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Ab initio calculation of the total energy and elastic properties of Laves phase C15 Al_2RE (RE = Sc, Y, La, Ce–Lu)

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ABSTRACT

Ab initio calculations for the total energy and elastic properties of the C15-type Al_2RE (RE = Sc, Y, Lanthanide) at $T = 0$ K have been performed by using the projector augmented-wave (PAW) method within the generalized gradient approximation (GGA). The lattice constants, formation enthalpies, elastic constants, bulk modulus and its pressure derivatives of the C15-type Al_2RE are obtained. Poisson's ratios, Young's modulus, shear modulus and the ratios of elastic anisotropy are also estimated in the present work. By using the Debye–Grüneisen model, the Debye temperatures, Grüneisen constants and the coefficients of thermal expansion at $T = 300$ K are obtained for the C15-type Al_2RE. The present calculated results are in good agreement with reported experimental values and with other theoretical calculations available as well.

1. Introduction

Because of their excellent physical and chemical properties [1–10], Laves phases with formula A_2B have been considered for many important and attractive applications, such as superconducting materials, giant magnetostrictive materials, hydrogen storage materials and high-temperature structural materials. In the Al–RE system, there exist Laves phases. All the Al_2RE have Laves C15-type A_2B structure (Pearson symbol cF24, prototype Cu_2Mg) [11]. Systematic knowledge of the basic thermodynamic and mechanical properties of the Laves C15 Al_2RE phase is important for the novel material design and further scientific and technical investigations.

Many researches have been performed about the properties of the Al_2RE Laves phases. The magnetic excitation spectrum of the ferromagnetic Al_2Nd [12], and the magnetostriction of the Al_2Pr [13] and Al_2Tb [13], and some magnetic properties of the Al_2Pr [14], Al_2Er [15] and Al_2Gd [16] have been investigated. Recently, the magnetic entropy change and the magnetocaloric effect of the Al_2Dy, Al_2Er and Ni_2Dy have been studied [17]. Nevertheless, ground-state property of the Al_2RE was far to be understood.

Recently, *ab initio* calculations was successfully employed to study ground-state properties such as the structure and phase stabilities, formation enthalpy, electronic structures and elastic properties for the Laves phase compounds $TiCr_2$, $ZrCr_2$, $HfCr_2$ and $ZrMn_2$ by Chen et al. [18], and the electronic structure of the Laves phase intermetallics LnM_2 (Ln = Y, La–Lu, M = Mg, Al) by Orgaz [19]. In the present work, the thermodynamic and mechanical properties of the Laves C15 Al_2RE are calculated using density functional theory. This paper was organized as follows. The details of *ab initio* calculations using the PAW method within the GGA are described in Section 2, calculations for the formation enthalpies and lattice constants of the Laves C15 Al_2RE in Section 3, and elastic constants of the Laves C15 Al_2RE based on equilibrium volume in Section 4. In Section 5, the thermal properties of the Laves C15 Al_2RE are obtained by using the Debye–Grüneisen model. Conclusions are drawn in Section 6.

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2. Computational details

Ab initio calculations were performed by using the scalar relativistic all-electron Blöchl's projector augmented-wave (PAW) approach [20,21] within the generalized gradient approximation (GGA), as implemented in the highly-efficient Vienna *ab initio* simulation package (VASP) [22,23]. For the GGA exchange-correlation function, the Perdew–Wang parameterization (PW91) [24,25] was employed. A plane-wave energy cutoff of 360 eV was taken for all the Laves C15 Al_2RE phases. The k-point meshes for Brillouin zone sampling were constructed using the Monkhorst–Pack scheme [26] and a $15 \times 15 \times 15$ k-points mesh are used in all Al_2RE compounds, and the total energy is converged to be better than 5 meV/atom. Spin polarization with ferromagnetic ordering was used in all calculations and we found all the C15 Al_2RE alloys considered here are not magnetic. In the present calculation, the potpaw_GGA pseudopotentials of Al, Sc, Y_sv, La, RE_3 (RE = Ce, Pr, Nd, Pm, Sm, Gd, Tb, Dy, Go, Er, Tm, Lu), Eu_2, Yb_2 are used.

In order to obtain the equilibrium unit cell volumes, the total energy calculations were performed for each structure with a set of volumes, with all atoms occupying their ideal lattice sites. Those total energies as a function of volume were then fitted to the Rose's equation of state [27]. Then the equilibrium volume (Ω_0), the formation enthalpy, the bulk modulus and its pressure derivative $(\partial B/\partial P)_T$ were evaluated.

The formation enthalpy for the C15-type Al_2RE alloys was calculated by the following equation:

$$\Delta H(\mathrm{Al_2RE}) = E_{\mathrm{total}}(\mathrm{Al_2RE}) - 2E_{\mathrm{total}}(\mathrm{Al}) - E_{\mathrm{total}}(\mathrm{RE}) \tag{1}$$

where $E_{\mathrm{total}}(\mathrm{Al_2RE})$, $E_{\mathrm{total}}(\mathrm{Al})$, and $E_{\mathrm{total}}(\mathrm{RE})$ are the calculated total energies (per atom at $T = 0$ K) of the C15-type Al_2RE compounds, Al and RE, respectively. During calculation, Al, Ce, and Yb are of fcc structure, Eu of bcc structure, La, Nd, Pr and Pm with dhcp structure, and Sc, Y, Gd, Tb, Dy, Ho, Er, Lu with hcp structure.

3. Equilibrium lattice constant and formation enthalpy

The calculated lattice constants, formation enthalpies, bulk modulus and its pressure derivative for the C15-type Al_2RE are listed in Table 1. The reported experimental data and theoretical results available are also included for comparison. Zhu et al. [28] have critically reviewed the formation enthalpies of binary Laves phases, and pointed out that Miedema's theory is capable of predicting the formation enthalpy of transition-metal lanthanide Laves-phase systems [29,30]. However, a comparative analysis of the calculated data by Miedema's theory and the reported experimental data clearly shows that discrepancies between the calculated and measured data are commonly of the order of 0.07–0.28 eV/atom. As a good alternative method, *ab initio* calculations based on density functional theory can provide accurate formation enthalpies of Laves phases [31].

3.1. Al_2Sc

The lattice constant of the C15-type Al_2Sc has been obtained to be 7.580 Å [32]. Same value has been reported by Croft and Levine [33]. From the Ruderer et al's experiment [34], the lattice constant of Al_2Sc is about 7.600 Å. Schuster et al. [35] and Cacciamni et al. [36] also measured the lattice constants of the Al_2Sc, which was respectively reported to be 7.5748 Å and 7.578 Å. The present calculated value is 7.573 Å. Obviously, the calculated lattice constant in this work agrees well with all reported values.

Formation enthalpy of Al_2Sc reported by Cacciamni et al. [36] is −0.489 eV/atom. Using acid solution calorimetry method, Pyagai et al. [37] determined the formation enthalpy of the Al_2Sc to be −0.974 eV/atom. Recently, by using the VASP code, formation enthalpy for the Al_2Sc was calculated to be −0.488 eV/atom [31], which is much close to the experimental data of Cacciamni et al. [36] and the present calculated value (−0.488 eV/atom).

Asta et al. [38] also studied the Al–Sc system by using local density approximation (LDA) with in the VASP code, and the calculated bulk modulus is 94 GPa for the Al_2Sc alloy. The bulk modulus calculated by Mayer et al. [39] is 92 GPa with NFP method. Anton and Schmidt [40] investigated the elastic constants of Laves phases by density functional theory, and obtained the bulk modulus of the Al_2Sc as 91 GPa employing the augmented spherical wave (ASW) and the full potential linear muffin-tin orbitals with gradient correction (FLG) band calculations. The present calculated value (89.49 GPa) is in good agreement with the full potential calculations.

3.2. Al_2Y

The lattice constant of Al_2Y has been studied in many literatures. Rao et al. [41] obtained the single crystal of the Al_2Y with the Czochralski method, and the lattice constant of Al_2Y was found to be 7.8611 Å at room temperature. Other values, 7.855 Å [42], 7.864 Å [43], 7.8654 Å [44] and 7.8687 Å [45], were also reported. It is clear that all the reported values for lattice constant of Al_2Y are comparable. In this work, the lattice constant of Al_2Y is calculated to be 7.881 Å, in good agreement with all the experimental values.

Formation enthalpy for the compound Al_2Y reported by Snyder [44] is −0.838 eV/atom. By a high-temperature calorimetry, a value of formation enthalpy of Al_2Y, −0.522 eV/atom, was measured [46]. Later, by means of liquid-metal solution calorimetry, Timofeev et al. [47] found that the formation enthalpy for the Al_2Y is −0.554 eV/atom. In this work, formation enthalpy of Al_2Y is calculated to be −0.540 eV/atom, which is consistent to the experimental values except the value published by Snyder [46].

The bulk modulus of the Al_2Y was obtained 82 GPa and 89 GPa respectively by using FLG and ASW band calculations [40]. Mayer et al. [39] calculated the bulk modulus of the Al_2Y to be 86 GPa by using NFP method. The experimental value of the bulk modulus for the Al_2Y was reported to be 82 GPa [45]. Compared with experimental value and other theoretical calculations, the present calculated bulk modulus (79.41 GPa) is reasonable.

3.3. Al_2La

Schiltz and Smith [45] firstly measured the lattice constant of Al_2La and obtained a value of 8.1495 Å. Other close values were later reported to be 8.1489 Å [48], 8.14 Å [49] and 8.125 Å [50], respectively. It indicates that the present calculated value (8.150 Å) is in good agreement with all experimental data.

Formation enthalpy for the compound Al_2La reported by Jung et al. [46] is −0.517 eV/atom. Using calorimetry, Sommer et al. [51] determined the formation enthalpy for the Al_2La to be −0.488 eV/atom. By same method, Colinet et al. [53] found that the formation enthalpy for Al_2La is −0.562 eV/atom. Recently Borzone et al. [52] obtained the formation enthalpy for Al_2La to be −0.523 eV/atom. Despite of a small deviation from above experimental data, the present calculated formation enthalpy (−0.506 eV/atom) is still acceptable.

Many authors have studied the bulk modulus of Al_2La. Schiltz and Smith [45] reported that the bulk modulus of Al_2La is 71 GPa. Using NFP method, Mayer et al. [39] calculated the bulk modulus of 76 GPa. By employing FLG and ASW band calculations respectively, Anton and Schmidt [40] also obtained the bulk moduli of 71 GPa and 64 GPa. The bulk modulus of the Al_2La reported by Vedel et al. [50] is 70 GPa. The present calculated value is 66.69 GPa. Clearly, the present value is close to that calculated one, 64 GPa.