

FIRST PRINCIPLES CALCULATIONS FOR STRUCTURAL AND MECHANICAL PROPERTIES OF POLAR INTERMETALLICS TYPE LAVES PHASES YM_2 (M: NI, CU AND ZN)

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Abstract

Polar intermetallics type Laves phases play in recent years a very important role in the field of metallurgy, and subject to a large number of works related among other things to their crystal chemistry and stability of their structures. In this paper we used a simulation study and *ab initio* based on the DFT, to examine the structural stability and to appreciate the mechanical properties of these compounds YM_2 (M: Cu, Zn, Ni).

Keywords: *Ab initio methods, Intermetallics, Laves phases, Structural and mechanical properties, Theory of Functional Density DFT.*

Résumé

Les intermétalliques polaires de type phases de Laves jouent ces dernières années un rôle très important dans le domaine de métallurgie, faisant ainsi l'objet d'un très grand nombre de travaux relatifs entre autre à leur cristallographie et la stabilité de leurs structures. Dans ce travail nous avons utilisé l'étude par simulation *ab initio* et en se basant sur la DFT, pour examiner la stabilité structurale et pouvoir apprécier les propriétés mécaniques de ces composés YM_2 (M : Cu, Zn, Ni).

Mots clés : *Les méthodes Ab initio, la Théorie de la Fonctionnelle de la Densité, les Intermétalliques, phases de Laves, propriétés structurales et mécaniques.*

ملخص

لعبت السبائك القطبية من نوع Laves في السنوات الأخيرة دورا هاما في مجال علم المعادن، و تخضع لعدد كبير من الأعمال ذات الصلة بالكيمياء الخاصة بهذه المواد و باستقرار هياكلها، و في هذه المنشورة و باستعمال دراسة المحاكاة و استنادا على طريقة *ab initio* و على أساس DFT قمنا بدراسة الاستقرار الهيكلي و تقييم الخواص الميكانيكية لهذه المركبات YM_2 (M :Cu, Zn, Ni).

الكلمات المفتاحية : *طريقة ab initio ، المحاكاة باستعمال DFT ، السبائك ، السبائك القطبية من نوع Laves ، الخصائص الهيكلية الإلكترونية و الميكانيكية.*

I. INTRODUCTION

Metals and metal alloys have an unquestionable technological interest. Most of the metals market is the construction or transportation. Although softer than most ceramics, they present an important property in these two sectors, namely the ductility. Their lack of rigidity is mitigated by the addition of different elements in varying concentrations. Intermetallics, meanwhile, are not only inherently more rigid than the pluparts alloys, but they combine lightness with rigidity to considerable advances in terms of energy saving. While their rigidity results from the polarity of chemical bonds present, their light comes from their crystal structures open unlike those very compact alloys. Indeed, the intermetallic most used, particularly those based on aluminum, crystallize in a CsCl (B2) structure. However, the B2 structure with no sliding system, the ductility of these intermetallic is greatly reduced, and thus they suffer a fragility unwelcome at room temperature. Currently, palliative solutions are adopted including the use of alloying elements (especially boron or carbon) to reduce the fragility intragranular.

An intermediate solution could be in the intermetallic crystallizing Laves phases. Indeed, many of the compounds IIA-IIA, IIA-M (where M is a transition element or a noble metal) structures are less compact than those usually adopted by metals (fcc or hcp) but a little less open than the CsCl(B2) structure. These compounds are mostly polar, favoring an intrinsic stiffness, and more compact structures (C14, C15 and C36) gives them a significant ductility. However, one point remains, these compounds often undergo phase transformations, including to and from the orthorhombic structure $CeCu_2$ [1-3].

In this paper, we propose to examine the structural stability of polar intermetallic compounds YCu_2 , YZn_2 and YNi_2 . To do this, the calculation of the variation in the total energy based on the parameters of the structure will determine transition pressures and to assess the mechanical stability through the elastic constants [4].

The class of an intermetallic compound as a Laves phases is purely based on 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) [5-8]. An orthorhombic structure also exists where a number of AB_2 intermetallics are observed, namely the $CeCu_2$ -type structure (Fig. 1).

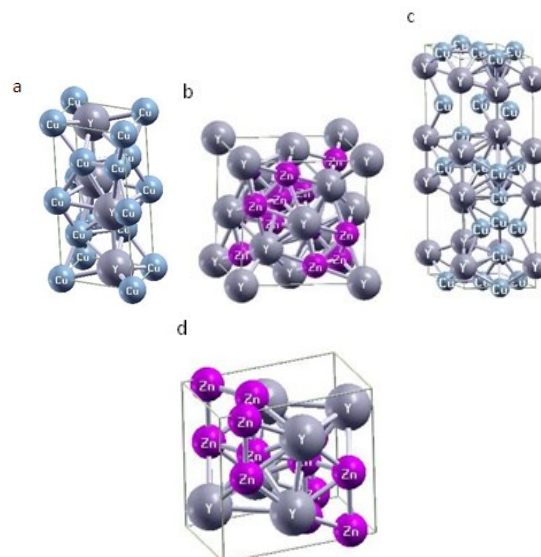


Fig.1. Crystal structures of C14 (a), C15 (b) and C36 (c) AB_2 type Laves phases and $CeCu_2$ (d) type orthorhombic structure.

First-principles density functional theory calculations have been widely used to shed light on the electronic structural and mechanical properties of Laves phase compound. Linear muffintin orbital (LMTO-NFP) was used by two groups to study these compounds. Mayer et al. [9] studied the MAI_2 ($M = Ca, Y, Sc$ and La) and MCr_2 ($M = Ti, Zr, Nb$ and Ta), Kumar and Miracle [10], Kumar et al. [11] studied the MCr_2 ($M = Ti, Zr, Ta, Nb, Sc, Y,$ and La). Other three groups have used the Vanderbilt-type ultrasoft pseudopotential (USPP) incorporated in the Vienna ab initio simulation package (VASP), Tao et al. [12] and studied MAI_2 ($M = Sc, Y, La,$ and $Ce-Lu$), Ouyang et al. [13] studied the MMg_2 ($M = La, Ce, Pr, Nd, Pm, Sm,$ and Gd), Kal et al. [14] studied the MZn_2 ($M = Ca$ and Sr) and MAI_2 ($M = Sr$ and Ba). Their results showed that density functional theory DFT calculations can give satisfactory results that would often not be easy to obtain directly from experiments.

II. CALCULATION METHODS AND CRYSTAL STRUCTURES:

Calculations were performed using the VASP [15–17] code based on the density functional theory (DFT) [18,19]. Ultrasoft Vanderbilt type pseudopotentials [20] were used to describe the interactions between ions and electrons. The generalized gradient approximation (GGAPW91) of Perdew et al. [21] was applied to evaluate the exchange–correlation energies of all examined structures.

Sampling of the Brillouin zone was done via $13 \times 13 \times 13$ (cubic C15 structure), $13 \times 13 \times 11$ (C14 and C36 structure) and $11 \times 9 \times 9$ ($CeCu_2$ orthorhombic structure) k-points grid generated according to the Monkhorst–Pack scheme [22] for

YCu₂, YZn₂ and YNi₂, respectively. The cut-off energy restricting the number of plane waves in the basis set was set to 310 eV for YCu₂, YZn₂ and YNi₂ compounds.

III. ENTHALPY OF FORMATION

In order to obtain the most energetically stable structure amongst the four structures mentioned previously, the formation enthalpy for both tow compounds YM_2 (M: Cu, Zn) was evaluated by the following equation:

$$\Delta H_f = E_{tot}^{YM_2} - (E_{solid}^Y + 2E_{solid}^M) \quad (1)$$

E_{solid}^Y and E_{solid}^M represent the energy per atom of A and B in solid states.

At zero Kelvin and under pressure zero Pa, the enthalpy equals to the energy, that is $\Delta E_f (YM_2) = \Delta H_f (YM_2)$ [23].

IV. RESULTS AND DISCUSSION

IV.1. Enthalpy of Formation

Using Eq. (1), we calculated the enthalpies of formations of both compounds. Results are presented in Table 1. We can see that the enthalpy of formation for YCu₂ is -0.617, -0.546, -0.585, -0.884 eV/atom for C14, C15, C36 and CeCu₂ structures, respectively.

TABLE 1: ENTHALPY OF FORMATION FOR YCu₂, YZn₂ AND YNi₂

	$\Delta H_f^{YCu_2}$ (eV/atom)	$\Delta H_f^{YZn_2}$ (eV/atom)	$\Delta H_f^{YNi_2}$ (eV/atom)
CeCu ₂	-0.884	-1.188	3.107
C14	-0.617	-1.058	-1.405
C15	-0.585	-1.137	-1.485
C36	-0.546	-1.108	-1.442

These values are greater than -1.058, -1.137, -1.108, -1.188 eV/atom for YZn₂. From the values of the enthalpy of formation in each AB₂ type binary Laves phase, we can see that the lowest enthalpy of formation for YCu₂ and YZn₂ is of CeCu₂ structure. They correspond to the relatively stronger alloying ability of CeCu₂-YCu₂, CeCu₂-YZn₂ in each binary Laves phase.

The values of the enthalpy of formation for YNi₂ are 3.107, -1.405, -1.485 and -1.442 eV/atom for CeCu₂, C14, C15 and C36 respectively. From the values of the enthalpy of formation in each AB₂ type binary Laves phase, we can see that the lowest enthalpy of formation for YCu₂ and YZn₂ is of CeCu₂ structure. They correspond to the relatively stronger alloying ability of CeCu₂-YCu₂, CeCu₂-YZn₂ in each binary Laves phase. The lowest enthalpy of formation for the YNi₂ are for the C15 cubic structure, and with a positive enthalpy of formation for CeCu₂, YNi₂ is not stable.

IV.2. Elastic Properties

The elastic properties play an important role in providing valuable information about the binding characteristic between adjacent atomic planes. Anisotropic characters of binding and structural stability are usually defined by the elastic constants C_{ij} . These constants have been often related to the shear modulus G and Young's modulus E. Ab initio calculation of the elastic constants requires precise methods. For obtaining the elastic constants from their known structure a popular approach [24–26], which is based on the analysis of the changes in calculated total energy values resulting from changes in the strain, is used.

To appreciate the mechanical properties of these intermetallic compounds, the calculation of elastic constants for YCu₂, YZn₂ and YNi₂ is paramount and has been done for different structures type Laves phases (Hexagonal C14, C36 and Cubic C15) and the most stable structure, namely the orthorhombic structure CeCu₂.

A cubic structure (C15) is characterized by three independent elastic constants: C_{11} , C_{12} and C_{44} and five elastic constants (C_{11} , C_{12} , C_{13} , C_{33} , C_{44}) for the hexagonal structure (C14 and C36). The orthorhombic structure (CeCu₂) is characterized by the elastic constants (C_{11} , C_{22} , C_{33} , C_{44} , C_{55} , C_{66} , C_{12} , C_{13} , C_{23}). The obtained elastic constants values for YCu₂ and YZn₂ are given in Table 2. Note that the elastic constants of these compounds were not measured experimentally.

IV.2.1. The CeCu₂ Orthorhombic Structure

For an orthorhombic structure, the bulk modulus B and the shear modulus G are calculated using the approximation of Voigt (v) and Reuss (r), using the following expressions:

$$G_V = \frac{1}{15}(C_{11} + C_{22} + C_{33}) - \frac{1}{15}(C_{12} + C_{13} + C_{23}) + \frac{1}{15}(C_{44} + C_{55} + C_{66}) \quad (2)$$

$$\frac{1}{G_R} = \frac{4}{15}(S_{11} + S_{22} + S_{33}) - \frac{4}{15}(S_{12} + S_{13} + S_{23}) + \frac{3}{15}(S_{44} + S_{55} + S_{66}) \quad (3)$$

$$B_V = \frac{1}{9}(C_{11} + C_{22} + C_{33}) + \frac{2}{9}(C_{12} + C_{23} + C_{13}) \quad (4)$$

$$\frac{1}{B_R} = (S_{11} + S_{22} + S_{33}) + 2(S_{12} + S_{23} + S_{13}) \quad (5)$$

The elastic behavior of the material depends on the bulk modulus B and shear modulus G as follows:

$$G = \frac{1}{2}(G_R + G_V) \quad , \quad B = \frac{1}{2}(B_R + B_V) \quad (6)$$

Young's modulus E and Poisson's ratio ν depend on the values of B and G previously computed and are defined by the following relationships:

$$E = \frac{9BG}{3B + G} \quad , \quad \nu = \frac{3B - 2G}{2(3B + G)} \quad (7)$$

With:

$$\left\{ \begin{array}{l} S_{11} = \frac{C_{22}C_{33} - C_{23}^2}{D} \\ S_{22} = \frac{C_{11}C_{33} - C_{13}^2}{D} \\ S_{33} = \frac{C_{11}C_{22} - C_{12}^2}{D} \\ S_{44} = \frac{1}{C_{44}} \\ S_{55} = \frac{1}{C_{55}} \\ S_{66} = \frac{1}{C_{66}} \\ S_{12} = \frac{C_{12}C_{33} - C_{13}C_{23}}{D} \\ S_{13} = \frac{C_{12}C_{23} - C_{13}C_{22}}{D} \\ S_{23} = \frac{C_{11}C_{23} - C_{13}C_{12}}{D} \end{array} \right. \quad (8)$$

And:

$$D = C_{11}C_{22}C_{33} + 2C_{12}C_{13}C_{23} - C_{23}^2C_{11} - C_{12}^2C_{33} - C_{13}^2C_{22} \quad (9)$$

The calculated elastic constants C_{ij} are shown in Table 2, and the bulk modulus B (GPa), Shear modulus G (GPa), Young modulus E (GPa), poisson's ratio ν and and ratio of the shear modulus to bulk modulus (G/B) are represented in the table 3. From Table 3, we can see that both examined compounds, YCu_2 , YZn_2 and YNi_2 , have low bulk and shear modulus, indicating that these materials have low hardness.

The B/G ratio provides information about the ductility of the material, in this case, if the B/G is higher than 1.75, the compound should has an appreciable ductility.

The B/G ratio of these compounds in the orthorhombic structure is close to 2.4, much higher than the critical value of 1.75, and we can also see that the Young's modulus E , which provides information on the stiffness of the material, is weak. Poisson's ratio is generally characteristic of a polar covalent bonding, when it is between -1 and +0.5. This validates the results previously obtained by

Benabadji et al. [27] with the analysis of the electronic properties.

IV.2.2. The C15 Cubic Structure :

For the C15 cubic structure, there are three independent single-crystal elastic constants: bulk modulus $B = (C_{11} + 2C_{12})/3$, tetragonal shear modulus $C' = (C_{11} - C_{12})/2$ and trigonal shear modulus C_{44} . The three elastic constants were calculated by using the scheme described by Mehl et al. [26] in detail. The polycrystalline elastic moduli can be obtained by averaging of single elastic constants in several schemes. The Voigt shear modulus G_V [28] and Reuss shear modulus G_R [29] are the theoretical upper and lower bounds of the true polycrystalline shear modulus, respectively, and are formulated as [30]:

$$G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5} \quad (10)$$

$$G_R = \frac{5(C_{11} - C_{12})C_{44}}{3(C_{11} - C_{12}) + 4C_{44}} \quad (11)$$

The average shear modulus G can be obtained by the expression:

$$G = \frac{1}{2}(G_V + G_R) \quad (12)$$

The Young's modulus E can be expressed as

$$E = \frac{9BG}{3B + G} \quad (13)$$

The Poisson's ratio ν and elastic anisotropy A can be obtained by the following expressions from the calculated elastic constants.

$$\nu = \frac{3B - 2G}{2(3B + G)} \quad (14)$$

$$A = 2 \frac{C_{44}}{C_{11} - C_{12}} \quad (15)$$

IV.2.3. The C14 And C36 Hexagonal Structures

For the C_{14} and C_{36} hexagonal structures, the bulk modulus B and the shear modulus G can be obtained by the following expressions:

$$B = \frac{2}{9} \left[C_{11} + C_{12} + 2C_{13} + \frac{1}{2}C_{33} \right] \quad (16)$$

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$$G = \left\{ C_{44} \left[\frac{C_{44}(C_{11} - C_{12})}{2} \right]^{1/2} \right\}^{1/2} \quad (17)$$

$$E = \frac{[C_{33}(C_{11} + C_{12}) - 2C_{13}^2](C_{11} - C_{12})}{C_{11}C_{33} - C_{13}^2} \quad (18)$$

The Young's modulus E , the Poisson's ratio ν and elastic anisotropy A are calculated using the following expressions.

$$\nu = \frac{C_{12}C_{33} - C_{13}^2}{C_{11}C_{33} - C_{13}^2} \quad (19)$$

$$A = \frac{C_{11} - C_{12}}{2C_{44}} \quad (20)$$

TABLE 2 :THE CALCULATED ELASTIC CONSTANTS FOR YCu_2 AND YZn_2 CRYSTALLIZED IN LAVES PHASES AND IN $CeCu_2$ -ORTHORHOMBIC STRUCTURE.

	C_{11} (GPa)	C_{22} (GPa)	C_{33} (GPa)	C_{44} (GPa)	C_{55} (GPa)	C_{66} (GPa)	C_{12} (GPa)	C_{13} (GPa)	C_{23} (GPa)
YCu_2									
$CeCu_2$	85.761	36.909	31.262	9.475	15.748	9.907	19.734	23.009	8.025
C15	133.124	-	-	32.935	-	-	67.375	-	-
C14	113.136	-	52.724	20.053	-	-	20.761	29.821	-
C36	114.634	-	13.558	15.489	-	-	18.999	14.730	-
YZn_2									
$CeCu_2$	74.960	33.958	24.487	8.013	12.730	7.116	137.718	69.667	-78.79
C15	86.902	-	-	27.058	-	-	27.915	-	-
C14	127.511	-	44.987	22.723	-	-	17.351	-2.268	-
C36	109.79	-	10.368	15.291	-	-	4.700	9.898	-
YNi_2									
C15	164.162	-	-	34.141	-	-	96.724	-	-

TABLE 3: Presentation of Bulk Modulus B (GPa), Shear Modulus G (GPa), Young's Modulus E (GPa), Anisotropy Factor A , Poisson's Ratio ν , Ratio B/G and Chauchy Pressure (C_{12} - C_{44}) (GPa) for YCu_2 and YZn_2 compounds.

	B (GPa)	G (GPa)	E (GPa)	A	ν	B/G
YCu_2						
$CeCu_2$	28.586	11.870	31.280	-	0.317	2.408
C15	89.291	32.875	87.978	1.002	0.336	2.716
C14	48.867	24.704	96.111	2.303	0.040	1.978
C36	37.749	20.191	98.539	3.087	0.030	1.869
YZn_2						
$CeCu_2$	23.995	9.854	26.002	-	0.560	2.435
C15	47.577	29.496	68.941	0.917	0.258	1.612
C14	36.182	32.303	125.06	2.424	0.135	1.120
C36	30.990	20.819	100.116	3.436	-0.047	1.488
YNi_2						
C15	119.2	33.97	93.07	1.012	0.369	3.509

The bulk modulus B , shear modulus G , Young's modulus E , Poisson's ratio ν and anisotropy factor A for both cubic and hexagonal structures are presented in the table 3.

When they crystallize in Laves phases, these compounds have bulk and shear modulus much higher compared to the orthorhombic structure. We conclude that the Laves phases have good hardness. This information is cross with the close packing of atoms in this structure.

For the first compound YCu_2 when it crystallizes in the cubic C15 structure, anisotropy factor is near unity, so an isotropic elasticity. This is also valid for the YZn_2 and YNi_2 ($A = 0.917$, and 1.012) respectively.

We note that the B/G ratio of YNi_2 crystallized in C15 phase and YCu_2 in three phases C14, C36 and C15 are clearly better than the YZn_2 in the same structures, indicating that the YNi_2 and YCu_2 is more ductile compared to YZn_2 .

We also note that both compounds have a high Young's modulus E , so a good intrinsic stiffness due to the polar nature of chemical bonds. This is confirmed by the value of Poisson's ratio between -1 and 0.5 .

In contrast to conventional intermetallic crystallizes most of them in structures B2 making them fragile and largely reduced their ductility, polar intermetallic phases type Laves while being hard have appreciable ductility, coupled with an intrinsic rigidity.

V. CONCLUSION

In this work we analyzed structural and mechanical properties of polar intermetallic materials, The major goal was to predict the better hard and rigid polar intermetallic materials with an appreciable ductility. The present results clearly demonstrate that we concludes that YCu_2 and YZn_2 compounds crystallized in $CeCu_2$ orthorhombic structure does not have good hardness and rigidity compared to Laves phases structure (Hexagonal C14, C36 and cubic C15), and the YNi_2 crystallized in C15 cubic structure present a high ductility and good hardness and rigidity. However, our results confirm that Laves phases present very interesting mechanical properties, in particular high hardness and rigidity resulting from the difference in electronegativity of both elements.

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