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First-principles study of the binary intermetallics in the Cu-Lu and Cu-Pm systems

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ABSTRACT

We present a first principle study of the structural, elastic and energetic properties of the Cu_aX_b (X=Lu, Pm) compounds, within the first principles density functional theory (DFT). The equilibrium volume, lattice constant, enthalpy of formation and the elastic constant are calculated using the full-potential linearized augmented plane-wave [FP-LAPW] method in the generalized gradient approximation (GGA) scheme. The CuLu, Cu_2Lu, Cu_5Lu, CuPm, Cu_2Pm, Cu_4Pm, Cu_5Pm and Cu_6Pm were investigated in their similar Cu-Lanthanide structure prototype compounds observed experimentally. The Cu_7Lu_2, Cu_9Lu_2 and Cu_7Pm_2 intermetallics reported without prototype structure, was also investigated by inspecting several hypothetical structures. The most stable structure for the Cu_7X_2 compounds was found to be the orthorhombic structure in the Ag_7Yb_2 prototype. For the Cu_9Lu_2 compound the two structures studied have a positive enthalpy, implying that it is not a ground state for both tested.

1. INTRODUCTION

Copper is a very common substance that is naturally present in the environment and diffuses into the environment through natural phenomena. It is used enormously, for example in industry and in agriculture; on the other hand promethium Pm and lutetium Lu are counted among lanthanide compounds. The lanthanides alloys are widely used in the industries applications as catalysts, in streetlights, searchlights, and in the high-intensity lighting present in sports stadiums. They form alloys with many other metals, and these alloys exhibit a wide range of physical properties. We did not find an experimental study for the phase diagram of the Cu-Pm and Cu-Lu systems. The only theoretical studies previously proposed for Cu-Pm and Cu-Lu are from Subramanian and Laughlin [1, 2] which proposes a theoretical phase diagram based on the similarity of the binary phase diagrams of Cu-Lanthanide, as the Cu-Ce, Cu-Pr, Cu-Sm and Cu-Nd systems. Hence, they proposed the existence of the compounds CuPm, Cu_2Pm, Cu_4Pm, Cu_5Pm, Cu_6Pm and Cu_7Pm_2. The structure prototype of these compounds is inspired from the Cu-Ce binary system which has been studied by several authors [3-6]. All of these compounds crystallize in the orthorhombic structure except the Cu_5Pm which is hexagonal in Cu_5Ce prototype and the Cu_7Pm_2 which they did not propose a prototype. The prototypes of the other compounds are also distinguished, CuPm and Cu_6Pm formed in FeB and Cu_6Ce prototype respectively; Cu_2Pm to Cu_2Ce as a prototype and the last Cu_4Pm crystallizes in a Cu_4Ce prototype. The Cu-Lu system is similar to Cu-heavy Lanthanide, and its compounds which have been proposed are CuLu, Cu_2Lu, Cu_5Lu in the prototypes structure form of the CsCl, Cu_2Ce and $AuBe_5$ respectively, and Cu_7Lu_2, Cu_9Lu_2 without prototype. The crystal parameters for these intermediate phases were estimated on the basis of the systematic of crystallographic data in the Cu- Lanthanide systems.

The aim of the present work, based on first-principles calculations, is to investigate the relative stabilities of the different compounds involved in the Cu-Lu and Cu-Pm systems, and predicting a stable structure for the Cu_7X_2 (X= Lu, Pm) compound. Having our calculations performed at 0 K, we will be mainly focusing on the determination of the ground state line of these systems.

2. COMPUTATIONAL DETAILS

We employed for the ground state energy the full potential linearized augmented plane wave [FP-LAPW] based on density functional theory (DFT)] [7], as implemented in WIEN2K code [8, 9]. For structural and elastic properties, the exchange correlation potential was calculated using the generalized gradient approximation (GGA) in the form proposed by Perdew et al. [10]. In order to achieve energy eigenvalues convergence, the wave functions in the interstitial region were expanded in plane waves with a cut off of K_{max} = 9/Rmt, where Rmt denotes the smallest atomic sphere radius and K_{max} gives the magnitude of the largest k-vector in the plane wave expansion. The k-point meshes for Brillouin zone sampling were constructed using the MonkhorstPack scheme [11]; the (12x12x12) k-points mesh was used for all calculations. The structures of our studied compounds are optimized by calculating the total energy as a function of volume. The results are fitted according to the Murnaghan equation of state [12] to obtain the ground-state properties given by

$$E(V) = E_0 + \frac{B_0}{B'(B'-1)}\left[V\left(\frac{V_0}{V}\right)^{B'} - V_0\right] + \frac{B_0}{B'}(V - V_0) \quad (1)$$

where E(V) is the internal energy, V_0 and E_0 are the equilibrium volume and energy, at zero pressure, V is the deformed volume, B_0 is the bulk modulus, and B' is the derivative of the bulk modulus.

The enthalpy of formation is obtained by calculating the difference between the energy of the compound and the energy of its constituents according to the following equation:

$$\Delta H_f(Cu_aX_b) = E_{tot(Cu_aX_b)} - [aE_{Cu} + bE_X] \quad (2)$$

where $\Delta H_f(Cu_aX_b)$ is the enthalpy of formation of the compound Cu_aX_b. $E_{tot}(Cu_aX_b)$, E_{cu} and E_X are the ground state energies.

The elastic properties define how a material under stress deforms and then recover and return to its original shape after stress ceases. We used the calculation of the elastic stiffness constant C_{ij} to check the mechanical stability of the Cu_7X_2 compounds. The strain–stress method [13] are used, in which the relaxed unit cell under hydrostatic stress tensor was linearly deformed, then the stress tensor was calculated self-consistently after relaxing forces.

3. RESULTS AND DISCUSSION

3.1 Pure elements: Cu, Lu and Pm

We have evaluated the energies of the pure elements Cu, Lu and Pm in their observed structures at room temperature. The calculated lattice constants are summarized in table 1. We compared our results with the experimental data [14-16] and those obtained by the VASP code [17]. A good agreement has been obtained with the available results from literature.

The promethium Pm has two structures, α (hexagonal) and a β (cubic). Our calculation of the ground state energy indicate that the hexagonal form is the most stable one that's why we used it to calculate the enthalpy of formation

3.2 Cu-Lu system

Only three compounds in the Cu-Lu systems are known: CuLu, Cu_2Lu and Cu_5Lu. Subramanian and Laughlin [18] have estimated phase diagram by systematic considerations of binary Cu-rare-earth systems and knowing the stoichiometry of some intermediate phases. Two intermetallics Cu_9Lu_2 and Cu_7Lu_2 were assumed to exist, for analogous phases are present in the Cu-RE (RE = Gd, Dy and Er) systems.

Iandelli and Palenzona [19] reported the cubic $AuBe_5$-type structure for Cu_5Lu. Storm and Benson [20] reported the formation of Cu_2Lu with the orthorhombic $CeCu_2$-type structure, and Dwight [21] reported the cubic CsCl-type structure for CuLu compound.

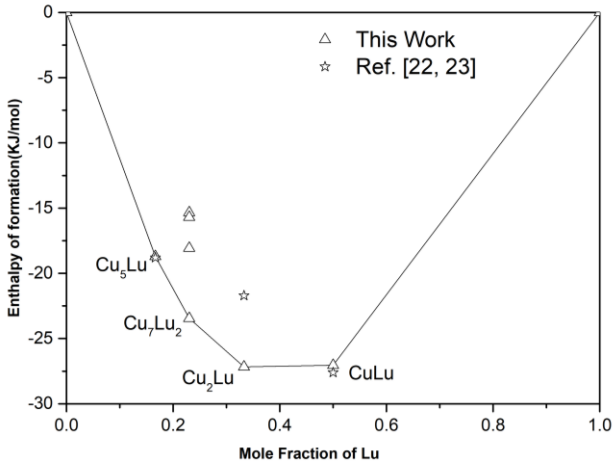

Figure 1. Enthalpies of formation of Cu-Lu intermetallics

By minimizing the total energies, we obtained the equilibrium lattice constants of these compounds, and the results are summarized in table 2. The experimental results are reasonably reproduced with differences less than 1%. Calculated enthalpies of formation are presented in table 3 and figure 1 compared with the experimental data [22, 23], where a good agreement is obtained with the experimental uncertainties.

The existence of the intermetallic Cu_7Lu_2 and Cu_9Lu_2 has not confirmed in any work. There is no structural data of these compounds. To calculate the enthalpy of formation of this supposed compound, and since there are no structural data in literature, we tried out several structures. We have found six crystal structures for the A_7B_2 compound and two crystal structures for the A_9B_2. The calculated enthalpies of formation of the Cu_9Lu_2 compound in the two structures studied (Pd_9Si_2 type, space group Pnma and Al_9Co_2 type, space group $P12_1/c1$) performed a positive enthalpy, which mean that it is not a ground state for both tested.

Table 1. Calculated lattice parameters and bulk modulus of the pure elements Cu, Lu and Pm

element	Pearson Symbol	Space group	Lattices Parameters (nm)				B_0 (GPa) (This Work)
				This Work	VASP[a]	Exp.	
Cu	cF4	*Fm-3m*	a	0.363	0.362	0.363[b]	139.37
Lu	hP2	*P63/mmc*	a	0.349	0.351	0.350 [c]	47.11
			b	0.349	0.351	0.350	
			c	0.552	0.547	0.556	
αPm	hP4	*P63/mmc*	a	0.314	0.367	0.365 [d]	36.33
			b	0.314	0.367	0.365	
			c	1.011	1.606	1.165	

(a) Ref. [17] (b) Ref. [14] (c) Ref. [15] (d) Ref. [16]

Table 2. Calculated and experimental lattice parameters and bulk modulus of Cu-Lu intermetallics

Phases	Pearson Symbol	Space group	Lattice Parameters (nm)			B_0 (GPa) This work
				This work	Exp.	
Cu_5Lu	cF24	$F\bar{4}3m$	a	0.7003	0.6970[(a)]	115.14
Cu_2Lu	oI12	*Imma*	a b c	0.429 0.666 0.726	0.424[(b)] 0.663 0.722	93.20
CuLu	cP2	$Pm\bar{3}m$	a	0.340	0.339[(c)]	78.09

(a) Ref. [19] (b) Ref. [20] (c) Ref. [21]

Table 3. Enthalpies of formation of Cu-Lu intermetallics (kJ/mol)

Compound	This Work	Exp. [22, 23]
Cu_5Lu	-18.70	-18.8±1.9
Cu_2Lu	-27.18	-21.7±5.3
CuLu	-27.04	-27.6±2.3

For the compound Cu_7Lu_2, we calculated the equations of state of the six proposed structures (Figure 2). As we can see the orthorhombic structure (space group Cmcm) is the stable phase. Lattice parameters and enthalpies of formation are listed in table 4. The lower enthalpy is obtained with orthorhombic structure. The results show that the enthalpy of formation of this structure breaks the convex hull (Figure 1). The different crystalline structures proposed for the Cu_7Lu_2 are shown in figure 3.

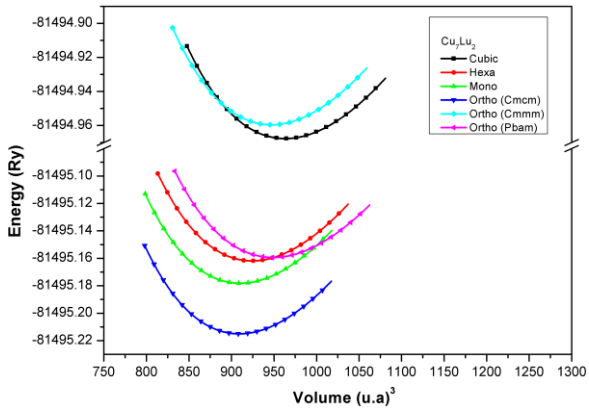

Figure 2. Calculated total energies as a function of volume of the suspected structures for the Cu_7Lu_2 compound

Table 4. Enthalpies of formation and bulk modulus of Cu_7Lu_2 in different suspected structures

Prototype	Pearson Symbol	Space group	Lattice Pramettres (nm)		H^{for} (kJ/mol)	B_0 (GPa)
Al_7Th_2	oP18	*Pbam*	a b c	0.534 1.044 0.503	-15.33	101.89
Ni_7Zr_2	mC36	*C2/m*	a b c	0.492 0.862 1.276	-18.07	108.49
Ag_7Yb_2	oS36	*Cmcm*	a b c	0.853 0.497 1.267	-23.45	107.60
Ge_2Li_7	oC36	*Cmmm*	a b c	0.921 1.316 0.461	+13.80	90.97
Sb_2Tl_7	cI54	*Im-3m*	a	0.950	+12.63	89.65
Ce_2Ni_7	hP36	*P6₃/mmc*	a c	0.503 2.497	-15.69	109.24

To verify the mechanical stability of this compound, we calculated its elastic stiffness constants and bulk modulus B_H (Table 5), and we checked them with all stability conditions for orthorhombic structures given by Wu et al. [24]:

$$\begin{cases} C_{11} > 0, \quad C_{22} > 0, C_{33} > 0, \\ C_{44} > 0, \quad C_{55} > 0, \quad C_{66} > 0 \\ [C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] > 0 \\ (C_{11} + C_{22} - 2C_{12}) > 0 \\ (C_{11} + C_{33} - 2C_{13}) > 0 \\ (C_{22} + C_{33} - 2C_{23}) > 0 \end{cases} \quad (3)$$

B_H is the bulk modulus given according to the Hill approximation [13] as:

$$B_H = \frac{1}{2}\left(B_{Reuss} + B_{Voigt}\right) \quad (4)$$

where B_{Reuss} and B_{Voigt} are the bulk modulus given by Reuss [25] and Voigt [26] approximations respectively.

The obtained values satisfy all this stability conditions, which confirm its mechanical orthorhombic structure stability, and the bulk modulus B_H is in good agreement with the one calculated by the Murnaghan equation.

To the best of our knowledge, there are no experimental and other theoretical data in literature for the elastic constants (C_{ij}) and bulk modulus of this compound for comparison, so we consider the present results as prediction study which still awaits an experimental confirmation.

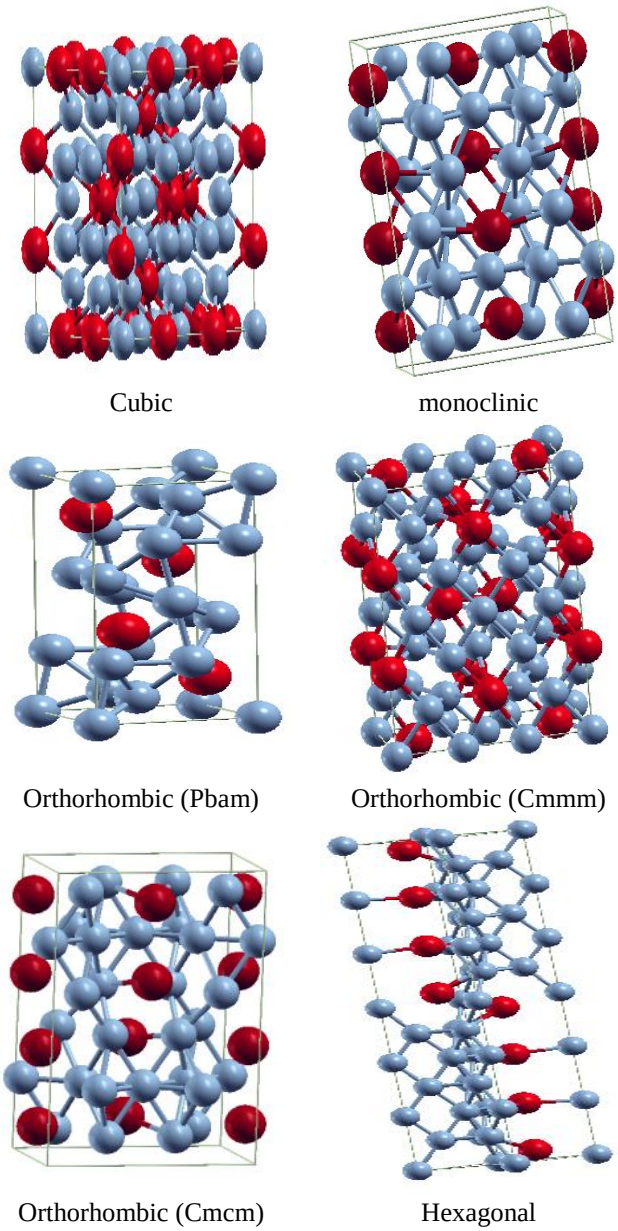

Figure 3. Schematic representation of the six proposed structures for the Cu_7Lu_2 compound

Table 5. Elastic stiffness constants and bulk modulus of the Cu_7Lu_2 and Cu_7Pm_2 compound

	Cu_7Lu_2	Cu_7Pm_2
C_{11}	187.85	164.04
C_{12}	78.02	52.54
C_{13}	68.40	49.71
C_{22}	177.23	142.24
C_{23}	76.59	42.91
C_{33}	174.17	117.15
C_{44}	42.84	30.69
C_{55}	37.24	46.28
C_{66}	49.76	46.95
B_H	109.40	78.32
B_0^{Murn}	107.60	92.61

3.3 Cu-Pm system

This system has not been studied experimentally till now. By comparison with other Cu-rare-earth systems and interpolating the data which could be expected for the Cu-Pm system, Subramanian and Laughlin [1] have proposed a phase diagram with six compounds: Cu_6Pm, Cu_5Pm, Cu_4Pm, Cu_2Pm CuPm and Cu_7Pm_2.

Lattice parameters for these intermetallics, except Cu_7Pm_2, were estimated by Subramanian and Laughlin [1] on the basis of the systematic of crystallographic data in the Cu lanthanide systems. We have not found any information for the Cu_7Pm_2 compound.

Lattice parameters and enthalpies of formation of the five known compounds obtained from first principles calculations, are reported in table 6 and figure 4. As we can see the Cu_4Pm has a positive enthalpy of formation, so it's impossible to form this compound. While for the compound CuPm which is not in the ground state, it is at least no stable at 0 K.

For the Cu_7Pm_2, since we have not found any information concerning its structure, six crystal structures for the A_7B_2 compound like the Cu_7Lu_2 intermetallics are calculated. The equations of state of the six structures are shown in figure 5, lattice parameters and enthalpies of formation are presented in table 7. The lower enthalpy is obtained with orthorhombic structure (space group Cmcm). The results show that even with this structure the calculated enthalpy of formation does not breaks the convex hull (Figure 4).

Table 6. Lattice parameters, enthalpies of formation and bulk modulus of Cu-Pm intermetallics

Phases	Pearson Symbol	Space group	Lattice Prametres (nm)	This work	Estim. [1]	H^{for} (KJ/mol)	B_0 (GPa)
Cu_6Pm	oP28	*Pnma*	a	0.804	0.807	8.35	103.30
			b	0.506	0.505		
			c	1.007	1.008		
Cu_5Pm	hP6	*P6/mmm*	a	0.510	0.509	-8.70	100.89
			c	0.407	0.410		
Cu_4Pm	oP20	*Pnma*	a	0.485		+13.09	85.68
			b	0.470			
			c	1.386			
Cu_2Pm	oI12	*Imma*	a	0.432	0.437	-11.63	72.99
			b	0.689	0.696		
			c	0.729	0.704		
CuPm	oP8	*Pnma*	a	0.715	0.722	-4.92	50.21
			b	0.450	0.454		
			c	0.548	0.553		

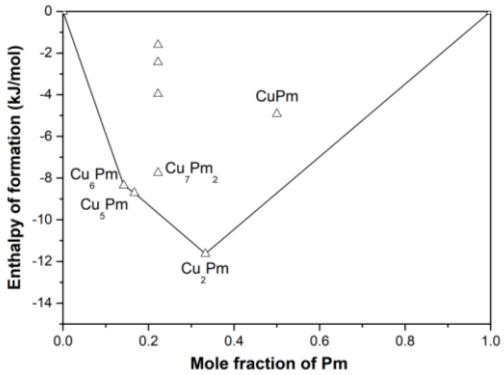

Figure 4. Enthalpies of formation of Cu-Pm intermetallics

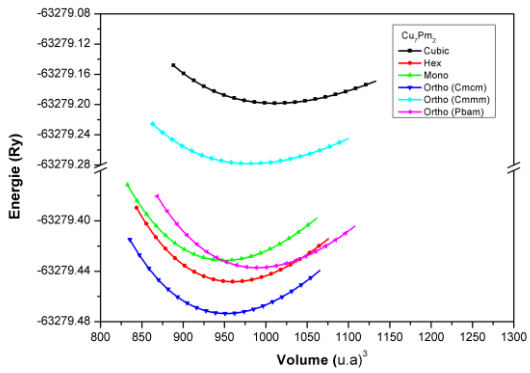

Figure 5. Calculated total energies as a function of volume of the suspected structures for the Cu_7Pm_2

Table 7. Lattice parameters, enthalpies of formation and bulk modulus of Cu_7Pm_2 in different suspected structures

Prototype	Pearson Symbol	Space group	Lattice Parameters (nm)		H^{for} (KJ/mol)	B_0 (GPa)
Al_7Th_2	oP18	*Pbam*	a b c	0.5417 1.0587 0.5100	-2.44	85.77
Ni_7Zr_2	mC36	*C2/m*	a b c	0.4992 0.8750 1.2956	-1.60	93.15
Ag_7Yb_2	hP18	*Cmcm*	a b c	0.8663 0.5049 1.2863	-7.74	92.61
Ge_2Li_7	oC36	*Cmmm*	a b c	0.9326 1.3334 0.4673	+20.75	84.21
Sb_2Tl_7	cI54	*Im-3m*	a	0.9646	+32.41	74.17
Ce_2Ni_7	hP36	*P 63/mm c*	a c	0.5094 2.5281	-3.9618	91.22

We have also calculated the elastic stiffness constants for this structure (Table 5). The obtained values satisfy all stability conditions (Eq. 3). So the stability of this compound at finite temperature may be explained by entropic effects that are related to vibrational state.

4. CONCLUSIONS

Through first-principles local density functional calculations, we have investigated the ground state line of the Cu-Lu and Cu-Pm systems. We have calculated the enthalpies of formation of eight compounds which there structure are known, and three suspect intermetallics (Cu_7Lu_2, Cu_9Lu_2 and Cu_7Pm_2). The established ground state shows that: (i) the compounds CuLu, Cu_2Lu, Cu_5Lu and Cu_7Lu_2 are ground state; (ii) the Cu_7Pm_2 is not stable at 0K but may be stable at finite temperature since its mechanically stable in the orthorhombic (Cmcm) structure; (iii) the compounds Cu_9Lu_2, Cu_4Pm and CuPm are not stable at 0 K. The current results suggest that further experimental investigation is needed for the Cu-Lu and Cu-Pm systems

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NOMENCLATURE

V_0	equilibrium volume
E_0	internal energy
E_{tot}	Total energy
B_0	bulk modulus
B'	derivative of the bulk modulus
ΔH^f	enthalpy of formation of the compound
C_{ij}	Elastic stiffness constants