Ab initio study of the thermodynamic properties of rare-earth-magnesium intermetallics MgRE (RE = Y, Dy, Pr, Tb)

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Abstract
We have performed an ab initio study of the thermodynamical properties of rare-earth–magnesium intermetallic compounds MgRE (RE = Y, Dy, Pr, Tb) with B2-type structures. The calculations were carried out in the framework of density functional theory and density functional perturbation theory in combination with the quasiharmonic approximation. The phonon-dispersion curves and phonon total and partial density of states have been investigated. Our results show that the contribution of RE atoms is dominant in phonon frequency, and this character agrees with the previous discussion by using atomistic simulations. The temperature dependence of various quantities such as thermal expansion, bulk modulus and heat capacity is obtained. Electronic contributions to the specific heat are discussed, and are found to be important for the calculated MgRE intermetallics.

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1. Introduction
Magnesium (Mg) alloys have been attracting much attention and are especially attractive for applications in the aeronautical and automotive industries because of their strength to weight ratios [1]. However, traditional Mg alloys often show low strength and creep resistance at high temperature, and this feature is a very serious problem that limits their applications. Recently, it has been reported that some rare-earth–Mg intermetallic compounds MgRE (where RE indicates a rare-earth element) with B2-type structure (CsCl-type structure) have good creep and high-temperature strength [2–4]. Hence MgRE intermetallics are extremely attractive structural materials for applications in automobile parts and aerospace industries, while various studies of the magnetic properties, linear and nonlinear elasticity, stacking fault and thermal properties of B2-MgRE intermetallics have been undertaken [5–12]. Recently, Wu et al [13] have performed atomistic simulations to study the thermodynamical properties of MgY, MgDy and MgPr by using the modified analytic embedded atom method, and their results are generally in agreement with experimental data and other theoretical results. However, since the ionic degrees of freedom are treated classically in their study, this simulation is not valid at temperatures comparable to or lower than the Debye temperature. In addition, the first-principles calculation indicates that the Fermi level occurs above a peak in the electronic density of states (DOS) and B2-MgRE intermetallics have large electronic DOS at the Fermi level [7]. Therefore, the thermal electronic excitations contribution to the thermal properties must be considered. The exact calculations of the thermodynamic properties for intermetallic compounds of Mg with RE metals, especially the phonon and electron contributions being considered, have received little attention.

It is obviously crucial to take into account thermodynamic properties such as thermal-expansion coefficients, specific heat at constant volume and constant pressure, and temperature-dependent bulk modules in the investigation of the properties of MgRE intermetallics as
well as their applications. A simplified method for thermal expansion calculations is in the framework of density functional theory (DFT) with a Debye–Grüneisen-based model [14]. A more accurate approach is first-principles DFT treatments within the quasiharmonic approximation (QHA), which provides a reasonable description of the thermodynamical properties of many bulk materials below the melting point [15–19]. QHA lets one take into account the anharmonicity of the potential at first order: vibrational properties can be understood in terms of the excitation of the noninteracting phonon. The exact calculations of phonon frequencies at every point of the Brillouin zone can be achieved by the density functional perturbation theory (DFPT) [20]. Today, QHA based on DFPT has been applied with great success to several complex materials such as alloys (NiAl and NiAl3 [21]), perovskite (MgSiO3 [22]) and hexaborides (LaB6 and CeB6 [23]).

In this paper, we apply first-principles calculations within QHA to study the thermodynamic properties of light RE MgPr, heavy RE MgY, MgDy and MgTb intermetallics with B2 structures. The phonon-dispersion curves and phonon DOS have been discussed. Thermal expansions, temperature dependence of isothermal bulk modules and heat capacities at constant volume and constant pressure are presented. In addition, we consider the electronic contribution to the thermal properties, and our results show that the effects of thermal electronic excitations for MgRE (RE = Y, Dy, Pr, Tb) are remarkable.

2. Theory

The equilibrium lattice volume \( V \) of a crystal with cubic symmetry at any temperature \( T \) is obtained by minimizing the Helmholtz free energy, \( F \), of a system. The free energy at temperature \( T \) and constant volume \( V \) is given by

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

where \( E_0(V) \) is the ground state \( (T = 0 \text{ K}) \) total energy of the crystal and \( F_{\text{ vib}}(V, T) \) is the vibrational energy that comes from the phonon contribution. Within the QHA, \( F_{\text{ vib}}(V, T) \) is written in the form

\[
F_{\text{ vib}}(V, T) = \frac{1}{2} \sum_{\mathbf{q}} \hbar \omega_{\mathbf{q}}(V)
+ k_B T \sum_{\mathbf{q}} \ln \left[ 1 - \exp \left( - \frac{\hbar \omega_{\mathbf{q}}(V)}{k_B T} \right) \right].
\]

Here, the sum is over all three phonon branches \( \lambda \) and over all wave vectors \( \mathbf{q} \) in the first Brillouin zone, \( k_B \) is the Boltzmann constant, \( \hbar \) is the reduced Planck constant and \( \omega_{\mathbf{q}}(V) \) is the frequency of the phonon with wave vector \( \mathbf{q} \) and polarization \( \lambda \), evaluated at constant volume \( V \). The first and second terms of equation (2) represent the zero point \(( \langle F^{\text{ ph}} \rangle )\) and thermal energies \(( \langle F^{\text{ th}} \rangle \)), respectively. For the thermal electronic contribution to free energy, \( F_{\text{el}} = E_{\text{el}} - TS_{\text{el}} \). The electronic energy \( E_{\text{el}} \) due to thermal electronic excitations is given by

\[
E_{\text{el}}(V, T) = \int_0^\infty n(\varepsilon, V) f(\varepsilon) \varepsilon \, d\varepsilon - \int_0^\infty n(\varepsilon, V) \varepsilon \, d\varepsilon,
\]

where \( n(\varepsilon, V) \), \( f(\varepsilon) \) and \( \varepsilon_p \) represent the electronic DOS, the Fermi–Dirac distribution and the Fermi level, respectively. The electronic entropy \( S_{\text{el}} \) is formulated as

\[
S_{\text{el}}(V, T) = -k_B \int_0^\infty n(\varepsilon, V) [f(\varepsilon) \ln f(\varepsilon)
+ (1 - f(\varepsilon)) \ln(1 - f(\varepsilon))] \, d\varepsilon.
\]

Usually, it is assumed that the electronic contribution to total free energy can be negligible.

To calculate free energy, one must be able to calculate frequencies over the entire Brillouin zone, and this can be done exactly using DFPT calculations. Furthermore, this calculation must be performed at various values of lattice parameter \( a \) in the case of isotropic thermal expansion for the B2-type structure crystal. The equilibrium lattice constant at temperature \( T \) is obtained by minimizing \( F \) with respect to \( a \). The coefficient of volume thermal expansion is given by

\[
\alpha(T) = \frac{1}{V} \left( \frac{dV(T)}{dT} \right)
\]

and the linear thermal expansion is described by

\[
\epsilon(T) = \frac{a(T) - a(T_c)}{a(T_c)},
\]

where \( a(T_c) \) is equilibrium lattice constant \( a(T) = [V(T)]^{1/3} \) at \( T_c = 300 \text{ K} \).

Once the phonon spectrum is obtained, we can easily compute the temperature dependence of the vibrational specific heat capacity \( C_V \) and the entropy \( S \) at constant volume, as described by

\[
C_{V}^{\text{ph}} = \sum_{\mathbf{q}} k_B \left( \frac{\hbar \omega_{\mathbf{q}}(V)}{2k_B T} \right)^2 \cosh^2 \left( \frac{\hbar \omega_{\mathbf{q}}(V)}{k_B T} \right)
\]

and

\[
S_{\text{ph}} = -k_B \sum_{\mathbf{q}} \ln \left( \frac{2 \sinh \frac{\hbar \omega_{\mathbf{q}}(V)}{2k_B T}}{2 \cosh \frac{\hbar \omega_{\mathbf{q}}(V)}{2k_B T}} \right),
\]

respectively. In addition, at constant volume the electronic heat capacity can be obtained from

\[
C_{V}^{\text{el}} = T \left( \frac{\partial S_{\text{el}}}{\partial T} \right)_V
\]

and we denote total specific heat at constant volume as \( C_V = C_{V}^{\text{ph}} + C_{V}^{\text{el}} \).

\( C_p \), the specific heat at constant pressure, can then be computed by using the relation

\[
C_p = C_V + \alpha^2 BVT,
\]

where \( B(T) = -1/V \partial^2 F/\partial V^2 \) is the bulk modulus.
3. Computational details

The first-principles calculations within DFT were performed using the VASP program [24–26]. We employed the projector-augmented wave (PAW) method [27, 28]. The Perdew–Burke–Ernzerhof (PBE) [29, 30] exchange-correlation functional for the generalized gradient approximation (GGA) was used. The structures were relaxed without any symmetry constraints with a cutoff energy of 600 eV for all calculated intermetallics. The Brillouin zones of the unit cells were represented by the Monkhorst–Pack special \( k \)-point scheme [31] with \( 21 \times 21 \times 21 \) grid meshes. The radial cutoffs of the PAW potentials of Mg, Y, Dy, Pr and Tb were 1.41, 1.72, 1.58, 1.61 and 1.58 Å, respectively. The 3s electrons for Mg, the 4s, 4p, 4d and 5s electrons for Y, and the 4f and 6s electrons for Dy, Pr and Tb were treated as valence electrons and the remaining electrons were kept frozen. In order to deal with the possible convergence problems of metals, a smearing technique was employed using the Methfessel– Paxton scheme [32], with added smearing of 0.05 eV.

We took the supercell approach within the framework of the force-constants method for the phonon calculations. Real-space force constants of the supercell were calculated in the DFPT implemented in the VASP code\(^1\) from forces on atoms with atomic finite displacements, and the phonon frequencies were calculated from the force constants using the PHONOPY package [33]\(^2\). From the full phonon spectrum, the lattice vibration free energies were calculated. Since the chosen supercell size strongly influences the thermal properties, we compared the vibrational free energies of the \( 3 \times 3 \times 3 \) supercell with those of the \( 4 \times 4 \times 4 \) supercell at 300 and 1000 K, and found that the energy fluctuations between the \( 3 \times 3 \times 3 \) and \( 4 \times 4 \times 4 \) supercells are less than 0.01%. So an adequate supercell size consisting of \( 3 \times 3 \times 3 \) unit cells was chosen to calculate the thermal properties for all calculated intermetallics; however, it has to be considered that Grabowski et al [34] reported that a small error in phonon calculation may bring about significant changes in the calculated thermal properties, especially at high temperatures. The thermal electronic energies and entropies were evaluated using one-dimensional integrations from the self-consistent DFT calculations of electronic DOS using Fermi–Dirac smearing as shown in equations (3) and (4). In order to obtain the temperature dependence of lattice parameters, we calculated total free energy at temperature points with a step of 1 K from 0 to 1000 K at 15 volume points. At each temperature

\(^1\) VASP—the guide http://cms.mpi.univie.ac.at/vasp/vasp.html

\(^2\) Phonopy http://phonopy.sourceforge.net
4. Results and discussions

4.1. Phonon-dispersion curves and phonon DOS

The calculated phonon-dispersion curves of four intermetallic compounds, which were calculated using $3 \times 3 \times 3$ supercells, are displayed in figure 1. The phonon properties of all calculated intermetallics were computed within the GGA in the B2-type structure, with space group symmetry Pm3m(221), in which the Mg atom is positioned at $(0, 0, 0)$ and the RE (RE = Y, Dy, Pr, Tb) atoms at $(0.5, 0.5, 0.5)$. These materials contain two atoms per primitive cubic unit cell. Owing to the symmetry, the dispersion curves are shown along the high-symmetry direction $\Gamma-X-M-\Gamma-R$ of the Brillouin zone. These dispersion curves have a common framework. There is a phonon band gap starting around $3$ THz. The maximum value of acoustic modes for MgY is slightly greater than $3$ THz and those for MgDy, MgTb and MgPr are slightly lighter than this value, since the atomic mass of Y is smaller than those of Dy, Tb and Pr.

The phonon DOSs including the partial DOS (PDOS) and the total DOS (TDOS) are shown in figure 2. Sampling a $51 \times 51 \times 51$ Monkhorst–Pack grid for phonon wave vectors $q$ is found to be sufficient in order to obtain the mean relative error in each channel of phonon DOS. The flat regions of phonon-dispersion curves, which correspond to the peaks in the phonon PDOS, indicate localization of the states, i.e. they behave like ‘atomic states’ [19]. For the four intermetallics, we find that the DOSs are mostly composed of Mg states above the phonon band gap because its atomic mass is lighter than those of the RE elements (RE = Y, Dy, Pr, Tb). Our results agree with the previous theoretical investigation in which the contribution of RE atoms is dominant in phonon frequency because they are heavier than Mg atoms [13].

4.2. Bulk properties and thermal expansion

The present results of the equilibrium lattice constants $a_0$ and isothermal bulk modulus $B_0$ at $T = 0 \text{K}$ for MgRE (RE = Y, Dy, Pr, Tb) intermetallics together with the available experimental values [36] and the previous calculated results [7] are shown in table 1. Our calculated results for the equilibrium lattice constants are within 0.8% of the experimental values, and show excellent agreement with the previous theoretical results. For the bulk modulus $B_0$ values
Table 1. Equilibrium lattice constants $a_0$ and bulk modulus $B_0$ at $T = 0$ K for MgRE (RE = Y, Dy, Pr, Tb) in our calculation in comparison with the previous calculated and experimental results.

|          | MgDy       | MgY       | MgTb       | MgPr       |
|----------|------------|-----------|------------|------------|
| $a_0$ (Å) | 3.778, 3.765$^a$, 3.759$^b$ | 3.795, 3.796$^c$, 3.796$^b$ | 3.789, 3.781$^a$, 3.781$^b$ | 3.910, 3.901$^c$, 3.912$^b$ |
| $B_0$ (GPa) | 41.35, 42.32$^c$ | 41.25, 42.06$^a$ | 40.84, 41.89$^b$ | 36.86, 37.20$^a$ |

$^a$Wu and Hu [7].  
$^b$Villars and Calvert [36] experiment.

that are obtained from Vinet EOS, the present results are within 1.9% error from the previous calculated values. The isothermal bulk modulus as a function of temperature $B(T)$ is shown in figure 3. Among the four intermetallic compounds, through the temperature range, heavy RE MgDy and light RE MgPr have the highest and lowest bulk moduli, respectively, i.e. MgDy is the most incompressible and MgPr is the most compressible. This indicates that the mechanical properties of MgRE intermetallics can be further improved by the addition of heavy RE metals [13]. With increasing temperature, the bulk moduli of the four intermetallics decrease and the differences among the bulk moduli almost remain unchanged. This character demonstrates that MgRE intermetallics can retain their mechanical properties through a wide temperature range and have good high-temperature stability, and agrees well with recent reports that the MgRE intermetallics have good strength at high temperature in comparison with traditional Mg alloys [2–4].

The temperature dependence of the linear thermal expansion $\epsilon$ defined by equation (6) of the four MgRE intermetallics is shown in figure 4. The linear expansions of the four compounds are MgTb > MgPr > MgDy > MgY; however, the differences among them are small. The coefficient of the volume thermal expansion $\alpha$ as a function of temperature is shown in figure 5. With increasing temperature, the thermal expansion grows rapidly up to $\sim$400 K, and the slopes become smaller and nearly constant at high temperature. Below $\sim$200 K, those of MgDy, Mg Tb and MgPr are equivalent and are greater than that of MgY. The reason can be understood from the electron configurations of the corresponding elements. We have electron structures with Mg(3s$^2$), Y(4d$^1$5s$^2$), Dy(4f$^{10}$6s$^2$), Pr(4f$^3$6s$^2$) and Tb(4f$^9$6s$^2$). All the elements have two s electrons, and the outermost shell of RE element Y includes the d electrons while the other elements include f electrons. So the thermal expansion of MgY is smaller than those of MgDy, MgPr and MgTb. At high temperatures, those of MgTb and MgPr tend to be equivalent.

4.3. Specific heat

Once the phonon spectrum over the entire Brillouin zone is available, the vibrational heat capacity at constant volume $C_V^{\text{vib}}$ can be calculated by equation (7), whereas the electronic
contribution to heat capacity at constant volume $C_V^{el}$ can be obtained from the electronic DOS using equation (9). Then, the specific heat at constant pressure $C_P$ can be computed by equation (10). As a comparison, both $C_V$ values, including and excluding electronic contribution, are plotted. We display the results in figure 6. As temperature increases, $C_V^{vib}$ tends to the classical constant 6R, and $C_V^{el}$ and $C_P$ still increase. At low temperatures below $\sim 200$ K, the discrepancy between $C_P$ and $C_V$ can be neglected. For thermal electronic contributions to specific heat, we find that $C_V^{el}$ is not negligible at high temperature although smaller than $C_V^{vib}$. This character can be understood from the electronic DOS at the Fermi energy level $f(\varepsilon_F)$. For MgRE, they have large electronic DOS near the Fermi level. When we consider the electronic contribution, the theoretical $C_P$ keeps positive slopes obviously. $C_V^{el}$ is smaller than $C_V^{vib}$, but it is larger than the value $C_P - C_V = \alpha^2 BVT$. Usually, the electronic heat capacity can be expressed as $C_V^{el} = \gamma T$, where $\gamma$ is known as the electronic constant. As a guide to the eye, we should mention that the order of these quantities (from lower to higher) is $\gamma$(MgPr) < $\gamma$(MgDy) < $\gamma$(MgTb) < $\gamma$(MgY). As previously studied by Wu and Hu [7], the Fermi level for MgRE occurs above a peak in the electronic DOS; the bonding states are full, and filling of the anti-bonding states is sensitive to deviations in the local structure that affect the Fermi level; so the electronic excitations affecting the thermal properties are remarkable. From figure 6, it is clear that the electronic contribution should be considered for MgRE intermetallics.

5. Conclusions

In conclusion, the thermal properties of MgRE intermetallics (RE = Y, Dy, Pr, Tb) with B2 structures, such as thermal expansion, bulk modulus and heat capacities at constant volume and constant pressure, as a function of temperature are studied by using DFT and DFPT in combination with QHA. The contribution of RE atoms is dominant in phonon frequency since the Mg atomic mass is lighter than those of the RE elements. Through the temperature range, heavy RE MgDy is the most incompressible and light RE MgPr is the most compressible. With increasing temperature, the bulk moduli of the four intermetallics decrease and the differences among the bulk moduli almost remain unchanged. In thermal expansion, we find MgTb > MgPr > MgDy > MgY at high temperature, and below $\sim 200$ K those of MgDy, MgTb and MgPr are equivalent and are greater than that of MgY. The electronic contributions to the specific heat are discussed, and are found to be important for the calculated MgRE intermetallics.
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