaller thermal expansion than Al and Mg.

### 4.4.3 Elastic properties

The calculated \( c_{ij}^T \)'s and \( c_{ij}^S \)'s of Al, Mg at 298 K and the values for Al\(_{12}\)Mg\(_{17}\) at both 0 K and 298 K are listed in Table 4.3. Note that \( c_{ij}^T \) and \( c_{ij}^S \) are equal at 0 K from Equation 4.5. Table 4.3 also list the absolute uncertainty for each property of Al\(_{12}\)Mg\(_{17}\) at 0 K, which is treated as the maximum value of \( |A_i - A_{avg}| \), where \( A_i \) is the calculated value and \( A_{avg} \) the average value. We also compute the relative deviation through

\[ \sqrt{\frac{1}{3} \sum \left( \frac{c_i - c_{avg}}{c_{avg}} \right)^2} \]

where \( c_i \) is the calculated elastic constant from each \( |x| \), \( c_{avg} \) the
average value. The relative deviations are 0.4%, 1.3%, and 4.7%, for \( c_{11}, c_{12} \) and \( c_{44} \) at 0 K, respectively, indicating the good predictions of \( c_{ij} \). For both cubic and hcp phases, we note that that in all cases \( c_{ij}^T < c_{ij}^S \) except isothermal \( c_{44}^T \) and isentropic \( c_{44}^S \) are equal. In Table 4.3, the corresponding experimental data for Al [92], Mg [92], as well as the previous calculation for Al\(_{12}\)Mg\(_{17}\) [93] are included for comparison. The elastic moduli of these phases, bulk modulus (\( B \)) and shear modulus (\( G \)), can be calculated using single crystal constants by the following equations:

\[
B = \left( \frac{c_{11} + 2c_{12}}{3} \right)
\]

Equation 4.11

\[
G = \left( \frac{c_{11} - c_{12} + 3c_{44}}{5} \right)
\]

Equation 4.12

where \( c_{11} = (c_{11} + c_{22} + c_{33})/3 \), \( c_{12} = (c_{12} + c_{13} + c_{23})/3 \), and \( c_{44} = (c_{44} + c_{55} + c_{66})/3 \). It is worth mentioning that the value of bulk modulus derived from elastic constants by Equation 4.11 has a good agreement with the ones obtained by Equation 4.10. (Table 4.2).

Furthermore, Table 4.3 also summarizes the properties derived from calculated elastic constants of Al, Mg and Al\(_{12}\)Mg\(_{17}\) at 298 K, including Young’s modulus, Poisson’s ratio, and \( B/G \) ratio. Young’s modulus (\( E \)), the evaluation of the stiffness of the solid, is defined as \( E = \frac{(9BG)}{(G + 3B)} \). Al\(_{12}\)Mg\(_{17}\) has a larger value of Young’s modulus than both Al and Mg, indicating that Al\(_{12}\)Mg\(_{17}\) is stiffer than both pure Al and Mg. Poisson’s ratio \( \nu \) is employed to indicate the stability of the crystal against shear stress. The calculated results show that compared with the Al and Mg, Al\(_{12}\)Mg\(_{17}\) has a lower tenacity since it has a smaller value of Poisson’s ratio \( \nu \). It is also known that \( B/G \) introduced by Pugh [94] is associated with ductility (brittleness), where \( B \) is considered as the resistance to fracture, and \( G \) the resistance to plastic deformation. The critical value which separates ductile and
brittle is about 1.75. The calculated results show that both Al and Mg are ductile, while
Al\textsubscript{12}Mg\textsubscript{17} is brittle. We obtained the similar results of elastic constants for Al and Mg
compared with the experimental ones, while significantly large discrepancy for Al\textsubscript{12}Mg\textsubscript{17}
from the calculations by Wang et al. [93]. As expected, the derived mechanical properties
from elastic constants are also notable different from the previous calculation. For
example, Wang et al. [93] calculated \( B/G = 2.19 \) and hence predicted Al\textsubscript{12}Mg\textsubscript{17} to be
ductile. However, our prediction of the brittleness of Al\textsubscript{12}Mg\textsubscript{17} is confirmed by several
experimental observations [95-97].

To obtain a better understanding of the mechanical properties of Al\textsubscript{12}Mg\textsubscript{17}, the
electronic structure is calculated and shown in Figure 4.6 as well as the total density of
states of Al\textsubscript{12}Mg\textsubscript{17} and its angular-moment decomposition plots for Mg and Al. The total
densities of states for Al and Mg in Al\textsubscript{12}Mg\textsubscript{17} are compared with the ones in pure Al and
Mg. The comparison reveals that the DOS below the Fermi level for the Al atoms in
Al\textsubscript{12}Mg\textsubscript{17} become more localized than those in pure Al. This observation suggests that
hybridization between Al and Mg increases the bonding directionality of Al, implying
that the covalent-like bonding existed in Al\textsubscript{12}Mg\textsubscript{17}. As the localization of bonding
electrons is the dominant factor in governing the brittleness of the materials, the brittle
behavior of Al\textsubscript{12}Mg\textsubscript{17} can be explained.

Figure 4.7 shows temperature dependences of both \( c^T_{ij} \) and \( c^S_{ij} \) of Al\textsubscript{12}Mg\textsubscript{17}. Values of
elastic constants decrease monotonically with the increase of temperature. Two sets of
bulk modulus, shear modulus, and Young’s modulus as a function of temperature derived
by \( c^T_{ij} \) and \( c^S_{ij} \), respectively, are shown in Figure 4.8. It is noted that the temperature
dependence of bulk modulus derived by elastic constants is similar as the ones from Equation 4.10 as in Figure 4.5, showing a consistent estimation of the compressibility of this phase.

4.5 Conclusions

In this work, a comprehensive analysis of the structural, electronic, and vibrational properties of Al$_{12}$Mg$_{17}$ has been performed from first-principles. The calculated equilibrium lattice constants of all phases are in good agreement with experimental data. The thermodynamic properties of Al, Mg and Al$_{12}$Mg$_{17}$ are calculated within the quasiharmonic approximation, and the thermal electronic contribution due to thermal excitation is considered. The finite temperature thermodynamic properties of thermal expansion, heat capacities, and bulk modulus are calculated for all the phases. We have studied the temperature dependence of the single crystal elastic constants as well as polycrystalline elastic properties ($B$, $G$, $E$ and $\nu$) from first-principles. They indicate that Al$_{12}$Mg$_{17}$ is stiffer than Al and Mg and has a lower tenacity with a smaller Poisson’s ratio. In contradiction to the previous elastic constant calculation [93], we predicted that Al$_{12}$Mg$_{17}$ is brittle. We have demonstrated that the brittle behavior of Al$_{12}$Mg$_{17}$ is due to the localization of bonding electrons of Al. Our result of brittleness of Al$_{12}$Mg$_{17}$ is supported by the experimental observations [95-97].
Table 4.1 Details of the first-principles and phonon calculations, including the Pearson’s symbol and the space group of pure elements and compound [43], k-mesh used to calculate the electronic and phonon structures, the number of atoms in the supercell (SC) to perform the phonon calculation, the displacement (Δr) of disturbed atom from its equilibrium position, and the cutoff distance (R_{cut}) used for the fitting range of force constants.

<table>
<thead>
<tr>
<th>Pearson symbol</th>
<th>Space group</th>
<th>k-mesh electron</th>
<th>SC</th>
<th>k-mesh phonon</th>
<th>Δr (Å)</th>
<th>R_{cut} phonon (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>cF4</td>
<td>Fm̅3m</td>
<td>35 × 35 × 35</td>
<td>32</td>
<td>6 × 6 × 6</td>
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</tr>
<tr>
<td>Mg</td>
<td>hP2</td>
<td>P6₃/mmc</td>
<td>25 × 25 × 15</td>
<td>36</td>
<td>6 × 6 × 6</td>
<td>0.1</td>
</tr>
<tr>
<td>Al_{12}Mg_{17}</td>
<td>cI58</td>
<td>I₄̅3m</td>
<td>6 × 6 × 6</td>
<td>58</td>
<td>4 × 4 × 4</td>
<td>0.1</td>
</tr>
</tbody>
</table>
Table 4.2 Calculated properties of Al$_{12}$Mg$_{17}$ at 0 K and 298K (with both phonon and thermal electronic contributions). The results include lattice parameters ($a_0$), equilibrium volume ($V$), bulk modulus ($B_0$), pressure derivative of bulk modulus ($B_0'$), enthalpy of formation $\Delta H$, heat capacity ($C_p$), and linear thermal expansion ($\alpha_L$).

<table>
<thead>
<tr>
<th></th>
<th>0 K</th>
<th>298 K</th>
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</thead>
<tbody>
<tr>
<td>$a_0$ (Å)</td>
<td>10.53</td>
<td>10.54$^a$</td>
</tr>
<tr>
<td>$V_0$ (Å$^3$/atom)</td>
<td>20.15</td>
<td>20.19</td>
</tr>
<tr>
<td>$\Delta H$ (kJ/mol-atom)</td>
<td>-2.64</td>
<td>-3.78$^c$, -0.97$^d$, -3.58$^e$</td>
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<tr>
<td>$B_0$ (GPa)</td>
<td>49.53</td>
<td>49.6$^b$</td>
</tr>
<tr>
<td>$B_0'$</td>
<td>4.44</td>
<td></td>
</tr>
<tr>
<td>$B^T$ (GPa)</td>
<td></td>
<td></td>
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<tr>
<td>$B^s$ (GPa)</td>
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<tr>
<td>$C_p$ (J mol$^{-1}$K$^{-1}$)</td>
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<tr>
<td>$\alpha_L$ (10$^{-6}$K$^{-1}$)</td>
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</table>

$^a$The experimental lattice parameters are reported at room temperature [43].

$^b$Calculated value [93].

$^c$Experimental data by Brown and Pratt [86].

$^d$Experimental data by Predel and Hulse [87].

$^d$Calculated value from reference [88].
Table 4.3 Calculated $c_{ij}^T$'s and $c_{ij}^S$'s (GPa) of Al, Mg at 298 K, in comparison with experimental data. Calculated $c_{ij}^T$'s and $c_{ij}^S$'s (GPa) of Al$_{12}$Mg$_{17}$ at both 0 K and 298 K compared with previous calculation.

<table>
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<tr>
<th></th>
<th>$c_{11}$</th>
<th>$c_{12}$</th>
<th>$c_{13}$</th>
<th>$c_{33}$</th>
<th>$c_{44}$</th>
<th>$B$</th>
<th>$G$</th>
<th>$E$</th>
<th>$V$</th>
<th>$B/G$</th>
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<td>$c_{ij}^T(298)$</td>
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<td></td>
<td>103.1</td>
<td>56.1</td>
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<td>71.9</td>
<td>0.33</td>
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<td>$c_{ij}^S(298)$</td>
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<td>29.3</td>
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<td>27.2</td>
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<td>0.33</td>
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<td></td>
<td>$c_{ij}^T(298)$</td>
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<tr>
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<td>53.8</td>
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<td>33.9</td>
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<td>59.28</td>
<td>25.9</td>
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<td>61.35</td>
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<td>35.3</td>
<td>17.2</td>
<td>44.5</td>
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<tr>
<td>Al$<em>{12}$Mg$</em>{17}$</td>
<td>$c_{ij}^T(298)$</td>
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<td>31.6</td>
<td>77.8</td>
<td>0.23</td>
<td>1.52</td>
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<td>30.7</td>
<td>49.4</td>
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<td>78.1</td>
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<td>$c_{ij}^T(0)$</td>
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<tr>
<td></td>
<td>97.7±0.8</td>
<td>28.1±0.5</td>
<td>31.4±1.1</td>
<td>51.3±0.4</td>
<td>32.7±1.0</td>
<td>81.0±2.2</td>
<td>0.24±0.01</td>
<td>1.57±0.04</td>
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<td></td>
<td>Ref.\textsuperscript{b}</td>
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<tr>
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<td>20</td>
<td>48.3</td>
<td>22</td>
<td>57.3</td>
<td>0.3</td>
<td>2.19</td>
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</tr>
</tbody>
</table>

\textsuperscript{a} Reference [92], the experimental elastic constants at room temperature.

\textsuperscript{b} Reference [93], the calculated value at 0 K.
Figure 4.1 Calculated phonon dispersion curves for Al$_{12}$Mg$_{17}$ pertaining to the equilibrium lattice parameters at 298 K.
Figure 4.2 Thermodynamic properties: entropy ($S$), Gibbs energy ($G$) for $\text{Al}_{12}\text{Mg}_{17}$. The solid lines and dot lines are the calculated results with (Ph+El) and without (Ph) the thermal electronic contributions, respectively.
Figure 4.3 Temperature dependence of heat capacity of Al, Mg, and Al\textsubscript{12}Mg\textsubscript{17}. Solid and dashed curves show the calculated $C_p$, with and without thermal electronic contribution, respectively. Circles represent experimental data [89].
Figure 4.4 Temperature dependence of lineal thermal expansion for Al, Mg, and Al$_{12}$Mg$_{17}$. Solid and dashed curves show the calculated thermal expansion, with and without thermal electronic contribution, respectively. Circles [89] and triangles [90] represent experimental data.
Figure 4.5 Temperature dependence of bulk modulus for Al, Mg, and Al$_{12}$Mg$_{17}$. Solid and dashed curves show the $B^T$ and $B^S$, respectively. Circles [89] and triangles [90] represent experimental data.
Figure 4.6 Calculated total densities of states (DOSs) for $\text{Al}_{12}\text{Mg}_{17}$ and angular-momentum decomposition of Al and Mg. The solid lines are for Al or Mg in $\text{Al}_{12}\text{Mg}_{17}$ bulk and dashed lines are for pure Al or Mg bulk. The dotted line dictates Fermi level.
Figure 4.7 Temperature dependence of elastic constants for Al$_{12}$Mg$_{17}$. Solid and dashed curves show the calculated $c_{ij}^T$ and $c_{ij}^S$, respectively.
Figure 4.8 Calculated bulk modulus, shear modulus, and Young’s modulus as a function of temperature. Solid and dashed curves show the results derived from $c^T_{lm}$ and $c^S_{lm}$, respectively.
Chapter 5  Thermodynamic modeling of Mg–Ca–Ce system by combining first-principles and CALPHAD method

5.1  Introduction

Calcium and cerium are two important alloying elements used in magnesium alloys. They contribute to the performance improvement in the creep resistance and strength of Mg alloys at elevated temperatures [98]. To understand the effects of Ca and Ce on the phase stability of magnesium alloys, a complete thermodynamic description of the Mg-Ca-Ce system is desirable. Of the three constituent binary systems of the ternary system only thermodynamic modeling of Ca-Mg [36] and Ce-Mg [99] were previously carried out, but the thermodynamic description of the Ce-Mg system was not satisfactory. In particular, the predicted enthalpies of formation of Ce-Mg compounds did not agree well with the experimental data, in addition to the significant discrepancies between prediction and experiment for the solubility ranges of fcc and bcc phases. There was no existing thermodynamic description for the Ca-Ce system.

In the present work, the thermodynamic description for the Ca-Ce binary system is obtained through the CALPHAD approach, combining the available experimental data in the literature and the first-principles results calculated in this work. The thermodynamic description for the Ce-Mg binary system was updated using the CALPHAD approach by
incorporating additional experimental data [100]. The resulting thermodynamic description for the Mg-Ca-Ce system was then developed by combining the derived databases of the Ca-Ce and Ce-Mg systems from the present work with that of the Ca-Mg system in the literature [36].

5.2 First-principles calculations for bcc Ca-Ce solution

The isostructural enthalpies of mixing for the bcc Ca-Ce solid solutions were calculated by means of density functional theory [14]. Random solid solution phases could not be treated precisely with the implementation of the first-principles method developed for ordered structures [78-79, 101-102]. In the present work, the random structure was mimicked by a so-called special quasi-random structure (SQS). The concept of SQS was first proposed by Zunger et al. [24-25] for calculating the fcc solutions. The SQS possessed, within the given interaction ranges, the local pair and multi-site correlation functions of the corresponding random alloys. Jiang et al. and Shin et al. extended this approach to the bcc [26] and hcp [33] structures, respectively. In the present work, 16 atoms SQS [26] were employed to model the bcc Ca-Ce solid solution at three compositions of 0.25 0.50 and 0.75 mole fractions of Ce, respectively.

We employed the generalized gradient approximation (GGA) together with the projector augmented-wave (PAW) pseudo-potentials as implemented in the Vienna ab initio simulation package (VASP) [78-79, 101-102]. For the GGA exchange-correlation energy, we used the Perdew–Wang parameterization [80] (GGA-PW91). A constant cutoff energy of 390 eV was used. Due to the structure instability of bcc solutions only the cell volume was relaxed. The Monkhorst-Pack scheme was used for the Brillouin-
zone integrations [103]. 18×18×18 k-point was used for pure elements Ca and Ce, 8×8×6 for Ca$_{0.25}$Ce$_{0.75}$ and Ca$_{0.75}$Ce$_{0.25}$ bcc solutions, and 6×6×10 for Ca$_{0.50}$Ce$_{0.50}$. These settings of k-point roughly correspond to a 5,000 k-point meshes per reciprocal-atom. For Ca, only the 4s shell was treated as valence state. For Ce, the semi-core 5s5p shells were included as valence states. On selecting the potential for Ce, an additional test was tried between the one that had one electron frozen to the 4f state and the one that did not have electrons frozen to the 4f state. It was found that using the potential that did not have one electron frozen to the 4f state was essential to yield reasonable miscibility gap by the present modeling. In addition, more tests were performed for the bcc solutions with and without considering the magnetic contribution. It was found that considering the magnetic contribution was necessary. The calculated total energies of the bcc SQS together with experimental data [104-105] are given in Table 5.1. The derived enthalpies of mixing with the magnetic contribution are plotted in Figure 5.1.

### 5.3 Experimental data and previous modeling in the literature

The Ca-Mg system modeled by Zhong et al. [36] was accepted in the present work. The Ca-Ce binary system was previously studied by Zverev [106], Trombe [107], and Gschneider and Verkade [108]. Zverev[106] reported the liquidus and the mutual solubility of calcium in cerium using 99.5% Ce and 99.9% Ca. Trombe [107] observed that 1% Ca prevented Ce from forming fcc-Ce on cooling through the stabilization of bcc-Ce. The monotectic and eutectic temperatures of this system were evaluated by
Gschneidner and Verkade [108]. No thermochemical data of the Ca-Ce system has been reported in the literature.

Nayeb-Hashemi and Clark [109] reviewed experimental data for the Ce-Mg system. Crystal structure data for the Ce-Mg and Ca-Ce systems [110-111] are listed in Table 5.2. Based on the reviewed experimental data, Cacciamani et al. [99] evaluated the thermodynamic model parameters of the Ce-Mg system. However, the phase equilibria on the Ce-rich side and the liquidus of Mg$_{41}$Ce$_5$ were not well studied. More recently, some new experimental data on the Mg-rich and Ce-rich sides were reported in the literature [100], which could not be reproduced well by the exiting thermodynamic modeling. The Ce-Mg system thus needs to be remodeled in order to improve the agreement with experiments.

The Ce-Mg system was first studied by Vogel [112] using Ce with purity of 93.5 wt.%. Later, the phase equilibria in the composition range of 18-100 at.% Ce were re-investigated by using Ce with purity of 99.7 wt.% [113]. Liquidus curves across the phase diagram were also measured by Haughton and Schofield [114], Drits et al. [115], and Wood and Cramer [116]. The liquidus temperatures obtained by Wood and Cramer [116] is in closer agreement with those from Haughton and Schofield [114] but higher than both data from Haughton and Schofield [114] and Drits et al. [115]. In the present work, we adopted the experimental data of liquidus temperatures for alloys from 0 to 10 at.% Ce investigated by Haughton and Schofield [114] using metallography; and from 0 to 15 at.% Ce obtained by Wood and Cramer [116] by differential thermal analysis, metallography, and X-ray diffraction methods. The solid solubility of Ce in Mg was investigated by Haughton and Schofield [114]; by Weibke and Schmidt [117] using
thermoresistometry; by Park and Wyman [118] using X-ray lattice parameter measurements; and by Drits et al. [115], Crosby and Fowler [119] using resistivity and metallography analysis. The activity of Mg in liquid between 1083K and 1133K was determined by Bayanov et al. [120] using vapor pressure measurements. Pahlman and Smith [121] measured the enthalpies of formation of intermetallic compounds in the system. More recently, Saccone et al. [100] prepared the Mg-94 at.% Ce alloys to determine phase equilibria between liquid and bcc, between fcc and bcc; and between fcc and MgCe by Smith thermal analysis, which were not included in the previous modeling work by Cacciamani et al. [99].

5.4 Thermodynamic models

In this section, the thermodynamic models of two types of phases, i.e., solution phases and intermetallic compounds are presented.

5.4.1 Solution phases: liquid, fcc, bcc and hcp.

The Gibbs energy functions of pure Ca, Ce and Mg are taken from the SGTE database [122]. The liquid, fcc, bcc and hcp solution phases are described by means of the one-sublattice model (Ca, Ce, Mg) [123]. The molar Gibbs energy can be expressed as following:

Equation 5.1
\[ G_m^\theta = \sum x_i \phi_i^\theta + RT \sum x_i \ln x_i + \phi G_m^\theta \]

Equation 5.2
\[ \phi G_m^\theta = \sum_{i \neq j} x_i x_j \sum_{k=0}^n L_{i,j}^k (x_i - x_j)^k + x_{Ca} x_{Ce} x_{Mg} I_{Ca,Ce,Mg}^\theta \]
where $^0 \text{G}_i$ is the molar Gibbs energy of the pure element i with the structure $\Phi$, $^{\text{ex}} \text{G}_i$ the excess Gibbs energy expressed in the Redlich-Kister polynomial [124] as Equation 5.2: 

$$ k L_{i,j}^\phi $$

the $k$th binary interaction parameter between i and j, which may depend on temperature as A+BT with A and B being the model parameters. Due to the lack of experimental data in the ternary system, the ternary interaction parameter $I_{i,j,k}^\phi$ is assumed to be zero.

### 5.4.2 Intermetallic phases

The compounds in the Ce-Mg system, Mg$_{12}$Ce, Mg$_{17}$Ce$_2$, Mg$_{41}$Ce$_5$, Mg$_3$Ce, Mg$_2$Ce, and MgCe, are modeled as stoichiometric compounds using two-sublattice models, i.e., (Mg)$_a$(Ce)$_b$. Their Gibbs energy functions are described as:

$$ G^{Mg,Ce}_a = a^0 G_{Mg}^{hcp} + b^0 G_{Ce}^{fcc} + \Delta_f G^{Mg,Ce}_a $$

where $^0 G_{Mg}^{hcp}$ and $^0 G_{Ce}^{fcc}$ are the molar Gibbs energies of the pure element hcp Mg and fcc Ce, respectively. $\Delta_f G^{Mg,Ce}_a$ is the Gibbs energy of formation of the compound. It can be written as: $A^{Mg,Ce}_a + B^{Mg,Ce}_a T$, where $A^{Mg,Ce}_a$ and $B^{Mg,Ce}_a$ are the enthalpy and entropy of formation of the compound.
5.5 Evaluation of model parameters

All model parameters were evaluated using the Parrot module in Thermo-Calc software [125]. This program is able to consider all types of experimental data simultaneously. It works by minimizing the sum of errors of the collected experimental and first-principles data with given weights. The weight is chosen and adjusted based on the data uncertainties given in the original literature and the authors’ judgment by analyzing the experimental procedure and considering all data at the same time. The complete thermodynamic descriptions thus obtained are shown in Table 5.3 and Table 5.4 for the Ca-Ce and Ce-Mg binary systems, respectively. The reference state of the Gibbs energy of individual phase is the stable element reference (SER), i.e., the enthalpies of the pure elements in their stable states at 298.15K and 1 bar.

In the Ca-Ce system, the evaluation of modeling parameters was started with the liquid miscibility gap and followed by the bcc phase. The thermodynamic parameter $^0L$ of the liquid phase requires a positive value due to the miscibility gap, and was evaluated by using the experimental liquidus data. The thermodynamic parameters of the bcc phase were evaluated by combining the experimental data, including liquidus and monotectic, and the enthalpies of mixing from first-principles calculations. The parameters of the fcc and hcp phases were set arbitrarily to be the same as in the bcc phase as it was shown that fcc, bcc, and hcp have similar enthalpies of mixing [33].

The evaluation of model parameters in the Ce-Mg system began with the liquid phase followed by the bcc phase, and then the six stoichiometric compounds, fcc and hcp solution phases. Special attention was paid to liquid-bcc and bcc-fcc phase boundaries as they were not well reproduced by Cacciamani et al. [99]. The thermodynamic parameters
of the stoichiometric compounds were obtained by experimental enthalpies of formation and liquidus data.

5.6 Results and discussions

The evaluated parameters of the Ca-Ce system in the present work are listed in Table 5.3. The calculated phase diagram using these parameters is shown in Figure 5.2. Most of the experimental liquidus data were well reproduced. The calculated temperatures and phase compositions of the invariant reactions in the Ca–Ce system are listed in Table 5.5; the available experimental data are included for comparison. The degree of agreement is represented by the relative deviation formula, $\sqrt{\frac{\sum [ (C_i - B_i)/B_i ]^2 }{N}}$ where $C_i$ is the calculated results, $B_i$ the experimental data, and $N$ the amount of experimental data. The relative deviation is 30.0% between the experimental and calculated liquidus compositions for given temperatures. This large discrepancy is due to the very steep phase boundaries. The enthalpies of mixing calculated using these parameters are shown in Figure 5.1 in comparison with the data from first-principles calculations. The relative deviation of enthalpy of mixing is about 6.5% between the first-principles results and those calculated from the present thermodynamic description.

The thermodynamic description of the Ce-Mg system obtained in the present work is listed in Table 5.4 in comparison with the results from Cacciamani et al. [99]. The calculated enthalpies of formation of the Ce-Mg compounds are in much better agreement with the experimental data [121] than those calculated from the previous
model [99] (see Figure 5.3). The relative deviation for enthalpies of formation of the Ce-Mg compounds is 12.4% in the present work and 54.1% in the previous work [99]. Figure 5.4 shows the calculated vapor pressure over the Ce-Mg alloys in comparison with the experimental data [99]. The major disagreement in this figure corresponds to the measurements of alloys with 9 at.% and 14 at.% Ce, pertaining to the Mg_{12}Ce + Mg_{41}Ce_{5} and Mg_{41}Ce_{5} + Mg_{5}Ce phase fields identified by Pahlman and Smith [121]. In the Mg_{12}Ce + Mg_{41}Ce_{5} phase region, it is likely that the measurements may have not reached equilibrium due to the precipitation of Mg_{17}Ce_{2}, which can be stable at high temperatures. In addition, the samples with high concentrations of Mg might be oxidized at high temperatures. For the rest of the alloys which have low concentrations of Mg, the differences between the calculations and the experiments are within the experimental uncertainties in vapor pressure measurements. As shown in Figure 5.5, the calculated activities of Mg in the liquid phase agree well with experimental data [121] with the relative derivation being 5.1%, while the relative deviation is about 7.6% in the previous modeling work [99]. Figure 5.6 shows the presently calculated phase diagram in comparison with that of Cacciamani et al. [99] with experimental data superimposed. The phase diagram on the Mg-rich side is enlarged in Figure 5.7. The relative deviation is 1.1% between the experimental and calculated temperatures on the phase boundaries and 10.0% between the experimental and calculated phase boundaries compositions for given temperatures. The main differences are phase equilibria at the Ce-rich side.

The present calculation reproduces the experimental data better, especially on the peritectic temperature of Mg_{41}Ce_{5}, solubility of Mg in Ce and the stability of Mg_{17}Ce_{2} and Mg_{41}Ce_{5}. The peritectic reaction of liquid + Mg_{5}Ce → Mg_{41}Ce_{5} at about 908 K was
observed by Wood and Cramer [116]. They also reported the tendency of undercooling in the temperature range from 894K to 908K, which was illustrated by the cooling curve obtained by DTA measurements with a relatively high cooling rate of 100 °C/h [116]. Therefore, in the present work, we relied more on the experimental peritectic reaction temperature of $\text{liquid} + Mg_3Ce \rightarrow Mg_{41}Ce_5$ than those of the liquidus between liquid and $Mg_{41}Ce_5$. The calculated phase boundary has thus higher temperatures than those of experimental data in the range of 4 to 10 at. % of Ce. This can be further justified by considering the driving force for the formation of $Mg_{41}Ce_5$ from liquid. With the composition of $x_{Ce} = 0.09$, the calculated liquidus is at $T = 903$ K. Experimentally, the new phase was detected at $T = 896$ K [116] at which the calculated driving force is 40.77 J/mol.atom only. At a cooling rate of 100 °C/h, such a small undercooling could be expected. The invariant equilibria and congruent point in the Ce-Mg system are listed in Table 5.6 together with the experimental data. The relative derivation is 0.5% between the experimental invariant point temperatures and 14.7% between the experimental and calculated compositions at invariant reactions.

Figure 5.8 shows the calculated Ca-Mg binary phase diagram using the parameters from the literature [126]. Figure 5.9 shows the calculated liquidus projection of the Mg-Ca-Ce ternary system with the phases forming from the liquid phase during solidification. The isotherms are shown as the dotted lines with the numbers indicating the temperatures. Figure 5.10 shows the liquidus projection of the Ca-Mg edge. The invariant equilibria in the liquidus projection are listed in Table 5.7. As an example, the calculated isothermal section of the Mg-Ca-Ce ternary system is presented in Figure 5.11 at 880 K. With the
thermodynamic database available, other isothermal and isopleth sections can be readily calculated.

5.7 Summary

Thermodynamic modeling of the Ce-Mg system was carried out based on the available experimental data. For the Ca-Ce system, the enthalpies of mixing from first-principles calculations were used in addition to the experimental phase equilibrium data from the literature. The thermodynamic database of the Mg-Ca-Ce ternary system was obtained by combining the thermodynamic descriptions of the presently modeled Ca-Ce and Ce-Mg systems together with the Ca-Mg system in the literature.
Table 5.1 Enthalpies of mixing of bcc solutions

<table>
<thead>
<tr>
<th>Phase</th>
<th>ev/atom</th>
<th>Enthalpy of mixing (kJ/mol)</th>
<th>Calculated lattice parameter (Å)</th>
<th>Lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>-1.902</td>
<td>4.40</td>
<td>4.50 [104]</td>
<td></td>
</tr>
<tr>
<td>Ce</td>
<td>-5.732</td>
<td>3.756</td>
<td>4.11(1041K) [105]</td>
<td></td>
</tr>
<tr>
<td>Ce (with magnetic)</td>
<td>-5.732</td>
<td>3.759</td>
<td>4.11(1041K) [105]</td>
<td></td>
</tr>
<tr>
<td>Ca(<em>{0.25})Ce(</em>{0.75})</td>
<td>-4.538</td>
<td>22.719</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca(<em>{0.50})Ce(</em>{0.50})</td>
<td>-3.589</td>
<td>21.928</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca(<em>{0.75})Ce(</em>{0.25})</td>
<td>-2.688</td>
<td>16.488</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca(<em>{0.25})Ce(</em>{0.75}) (with magnetic)</td>
<td>-4.585</td>
<td>18.208</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca(<em>{0.50})Ce(</em>{0.50}) (with magnetic)</td>
<td>-3.599</td>
<td>20.989</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca(<em>{0.75})Ce(</em>{0.25}) (with magnetic)</td>
<td>-2.695</td>
<td>15.827</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 5.2  Crystal structures of phases in the Mg-Ca-Ce system

<table>
<thead>
<tr>
<th>Phase</th>
<th>Pearson Symbol</th>
<th>Space Groups</th>
<th>Strukturbericht Designation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>cI2</td>
<td>Im(\bar{3}m)</td>
<td>A2</td>
<td>[110]</td>
</tr>
<tr>
<td>Ce</td>
<td>cI2</td>
<td>Im(\bar{3}m)</td>
<td>A2</td>
<td>[110]</td>
</tr>
<tr>
<td>Mg</td>
<td>hP2</td>
<td>P6(_3)/mmc</td>
<td>A3</td>
<td>[110]</td>
</tr>
<tr>
<td>Mg(_{12})Ce</td>
<td>oI338</td>
<td>Im(mm)</td>
<td>...</td>
<td>[111]</td>
</tr>
<tr>
<td>Mg(<em>{17})Ce(</em>{2})</td>
<td>hP38</td>
<td>P6(_3)/mmc</td>
<td>...</td>
<td>[111]</td>
</tr>
<tr>
<td>Mg(<em>{41})Ce(</em>{5})</td>
<td>tI92</td>
<td>I4/m</td>
<td>...</td>
<td>[111]</td>
</tr>
<tr>
<td>Mg(_{3})Ce</td>
<td>cF16</td>
<td>Fm(\bar{3}m)</td>
<td>D03</td>
<td>[111]</td>
</tr>
<tr>
<td>Mg(_{2})Ce</td>
<td>cF24</td>
<td>Fd(\bar{3}m)</td>
<td>C15</td>
<td>[111]</td>
</tr>
<tr>
<td>MgCe</td>
<td>cP2</td>
<td>Pm(\bar{3}m)</td>
<td>B2</td>
<td>[111]</td>
</tr>
</tbody>
</table>
Table 5.3 Thermodynamic parameters of the Ca-Ce system, in SI unit

<table>
<thead>
<tr>
<th>Phase</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>$^0 L_{Ca,Ce}^{\text{liq}} = 44813$</td>
</tr>
<tr>
<td>Bcc</td>
<td>$^0 L_{Ca,Ce}^{\text{bcc}} = 85106$</td>
</tr>
<tr>
<td>Fcc</td>
<td>$^0 L_{Ca,Ce}^{\text{fcc}} = 85106$</td>
</tr>
<tr>
<td>Hcp</td>
<td>$^0 L_{Ca,Ce}^{\text{hcp}} = 85106$</td>
</tr>
</tbody>
</table>
Table 5.4  Thermodynamic parameters of the Ce-Mg system in comparison with the results of Cacciamani [99], in SI unit

<table>
<thead>
<tr>
<th>Phase</th>
<th>Cacciamani Work</th>
<th>Present Work</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>$0 L^\text{liq}_{\text{Ce,Mg}} = -39381.19 + 16.34052 T$</td>
<td>$0 L^\text{liq}_{\text{Ce,Mg}} = -36703 + 13.831 T$</td>
</tr>
<tr>
<td></td>
<td>$1 L^\text{liq}_{\text{Ce,Mg}} = 25338.56 - 11.86885 T$</td>
<td>$1 L^\text{liq}_{\text{Ce,Mg}} = 30962 - 17.297 T$</td>
</tr>
<tr>
<td></td>
<td>$2 L^\text{liq}_{\text{Ce,Mg}} = -15106.9$</td>
<td>$2 L^\text{liq}_{\text{Ce,Mg}} = -15090$</td>
</tr>
<tr>
<td>Bcc</td>
<td>$0 L^\text{bcc}_{\text{Ce,Mg}} = -27000 + 3.3 T$</td>
<td>$0 L^\text{bcc}_{\text{Ce,Mg}} = -27284 + 3.641 T$</td>
</tr>
<tr>
<td></td>
<td>$1 L^\text{bcc}_{\text{Ce,Mg}} = 25338.56 - 11.86885 T$</td>
<td>$1 L^\text{bcc}_{\text{Ce,Mg}} = 25374 - 11.872 T$</td>
</tr>
<tr>
<td></td>
<td>$2 L^\text{bcc}_{\text{Ce,Mg}} = -15106.9$</td>
<td>$2 L^\text{bcc}_{\text{Ce,Mg}} = -15094$</td>
</tr>
<tr>
<td>Fcc</td>
<td>$0 L^\text{fcc}_{\text{Ce,Mg}} = -15000 + 0.5 T$</td>
<td>$0 L^\text{fcc}_{\text{Ce,Mg}} = -11916 + 6.541 T$</td>
</tr>
<tr>
<td></td>
<td>---</td>
<td>$1 L^\text{fcc}_{\text{Ce,Mg}} = -13507$</td>
</tr>
<tr>
<td>Hcp</td>
<td>$0 L^\text{hcp}_{\text{Ce,Mg}} = -94337.51 + 79.95155 T$</td>
<td>$0 L^\text{hcp}_{\text{Ce,Mg}} = -94338 + 79.952 T$</td>
</tr>
<tr>
<td>Mg$_{12}$Ce</td>
<td>$\Delta_f G = -139880 + 84.5 T$</td>
<td>$\Delta_f G = -182973 + 132.873 T$</td>
</tr>
<tr>
<td>Mg$_{17}$Ce$_2$</td>
<td>$\Delta_f G = -217170.0 + 104.5 T$</td>
<td>$\Delta_f G = -318800 + 215.027 T$</td>
</tr>
<tr>
<td>Mg$_{41}$Ce$_5$</td>
<td>$\Delta_f G = -575000 + 299.0 T$</td>
<td>$\Delta_f G = -832250 + 578.399 T$</td>
</tr>
<tr>
<td>Mg$_3$Ce</td>
<td>$\Delta_f G = -76800 + 26.5 T$</td>
<td>$\Delta_f G = -75046 + 25.0 T$</td>
</tr>
<tr>
<td>Mg$_2$Ce</td>
<td>$\Delta_f G = -52744.6 + 15.163 T$</td>
<td>$\Delta_f G = -44457 + 7.073 T$</td>
</tr>
<tr>
<td>MgCe</td>
<td>$\Delta_f G = -46000.0 + 23.32 T$</td>
<td>$\Delta_f G = -27451 + 4.401 T$</td>
</tr>
</tbody>
</table>
Table 5.5 Invariant equilibria in the Ca-Ce binary system

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Experimental data</th>
<th>Present calculations, at.% Ce</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T, K, x&lt;sub&gt;1&lt;/sub&gt;</td>
<td>T, K, x&lt;sub&gt;1&lt;/sub&gt;, x&lt;sub&gt;2&lt;/sub&gt;, X&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>liquid 1 → bcc(Ce) + bcc(Ca)</td>
<td>1068 ~99.7</td>
<td>1061.7 99.8 99.98 0.0015</td>
</tr>
<tr>
<td>liquid 1 → bcc(Ca) + liquid 2</td>
<td>1108 ~0.2</td>
<td>1105.8 0.27 0.023 99.97</td>
</tr>
</tbody>
</table>
Table 5.6 Invariant equilibria in the Ce-Mg binary system

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Type</th>
<th>Experimental data at.% Ce</th>
<th>Present calculations, at.% Ce</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T, K</td>
<td>x₁</td>
<td>x₂</td>
</tr>
<tr>
<td>liquid $\rightarrow$ bcc $_A2 + MgCe$</td>
<td>Eutectic</td>
<td>961$^{[113]}$</td>
<td>65</td>
</tr>
<tr>
<td>liquid $\rightarrow$ MgCe + Mg₂Ce</td>
<td>Eutectic</td>
<td>984$^{[113]}$</td>
<td>53.5</td>
</tr>
<tr>
<td>liquid + Mg₅Ce $\rightarrow$ Mg₂Ce</td>
<td>Peritectic</td>
<td>1023$^{[113]}$</td>
<td>41</td>
</tr>
<tr>
<td>liquid + Mg₅Ce $\rightarrow$ Mg₈₁₇Ce₅</td>
<td>Peritectic</td>
<td>908$^{[116]}$</td>
<td>10</td>
</tr>
<tr>
<td>liquid + Mg₈₁₇Ce₂ $\rightarrow$ Mg₈₁₂Ce</td>
<td>Peritectic</td>
<td>894$^{[116]}$</td>
<td>8.5</td>
</tr>
<tr>
<td>liquid + Mg₈₁₂Ce $\rightarrow$ Mg₈₁₇Ce₂</td>
<td>Peritectic</td>
<td>889$^{[114]}$</td>
<td>7.5</td>
</tr>
<tr>
<td>liquid $\rightarrow$ Mg₈₁₂Ce + hcp $_A3$</td>
<td>Eutectic</td>
<td>865$^{[114]}$</td>
<td>4.3</td>
</tr>
<tr>
<td>Mg₅Ce $\rightarrow$ liquid</td>
<td>Congruent</td>
<td>1069$^{[113]}$</td>
<td>25</td>
</tr>
</tbody>
</table>
Table 5.7 Invariant reactions in the Mg-Ca-Ce liquidus projection

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Present calculations</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T, K</td>
<td>at.% Mg</td>
<td>at.% Ce</td>
</tr>
<tr>
<td>$MgCe + \text{liquid} \rightarrow Mg_2Ce + \text{liquid} \ 2$</td>
<td>918.56</td>
<td>57.44</td>
<td>32.71</td>
</tr>
<tr>
<td>$Mg_2Ce + \text{liquid} 2 \rightarrow Mg_3Ce + \text{liquid} 1$</td>
<td>920.63</td>
<td>69.20</td>
<td>26.87</td>
</tr>
<tr>
<td>$Mg_3Ce + \text{liquid} 1 \rightarrow Mg_2Ca + Mg_{41}Ce_5$</td>
<td>868.81</td>
<td>86.75</td>
<td>11.22</td>
</tr>
<tr>
<td>$Mg_{41}Ce_5 + \text{liquid} 1 \rightarrow Mg_{812}Ce + Mg_2Ca$</td>
<td>820.29</td>
<td>88.71</td>
<td>9.54</td>
</tr>
<tr>
<td>$\text{liquid} 1 \rightarrow Mg_2Ca + Mg_{812}Ce + hcp(Mg)$</td>
<td>790.30</td>
<td>88.30</td>
<td>5.57</td>
</tr>
<tr>
<td>$Mg_{17}Ce_2 + \text{liquid} 1 \rightarrow Mg_{41}Ce_5 + Mg_{812}Ce$</td>
<td>877.21</td>
<td>89.80</td>
<td>10.19</td>
</tr>
<tr>
<td>$\text{liquid} 1 + \text{liquid} 2 + bcc(Ce) \rightarrow MgCe$</td>
<td>866.62</td>
<td>28.82</td>
<td>35.14</td>
</tr>
<tr>
<td>$Mg_3Ce + \text{liquid} 2 \rightarrow bcc(Ca) + Mg_2Ca$</td>
<td>720.22</td>
<td>58.55</td>
<td>11.13</td>
</tr>
<tr>
<td>$\text{liquid} 1 + \text{liquid} 2 \rightarrow bcc(Ca) + Mg_3Ce$</td>
<td>766.21</td>
<td>51.39</td>
<td>23.67</td>
</tr>
</tbody>
</table>
Figure 5.1 Calculated enthalpy of mixing of bcc solutions at 298K as a function of Ce concentration in the Ca-Ce system, compared with first-principles calculations □.
Figure 5.2 Calculated Ca-Ce phase diagram compared with the experimental data

\(\Xi\) [106]; \(\Diamond\) [107]; \(\triangle\) \(\Box\) [127].
Figure 5.3 Enthalpy of formation of Ce-Mg compounds △ in comparison with the previous modeling □[99] and the experimental data ○.
Figure 5.4 Vapor pressures over Ce-Mg alloys with different Ce contents in comparison with the experimental data [121].
Figure 5.5 Calculated activities of Mg at 1133K in comparison with the experimental data $\Delta[121]$. 
Figure 5.6 Calculated Ce-Mg phase diagram in comparison with the previous modeling (dotted line) by G. Cacciamani et al. [99] and experimental data □[114]; ◊ [116]; △[113]; ○ [100].
Figure 5.7  Mg-rich corner of the Ce-Mg phase diagram in comparison with previous modeling (dotted line) [99] and experimental data □[114]; ◊ [116].
Figure 5.8 Calculated Ca-Mg phase diagram using the parameters from the literature [36].
Figure 5.9  Liquidus projection to the composition triangle in the Mg-Ca-Ce system.
Figure 5.10  Enlarged Ca-Mg edge of the liquidus projection.
Figure 5.11 Calculated isothermal section for the Mg-Ca-Ce system at 880K.


CHAPTER 6 SOLVUS BOUNDARIES OF (META)STABLE PHASES IN THE AL–Mg–Si SYSTEM: FIRST-PRINCIPLES PHONON CALCULATIONS AND THERMODYNAMIC MODELING

6.1 Introduction

Alloys based on the Al-Mg-Si system are widely used for engineering applications due to their excellent mechanical properties. In particular, the strength of Al-Mg-Si alloys can be significantly increased through age hardening, during which various metastable phases form. Although there are a wealth of metastable phases observed in these alloys, the generic precipitate formation sequence in Al-Mg-Si alloys is the following [128-130]:

Atomic clusters → Guinier-Preston (GP) zones → β” → β’ → β,

where β”, β’ and β represent the metastable Mg$_5$Si$_6$ and Mg$_{18}$Si$_{10}$ and the stable Mg$_2$Si compounds, respectively. The GP zones consist of distinctive clusters with compositions different from the overall alloy composition [131]. The needle-shaped β” phase is often considered the most effective hardening precipitate [129, 132], while the formation of the rod-shaped precipitate β’ phase can indicate that the alloy is over-aged [133].

Despite nearly one hundred years of study of this important system, accurate positions of the metastable phase boundaries are not known, which are needed for
quantitative simulation of the aging process. These phase boundaries are very difficult to determine reliably from experiments due to the transient nature of metastable phases. In the present work, first-principles density-functional theory calculations [78-79] are performed in an effort to obtain the key thermodynamic properties necessary to quantitatively predict the thermodynamic limit of these metastable boundaries. From static total energy calculations, we obtain the equilibrium structural properties of Mg, Si, $\beta$, $\beta'$ and $\beta''$ and the enthalpies of formation of $\beta$, $\beta'$ and $\beta''$. Using frozen-phonon calculations, we also ascertain the vibrational entropies of formation for each phase. This combination of first-principles calculated enthalpies and entropies for stable and metastable phases allows us to compare trends in the enthalpy vs. entropy for $\beta$, $\beta'$ and $\beta''$, as well as these thermodynamic functions with the observed precipitation sequence given above. Combining this first-principles thermodynamic information together with the Gibbs energy of the Al-rich solid solution containing Si and Mg (fcc phase) from the CALPHAD approach [134], we predict the stable and metastable phase boundaries for fcc/$\beta$, fcc/$\beta'$ and fcc/$\beta''$. Our work is guided by previous studies of the first-principle prediction of solvus boundaries in Al alloys. In particular, the solvus boundaries for stable phases in binary systems were investigated, e.g. Al-Sc [135] and Al-Si [136]. Subsequently, this work was extended to include, both stable and metastable phase boundaries in Al-Cu [137]. In the present work, we extend these previous studies by predicting solvus boundaries in the Al-Mg-Si ternary system, including both stable and metastable precipitate phases. In addition, our work explores the approach of combining first-principles calculated thermodynamic functions of the (meta)stable intermetallic
phases with CALPHAD data for the solid solution, in order to achieve more quantitatively accurate phase boundaries.

6.2 Method

In the present work, the first-principles calculations are performed by employing the Vienna *ab initio* simulation package (VASP) [78-79] with Vanderbilt ultrasoft pseudopotentials [138] and the generalized gradient approximation (GGA) [80]. The crystal structure data of $\beta$-Mg$_2$Si, $\beta'$-Mg$_{18}$Si$_{10}$, and $\beta''$-Mg$_5$Si$_6$ are summarized in Table 6.1 [139-142] with $\beta$ having the cubic CaF$_2$ structure [131], $\beta'$ hexagonal and $\beta''$ monoclinic structures [129, 132], respectively. We use an energy cutoff of 188.3 eV, i.e., 1.25 times of the energy cutoff of Si, higher than those of Al and Mg, suggested by VASP. All calculations are performed with complete relaxation of cell volume, cell vectors and cell-internal atomic positions. The Monkhorst-Pack scheme is used for the Brillouin-zone integrations [103]. The settings of k-points correspond roughly to an 8,000 k-point mesh per reciprocal-atom.

In this study, the Helmholtz free energies for Mg, Si, $\beta$, $\beta'$ and $\beta''$, are described by the harmonic approximation at the equilibrium volume [19-20, 143],

\[
F(T) = E_0 + F_{ph}(T),
\]

where $E_0$ is the first-principles ground state energy at 0 K, and $F_{ph}(T)$ [19-20, 143] the phonon contributions to the free energy. Since we are focused on the difference of thermodynamic properties (e.g. enthalpy of formation, entropy of formation) for
compounds compared with the pure elements. It is worth mentioning that the anharmonic effects can be neglected here. From the phonon density of states, the lattice vibrational free energy can be calculated through [19-20, 143]:

\[
F_{ph}(T) = k_B T \int \ln \left( 2 \sinh \left( \frac{\hbar \nu}{2 k_B T} \right) \right) g(\nu) d\nu,
\]

where \( T \) is the temperature, \( k_B \) the Boltzmann constant, \( \hbar \) the Planck constant, and \( g(\nu) \) the phonon density of states as a function of phonon frequency \( \nu \). At zero pressure, the internal energy and Helmholtz free energy are equal to the enthalpy and Gibbs energy, respectively.

The vibrational properties of the structures can alternatively be characterized by their Debye temperatures \( \Theta_D \), which can be calculated by [144-145]:

\[
k_B \Theta_D = h v_D(n)
\]

\[
v_D(n) = \left( \frac{n + 3}{3} \right) \int_0^\infty \nu^n g(\nu) d\nu \quad (n \neq 0, n > -3),
\]

where \( v_D(n) \) is the Debye cutoff frequency. The cutoff frequency for \( n = -2 \) is used in this work, and hence the integrals in Equation 6.3 and Equation 6.4 can get \( \Theta_D(-2) \). \( \Theta_D(-2) \) has an important physical meaning as it is related to the root-mean-square amplitude of thermal oscillations according to the Debye-Waller theory [146-147].

The phonon density of states ( \( g(\nu) \) in Equation 6.2) for hcp-Mg, diamond-Si, \( \beta\)-Mg\(_2\)Si, \( \beta'\)-Mg\(_{18}\)Si\(_{10}\) and \( \beta''\)-Mg\(_5\)Si\(_6\) are calculated using the supercell method implemented in the ATAT package [68] as the interface to the VASP code [78-79]. The
supercell method is based on the frozen phonon approximation through which the
to changes in total energy and forces are calculated in the direct space by displacing the
atoms from their equilibrium positions. The main steps for the first-principles phonon
calculation in ATAT are: (i) Assign the primitive unit cell and fully relax the primitive
unit cell by first-principles code (VASP in this work). (ii) Select the size of the supercell
according to the defined neighbor interaction distance, making perturbation to the atomic
positions, and calling the first-principles code to calculate the forces imposed on the
atoms. (iii) Fit the force constants from the forces and calculate the phonon frequencies
with the assigned cutoff range for force constants. The supercell sizes $N$ in the phonon
calculations for Mg, Si, $\beta$-Mg$_2$Si, $\beta'$-Mg$_{18}$Si$_{10}$ and $\beta''$-Mg$_5$Si$_6$ contained 52, 96, 96, 84,
and 88 atoms, respectively. The number of $k$ points, $N_k$, is determined through $N \times N_k = 4000$.

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

$$
\Delta_f H(Mg_xSi_y) = E(Mg_xSi_y) - \frac{x}{x+y} E(Mg) - \frac{y}{x+y} E(Si)
$$

Equation 6.5

where $E(Mg_xSi_y)$, $E(Mg)$ and $E(Si)$ are the energies of the compound $Mg_xSi_y$ and
constituents, hcp-Mg and diamond-Si, respectively.

To calculate the phase boundaries, the Gibbs energy of the fcc solution phase is
taken from the work by Feufel et al. [134] shown in Table 6.2. Ideally, one would use the
free energy of fcc also from the first-principles calculations. Indeed, in a recent study [D.
W. Shin and Z. K. Liu, "Enthalpy of mixing for ternary fcc solid solutions from special quasirandorn structures," *CALPHAD*, Vol.32, 2008, 74-81], the enthalpy of mixing in the ternary fcc Al-Mg-Si phase was calculated, showing the discrepancies with the data in the literature for the binary and the ternary systems. The present work focuses on developing an approach to insert the metastable phases into multi-component Al and Mg thermodynamic databases and demonstrating its feasibility. The enthalpies and entropies of formation of β, β’ and β’’ are obtained from first-principles calculations in the present work. The Gibbs energy of compounds can be described as:

\[
G_{Mg_{x}Si_{y}}^{Mg_{x}Si_{y}} = a^{0}G_{Mg}^{hcp} + b^{0}G_{Si}^{diamond} + \Delta_{f}H_{Mg_{x}Si_{y}}^{Mg_{x}Si_{y}} - T\Delta_{f}S_{Mg_{x}Si_{y}}^{Mg_{x}Si_{y}}
\]

where \(0G_{Mg}^{hcp}\) and \(0G_{Si}^{diamond}\) are the molar Gibbs energies of the pure element hcp Mg and diamond Si, from the widely accepted Scientific Group Thermodata Europe (SGTE) data [148], respectively. The Gibbs energy of formation of the compound can be written as:

\[
\Delta_{f}H_{Mg_{x}Si_{y}}^{Mg_{x}Si_{y}} - T\Delta_{f}S_{Mg_{x}Si_{y}}^{Mg_{x}Si_{y}}
\]

where \(\Delta_{f}H_{Mg_{x}Si_{y}}^{Mg_{x}Si_{y}}\) and \(\Delta_{f}S_{Mg_{x}Si_{y}}^{Mg_{x}Si_{y}}\) are the enthalpy and entropy of formation calculated from first-principles.

### 6.3 Results and discussion

#### 6.3.1 First-principles results

In this section, the calculated equilibrium lattice parameters, phonon density of states, together with the predicted finite temperature thermodynamic properties (entropy, enthalpy, and Gibbs energy) are presented and compared with the available experimental data.
Table 6.1 gives the predicted lattice parameters of hcp-Mg, diamond-Si, $\beta$-Mg$_2$Si, $\beta'$-Mg$_{18}$Si$_{10}$ and $\beta''$-Mg$_5$Si$_6$ at 0 K, which are in good agreement with the experimental data at room temperature. The phonon density of states (DOS) of Mg, Si, $\beta$-Mg$_2$Si, $\beta'$-Mg$_{18}$Si$_{10}$ and $\beta''$-Mg$_5$Si$_6$ calculated at the equilibrium volumes are plotted in Figure 6.1. The available Raman measurements [149-150] and the previous calculations [151-152] of Mg and Si are included for comparison, showing good agreement. The predicted frequency of Si is slightly lower than the measured ones due to a weak bonding of Si predicted by the present calculations. The calculated lattice parameter of 5.45 Å is slightly larger than the measured lattice parameter 5.43 Å [153] (see Table 6.1). The peak with frequency around 7.8 THz can not be reproduced in the present work, which has been previously noted as a disagreement between first-principles calculations and experimental phonon DOS [152, 154].

Comparing the phonon density of states of $\beta$-Mg$_2$Si, $\beta'$-Mg$_{18}$Si$_{10}$ and $\beta''$-Mg$_5$Si$_6$ as shown in Figure 6.1(c), the distributions of vibrational frequencies in the lower frequency region (e.g., less than 5 THz) increase from Si, $\beta$, $\beta'$, $\beta''$, to Mg, indicating the increase of phonon contributions to Gibbs energies from Si, $\beta$, $\beta'$, $\beta''$, to Mg (cf. Equation 6.2 and Figure 6.3). In principle, the higher value of the phonon density of states in the lower frequency region implies a weak bonding nature and correspondingly a lower Debye temperature [143]. In terms of the second-moment Debye cutoff frequencies calculated from phonon density of states in Figure 6.1, Table 6.1 summarizes the predicted Debye temperatures, which agree well with the available measurements [155-157]. It is shown that the Debye temperatures decrease from Si, $\beta$, $\beta'$, $\beta''$, to Mg, which is consistent with the distributions of phonon density of states in the lower frequency region. The increase
of Debye temperatures from $\beta''$, $\beta'$, to $\beta$ confirms again the strengthened bonds from $\beta''$, $\beta'$, to $\beta$.

In order to validate the first-principles phonon calculations, one of the most important steps is to calculate the phonon dispersion. To our knowledge, there is no experimental phonon data of $\beta$, $\beta'$ and $\beta''$, except for the measured $\Gamma$ point data of $\beta$-Mg$_2$Si. Figure 6.2 shows the calculated phonon dispersion for $\beta$-Mg$_2$Si pertaining to the equilibrium volume at 0 K, which are in good agreements with the available Raman [158] and infrared measurements measured at room temperature [159]. As Mg$_2$Si is known to be a small band gap semiconductor, we should note that the Coulomb interactions will cause the frequencies of longitudinal optical (LO) modes above those of transversal optical (TO) modes [160-162]. The LO/TO splitting occurs at the $\Gamma$ point of the Brillouin zone, and only for infrared active modes. However, the supercell method used in the present work cannot be employed to estimate the LO/TO splitting directly. And it should be mentioned that the LO modes contribute very little to the phonon DOS’s, because they differ from TO modes only in a small volume of the reciprocal lattice in the vicinity of the $\Gamma$ point [163]. Therefore, the present work does not take into account the influences of LO/TO splitting.

From the harmonic approximation, Figure 6.3 shows the phonon contribution to enthalpies, entropies and Gibbs energies of Mg, Si, $\beta$-Mg$_2$Si, $\beta'$-Mg$_{18}$Si$_{10}$ and $\beta''$-Mg$_5$Si$_6$, where the total energy at 0 K is excluded. Note the diverse values of enthalpy at 0 K indicating the zero-point vibrational energies for each phase are different, whereas with increasing temperature, the vibrational contributions to enthalpy are approaching to classical limit of $3RT$ regardless of different materials. Only small differences of
enthalpy exist among $\beta$-Mg$_2$Si, $\beta'$-Mg$_{18}$Si$_{10}$ and $\beta''$-Mg$_5$Si$_6$, while there are more significant differences among the calculated vibrational entropies. The entropy of $\beta''$ increases with temperature more quickly than those of $\beta$ and $\beta'$ phases. Consequently, the Gibbs energy of $\beta''$-Mg$_5$Si$_6$ decreases faster than those of $\beta$-Mg$_2$Si and $\beta'$-Mg$_{18}$Si$_{10}$ at high temperatures.

The predicted room temperature (298 K) entropies and enthalpies of formation of $\beta$, $\beta'$, and $\beta''$ phases are listed in Table 6.3. These quantities are calculated from a combination of the total energy at 0 K and thermodynamic phonon contributions. The enthalpies of formation calculated at 298 K decrease in the same order as the observed precipitation sequence: $\Delta H (\beta''$-Mg$_5$Si$_6) > \Delta H (\beta'$-Mg$_{18}$Si$_{10}) > \Delta H (\beta$-Mg$_2$Si). The first-principles calculations show a correlation between decreasing energy and increasing Mg:Si ratio as the precipitation process proceeds, consistent with previous first-principles calculations by Ravi and Wolverton [164]. Table 6.3 also includes a comparison between the experimental enthalpies of formation of $\beta$-Mg$_2$Si, prior first-principles calculations [164], and the COST507 database [134]. The experimental values of the enthalpy of formation of Mg$_2$Si scatter over a large range. In view of the large difference in the melting points of Mg and Si as well as the large differences of their vapor pressures and densities, preparation of Mg-Si alloys can be extremely difficult. On the other hand, in the isopiestic technique, the Mg-Si alloy is obtained directly from a vapor pressure experiment taking advantage of the large difference in vapor pressures of the elements. Therefore, among all the techniques, we suggest that the isopiestic technique employed by Eldridge et al. [165] is more suited for this system compared with the other vapor pressure measurements as suggested by Geffken and Miller [166]. More recently, the
value of the enthalpy of formation of Mg₂Si determined by Feufel et al. [134] is -21.12±2.54 kJ/mole-atom. Values of the standard enthalpy of formation of Mg₂Si determined by Eldridge et al. [165], Rao et al. [167], and Feufel et al. [134] from vapor pressure, emf, and calorimetric methods are in accord with each other. The first-principles calculated enthalpy of formation for β-Mg₂Si at 298K is about ~19% (~4 kJ/mole-atom) less negative than these values. We also compare our results with those of Ravi and Wolverton [164] who have recently reported enthalpies of formation of β’'-Mg₅Si₆, β'-Mg₂Si and β-Mg₂Si precipitates from first-principles. We see in Table 6.3 that the enthalpy of formation of β’ in [164] is slightly less negative than the present value. It should be noted that the present work used the crystal structure of β’ proposed by Andersen et al. [168] while the prior work [164] assumed a different crystal structure with composition Mg₁.₈Si. The enthalpies of formation are listed in Table 6.3. We note that the crystal structure of β’ proposed by Andersen et al [168] yields lower total energy in the DFT calculations. The calculated values of lattice parameters for β’ phase are also in good agreement with measurements, as shown in Table 6.1. We assert that the crystal structure and composition of β’ proposed by Andersen et al. [168] is supported by our first-principle calculations. Table 6.3 also gives the calculated vibrational entropies of formation for stable and metastable phases. It can be seen that the entropies of formation calculated at 298 K decrease in the same order as the enthalpies of formation: ΔS (β’'-Mg₅Si₆) > ΔS (β’-Mg₁₈Si₁₀) > ΔS (β-Mg₂Si). The stable phase has the lowest entropy of formation. This correlation between entropies and enthalpies of formation has also previously been found in DFT studies the Al-Cu system [137]. Due to the fact that the standard entropy determined from integration of the low temperature heat capacities can
have significant uncertainty [166], we consider the very small magnitude of our calculated entropy of formation of β-Mg$_2$Si -1.8J/K mol-atom to be in reasonably good agreement with the COST507 database value of -2.68J/K mol-atom, based on the experiment by Geffken and Miller [166].

6.4 Phase diagram of Al solvus

In this section, we use our DFT calculated thermodynamic properties to calculate the (meta)stable phase stabilities of β”, β’ and β phases. The Gibbs energy function of the fcc phase is taken from Feufel et al. [134] and is shown in Table 6.2. For the stable β-Mg$_2$Si and metastable β’ and β” phases, the enthalpies and entropies of formation are calculated from first-principles.

The calculated phase boundaries of fcc/β are shown in the vertical section from Al to Mg$_2$Si in Figure 6.4, compared with experimental data and those calculated from the COST507 database. We note that there is considerable scatter in the reported experimental data for the ternary solubility of the stable β-Mg$_2$Si phase in an Al solid solution. Due to the fact that the starting materials contained relatively high impurities, e.g. 99.98 wt. % Mg and 98.64 wt. % Si [169]; 97.90 wt. % Mg and 99.48 wt.% Si [170] and the fact that the investigation was done with very low concentration of Mg, the data are not considered to be accurate. The degree of agreement between the two phase boundaries is represented by the relative deviation in calculated temperatures,

$$\sqrt{\frac{\sum_{i}[(C_i - B_i)/B_i]^2}{N}}$$

where $C_i$ and $B_i$ represent the two sets of data, and $N$ the number of experimental data points. Given the fact that we have no adjustable or fitting parameters
in the present calculations, we find the first-principles phase boundaries to be in very good agreement with COST507 database with the relative deviation of solvus of fcc/β about 6.7%.

Even though the solvus boundary of β from first-principles is in reasonably good agreement with COST507, in order for us to make quantitative predictions of the metastable β’ and β” solvus boundaries, we wish to adjust our solvus curves slightly such that the calculated solvus of β agrees precisely with COST507. To achieve this, we apply correction parameters, \( k_H \) and \( k_S \), which are the ratios between the enthalpies and entropies of formation for \( \beta\text{-Mg}_2\text{Si} \) phase from COST507 database and first-principles:

\[
\begin{align*}
\Delta_f H_{\beta\text{-Mg}_2\text{Si}}^{\text{COST507}} & = \Delta_f H_{\beta\text{-Mg}_2\text{Si}}^{\text{first-principles}} \\
\Delta_f S_{\beta\text{-Mg}_2\text{Si}}^{\text{COST507}} & = \Delta_f S_{\beta\text{-Mg}_2\text{Si}}^{\text{first-principles}}
\end{align*}
\]

where \( \Delta_f H_{\beta\text{-Mg}_2\text{Si}} \) and \( \Delta_f S_{\beta\text{-Mg}_2\text{Si}} \) correspond to enthalpy of formation of \( \beta\text{-Mg}_2\text{Si} \) phase from COST507 database and first-principles, respectively. The entropy of formation of \( \beta\text{-Mg}_2\text{Si} \) phase from COST507 database and first-principles are represented by \( \Delta_f S_{\beta\text{-Mg}_2\text{Si}}^{\text{COST507}} \) and \( \Delta_f S_{\beta\text{-Mg}_2\text{Si}}^{\text{first-principles}} \). The correction parameters are then applied to scale the values of \( \Delta_f H_{\beta\text{-Mg}_2\text{Si}}^{\text{first-principles}} \), \( \Delta_f H_{\beta\text{-Mg}_2\text{Si}}^{\text{first-principles}} \), \( \Delta_f S_{\beta\text{-Mg}_2\text{Si}}^{\text{first-principles}} \), and \( \Delta_f S_{\beta\text{-Mg}_2\text{Si}}^{\text{first-principles}} \) calculated from first-principles for β’ and β” phases. The modified enthalpic and entropic parameters for metastable phases can in turn be expressed as:

\[
\Delta_f H_{\beta\text{-Mg}_2\text{Si}}^{\text{modified}} = k_H \times \Delta_f H_{\beta\text{-Mg}_2\text{Si}}^{\text{first-principles}}
\]
Equation 6.10
\[ \Delta_f S_{\text{modified}}^{MgSi} = k_s \Delta_f S_{\text{first-principles}}^{MgSi} \]

The correction parameters and modified parameters for stable and metastable phase are shown in Table 6.4.

Figure 6.5 shows the predicted phase boundaries of fcc/β, fcc/β’ and fcc/β’’ in the isopleth of 0.76 at. % Si from first-principles calculations. In this figure, the Gibbs energy function of the fcc phase is taken from Feufel et al. [134]. Using the first-principles enthalpies and entropies of formation of three precipitate phases, the solvus curves are predicted and shown as solid curves. Dashed lines indicate the predicted solvus curves by using the modified parameters as shown in Table 6.4. The width of the bands indicated the estimated uncertainty in solvus curves. Even though the experimental solubility data is very scattered due to the transitory feature of the metastable phases, the measured stability ranges for β’-Mg\(_{18}\)Si\(_{10}\) and β’’-Mg\(_{5}\)Si\(_{6}\) phases [128, 130, 171-174] are well captured in our predictions.

It should be pointed out that the above calculated phase boundaries represent the thermodynamic limits of phase equilibria, while the experimentally measured ones are affected by the interfaces between fcc and precipitates. Typically, an interface changes from coherent, semi-coherent to incoherent due to the interplay between the interfacial energy and the strain energy associated with the size of precipitates. As the first precipitate formed during low-temperature aging, β’’ has a coherent interface with the fcc matrix, while the interfaces of β’ and β with the fcc matrix are semi-coherent and incoherent, respectively [175]. In our prior study, the coherent interfacial energy and strain energy of β’’ were predicted to be around 100 mJ m\(^{-2}\) and 0.45 kJ/mole-atom,
respectively [176]. The typical semi-coherent and incoherent interfacial energies are from 300 – 1000 mJ m⁻² [176-177], along with smaller strain energies because of the less deformation. As both interfacial and strain energies increase the Gibbs energy of precipitates, and hence result in increasing the solubility of (meta)stable phases in the fcc solution phase. Different experimental measurements of the metastable solvus reported in the literature might have been carried out at the different stages of the transitions, contributing to the significant scattering of phase boundary data.

6.5 Summary

Using first-principles calculations, we have computed the thermodynamic properties of (meta)stable precipitates in the Al-Mg-Si system. Along with the T=0K first-principles total energies, we use the frozen phonon approximation to calculate the enthalpies and entropies of formation of β-Mg₂Si, β’-Mg₁₈Si₁₀ and β”'-Mg₅Si₆ phases. We find that the phonon contributions to Gibbs energies increase from β, β’ to β” and thus the bonding of Mg-Si weakens from β, β’ to β”’. The metastable β”’ phase has the highest entropy and the weakest bonding among all the precipitates. The predicted enthalpy and entropy of formation for β-Mg₂Si at room temperature are in good agreement with the available experimental data. The Gibbs energies of formation of the precipitates from first-principles calculations are used to predict the solvus of metastable phases, and are in good agreement with the (admittedly scattered) experimental data from aging experiments.
Table 6.1 Calculated and experimental lattice parameters (Å) and Debye temperature $\Theta_D$ (K)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Space group</th>
<th>Lattice parameter (Å)</th>
<th>$\Theta_D$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
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<td>Exp.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>Si</td>
<td>Fd$\bar{3}$m</td>
<td>5.45</td>
<td></td>
</tr>
<tr>
<td>$\beta$-Mg$_2$Si</td>
<td>Fm$\bar{3}$m</td>
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<tr>
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<td>4.14</td>
</tr>
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<td>$\beta''$-Mg$_5$Si$_6$</td>
<td>C2/m</td>
<td>14.24</td>
<td>4.07</td>
</tr>
</tbody>
</table>
Table 6.2 Thermodynamic parameters of fcc phase in the Al-Mg-Si system, in SI unit

Fcc description:

\[ G_m^{fcc} = \sum x_i^0 G_i^{fcc} + RT \sum x_i \ln x_i + \sum_{i<j} x_i x_j \sum_{k=0}^{n} L_{i,j}^{fcc} (x_i-x_j)^k \]

<table>
<thead>
<tr>
<th>Parameters</th>
<th>[0 L_{Al,Mg}^{fcc} = 4971 - 3.5T ]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[1 L_{Al,Mg}^{fcc} = 900 + 0.423T ]</td>
</tr>
<tr>
<td></td>
<td>[2 L_{Al,Mg}^{fcc} = 950 ]</td>
</tr>
<tr>
<td></td>
<td>[0 L_{Al,SI}^{fcc} = -3143.78 + 0.29397T ]</td>
</tr>
<tr>
<td></td>
<td>[0 L_{Mg,SI}^{fcc} = -7148.79 + 0.89361T ]</td>
</tr>
</tbody>
</table>
Table 6.3 Enthalpy and entropy of formation, $\Delta_f H$ (kJ/mol-atom) and $\Delta_f S$ (J/K mol-atom), at 298K, respectively

<table>
<thead>
<tr>
<th>Phase</th>
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<th>Method</th>
<th>$\Delta_f S$</th>
<th>Method</th>
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<td>emf [167]</td>
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<td>-21.10</td>
<td>calorimetry [134]</td>
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Table 6.4 Enthalpy and entropy of formation $\Delta_f H$ (kJ mol$^{-1}$) and $\Delta_f S$ (J mol$^{-1}$K$^{-1}$), respectively, in per mole of atom unit

<table>
<thead>
<tr>
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<th>First-principles calculations</th>
<th>Thermodynamic database [134]</th>
<th>Correction</th>
<th>Modified parameters</th>
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<td>$\Delta_f S^a$</td>
<td>$\Delta_f H^b$</td>
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<td>-1.8</td>
<td>-21.74</td>
<td>-2.68</td>
</tr>
<tr>
<td>$\beta'$-Mg$<em>{18}$Si$</em>{10}$</td>
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<td>N/A</td>
<td>N/A</td>
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<tr>
<td>$\beta''$-Mg$_5$Si$_6$</td>
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<td>4.5</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

$\Delta_f H^a$ enthalpy of formation from first-principles calculations

$\Delta_f H^b$ enthalpy of formation from COST507 thermodynamic database

$\Delta_f S^a$ entropy of formation from first-principles calculations

$\Delta_f S^b$ entropy of formation from COST507 thermodynamic database
Figure 6.1 Phonon density of states for Mg, Si, β-Mg₂Si, β’-Mg₁₈Si₁₀ and β”-Mg₅Si₆ phases in comparison with the available experimental data [149-150] and previous calculations [151-152].
Figure 6.2 Calculated phonon dispersion curves of β-Mg₂Si pertaining to the equilibrium volume at 0 K, and experimental frequencies [158-159] at the Γ point are compared. Note that the LO/TO splitting is not calculated for the infrared active mode.
Figure 6.3  Vibrational contributions to entropy (S), enthalpy (H), and Gibbs energy (G) for Mg, Si, β-Mg$_2$Si, β'-Mg$_{18}$Si$_{10}$ and β''-Mg$_5$Si$_6$ phases, in per mole of atom.
Figure 6.4 Calculated solvus boundaries in the isopleth from Al to Mg$_2$Si in the present work (solid line) in comparison with COST507 database [134] (dotted line) and literature data (○ △ □ ▶) fcc-β solidus [134, 169-170, 188].
Figure 6.5 Calculated solvus boundaries in the isopleth of 0.76 at.% Si with (■) fcc+β’ phase region [128, 130, 171, 173]; (◆) fcc+β” phase region [128, 172-174]; and soluvs of fcc/β from COST507 [134]. The solid lines indicate the solvus using first-principles enthalpies of formation and entropies for three precipitates. The dashed lines represent the solvus using modified enthalpic and entropic parameters. The width of the bands indicates the uncertainty in solvus.
CHAPTER 7 THERMODYNAMIC MODELING OF THE Mg-AL-CA SYSTEM

7.1 Introduction

Mg-Al based alloys, possessing the best strength to weight ratio among the common structural materials, have received increasing attention due to their applications in automotive and aerospace industries. However, despite the high specific strength, these alloys have limited use as structural materials due to their poor creep resistance at high temperatures, mainly caused by the softening of the intermetallic phase Al$_{12}$Mg$_{17}$ at elevated temperatures [4-5]. Significant improvements can be achieved by alloying. Additions of rare earth elements show improvement in mechanical properties as a result of formation of strengthening precipitates [7-8], but they incur high costs. As a lower cost element, the addition of Ca provides additional ways to improve the creep resistance of Mg-Al base alloys through the replacement of the Al$_{12}$Mg$_{17}$ phase by more stable Laves phases [11-12]. Therefore, the ternary Mg-Al-Ca alloys have received increasing attention in the past few years, especially the Laves phases in Mg alloys due to their excellent physical and chemical properties. Despite the interesting properties of these alloys, there are only quite a few existing theoretical investigations on the structures and stability of these Laves phases in the Mg-Al-Ca system and most of them were studied for 0 K [10, 189].

To better understand the alloying behavior of Ca on Mg-Al alloys, it is important to determine the thermochemical properties of the Laves phases. A general two-sublattice
model \((\text{Mg, Al, Ca})_2(\text{Mg, Al, Ca})_1\) is used to represent the Laves phases (C14, C15, and C36) with homogeneity ranges as discussed in [10, 190]. It is found that the energetics for end-members with one element in each sublattice remain to be developed due to the lack of data, especially for the nonstable ones. In the current work, we present a systematic theoretical study on the structural, vibrational, and thermodynamic properties of \(A_2B\) type Laves phase with C14, C15, and C36 structures from first-principles. The total energies of all the nine end-members in the Laves phases C14, C15 and C36 structures are calculated and fitted by an equation of state (EOS). For the stable phases, e.g. C14-Mg\(_2\)Ca and C15-Al\(_2\)Ca, the vibrational properties are firstly predicted from phonon calculations. Subsequently, the Debye temperature evaluated from phonon properties is employed to adjust the scaling factor \((s)\) in Debye_Grüneisen model by Moruzzi et al. [191]. Herein, the vibrational properties through Debye_Grüneisen model are compared with those obtained from phonon calculations. For nonstable end-members, it is impossible to perform either the phonon calculations or experiments to estimate their vibrational properties. However, from the analysis of thermodynamic properties for stable end-members, we propose to predict the thermodynamic properties of nonstable \(A_2B\) type Laves phases using Debye_Grüneisen model by Moruzzi et al. [191] and Wang et al. [192]. The results of this work are expected to enhance the understanding of phase stability in the Mg-Al-Ca ternary system, and the approaches developed are extensible to other materials and for developing self-consistent and robust thermodynamic databases.

### 7.2 Methodology

Under the quasiharmonic approximation, the Helmholtz free energy, \(F\), of a system at temperature \(T\) and volume \(V\) is given by [19-23]
Equation 7.1 \[ F(V,T) = E_0(V) + F_{vib}(V,T) + F_{el}(V,T) \]

where \( E_0(V) \) is the first-principles static energy at 0 K and volume \( V \), \( F_{vib}(V,T) \) the lattice vibrational contributions to the free energy, and \( F_{el}(V,T) \) the thermal electronic contributions. Within the quasiharmonic approximation, the anharmonic effect is accounted by the harmonic approximation at several volumes.

From phonon density of states, the lattice vibrational free energy can be calculated through [19-21]:

Equation 7.2 \[ F_{vib}(V,T) = k_B T \int_0^\infty \ln[2\sinh \frac{h\nu}{2k_B T}] g(\nu,V) d\nu \]

where \( T \) is the temperature, \( k_B \) the Boltzmann constant, \( \hbar \) the Planck constant, and \( g(\nu,V) \) the phonon density of states as a function of phonon frequency \( \nu \) and volume \( V \).

The vibrational properties can be alternatively characterized by their Debye temperatures \( \Theta_D \) [4, 22, 191]:

Equation 7.3 \[ k_B \Theta_D(n) = \hbar \nu_D(n) \]

Equation 7.4 \[ \nu_D(n) = \left[ \frac{n+3}{3} \int_0^\infty v^n g(v) dv \right]^{1/n} (n \neq 0, n > 3), \]

where \( \nu_D(n) \) is the Debye cutoff frequency. The second moment cutoff frequency (\( n=2 \)) is used in this work, since \( \Theta_D(2) \) corresponds to the Debye temperature obtained from heat capacity data [4, 144].

Consequently, the vibrational Helmholtz free energy can be estimated by Debye model through the Debye temperature, \( \Theta_D \).
Equation 7.5 \[ F_{\text{ab}}(V, T) = \frac{9}{8} k_B \Theta_D + k_B T \left\{ 3 \ln \left[ 1 - \exp \left( -\frac{\Theta_D}{T} \right) \right] - D \left( \frac{\Theta_D}{T} \right) \right\} \]

where \( D \left( \frac{\Theta_D}{T} \right) \) is the Debye function with \( \Theta_D \) determined by via phonon frequencies. In terms of Debye-Grüneisen model by Moruzzi et al. [191], \( \Theta_D \) is given by:

Equation 7.6 \[ \Theta_D = s AV_0^{1/6} \left( \frac{B_0}{M} \right)^{1/2} \left( \frac{V_0}{V} \right)^{\gamma} \]

where \( M \) is the atomic mass, \( s \) the scaling factor with a default value of 0.617 as discussed by Moruzzi et al. [191], \( \gamma \) the Grüneisen constant, \( V_0 \) the 0 K static equilibrium volume, \( B_0 \) the bulk modulus calculated at \( V_0 \), \( B'_0 \) the derivative of \( B_0 \) against \( P \), \( \gamma = (1 + B'_0) / 2 - x \) with \( x = 1 \) for low temperatures and \( x = 2/3 \) for high temperatures [191].

Without using the Grüneisen constant, another method to calculate the Debye temperature was proposed by Wang et al. [22, 192]:

Equation 7.7 \[ \Theta_D = s AV^{1/6} \left\{ \frac{1}{M} \left[ B - \frac{2(\lambda + 1)}{3} P \right] \right\}^{1/2} \]

where \( B \) is the bulk modulus calculated from the 0 K static total energy curve at a given volume \( V \), \( P \) the pressure calculated from the 0 K static total energy curve at \( V \), \( \lambda = -1, 0, \) and 1 correspond to the thermodynamic theories of Slater [193], Dugdale and MacDonald [194], and the free volume theory [195], respectively. It should be noted that the case of \( \lambda = -1 \) by Wang et al. [192] is equivalent to the high temperature case by Moruzzi et al. [191] and that the case of \( \lambda = 0 \) by Wang et al. [192] is equivalent to low temperature
case by Moruzzi et al. [191]. Since the present interest is focused at the relatively high temperature region of the phase diagram, all the calculations using Debye_Grüneisen models of Moruzzi et al. [191] and of Wang et al. [192] are carried out at high temperature with \( x = 2/3 \) and \( \lambda = -1 \), respectively. When possible, the scaling factors for the Debye_Grüneisen models are determined by making the Debye temperatures from Equation 7.6 or Equation 7.7 equal to the Debye temperature obtained by phonons (Equation 7.4).

### 7.3 First-principles computational details

In the present work, first-principles calculations were performed by using the projector-augmented wave (PAW) method as implemented in VASP [78-79]. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [80] is used for the exchange-correlation functional. The electronic configurations considered are \( 3s^23p^1 \) for Al, \( 3s^2 \) for Mg, and \( 3p^64s^2 \) for Ca, respectively. We use the energy cutoff of 320 eV, i.e., 1.3 times the highest energy cutoff among Al, Mg and Ca as suggested by VASP. The crystal structures of Laves C14, C15, and C36 are summarized in Table 7.1. The Monkhorst-Pack scheme is used for the Brillouin-zone integrations [42] of Al, Ca, Laves C15 and Laves C36, while \( \Gamma \)-centered \( k \)-mesh is used for Mg and Laves C14.

The phonon calculations of C14-Mg\textsubscript{2}Ca and C15-Al\textsubscript{2}Ca are carried out by using the supercell method implemented in the ATAT package [68] with VASP code as the computational engine. The supercell method is based on the frozen phonon
approximation through which the changes in forces acting on atoms are calculated in the
direct space by displacing the atoms from their equilibrium positions.

Table 7.1 shows the detailed settings for first-principles calculations, including the
space group, the size of $k$-mesh for electronic structure calculations and in the perturbed
supercell for phonon calculations, the number of atoms in the supercell for phonon
calculations; the setting of displacement from the equilibrium atomic position, and the
cutoff distance used to fit the force constants and phonon properties.

### 7.4 Thermodynamic models

Thermodynamic modeling through the CALPHAD approach is based on the
Gibbs energy of individual phases. In this ternary system, there are two types of phases:
(i) solution phases such as the liquid phase, Fcc, Hcp and Bcc phases, and (ii) two-
sublattice intermetallic phases such as C14, C15, and C36 Laves phases. The molar Gibbs
energy of a solution phase can be described as [31-32]:

\[
G_m^\Phi = \sum_{i=1}^{n} x_i \ G_i^0 + RT \sum_{i=1}^{n} x_i \ \ln x_i + \sum_{\Phi} G^\Phi_m
\]

\[
\sum_{\Phi} G^\Phi_m = \sum_{i} \sum_{j \neq i} x_i x_j \sum_{k=0}^{n} L_{i,j}^k (x_i - x_j)^k + x_i x_j x_k I^\Phi
\]

where $G_i^0$ is the molar Gibbs energy of the pure element $i$ with the structure $\Phi$, $G_i^\Phi$ the excess Gibbs energy expressed in the Redlich-Kister polynomial as Equation 6.2;

\[ k L_{i,j}^k \] the $k^{th}$ binary interaction parameter between $i$ and $j$, which normally vary linearly

with temperature at high temperatures.
In the present study, the Gibbs energy of C14, C15 and C36 Laves phases can be described using the general two-sublattice model \((\text{Mg, Al, Ca})_2(\text{Mg, Al, Ca})_1\), with the molar Gibbs energy expressed as:

\[
G^\phi_m = G^0 + G^\text{ideal}_m + G^\phi^x_m
\]

\(G^0\) is defined by the ‘end-members’ with only one component in each sublattice of the \(\Phi\) phase, i.e. \((\text{Al})_2(\text{Al})_1\), \((\text{Al})_2(\text{Mg})_1\), \((\text{Ca})_2(\text{Al})_1\), \((\text{Ca})_2(\text{Ca})_1\), \((\text{Ca})_2(\text{Mg})_1\), \((\text{Mg})_2(\text{Al})_1\), \((\text{Mg})_2(\text{Ca})_1\), and \((\text{Mg})_2(\text{Mg})_1\), respectively. It can be described as:

\[
G^\phi^0 = y^I_A y^I_B G^\phi^0_{\text{Al-Al}} + y^I_A y^I_Ca G^\phi^0_{\text{Al-Ca}} + y^I_Ca y^I_Mg G^\phi^0_{\text{Ca-Mg}} + y^I_Ca y^I_Ca G^\phi^0_{\text{Ca-Ca}}
\]

where \(y^I\) and \(y^II\) are the site fraction of elements (Al, Mg, Ca) in the first and second sublattices, respectively.

\(G^\text{ideal}_m\) is the ideal Gibbs energy of mixing, which can be described as:

\[
G^\text{ideal}_m = 2RT\left(y^I_A \ln y^I_A + y^I_B \ln y^I_B\right) + RT\left(y^I_Ca \ln y^I_Ca + y^I_Mg \ln y^I_Mg\right)
\]

\(G^\phi^x_m\) is the excess Gibbs energy of mixing and expressed as:

\[
G^\phi^x_m = y^I_A y^I_B \left(\sum_{k=0}^i L_{A,B,A}(y^I_A - y^I_B)^k + \sum_{k=0}^i L_{A,B,B}(y^I_A - y^I_B)^k\right) + y^I_Ca y^I_Ca \left(\sum_{k=0}^i L_{A,B,A}(y^I_Ca - y^I_Ca)^k + \sum_{k=0}^i L_{A,B,B}(y^I_Ca - y^I_Ca)^k\right)
\]

\(L_{A,B,A}^k (L_{A,B,B}^k)\) is the interaction parameter between component A and B in the first (second) sublattice.

The enthalpies of formation of all end-members are from our first-principles calculations.
7.5 Results and discussion

7.5.1 Evaluation of enthalpies for all end-members

The total energy of each end-member is calculated as a function of volume and fitted by the 4-parameter Birch-Murnaghan equation of state [22, 84, 196]:

Equation 7.13 \( E(V) = a + bV^{-2/3} + cV^{-4/3} + dV^{-6/3} \)

Herein, the structural properties including the equilibrium volume, enthalpy of formation, bulk modulus and its pressure derivative for each end-member at 0 K are determined, and compared with available data as listed in Table 7.2. Note that most of \( B_0' \) values are 3~6, which is within the range of values for nearly all the materials. Figure 7.1 shows the calculated enthalpy of formation of each A\(_2\)B type Laves phase, in comparison with the CALPHAD modeled results for the Mg-Al-Ca [197], Al-Ca [198], and Mg-Ca [36] databases. The solid line represents the perfect agreement between the first-principles values and CALPHAD assessments, and two dashed lines define an error bar of ±5 kJ/mol. The value of ±5 kJ/mol is chosen due to the uncertainty for most experimental studies of enthalpies of formation. The calculated results compared favorably with each other with the differences within ±5 kJ/mol except for the C14-Al\(_2\)Ca and C15-Mg\(_2\)Ca phases. Such discrepancy is due to the arbitrary enthalpies of formation values used in CALPHAD assessments since both of these two are nonstable phases. The enthalpies of formation of C14, C15, and C36 structures with the same composition have similar values with those for Al\(_2\)Ca, Mg\(_2\)Ca, and Al\(_2\)Mg being negative. Al\(_2\)Ca has the lowest enthalpy of formation in their respective structures with the value being the lowest for the
C15 structure, which is consistent with its stability in the Al-Ca binary system [198]. For the composition of Mg₂Ca, the C14 structure has the lowest energy among three structures, which is consistent with the fact that it is the stable phase in the Mg-Ca system [36]. As for \( V_0 \) and \( B_0 \), all the calculations reveal the same trend: the one with the larger equilibrium volume showing lower bulk modulus.

### 7.5.2 Evaluation of entropies for all end-members at 298 K

Figure 7.2 shows the phonon density of states (DOS’s) for C14-Mg₂Ca and C15-Al₂Ca at their equilibrium volumes at 298 K. We note that in the low frequency region, the phonon DOS of C14-Mg₂Ca has higher values than that of C15-Al₂Ca, indicating that C14-Mg₂Ca has the larger phonon contributions to Gibbs energy from the vibrational entropy [199]. In principle, the higher value of the phonon density of states in the lower frequency region implies a weak bonding nature and correspondingly a lower Debye temperature [21]. Table 7.3 summarizes the estimated second moment Debye temperatures at the theoretical equilibrium volumes from phonon calculations. It is shown that C14-Mg₂Ca has a lower Debye temperature, confirming again its weaker bonding than that of C15-Al₂Ca.

By using the calculated Debye temperatures from phonon, the scaling factor, \( s \), in Debye_Gr"eneisen model can be adjusted, with the value of 0.67 and 0.7 for C14-Mg₂Ca and C15-Al₂Ca, respectively. The temperature dependent vibrational enthalpies, entropies, and heat capacities of C15-Al₂Ca and C14-Mg₂Ca are shown in Figure 7.3, including the ones from phonon calculations, Debye_Gr"eneisen model with the suggested scaling factor (\( s=0.617 \)) by Moruzzi et al. [191], and Debye_Gr"eneisen model with the adjusted \( s \).
Note that the thermal electronic contributions are included in this work. The calculated vibrational enthalpies shown in Figure 7.3(a) are almost identical regardless of calculation methods. In Figure 7.3(b), the entropy is calculated from \( S = -\left(\frac{\partial F}{\partial T}\right)_V \) under \( P=0 \). The predictions from phonon calculations and Debye_Gr"uneisen model using the adjusted \( s \) show consistency and are in good agreement with recommended values (0.617) [200] as well. Regarding the Debye_Gr"uneisen model using the suggested \( s \) (\( s=0.617 \)), the evaluated entropies are slightly higher than those from phonon calculations, e. g. about 6.2% and 7.7% for \( \text{Mg}_2\text{Ca} \) and \( \text{Al}_2\text{Ca} \) at 900K, respectively. The heat capacity at constant pressure is estimated by \( C_p = C_v + \beta^2 BTV \), where \( C_v \) is the heat capacity at constant volume calculated by \( C_v = -T\left(\frac{\partial S}{\partial T}\right)_V \), and \( \beta, B, T, \) and \( V \) are the volume thermal expansion coefficient, bulk modulus, temperature and volume, respectively. Table 7.4 summarizes the calculated equilibrium volume, enthalpy of formation, entropy of formation, bulk modulus, heat capacity, and linear thermal expansion at 298 K for both \( \text{C}_{15}\text{-Al}_2\text{Ca} \) and \( \text{C}_{14}\text{-Mg}_2\text{Ca} \). Vibrational contributions evaluated from phonon calculations, Debye_Gr"uneisen model with the adjusted \( s \), and Debye_Gr"uneisen model with the suggested \( s=0.617 \) [191] are also compared in Table 7.4, showing the consistent prediction of thermodynamic properties and good agreement with the available experimental data as well. At room temperature, the larger volume, the lower bulk modulus, and the lower enthalpy of formation of \( \text{C}_{14}\text{-Mg}_2\text{Ca} \) with respect to those of \( \text{C}_{15}\text{-Al}_2\text{Ca} \) confirm again the weaker bonds in \( \text{C}_{14}\text{-Mg}_2\text{Ca} \). By considering the thermodynamic properties of stable \( \text{C}_{15}\text{-Al}_2\text{Ca} \) and \( \text{C}_{14}\text{-Mg}_2\text{Ca} \), it is found that (i) with the phonon and thermal electronic contributions included, the thermodynamic properties can be well described; (ii) the vibrational enthalpy and heat capacity calculated from the
suggested scaling factor ($s$) are almost identical with the ones calculated with adjusted $s$ in Debye_Gruneisen model and in good agreement with phonon calculations and experiments, and (iii) the entropy predicted by Debye_Gruneisen model with $s=0.617$ is about 6~7% higher than that from Debye_Gruneisen model with adjusted $s$ at high temperature (900 K).

Except C14-Mg$_2$Ca and C15-Al$_2$Ca phases, the other end-members with A$_2$B type Laves structures are not stable in the Mg-Al-Ca system, and hence their vibrational properties cannot be obtained from phonon calculations. In the present work, their thermodynamic properties are investigated by the Debye_Gruneisen model with the scaling parameter $s=0.617$ [191]. The calculated entropies of formation for each A$_2$B structure at 298 K are shown in Figure 7.4 as a function of difference in metallic radius between A and B, $\Delta r$, in comparison with those calculated from the Al-Ca [198], Mg-Ca [36], and Al-Mg-Ca [197] databases. The discrepancies are expected especially for the nonstable phases as there were no experimental data to evaluate the entropies of formation of nonstable structures in the database development. For example, entropies of formations of nonstable C15-Al$_2$Al, C15-Ca$_2$Ca, and C15-Ca$_2$Al are assumed to be the same as the stable phase C15-Al$_2$Ca. It is observed that Al$_2$B has the most negative values of entropies of formation, while Ca$_2$B has the most positive values. In each group of Al$_2$B, Mg$_2$B, and Ca$_2$B, we note that the entropy of formation becomes less negative (more positive) when $\Delta r$ increases. It can be understood that when the atom B is smaller than the atom A in A$_2$B, the contact between the B atom and its neighbors becomes poorer resulting in weak A-B bonding and high entropy. The relationship between entropy of formation and $\Delta r$ in L1$_2$ phases also shows a similar trend [201].
The bonding strength can be alternatively illustrated by bulk modulus since bulk modulus is proportional to the average stretching force constant [202]. In Figure 7.5, bulk modulus of a compound with respect to its pure elements, e.g. $\Delta B(\text{Al}_2\text{Ca}) = B(\text{Al}_2\text{Ca}) - \frac{2}{3}B(\text{Al}) - \frac{1}{3}B(\text{Ca})$, are presented as a function of $\Delta r$. It is shown that $\Delta B$ becomes more negative as $\Delta r$ increases, showing weaker bonding in the compound. From both Figure 7.4 and Figure 7.5, the relationship between $\Delta S$ and $\Delta B$ are illustrated in Figure 7.6, demonstrating that the stronger bonding of a compound can be represented by a more positive (less negative) $\Delta B$ with a more negative (less positive) $\Delta S$.

For phases with the same element A in $\text{A}_2\text{B}$, it is worth noting that the more negative entropy of formation corresponds to a more negative enthalpy of formation (see Table 7.2). A more negative enthalpy of formation is an indicator of a stronger interatomic bonding and stronger bonding leads to lower vibrational entropies, and hence a more negative entropy of formation.

Furthermore, the entropies of formation of $\text{A}_2\text{B}$ are also estimated by the Debye_Grüneisen model of Wang et al. and compared with Debye_Grüneisen model of Moruzzi et al. in Figure 7.7. A perfect agreement between the calculated and experimental values is indicated by the solid line, where an error bar of ±0.5 J/mol K are shown by the dashed lines. The calculated entropies of formation from two models are consistent with each other, and the differences are within ±0.5 J/mol K in all cases.
7.5.3 Evaluation of model parameters and results

Although the Mg-Al-Ca system has been studied by several authors [197, 203-205], there are still many unsolved questions. This system contains three Laves phases: C14, C15 and C36. All these Laves phases have wide ranges of homogeneity, but the precise stability range and solubility range are still unknown.

The four isothermal phase diagram sections, calculated from the present thermodynamic model and shown in Figures 8.1~8.4, emphasize the significant changes within the Mg–Al–Ca system between 563K and 773K. The results are compared with available experimental data as superimposed. The isothermal section at 563K is shown in Figure 7.8. The ternary Laves phase C36 is not yet stable at this temperature. The experimental data [206-207] are reproduced very well by the calculation. At 643K, as shown in Figure 7.9, the C36 phase is predicted to be stable in the composition of Al₂(Mg,Ca). While in the Mg-rich corner, C36 is not stable, showing the good agreement with the experimental observations [206-207]. At 673K, the Laves_C36 phase becomes stable in the composition of Al₂(Mg, Ca) and (Mg,Al)₂(Ca). The latest experimental phase analysis data [205] are included in Figure 7.10, and it can support our predictions. Only two data [208] do not fit: those in the Mg-rich corner. It is possibly because of its single point analysis. When temperature goes up, C36 phase has a quite substantial solubility range, extending from (Mg,Al)₂(Ca) to Al₂(Mg, Ca), as shown in Figure 7.11. The binary Al-Mg compounds are already molten at this temperature; a second liquid region emerges from the Ca-rich side.
7.6 Summary

In the present work, a systematic analysis on the structural, vibrational, and thermodynamic properties of the A_2B type Laves phases with C14, C15, and C36 structures in the Mg-Al-Ca system has been performed using first-principles methods. Energy vs. volume (E-V) equations of state (EOS) are fitted to the first-principles calculations. Through the use of the supercell method with quasiharmonic corrections, the vibrational properties of fcc-Al, hcp-Mg, fcc-Ca, C14-Mg_2Ca, C15-Al_2Ca are calculated. It is shown that C14-Mg_2Ca has weaker bonds with respect to C15-Al_2Ca, which is confirmed by its larger volume, lower bulk modulus, and lower enthalpy of formation. Furthermore, a comparative study of stable structures is performed between phonon and Debye_Gr"uneisen model with scaling parameter adjusted from phonon calculation and suggested in the literature. It is found that those calculations show the consistent thermodynamic properties of C14-Mg_2Ca and C15-Al_2Ca. In addition, the thermodynamic properties of the nonstable A_2B type Laves structures are predicted by both Debye_Gr"uneisen and Debye_Wang models. Using the first-principles results for all the end-members, the thermodynamic database of the Mg-Al-Ca system is developed.
Table 7.1 Details of the first-principles and phonon calculations, including the space
group of pure elements and compounds [43], \( k \)-mesh used for the electronic and phonon
structures, the number of atoms in the supercell (SC) for phonon calculations, the
displacement (\( \Delta r \)) of disturbed atom from its equilibrium position, and the cutoff distance
(\( R_{\text{cut}} \)) for the fitting range of force constants.

<table>
<thead>
<tr>
<th>EOS Calc.</th>
<th>Space group</th>
<th>k-mesh</th>
<th>Phonon Calc.</th>
<th>SC Atoms</th>
<th>k-mesh phonon</th>
<th>( \Delta r ) (Å)</th>
<th>( R_{\text{cut}} ) phonon (Å)</th>
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<td>Al</td>
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<td>Ca</td>
<td>32</td>
<td>( 6 \times 6 \times 6 )</td>
<td>0.1</td>
<td>7</td>
</tr>
<tr>
<td>Mg</td>
<td>( P6_3/mmc )</td>
<td>( 25 \times 25 \times 15 )</td>
<td>Mg</td>
<td>36</td>
<td>( 6 \times 6 \times 6 )</td>
<td>0.1</td>
<td>6</td>
</tr>
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<td>( P6_3/mmc )</td>
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<td>( 5 \times 5 \times 5 )</td>
<td>0.1</td>
<td>7</td>
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<tr>
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<td>48</td>
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<tr>
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<td>( P6_3/mmc )</td>
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</table>
Table 7.2  Calculated equilibrium volume \((V_0)\), enthalpy of formation \((\Delta H)\), bulk modulus \((B_0)\), and pressure derivative of bulk modulus \((B'_0)\) of binary laves phases at 0 K.

<table>
<thead>
<tr>
<th>Structure</th>
<th>(V_0) (Å(^3)/atom)</th>
<th>(\Delta H) (kJ/mol)</th>
<th>(B_0) (GPa)</th>
<th>(B'_0)</th>
</tr>
</thead>
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<tr>
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<td>76.4</td>
<td>4.80</td>
</tr>
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<td>21.693</td>
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<td>38.345</td>
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<td>C15</td>
<td>44.172</td>
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<td></td>
<td>C36</td>
<td>44.017</td>
<td>8.32</td>
<td>16.1</td>
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*Calculated results at 0 K from references*

*b* Experimental results at 298 K

*c* Experimental results at 298 K are in Table 4
Table 7.3 Debye frequency and Debye temperatures of Al, Mg, Ca, C14-Mg2Ca, and C15-Al2Ca.

<table>
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<tr>
<th></th>
<th>Debye Temperature (K)</th>
<th>Debye cutoff frequency (THz)</th>
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<tr>
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<td>Calc. (a)</td>
<td>Exp. [179]</td>
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<tr>
<td>Al</td>
<td>400</td>
<td>396 [179]</td>
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<tr>
<td>Mg</td>
<td>323</td>
<td>325 [179], 323 [144], 320 [4]</td>
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<tr>
<td>C14-Mg2Ca</td>
<td>277</td>
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<tr>
<td>C15-Al2Ca</td>
<td>377</td>
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</table>

\(a\) Derived from the second moment of phonon DOS.

\(b\) Calculated Debye cutoff frequency from the eighth neighbor Born-von Karman model.
Table 7.4 Thermodynamic properties of stable intermetallic compounds at 298 K.

<table>
<thead>
<tr>
<th></th>
<th>( V_{298} ) (Å(^3)/atom)</th>
<th>( \Delta H ) (kJ/mol)</th>
<th>( \Delta S ) (J/mol)</th>
<th>( B^T ) (GPa)</th>
<th>( C_p ) (J mol(^{-1})K(^{-1}))</th>
<th>( \alpha_L ) (10(^{-6})K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>C14-Mg(_2)Ca</strong></td>
<td></td>
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<tr>
<td>Phonon</td>
<td>28.953</td>
<td>-12.12</td>
<td>-0.68</td>
<td>27.0</td>
<td>24.95</td>
<td>27.32</td>
</tr>
<tr>
<td>Debye_Gr&quot;u (\gamma=0.67)</td>
<td>29.043</td>
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<td>-0.84</td>
<td>28.0</td>
<td>25.10</td>
<td>29.45</td>
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<tr>
<td>Debye_Gr&quot;u (\gamma=0.617)</td>
<td>29.037</td>
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<td>-0.54</td>
<td>28.0</td>
<td>25.24</td>
<td>29.73</td>
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<tr>
<td>Ref.</td>
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<td>-0.99[200] [215],</td>
<td>27.71[4]</td>
<td>25.20[4], 24.58</td>
<td>25.72[4]</td>
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<td>-12.7 ± 0.63 [216],</td>
<td>-1.7[36] [216],</td>
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<tr>
<td></td>
<td></td>
<td>-13.0 ± 0.88 [217]</td>
<td>-0.46[4] [217],</td>
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<td>-12.44 [4]</td>
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<tr>
<td><strong>C15-Al(_2)Ca</strong></td>
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<td>Phonon</td>
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<td>-3.99</td>
<td>51.9</td>
<td>11.91</td>
<td>18.22</td>
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<tr>
<td>Debye_Gr&quot;u (\gamma=0.7)</td>
<td>21.917</td>
<td>-34.60</td>
<td>-3.52</td>
<td>52.8</td>
<td>12.11</td>
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<tr>
<td>Debye_Gr&quot;u (\gamma=0.617)</td>
<td>21.911</td>
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<td>-2.71</td>
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<td>12.29</td>
<td>21.97</td>
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<td>-33.4±0.6[219],</td>
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<td>-34.3±3.5[220],</td>
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<td>-29.4±0.9[221]</td>
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Figure 7.1  Enthalpies of formation for the Al-Mg-Ca ternary system in a variety of Laves structures. Where C15 structures of Al$_2$Ca, Al$_2$Al, Ca$_2$Al, and Ca$_2$Ca are from the thermodynamic database by Ozturk et al. [198], while C14 structures of Mg$_2$Ca, Mg$_2$Mg, Ca$_2$Mg and Ca$_2$Ca are from the thermodynamic database by Zhong et al. [36], and C14-Al$_2$Ca, C15-Mg$_2$Ca, C36 structures of Al$_2$Mg, and Al$_2$Ca are from the thermodynamic database by Janz et al. [197].
Figure 7.2 Phonon DOS’s of the C14-Mg$_2$Ca and C15-Al$_2$Ca at their equilibrium volumes from first-principles calculations.
Figure 7.3  Thermodynamic properties of vibrational enthalpy (H), entropy (S), and heat capacity (C_p) for Al_2Ca and Mg_2Ca from phonon calculations (—), Debye model with s=0.617 (…), and Debye model with adjusted s (— —) together with available experiments (○) [200].
Figure 7.4 Entropies of formation at 298K for the end-members in the Al-Mg-Ca ternary system plotted with respect to their relative pure elements, in comparison with the values from thermodynamic databases. Where C15 structures of Al$_2$Ca, Al$_2$Al, Ca$_2$Al, and Ca$_2$Ca are from the thermodynamic database by Ozturk et al. [198], while C14 structures of Mg$_2$Ca, Mg$_2$Mg, Ca$_2$Mg and Ca$_2$Ca are from the thermodynamic database by Zhong et al. [36], and C14-Al$_2$Ca, C15-Mg$_2$Ca, C36 structures of Al$_2$Mg, and Al$_2$Ca are from the thermodynamic database by Janz et al. [197].
Figure 7.5  Bulk modulus relatively to its pure elements for the end-members in the Al-Mg-Ca ternary system in comparison with the available data (△[4] ▽○[189] and □[212]) in the literature.
Figure 7.6 Entropies of formation at 298K for the end-members in the Al-Mg-Ca ternary system as a function of bulk modulus relative to its pure elements.
Figure 7.7 Comparison of calculated entropies of formation at 298 K for the end-members in the Mg-Al-Ca systems from Debye_Grüneisen models by Moruzzi et al. [191] and by Wang et al. [192]. The solid line shows unity (y=x) while the dashed lines present an error range of ±0.5 J/mol K.
Figure 7.8 Calculated isothermal section at 563K, in compare with experimental data [206-207].
Figure 7.9 Calculated isothermal section at 643K, in compare with experimental data[206-207].
Figure 7.10 Calculated isothermal section at 673K, in compare with experimental data [205-208].
Figure 7.11 Calculated isothermal section at 773K, in compare with experimental data [208].
Chapter 8 Conclusions and Future work

8.1 Conclusion

In this thesis, thermodynamic properties of Mg based alloys have been studied from first-principles and CALPHAD approaches. The main contributions of the present work include:

1. 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 lattice parameters and enthalpies of formation of binary compounds in these systems are calculated. Herein, the phase stabilities at 0 K are predicted. 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.

2. A comprehensive analysis of Al_{12}Mg_{17} has been performed from first-principles. The finite temperature thermodynamic properties of thermal expansion, heat capacities, and bulk modulus are analyzed. We have studied the temperature dependence of the single crystal elastic constants as well as polycrystalline elastic properties (B, G, E and v). The predicted brittleness of Al_{12}Mg_{17} is explained by calculated density of states and supported by the experimental observations.

3. Thermodynamic modeling of the Ce-Mg system was carried out based on the available experimental data. While for the Ca-Ce system, the enthalpies of mixing from first-principles calculations were used in addition to the experimental phase
equilibrium data. The thermodynamic database of the Mg-Ca-Ce ternary system was herein developed by its three constitutional binaries.

4. The thermodynamic properties for three phases (β-Mg_2Si, β’-Mg_{18}Si_{10} and β’’-Mg_5Si_6) in the Al-Mg-Si system using first-principles total energies and frozen phonon calculations. Predicted phase boundaries in Al-rich corner show good agreement with available phase stability measurements. The present work demonstrates the capability of first-principles calculations in predicting Gibbs energies of both stable and metastable phases.

5. First-principles calculations and CALPHAD approach are combined to investigate the phase equilibria in the Mg-Al-Ca system. First, first-principles calculations predict the structural, vibrational, and thermodynamic properties of the A_2B type Laves phases with C14, C15, and C36 structures. A comparative study of stable structures is performed between phonon and Debye_Grüneisen model, showing the consistent thermodynamic properties of C14-Mg_2Ca and C15-Al_2Ca. Therefore, Debye_Grüneisen and Debye_Wang models are employed to predict the thermodynamic properties of the nonstable A_2B type Laves structures, including both enthalpy and entropy of formation at room temperature. Those results are used to update the thermodynamic database of Mg-Al-Ca system. A good agreement is achieved by comparing with various experimental data at different temperatures.

### 8.2 Future works
1. First-principles calculations predict the existence of Laves_C36 phases in Mg-Al-Ca system, and it is validated by the experimental observations. However, recent publications regarding the stability range of Laves_C36 phase are conflicted with each other. More experiments are needed, especially for solubility range and stability range of ternary Laves_C36-Mg₂(Al,Ca) and Al₂(Mg,Ca) phases.

2. Since it is almost impossible to calculate the liquid phase from first-principles calculations due to the lack of long range ordering. Herein, exploration study of liquid phase by ab initio molecular dynamics (AIMD) method is desired. And we may apply this method to Ni and Ni based system.
Reference:


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VITA

Hui Zhang was born in Beijing, China. She graduated from Peking University, China in July 2004 with a B.S. degree in Chemistry. Afterwards, she joined the Pennsylvania State University, University Park, for her Ph. D. degree in Materials Science and Engineering. She received the CALPHAD Scholarship in 2007 and the Kennametal Graduate Fellowship Award in 2008. She authored or co-authored 15 peer reviewed journal publications during her Ph.D. study. Some publications are listed below:


