First-principles study of structural and electronic properties of Laves phases structures YM$_2$ (M = Cu and Zn)

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Abstract. First-principles calculations have been carried out to investigate the structural properties and electronic structure of the main binary Laves phase YCu$_2$ and YZn$_2$ with C14, C14, C36 and CeCu$_2$ structures in Cu-Y-Zn alloy, respectively. The total energies of Laves phases with various occupations of nonequivalent lattice sites in all four structural forms have been calculated Ab initio by a pseudopotential VASP code. The optimized structural parameters were in very good agreement with the experimental values. The calculated heat of formation showed that the CeCu$_2$-YCu$_2$ and YZn$_2$ Laves phase was of the strongest alloying ability and structural stability. The electronic density of states (DOS) and charge density distribution were given.

1. INTRODUCTION

This paper concentrates on a particular class of intermetallic phases, the so-called Laves phases. These phases, which form the largest group of intermetallic with more than 1400 representatives, have the ideal composition AB$_2$. An intermetallic compound is classified as a Laves phase purely on the basis of the geometry of the crystal structure. The Laves phases crystallize in three structure types: cubic MgCu$_2$ (C15), hexagonal MgZn$_2$ (C14) and hexagonal MgNi$_2$(C36) [1–4]. An orthorhombic structure also exists where are observed a number of AB$_2$ intermetallics, namely the CeCu$_2$-type structure.

In the past decades several heuristic approaches to describe the stability have been applied to the family of Laves phases. In particular geometrical concepts relying on symmetry, packing density or electronic factors like valence electron concentration or the difference in electronegativity have been considered. However, these concepts are of limited value. They have turned out to be of low predictability even in binary systems and they are inapplicable for extrapolation, e.g., by introducing more components.

The exploration of Laves phases as materials components has revealed many problems in our understanding of intermetallics. A breakthrough in the targeted development of materials with superior properties based on intermetallics compared to steel alloys can only be expected after a much better understanding of their stability and chemical bonding [5]. First-principles density functional theory calculations have been broadly used to study the electronic structure and mechanical properties of laves phase compound. Two groups have used the linear muffin-tin orbital (LMTO-NFP) to study these compounds. B. Mayer et al. [6] studied the MAl$_2$ (M=Ca, Y, Sc and La) and MCr$_2$ (M=Ti, Zr, Nb and Ta), K.S. Kumar et al. [7,8] studied theMCr$_2$ (M=Ti, Zr, Ta, Nb, Sc, Y, La), other three groups have used the Vanderbilt-type ultrasoft pseudopotential (USPP) incorporated in the Vienna ab initio simulation package (VASP), Xiaoma Tao et al. [9] studied MAl$_2$ (M=Sc, Y, La, Ce–Lu), Yifang Ouyang et al. [10] studied the MMg$_2$ (M=La, Ce, Pr, Nd, Pm, Sm, Gd), Subhadeep Kal et al. [11] studied the MZn$_2$ (M=Ca and Sr) and MAl$_2$ (M=Sr and Ba); Their results showed that density functional theory (DFT) calculations can give satisfactory values that would often be otherwise difficult to obtain directly from experiments. In this paper, we have performed ab initio calculations to investigate the stability, electronic and structural properties of YCu$_2$ and YZn$_2$.

2. CALCULATION METHODS AND CRYSTAL STRUCTURES

Calculations were performed using the VASP [12–14] code based on the density functional theory (DFT) [15,16]. Ultrasoft Vanderbilt-type pseudopotentials [17] were used to describe the interactions between ions and electrons. The generalized gradient approximation (GGAPW91) due to Perdew and Wang [18] was applied to evaluate the exchange-correlation energies of all examined structures. Sampling of the Brillouin zone was done via $9 \times 9 \times 9$ and $11 \times 11 \times 11$ k-point grid generated according to the Monkhorst–Pack scheme [19] for YCu$_2$ and YZn$_2$ respectively. The cut-off energy restricting the number of plane waves in the basis set was set to 292.2 eV for YCu$_2$ and 261.9 eV for YZn$_2$.

Laves phases belong to the class of Frank–Kasper phases showing topologically close-packed structures. They have the general composition AB$_2$ with the larger A atoms in the centre of a 16-atom Frank–Kasper polyhedron and the smaller B atoms in the centers of icosahedra. The coordination number for the A atoms is 16 (4A and 12B atoms) and 12 (6A and 6B atoms) for the B atoms. The closest packing of hard spheres of types A and B is obtained for the radius ratio $r_A/r_B = (3/2)^{1/2}$ $\approx$ 1.225 [20].

The structural relaxation and optimization have been performed from the above configurations. The energies of these AB$_2$ Laves phases were minimized to determine the internal atomic coordinates. The obtained optimal atomic coordinates from energy minimization were Y 4f (0.33, 0.67, 0.062), Cu (Zn) 2a (0, 0, 0) and Cu (Zn) 6h (0.83,
Table 1. The calculated ground state properties of pure elements. Experimental values are listed in parentheses, cell parameters (a, b, c in Å), bulk modulus (GPa).

<table>
<thead>
<tr>
<th>Parameters/ metals</th>
<th>Y</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valence electrons</td>
<td>1s²d⁶</td>
<td>1s²d⁴p¹</td>
<td>1s²d⁴p²</td>
</tr>
<tr>
<td>Space group</td>
<td>P6₃/mmc</td>
<td>Fm3m</td>
<td>P6₃/mmc</td>
</tr>
<tr>
<td>Z</td>
<td>3</td>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>Cell angles</td>
<td>90/60</td>
<td>90</td>
<td>90/60</td>
</tr>
<tr>
<td>Cell constants</td>
<td>a = b</td>
<td>3.63</td>
<td>3.64</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>5.61</td>
<td>–</td>
</tr>
<tr>
<td>Bulk modulus</td>
<td>(3.65)²</td>
<td>(3.61)²</td>
<td>(2.66)²</td>
</tr>
<tr>
<td></td>
<td>(5.73)²</td>
<td>–</td>
<td>(4.95)²</td>
</tr>
<tr>
<td></td>
<td>(58.56)²</td>
<td>(137.0)²</td>
<td>(95.68)²</td>
</tr>
</tbody>
</table>

*Ref. [24].

0.66, 0.25) sites for C14 Laves phase structure, and 0.125, 0.125, 0.125) and Cu (Zn) 16d (0.50, 0.50, 0.50) sites for C15 Laves phase, and Y 4e (0, 0, 0.093), Y 4f (0.33, 0.67, 0.16), Cu (Zn) 6g (0.50, 0.50, 0.50) and Cu (Zn) 6h (0.16, 0.33, 0.25) sites for C36 Laves phase structure [21]. However, these compounds often pass through phase transformations, especially to and from the orthorhomic CeCu₂ structure and the optimal atomic coordinates for this structure were Ce 4e (0, 0.25, 0.5377) and Cu 8h (0, 0.0510, 0.1648) [22].

3. RESULTS AND DISCUSSIONS

3.1. Stability and structural properties

We performed these calculations to investigate structural competition between some Laves phase structures for the systems YCu₂ and YZn₂. As Laves phase structures we considered cubic MgCu₂ (C15), hexagonal MgZn₂ (C14) and hexagonal MgNi₂ (C36).

As shown in Table 1 the cell parameters of pure Cu and Zn are overestimated whereas, many previous calculations on transition metals clearly indicated that cell constants were usually underestimated with standard DFT method, even GGA is applied, and it is the same for the bulk modulus of the two elements. While the calculation of cell parameters and bulk modulus of pure Y are in good agreement with the experimental values.

The total energy as a function of the cell volume was fitted by Birch-Murnaghan equation of state [25]. Then the lattice constants of YCu₂ and YZn₂ Laves phases were calculated and listed in Table 1, together with the lattice constants of pure Y, Cu and Zn. It can be seen that the obtained results of the lattice parameters were close to the available other theoretical values, and the errors was not more than 0.1 Å.

Figure 1 summarizes the results in the form of total energy vs. volume curves. For the 6 valence electron system YZn₂ the cubic MgCu₂ structure is preferred over the hexagonal MgNi₂ and the hexagonal MgZn₂ structure, this is in disagreement with the result obtained by S. Kal et al. [26], while for the 4 valence electron system YCu₂ the hexagonal MgZn₂ structure is preferred over the MgNi₂ and the cubic MgCu₂ structure.

Hexagonal and cubic Laves phases attain the same equilibrium volume for a particular system. The more open packed CeCu₂ structure yields a higher equilibrium volume (by about 5%) compared to the close-packed arrangements. This is similar with to the other theoretical and experiment results [27]. The stabilization of the CeCu₂ structure over a close-packed arrangement increases from YCu₂ and YZn₂.

For YCu₂ and YZn₂ the crossing of the energy-volume curves of the close-packed Laves phase structures and the orthorhobic CeCu₂ structure. From this behavior theory predicts a high-pressure structural transition.
respectively, which are greater than \(-C_{36}\) and CeCu\textsubscript{2} structures the heat of formation for \(YCu_2\) occurs at a pressure \(P_{tr}\) (show Table 3).

<table>
<thead>
<tr>
<th>Structure</th>
<th>Pressure at transition (P_{tr}) (GPa)</th>
</tr>
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<tbody>
<tr>
<td>YCu\textsubscript{2}</td>
<td>16.7 (C14) – 17.5 (C36) – 28.5 (C15)</td>
</tr>
<tr>
<td>YZn\textsubscript{2}</td>
<td>19.5 (C14) – 14.8 (C36) – 12.2 (C15)</td>
</tr>
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</table>

At 0 K (which the calculations refer to) \(G = E + pV\). The difference in Gibbs-free energy \(G\) of two phases 1 and 2 at a given pressure \(p\) is given by the difference between intersections of parallel tangents \(p = -(\partial E_1/\partial V)_{h=1} = -(\partial E_2/\partial V)_{h=2}\) with the ordinate axis. A transformation occurs at a pressure \(p_{tr}\) at which the tangents coincide \((\Delta G = 0)\) [26]. With this so-called common tangent method transition pressures for a CeCu\textsubscript{2}-type to Laves phase structural change are estimated as 16.7 GPa (CeCu\textsubscript{2} to C14) and 12.2 GPa (CeCu\textsubscript{2} to C15) for YCu\textsubscript{2} and YZn\textsubscript{2} respectively (show Table 3).

In summary, theory reproduces correctly the experimental ground state structures for YCu\textsubscript{2} and YZn\textsubscript{2} and predicts pressure-induced structural phase transitions from the CeCu\textsubscript{2}-type to a Laves phase close-packing for the latter systems.

### 3.2. Enthalpy of formation

To investigate the alloying ability and stability, the formation energy \((\Delta E_f)\) of AB\textsubscript{2} type Laves phase were calculated by:

\[
\Delta E_f = E^{AB_2}_{\text{tot}} - (E^A_{\text{solid}} + 2E^B_{\text{solid}}) \tag{1}
\]

\(E^A_{\text{solid}}\) and \(E^B_{\text{solid}}\) represent the energy per atom of A and B in solid states.

At ambient conditions at the ground state (with temperature at zero Kelvin and pressure at zero bar), the enthalpy is equal to the energy, that is \(\Delta E_f(AB_2) = \Delta H_f(AB_2)\) [28].

From Figure 2, we can see that for C14, C15, C36 and CeCu\textsubscript{2} structures the heat of formation for YCu\textsubscript{2(a)} is \(-0.617, -0.546, -0.585, -0.884\) eV/atom respectively, which are greater than \(-1.058, -1.137, -1.108, -1.188\) eV/atom for YZn\textsubscript{2(b)}. From the values of the heat of formation in each AB\textsubscript{2} type binary Laves phase, we can see that the lowest heat of formation for YCu\textsubscript{2} and YZn\textsubscript{2} is of CeCu\textsubscript{2} structure, corresponding to the relatively stronger alloying ability of CeCu\textsubscript{2}-YCu\textsubscript{2}, CeCu\textsubscript{2}-YZn\textsubscript{2} in each binary Laves phase, respectively.

### 3.3. Electronic structure

#### 3.3.1. Densities of States

Electronic densities of state (DOS) and electron charge densities distributions were calculated to have a further insight into the bonding of YCu\textsubscript{2} and YZn\textsubscript{2} and then to reveal the underlying structural stability mechanism of these Laves phases.

Total and partial DOS of YCu\textsubscript{2} and YZn\textsubscript{2} are presented in Figure 3 and Figure 4.

As shown in Figure 3, the Cu-DOS plays a dominant and most important role in the total DOS of YCu\textsubscript{2}. In the YCu\textsubscript{2}- C14- C15- C36- CeCu\textsubscript{2} the Cu-DOS is mainly localized from about \(-5\) to \(-1\) eV. The same for the Y-DOS how have an important role in the Dos of YCu\textsubscript{2} in the YCu\textsubscript{2}- C14- C15- C36 the Y-DOS is mainly localized from about \(-1\) to \(2.75\) eV [29,30]. In Figure 6, we can see that the Zn-DOS have an important role in the DOS of YZn\textsubscript{2}. In the YZn\textsubscript{2}- C14- C15- C36 the Zn-DOS is mainly localized from about \(-8\) to \(-6\) eV, the same for the Y-DOS
Figure 5. The contour plots of charge densities (a) The (0 1 0) plan for CeCu₂-YCu₂, (b) The (0 1 0) plan for CeCu₂ – YZn₂.

3.3.2. Charge densities distribution

The charge-densities contour maps of CeCu₂-YCu₂ (a), CeCu₂-YZn₂(b) in (010) and (010) planes respectively, and C14-YCu₂(c), C15-YZn₂(d) in (1 0 0) and (0 1 0) planes respectively are presented in Figure 5.

Higher density region corresponds to the core electron distribution of Cu and Y atoms that contributes relatively little to the bonding. In Figure 5(a), Y atoms are almost spherical, but Cu atoms are a little deformed. The obvious overlap of electron densities between Cu and Cu indicates a covalent bonding between them. In contrast to the Cu-Cu bonding, there is no overlap of electron densities around Y atoms. The almost uniform electron distribution around Y atoms exhibits a metallic bonding between Y and Y and can be well described by the nearly free electron model. The charge density distribution maps exhibit mainly an ionic bonding between Cu and Y atoms, which is a common feature for the electronic structure of AB₂ type Laves phases. In Figure 5(b), the charge density distribution indicates that there is covalent bonding between Zn and Zn, ionic bonding between Y and Zn and metallic bonding between Y and Y [31].

4. SUMMARY AND CONCLUSION

In conclusion, the calculated result of the heat of formation show that YZn₂ phase has the strongest alloying ability as well as the highest structural stability, next YCu₂. Our two composed have a high-pressure transition phase from the CeCu₂ structure to Laves phase structures, the boundary between open packed, polyanionic, CeCu₂ – type phases and close packed Laves phases is primarily governed by the electronegativity difference between the A and B component. The application of pressure has the effect of decreasing the electronegativity difference between components in binary systems (Figure 5). Thus CeCu₂ – type polar intermetallics can be compressed into Laves phases.

The charge density distributions show that for YCu₂ and YZn₂ type Laves phase, there are metallic bonding between Y and Y, covalent bonding between Cu (Zn) and Cu (Zn), while between the Y and Cu (Zn) atoms, and this is consistent with the difference in electronegativity between Cu (Zn) and Y atoms. This charge accumulation is typically characteristic of a polar covalent bonding.

References


