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First principles account for large changes in electronic structure and bonding from LaCu to LaCuMg and LaCuMg₄

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Abstract

Increasing amounts of magnesium in LaCu intermetallic are shown to bring drastic electronic, chemical and mechanical changes. Based on DFT methodologies this is quantified for the cohesive energies, relative charge transfers, bulk modules, electronic structures and bonding properties for the three compounds LaCu, LaCuMg and LaCuMg₄. Particularly the cohesive energies increase with Mg amounts: This is illustrated by the increasing number of pair interactions: While in the binary the bonding is ensured by La–Cu, in the ternaries La–Cu, La–Mg and Cu–Mg interactions contribute to the bonding with the extra electrons brought by Mg occupying bonding states. Along the series, increasing magnesium contents lead to moderate increase of the compressibility.

Introduction

Magnesium rich compounds are of interest in the field of materials science for crystal chemistry fundamentals [1,2] and for different applications like corrosion resistance compounds such as within the Mg-Zn-RE ternary system (RE: Rare Earth) [3] as well as host compounds for hydrogen storage in the solid state [4,5]. In the La-Cu-Mg phase diagram [6] the Mg rich ternary compound LaCuMg₄ (1:1:4) was discovered and structurally determined from *ab initio* in the hexagonal UCoAl₄ -type structure with $P\bar{6}m2$ space group, cf. [7] for a

detailed description. The structure consists of *LaCuMg* planes interlayered by magnesium planes formed by three Mg (Fig. 1a). Mg-Mg distances are in the range of ~ 3 Å. This is close to the sum of Mg metallic radii, and metallic-like Mg networks can be expected. Note that short Mg–Mg connections are found in other ternary magnesium rich compounds as CeRu_2Mg_5 and $\text{Ce}_2\text{Ru}_4\text{Mg}_{17}$ [8]. The 1:1:4 structure presents similarities with equiatomic LaCuMg (1:1:1) which also crystallizes in the $P\bar{6}m2$ space group while adopting the ZrNiAl -type structure [7]. The additional Mg substructures lead to an almost doubling of the cell volume from 1:1:1 to 1:1:4. Another difference between the two structures is found in the two copper sites Cu1 and Cu2 (Table 1): whereas they occupy the same plane in LaCuMg_4 , they are found at $z = 0$ and $z = \frac{1}{2}$ in LaCuMg . As a consequence the structure consists of *LaCu1* planes interlayered by *Cu2Mg* along the hexagonal c axis (Fig. 1b). These structural modifications are likely to induce changes in the electronic structure and the bonding behaviors. They can be approached complementarily to crystal lattice determination with quantum theoretical methods to obtain the energies (total and cohesive) and the energy-volume equations of states (EOS) as well as the overlap populations (S_{ij}) analysis to describe the chemical bonding and the trends of charge transfers. Consequently the purpose of the paper is to provide an accurate account of the role played by increasing amounts of Mg along the series LaCu , LaCuMg and LaCuMg_4 with computational methods within the well established framework of the quantum density functional theory (DFT) [9,10].

2. Computational framework

Two methods were used complementarily. Firstly total-energy and force calculations were performed using the VASP package [11, 12] for optimizing the structures and establishing trends of charge transfers and the energy volume equations of states (EOS). The projector-augmented wave (PAW) method was used to solve the single-particle equations [12, 13]. Exchange and correlation effects were accounted for within the GGA following Perdew, Burke and Ernzerhof [14]. The optimization of the structural parameters was performed until the Hellmann–Feynman forces acting on the atoms were less than 10^{-2} eV.Å⁻¹ and stress components less than 10^{-3} eV.Å⁻³. The expansion of the Kohn-Sham orbitals was operated with a plane wave energy cutoff of 400 eV. The Brillouin-zone (BZ) integrals were approximated with a special precise k -point sampling following Monkhorst and Pack [15]: For the hexagonal structures of the ternary title compounds, this implies grid sizes of $24 \times 24 \times 8$ and $24 \times 24 \times 24$ for the orthorhombic structure of LaCu .

The charge density resulting from the calculations was analyzed with the theory of atoms in molecules (AIM) [16] as based purely on the electronic charge density. The so-called Bader analysis is particularly useful when trends between similar compounds need to be examined; consequently such a tool cannot allow evaluating absolute ionizations.

Secondly, for an account of the electronic structure and particularly of the properties of chemical bonding not available with VASP, the scalar relativistic full-potential augmented spherical wave (ASW) method was used [17-19]. Like above the DFT exchange and correlation effects were accounted for within the GGA treated with a different parameterization scheme [20]. For the valence states the ASW method uses the outermost shells to represent a minimal basis set with one of each kind, i.e. s , p , d , f . The matrix elements are constructed with partial waves up to $l_{\max}+1 = 4$ for La; $l_{\max}+1 = 3$ for Cu and $l_{\max}+1 = 2$ for Mg; l being the secondary quantum number. Self-consistency is considered as achieved when charge transfers and energy variation between two consecutive cycles were less than $10^{-8} \times e$ and 10^{-6} eV, respectively. The BZ integrations are performed using the linear tetrahedron method within its irreducible wedge [21]. The pair interactions between atomic constituents are discussed based on the crystal orbital overlap population S_{ij} with the COOP criterion [22]. Bonding, non-bonding and anti-bonding states are designated by positive, nil and negative COOP magnitudes along the y axis (cf. Figs. 4 and 5).

3. Geometry optimization, charge transfers and energy-volume EOS.

Geometry optimization and relative charge transfers.

Starting from the experimental structure parameters of LaCuMg and LaCuMg₄ [6, 7] given in Table 1, unconstrained geometry optimization runs were carried out. Similar calculations were done for LaCu which crystallizes in FeB-type orthorhombic structure ($Pnma$ space group) [23]. In both ternary compounds the hexagonal symmetry in $P\bar{6}m2$ space group is preserved after successive calculations with increasing precision of the BZ. As shown in Table 1, the fully relaxed structure parameters are found close to starting ones and the shortest interatomic distances are in fair agreement with experiment. Especially $d(\text{La-Cu})$ is smallest in LaCu and increases in the ternaries due to the cell expansion. In LaCuMg₄ the shortest metal-magnesium separations are for Cu-Mg1 and Cu-Mg2, and Cu-Mg3 in LaCuMg structure. It is important to mention that Cu1 located at (0,0,0) plane has the shortest separation with Mg in both compounds. Larger distances characterize the La-Mg connections.

This lets suggest different trends in charge transfers (Q/e) along the different substructures. The last columns of Tables 1 present the charge transfers showing the common trend of positively charged La and Mg and negatively charged copper. This follows from the relative electronegativities of the different chemical species: $\chi(\text{Cu}) = 1.90$; $\chi(\text{Mg}) = 1.31$ and $\chi(\text{La}) = 1.10$. The 1:1:4 ternary with highest Mg concentration clearly shows a reduced amount of transferred charges compared to LaCuMg and LaCu. For instance, the charge carried by La goes down from $+0.97e$ for LaCu through $+0.63e$ for 1:1:1 to $+0.58e$ for 1:1:4. Nevertheless the overall charge transfer from Mg is small. The lowest magnitudes are found in the 1:1:4 ternary approaching zero whereas Mg in 1:1:1 carries a positive charge of $0.18e$. Such small magnitudes are significant of covalent like bonding illustrated in next section.

Cohesive energies.

The question arises as to the role of Mg ‘adjunction/insertion’ in the binary intermetallic on the relative stabilities of the ternaries versus LaCu. This is quantified from examining the magnitudes of the cohesive energies.

$$E_{\text{coh.}} = E_{\text{total}}(\text{compound}) - \sum E(\text{constituents}) \text{ for one FU.}$$

The energies of the constituents were calculated in their ground state structures. Mg (hexagonal, with $2p^6$ semi-core states): -2.784 eV (2 atoms); La (hexagonal): -9.48 eV (2 atoms) and Cu (FCC): -3.715 eV (1 atom). The resulting $E_{\text{coh.}}$ are given in Table 1 per FU. The trends of $E_{\text{coh.}}(\text{LaCu}) = -0.35$ eV to $E_{\text{coh.}}(\text{LaCuMg}) = -0.67$ eV then $E_{\text{coh.}}(\text{LaCuMg}_4) = -1.41$ eV clearly show enhanced cohesion of the structures upon insertion of Mg and up to the Mg saturated 1:1:4 composition.

Energy-volume equations of states

The volume expansions from LaCu to LaCuMg (47%) and from LaCuMg to LaCuMg₄ (95%) is remarkably large and should have consequences on the compressibility of the compounds, i.e. the larger the volume the more compressible the compound. However the bonding between the nearest neighbors can hinder this effect and reduce the compressibility. The prevailing effect can be obtained through the energy-volume equations of state (EOS) for the three compounds. This proceeds from the E,V (energy-volume) set of calculations around the minima found from the geometry optimization (Table 1). The resulting $E = f(V)$ curves are

shown in Figs. 2. They have a quadratic variation which can be fitted with Birch EOS up to the 3rd order [24]:

$$E(V) = E_0(V_0) + (9/8)V_0B_0\left[\left(\frac{V_0}{V}\right)^{2/3}B' - 1\right]^2 + [9/16]B_0(B' - 4)V_0\left[\left(\frac{V_0}{V}\right)^{2/3} - 1\right]^3,$$

where E_0 , V_0 , B_0 and B' are the equilibrium energy, the volume, the bulk modulus and its pressure derivative, respectively. The fit results in the inserts of Fig. 2 show close values of equilibrium energies E_0 and volumes V_0 to the ones obtained by energy optimization (Table 1). All three B' values are close to 4, i.e. within range of usually obtained values [25]. The magnitude of $B_0(\text{LaCu}) = 53$ GPa (no experimental value is available to the best of our knowledge) is within range of binary *RET* intermetallics (T: transition metal of the 1st period) [25]. The relevant trend is in the decrease of B_0 from LaCu (53 GPa) to LaCuMg (49 GPa) then to LaCuMg₄ (44 GPa) with steps of $\Delta B_0 = 5$ GPa. This follows the increase of the volume especially from LaCuMg to LaCuMg₄ whereby the compound with the largest volume becomes most compressible under hydrostatic pressure. However the increase of compressibility is not large enough to assign the only effect to volume change and it can be proposed that the bonding between the atomic constituents is a limiting factor to large changes in compressibility.

4. All electrons calculations and chemical bonding.

In so far that the calculated crystal results are in fair agreement with experiment we used the latter for a full assessment of the electronic structure and the qualitative description of the chemical bonding based on the overlap populations. This allows independent comparisons between the results of the two methods in use. At self consistent convergence of the charges and of the (variational) energy, the amount and the sign of charge transfer are similar to the Bader analysis above.

Site projected density of states

The site projected densities of states (PDOS) are displayed in Fig. 3. The zero energy along the x axis is taken with respect to the Fermi energy (E_F). The valence band (VB) is characterized by Cu d states centered at ~ -3 eV. An inversion of the relative PDOS positions of Cu1 and Cu2 is observed between “1:1:1” and “1:1:4” compounds due to their belonging to different planes (at $z = 0$ and $z = 1/2$) in the former and to the same plane ($z = 0$) in the latter. Empty La $4f$ states are found at 2 eV, well above E_F within the conduction band (CB). Then

La is expected to contribute to the bonding with neighboring *ligands* mainly through the itinerant *d* states which are of low intensity and smeared over the VB. In particular, Mg (*s,p*) states are observed below the copper DOS crossing E_F (Fig. 3c). From the binary to the equiatomic ternary and the 1:1:4 compound a narrowing of the Cu and La PDOS can be observed. This arises from the volume increase leading to larger localization of the respective 3*d* and 4*f* states.

Chemical bonding

The resembling PDOS between the different species indicates the bonding between them through the quantum mixing between the valence states. Such bonding is rationalized based on the overlap matrix elements S_{ij} within the COOP scheme [22]. In as far as the atomic species exist with different stoichiometries -as in LaCuMg_4 with $Z=3$: $\text{La}_3\text{Cu}_1\text{Cu}_2\text{Mg}_{12}\text{Mg}_{21}\text{Mg}_{31}$ - one atom of each kind is considered in the plots for the sake of establishing comparisons.

- a- *LaCu and LaCuMg*. Looking firstly at the bonding within LaCu, Fig. 4a shows that within the valence band the La–Cu interaction between atoms with respectively empty and filled valence states is bonding throughout the VB with positive COOP magnitudes. Two main bonding regions are observed: at -4 eV and in the neighborhood of E_F . They correspond to the DOS positions of Cu-*d* and the itinerant part of La mainly constituted of La-*d*. The same feature is reproduced in panel b) relative to the COOP within LaCuMg characterized by bonding COOP throughout the VB albeit with a small anti-bonding contribution at the top of Cu-*d*. The plots are more complex due to the presence of several interactions: La–Cu1 and La–Cu2 are dominating with respect to Cu1–Mg and Cu2–Mg (Mg3 in Table 1). Note that in spite of the large La–Mg separation (~ 3.15 Å) there is a non-negligible La–Mg bonding in the neighborhood of E_F involving La-*d* states and Mg *s,p*. The overall bonding in LaCuMg is more differentiated and qualitatively larger than in the intermetallic. This further illustrates the origin of the larger cohesive energy (Table 1).
- b- *LaCuMg₄*. Due to the presence of several Mg substructures in the 1:1:4 compound, Fig. 5 details the different COOP in four panels. The La–Cu COOP shows a negligibly small magnitude La–Cu1 bond whereas the whole La–Cu bonding is ensured by La–Cu2. This follows from the different distances: $d(\text{La–Cu1}) = 4.2$ Å while $d(\text{La–Cu2}) = 3.15$ Å. Likewise Cu1–Mg1 bonding is negligibly small due to the large Cu1–Mg1

distance of 4.86 comparatively with Cu1–Mg2 2.62 Å and Cu1–Mg3 2.86. Opposite features are observed for Cu2–Mg1 (~2.9 Å) which is dominating over the other two bonds. The fourth panel 5d) indicates dominant La–Mg3 bonding with $d(\text{La-Mg3}) = 3.34 \text{ Å}$ while $d(\text{La-Mg1}) = 3.56 \text{ Å}$ and $d(\text{La-Mg2}) = 3.54 \text{ Å}$.

5. Conclusions

In this work we have reported original results of major effects brought by increasing amounts of magnesium to the electronic structure and hardness of La-Cu-Mg phases. Enhanced cohesive energies with respect to LaCu are identified, significant of improved stability due to Mg: While in LaCu binary the bonding is ensured by La–Cu interaction, in the ternary compounds La–Cu, La–Mg, and Cu–Mg contribute to the bonding and all electrons brought by Mg are located in bonding states thus providing enhanced cohesion to the crystal lattice. Compressibility increases along with the volume from LaCu to LaCuMg and LaCuMg₄. However its change of $\Delta B_0 \sim 5 \text{ GPa}$ is not large enough to assign the only role to volume increase and a hindering role is assigned to the chemical bonding. Charge transfers are within the range of metallic behavior best highlighted in the Mg rich LaCuMg₄ compound.

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Table 1 Experimental and calculated crystal data for the isostructural hexagonal LaCuMg₄ and LaCuMg ternary compounds and for LaCu binary in FeB structure.

a) LaCuMg₄

LaCuMg ₄ $P\bar{6}m2$, Z= 3 FU	Experimental [7]	Calc. (this work)	Calculated Bader charges (Q\ e)
$a / \text{\AA}$	10.3911	10.322	
$c / \text{\AA}$	4.5126	4.521	
$V / \text{\AA}^3$	421.98	417.50	
La (3f)	0.4064, 0, 0	0.407, 0, 0	+0.58
Cu1 (1a)	0, 0, 0	0, 0, 0	-0.81
Cu2 (2c)	1/3, 2/3, 0	1/3, 2/3, 0	-0.70
Mg1 (6k)	0.2935, 0.4746, 1/2	0.297, 0.480, 1/2	0
Mg2 (3f)	0.7475, 0, 0	0.746, 0, 0	+0.03
Mg3 (3g)	0.1696, 0, 1/2	0.166, 0, 1/2	+0.08
d(Cu1-Mg1)	2.62	2.62	
d(Cu1-Mg2)	2.86	2.84	
d(Cu2-Mg1)	2.90	2.87	
d(Cu2-La)	3.15	3.13	
Energy (eV) / 3FU		-46.87	$E_{\text{coh.}} = -1.41 \text{ eV/FU}$

b) LaCuMg

LaCuMg $P\bar{6}m2$, Z= 3 FU	Experimental [6]	Calc. (this work)	Calculated Bader charges (Q\ e)
$a / \text{\AA}$	7.725	7.597	
$c / \text{\AA}$	4.188	4.201	
$V / \text{\AA}^3$	216.44	210.2	
La (3f)	0.582, 0, 0	0.407, 0, 0	+0.63
Cu1 (1a)	0, 0, 0	0, 0, 0	-0.94
Cu2 (2c)	1/3, 2/3, 1/2	1/3, 2/3, 1/2	-0.77
Mg3 (3g)	0.256, 0, 1/2	0.166, 0, 1/2	+0.18
d(Cu1-Mg3)	2.79	2.76	
d(Cu2-La)	3.12	3.10	
Energy (eV) / 3FU		-32.11	$E_{\text{coh.}} = -0.67 \text{ eV/FU}$

c) LaCu

LaCu $Pnma$ Z= 4 FU	Experimental [23]	Calc. (this work)	Calculated Bader charges (Q\ e)
$a / \text{\AA}$	7.543	7.503	
$b / \text{\AA}$	4.616	4.562	
$c / \text{\AA}$	5.724	5.661	
$V / \text{\AA}^3$	199.30	195.39	
La (4c)	0.179, 1/4, 0.135	0.177, 1/4, 0.134	+0.97
Cu (4c)	0.035, 1/4, 0.626	0.035, 1/4, 0.608	-0.97
d(La-Cu)	3.01	3.0	
Energy (eV) / 4FU		-35.98	$E_{\text{coh.}} = -0.35 \text{ eV/FU}$

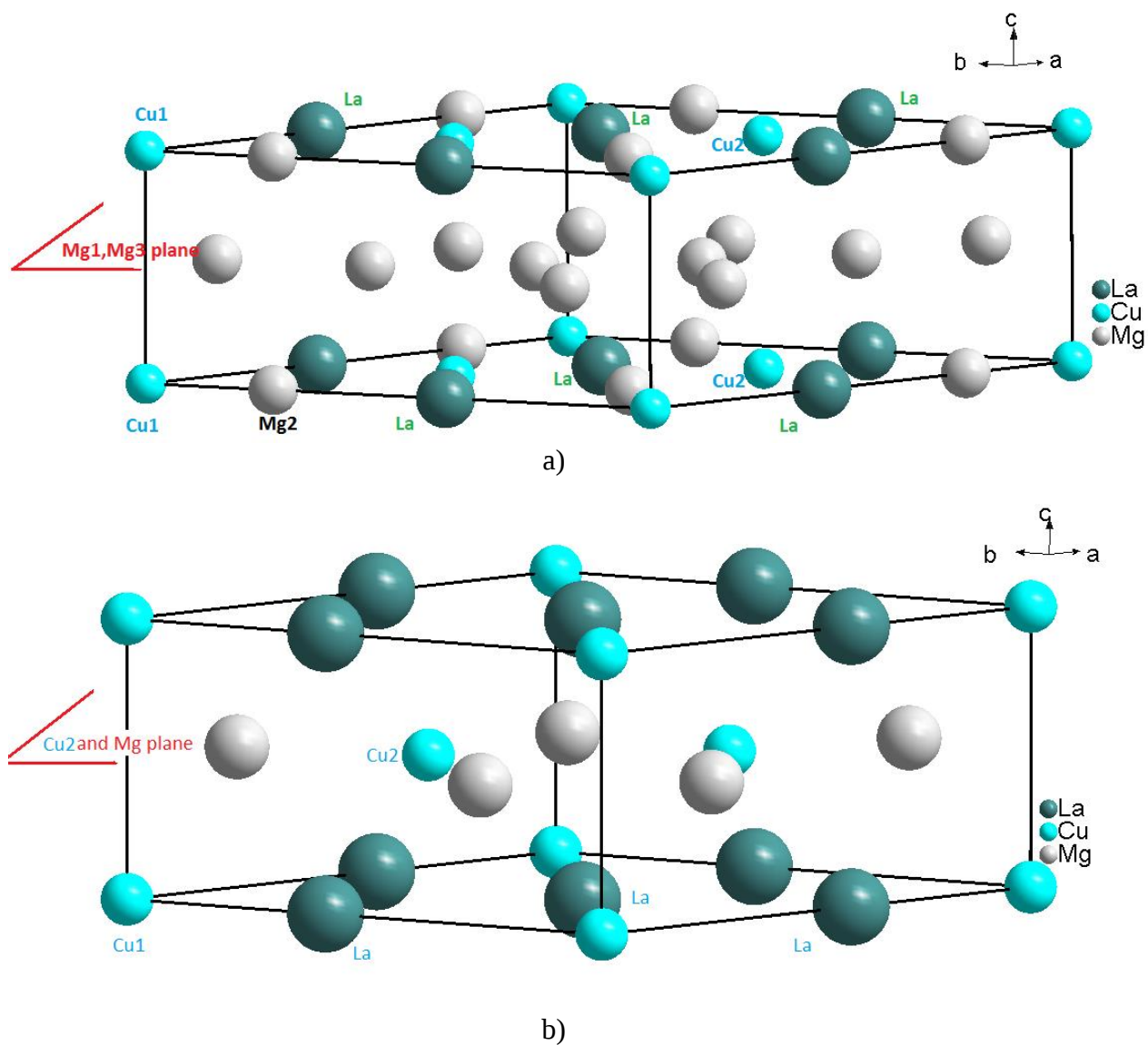


Fig.1. Sketches of the crystal structures of LaCuMg₄ (a) and LaCuMg (b)

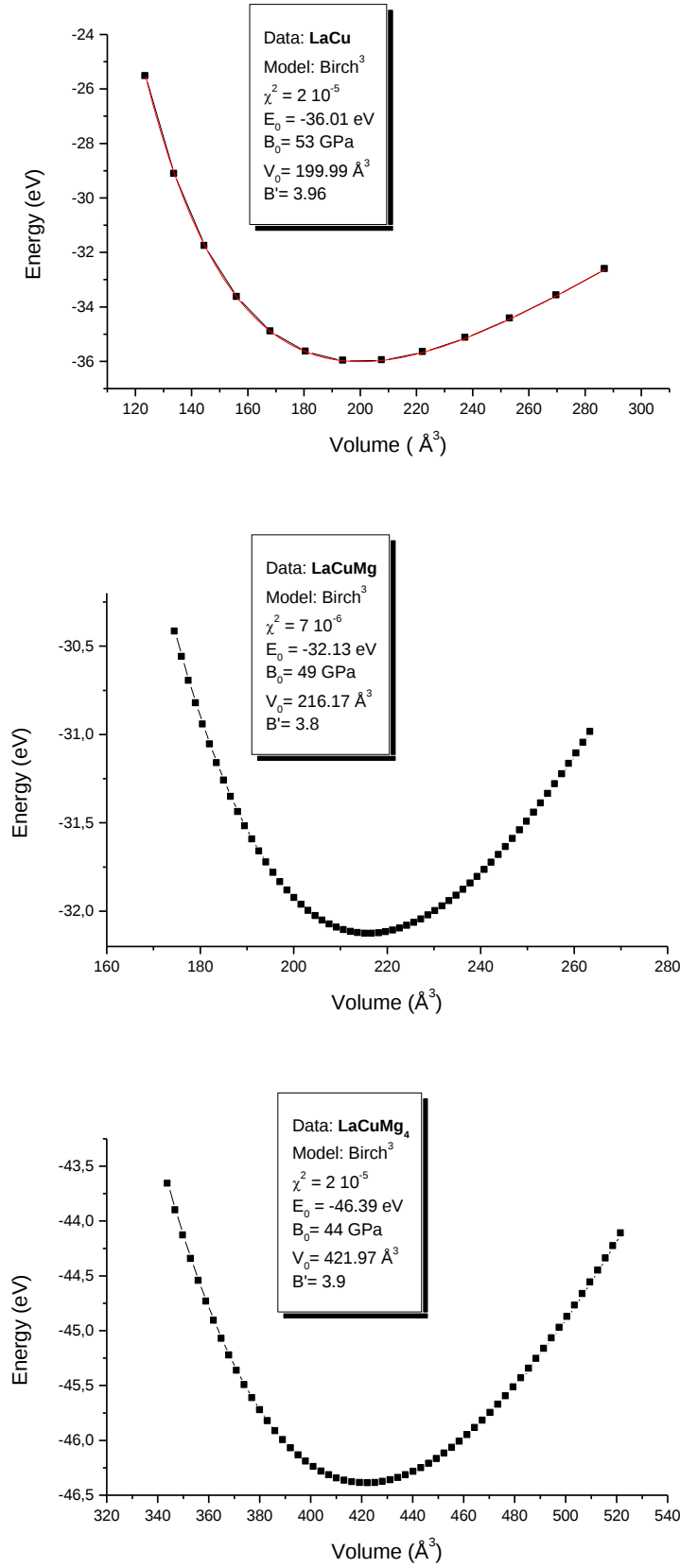


Fig.2. Energy volume curves and Birch EOS fit parameters (inserts) of LaCu (a), LaCuMg (b) and LaCuMg₄ (c).

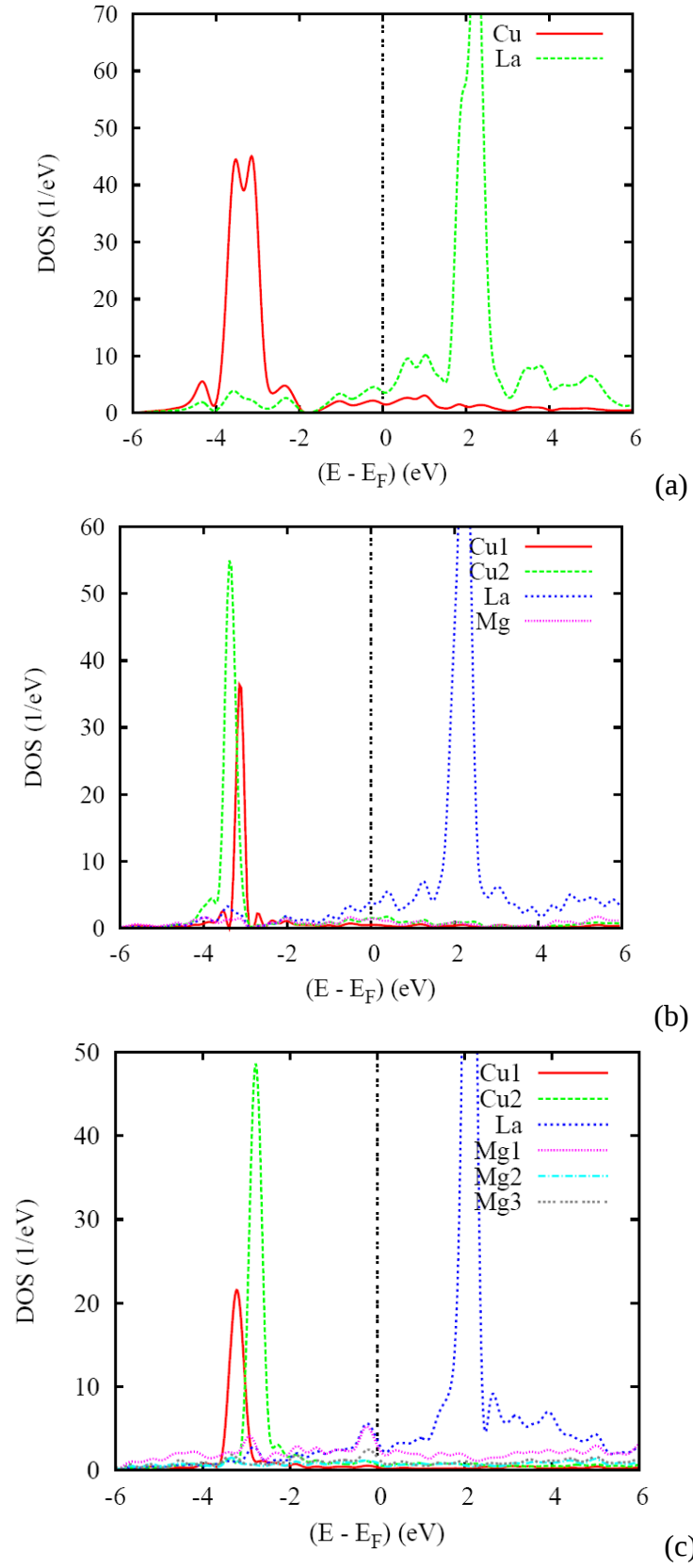


Fig.3. Site projected DOS for LaCu (a), LaCuMg (b) and LaCuMg₄ (c).

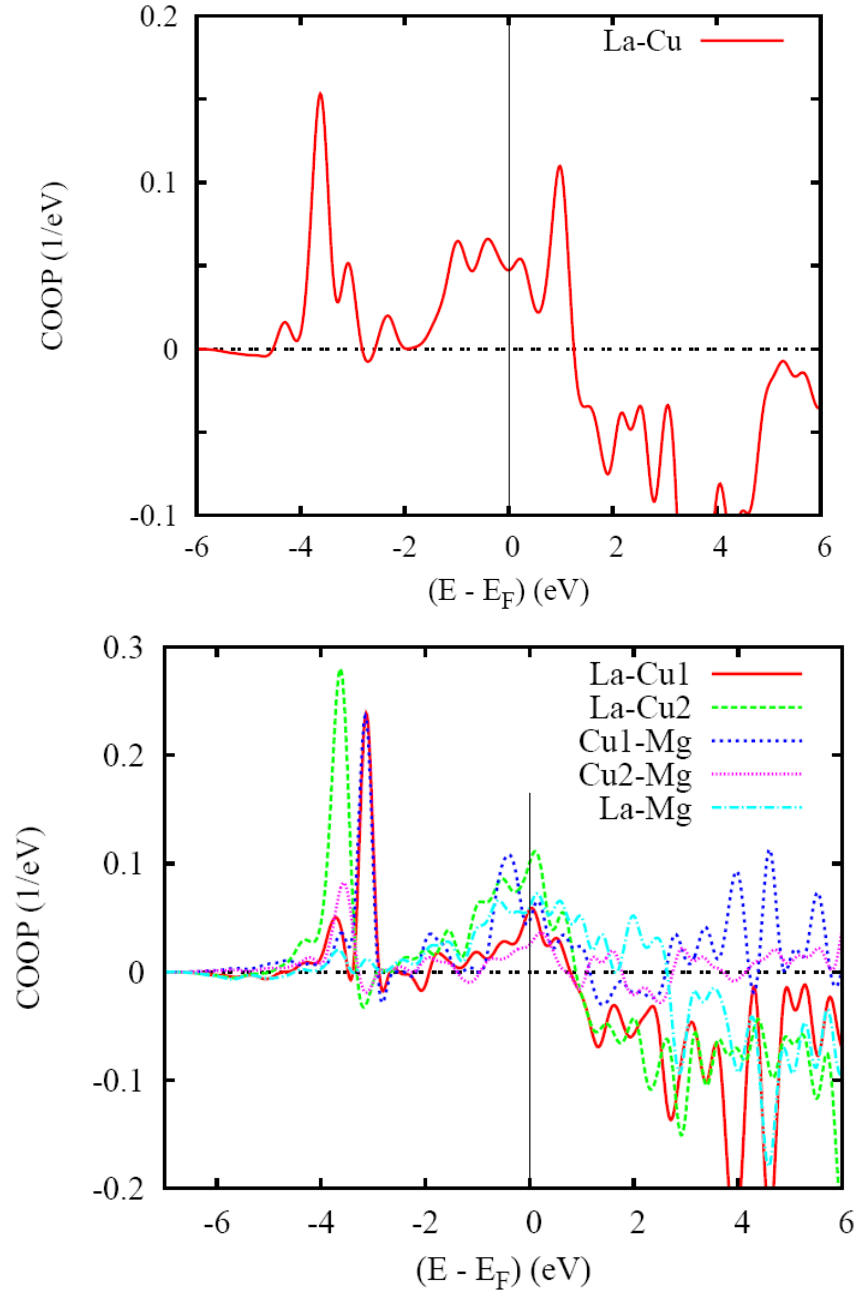


Fig.4. COOP of LaCu and LaCuMg

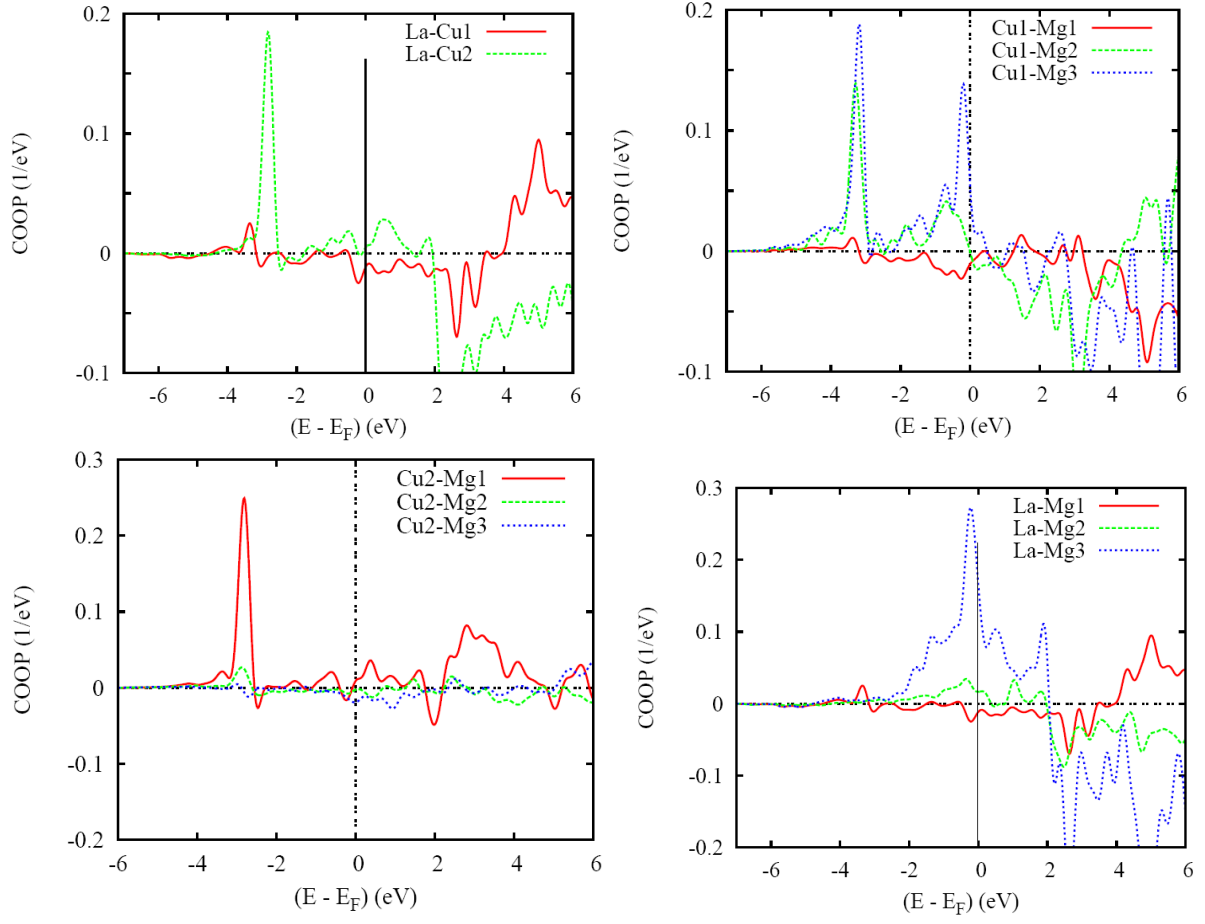


Fig.5. COOP of the different atom-to-atom interactions in LaCuMg₄