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First principles account for large changes in electronic structure and bonding from LaCu to LaCuMg and $LaCuMg_4$

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This work is dedicated to Prof. Joseph Matar.

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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 $LaCuMg_4$. 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.

1. 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 $LaCuMg_4$ (1:1:4) was discovered and structurally determined from *ab initio* in the hexagonal $UCoAl_4$ -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 $NdNiMg_5$ [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 $z = ½$ 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

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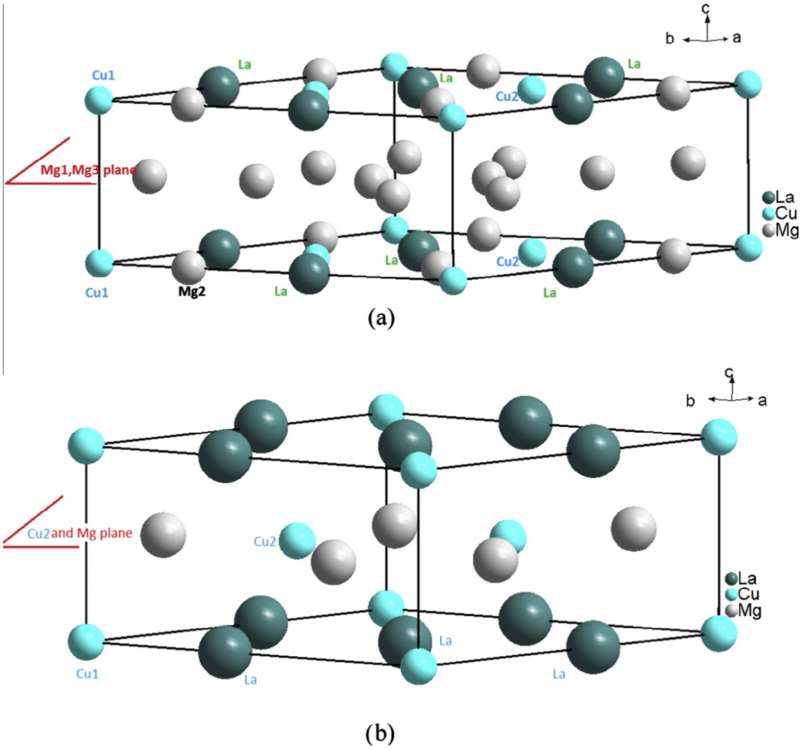

Fig. 1. Sketches of the crystal structures of $LaCuMg_4$ (a) and LaCuMg (b).

Table 1
Experimental and calculated crystal data for the isostructural hexagonal $LaCuMg_4$ and LaCuMg ternary compounds and for LaCu binary in FeB structure.

$LaCuMg_4$ $P\bar{6}m2$, $Z = 3$ FU	Experimental [7]	Calc. (this work)	Calculated Bader charges (Q/e)
a (Å)	10.3911	10.322	
c (Å)	4.5126	4.521	
V ($Å^3$)	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, ½	0.297, 0.480, ½	0
Mg2 (3f)	0.7475, 0, 0	0.746, 0, 0	+0.03
Mg3 (3g)	0.1696, 0, ½	0.166, 0, ½	+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	$E_{coh.}$=−1.41 eV/FU
LaCuMg $P\bar{6}m2$, $Z = 3$ FU	Experimental [6]	Calc. (this work)	Calculated Bader charges (Q/e)
a (Å)	7.725	7.597	
c (Å)	4.188	4.201	
V ($Å^3$)	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, ½	1/3, 2/3, ½	−0.77
Mg3 (3g)	0.256, 0, ½	0.166, 0, ½	+0.18
d(Cu1–Mg3)	2.79	2.76	
d(Cu2–La)	3.12	3.10	
Energy (eV)/3FU		−32.11	$E_{coh.}$ = −0.67 eV/FU
LaCu $Pnma$ $Z = 4$ FU	Experimental [23]	Calc. (this work)	Calculated Bader charges (Q/e)
a (Å)	7.543	7.503	
b (Å)	4.616	4.562	
c (Å)	5.724	5.661	
V ($Å^3$)	199.30	195.39	
La (4c)	0.179, ¼, 0.135	0.177, ¼, 0.134	+0.97
Cu (4c)	0.035, ¼, 0.626	0.035, ¼, 0.608	−0.97
d(La–Cu)	3.01	3.0	
Energy (eV)/4FU		−35.98	$E_{coh.}$ = −0.35 eV/FU