$\text{La}_4\text{Cu}_{3-x}\text{Zn}_x\text{MoO}_{12}$: Zinc Doped Cuprates with Kagomé lattices

Guobao Li, Liping You^a, Wutao Wei^b, Yue Lu^b, Jing Ju^c, Anders Wannberg^d, Håkan Rundlöf^d, Xiaodong Zou^e, Tao Yang, Shujian Tian, Fuhui Liao, Naoki Toyota^c, Jianhua Lin

State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China

liguobao@pku.edu.cn

^aElectron microscope Lab, Peking University, Beijing 100871, P.R.China.

^bStudents from The First High school attended to Beijing Normal University, Beijing, P. R. China.

^cPhysics Department, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

^dStudsvik Neutron Research Laboratory, Uppsala University, S-611 82 Nyköping, Sweden.

^eStructural Chemistry, Stockholm University, SE-10691 Stockholm, Sweden

Supporting Information

1. The conductivity of the $\text{La}_4\text{Cu}_{3-x}\text{Zn}_x\text{MoO}_{12}$ system

The conductivity was measured by impedance spectra with a HP4192A impedance analyzer (see Li et al., J. Solid State Chem. 2004, 177, 875-82 for details on the measurement of impedance spectra) and agrees well with Arrhenius' law as shown in Figure S1. It decreases when Zn-concentration increases.

Figure S1 Typical conductivity of the series $\text{La}_4\text{Cu}_{3-x}\text{Zn}_x\text{MoO}_{12}$ at different temperature.

2. Typical synthesis temperature for each sample.

Table S1 Typical synthesis temperature of $\text{La}_4\text{Cu}_{3-x}\text{Zn}_x\text{MoO}_{12}$

x	0	0.05	0.10	0.15	0.20	0.25	0.28	0.30	0.60
Temperature(°C)	1025	1025	1030	1040	1050	1050	1050	1060	1070
x	0.80	1.00	1.30	1.60	2.00	2.30	2.60	2.70	2.80
Temperature(°C)	1080	1100	1120	1140	1160	1180	1200	1200	1200

3. Lattice parameters of the samples in the series $\text{La}_4\text{Cu}_{3-x}\text{Zn}_x\text{MoO}_{12}$

Table S2 Lattice parameters of different phases in the series $\text{La}_4\text{Cu}_{3-x}\text{Zn}_x\text{MoO}_{12}$

x	a_o (Å) ^a	b_o (Å) ^a	c_o (Å) ^a	a_t (Å) ^b	b_t (Å) ^b	c_t (Å) ^b	α_t (°) ^b	β_t (°) ^b	γ_t (°) ^b	R factor	Unit Cell Volume (Å ³)
0.05	3.9574(3)	6.8544(4)	11.0066(2)							$R_{exp}=0.083$, $R_p=0.058$	$V_o=298.56(1)$
0.10	3.9583(2)	6.8554(3)	11.0070(2)							$R_{exp}=0.083$, $R_p=0.060$	$V_o=298.67(2)$
0.15	3.9591(3)	6.8570(4)	11.0074(1)							$R_{exp}=0.084$, $R_p=0.060$	$V_o=298.83(1)$
0.20	3.9598(2)	6.8585(4)	11.0078(2)							$R_{exp}=0.082$, $R_p=0.059$	$V_o=298.95(2)$
0.25 ^c	3.9598(2)	6.8585(4)	11.0078(2)	11.6950(2)	11.6941(2)	7.9277(2)	80.27(1)	99.80(1)	39.63(1)	$R_{exp}=0.084$, $R_p=0.058$	$V_o=298.95(2)$, $V_t=598.76(3)$
0.28 ^c	3.9598(2)	6.8585(4)	11.0078(2)	11.6950(2)	11.6941(2)	7.9277(2)	80.27(1)	99.80(1)	39.63(1)	$R_{exp}=0.084$, $R_p=0.059$	$V_o=298.95(2)$, $V_t=598.76(3)$
0.30				11.6950(2)	11.6941(2)	7.9277(2)	80.27(1)	99.80(1)	39.63(1)	$R_{exp}=0.077$, $R_p=0.058$	$V_t=598.76(3)$
0.60				11.6997(2)	11.7013(2)	7.9300(3)	80.24(1)	99.76(1)	39.63(1)	$R_{exp}=0.081$, $R_p=0.059$	$V_t=599.61(3)$
0.80				11.7087(5)	11.7050(4)	7.9319(3)	80.26(1)	99.76(1)	39.62(1)	$R_{exp}=0.067$, $R_p=0.050$	$V_t=600.33(3)$
1.00				11.7114(6)	11.7098(6)	7.9329(4)	80.26(1)	99.76(1)	39.58(1)	$R_{exp}=0.074$, $R_p=0.055$	$V_t=600.47(2)$
1.30				11.7190(5)	11.7151(2)	7.9359(4)	80.25(1)	90.75(1)	39.60(1)	$R_{exp}=0.077$, $R_p=0.055$	$V_t=601.34(2)$
1.60				11.7213(4)	11.7194(2)	7.9394(4)	80.28(1)	99.79(1)	39.60(1)	$R_{exp}=0.082$, $R_p=0.062$	$V_t=602.03(2)$
2.00				11.7315(4)	11.7266(3)	7.9430(4)	80.30(1)	99.79(1)	39.59(1)	$R_{exp}=0.076$, $R_p=0.056$	$V_t=603.07(2)$
2.30				11.7402(6)	11.7343(2)	7.9452(4)	80.27(1)	99.76(1)	39.57(1)	$R_{exp}=0.090$, $R_p=0.068$	$V_t=603.84(2)$
2.60 ^d				11.7404(6)	11.7384(3)	7.9456(5)	80.27(1)	99.76(1)	39.57(1)	$R_{exp}=0.139$, $R_p=0.093$	$V_t=604.07(2)$
2.70 ^d				11.7408(7)	11.7379(3)	7.9456(5)	80.27(1)	99.76(1)	39.57(1)	$R_{exp}=0.139$, $R_p=0.093$	$V_t=604.07(2)$
2.80 ^d				11.7405(6)	11.7380(4)	7.9456(5)	80.27(1)	99.76(1)	39.57(1)	$R_{exp}=0.139$, $R_p=0.093$	$V_t=604.06(2)$

^a a_o , b_o , c_o and V_o are the lattice parameters and unit cell volume for the orthorhombic phase SS1 in the space group Pmmn.

^b a_t , b_t , c_t , α_t , β_t , γ_t and V_t are the lattice parameters and unit cell volume for the triclinic phase SS2 in the space group P-1.

^cTwo phases model (the orthorhombic phase SS1 and the triclinic phase SS2) is used in the Rietveld refinement of the obtained X-ray diffraction data.

^dThere are some unknown phases in the sample, therefore the R factors are larger.

4 Rietveld refinement details for $\text{La}_4\text{Cu}_{2.90}\text{Zn}_{0.10}\text{MoO}_{12}$ (a sample of SS1) and the corresponding Rietveld Plot.

Table S3 Rietveld refinement details of $\text{La}_4\text{Cu}_{2.90}\text{Zn}_{0.10}\text{MoO}_{12}$ ^a

La1	-0.0005(1), 0.2500, 0.2460(1)	1
T1a ^b	0.2500, 0.7500, 0.4022(1)	0.5
T1b ^b	0.2500, 0.7500, 0.4438(1)	0.5
T2 ^b	0.9076(1), 0.25, 0.5985(1)	0.5
O1	0.0919(1), 0.7500, 0.3914(1)	1
O2	0.0703(1), 0.2500, 0.8899(1)	1
O3a	0.2500, 0.7500, 0.7550(1)	0.5
O3b	0.2500, 0.7500, 0.6594(1)	0.5
O4	0.2500, 0.2643, 0.3036(1)	0.5
R factor	$R_{\text{wp}}=0.092$, $R_{\text{p}}=0.066$	

^aSpace group *Pmmn* with $a=3.9583(2)$ Å, $b=6.8554(2)$ Å, $c=11.0066(2)$ Å, $V=298.674(8)$ (Å³)

^bMo, Cu, Zn atoms are mixed in this site.

Figure S2 Rietveld plot of the X-ray powder diffraction pattern for $\text{La}_4\text{Cu}_{2.90}\text{Zn}_{0.10}\text{MoO}_{12}$.

5 Rietveld refinement details for $\text{La}_4\text{Cu}_2\text{ZnMoO}_{12}$ (a sample of SS2) and the corresponding Rietveld plots.

Table S4 Rietveld refinement details of $\text{La}_4\text{Cu}_2\text{ZnMoO}_{12}$ in different models.

	Model A	Model B	Model C
Space group	P21/m	A-1	P -1
Lattice parameter	a=6.8708(4), b=11.0180(2), c=7.9309(5) Å, $\beta=90.00(1)^\circ$	a=7.9329(4), b=22.0367(6), c=7.9330(6) Å, $\alpha=89.99(1)^\circ$, $\beta=120.00(1)^\circ$, $\gamma=90.01(1)^\circ$	a=11.7114(6), b=11.7098(6), c=7.9329(4) Å, $\alpha=80.26(1)^\circ$, $\beta=99.76(1)^\circ$, $\gamma=39.60(1)^\circ$
Cell Volume	600.38(4) (Å ³)	1200.94(2) (Å ³)	600.47(2) (Å ³)
La1	0.2484(1), -0.0002(1), 0.1274(1)	0, 0, 0	0, 0, 0
La2	0.2493(1), -0.0016(1), 0.6221(1)	0.5, 0, 0	0, 0, 0.5
La3		0, 0.5, 0	0.5, 0.5, 0
La4		0.5, 0.5, 0	0.5, 0.5, 0.5
La5		-0.0005(1), 0.2491(1) 0.0063(1)	0.2554(1), 0.2429(1), -0.0005(1)
La6		0.4974(1), 0.2493(1), 0.5005(1)	0.7498(1), -0.2512(1), 0.4974(1)
Mo	0.4378(1), 0.25, 0.3618(1)	0.1336(1), 0.1268(1), 0.8423(1)	0.9691(1), -0.7155(1), 0.1336(1)
T1 ^a	0.4354(1), 0.25, 0.8718(1)	0.6411(1), 0.1218(1), 0.3160(1)	0.4378(1), -0.1943(1), 0.6411(1)
T2 ^a	0.9035(1), 0.25, 0.0960(1)	0.6584(1), 0.1238(1), 0.7851(1)	0.9089(1), -0.6613(1), 0.6584(1)
T3 ^a	0.9076(1), 0.25, 0.5985(1)	0.1688(1), 0.1259(1), 0.3287(1)	0.4546(1), -0.2028(1), 0.1688(1)
O1	0.4209(1), 0.0792(1), 0.3819(1)	0.3311(1), 0.7887(1), 0.6702(1)	0.4588(1), 0.1185(1), 0.3311(1)
O2	0.4112(1), 0.0836(1), 0.8810(1)	0.3251(1), 0.9569(1), 0.1542(1)	0.1111(1), 0.8027(1), 0.3251(1)
O3	0.9077(1), 0.0854(1), 0.1304(1)	0.8291(1), 0.7921(1), 0.1700(1)	0.9621(1), 0.6221(1), 0.8291(1)
O4	0.9070(1), 0.0847(1), 0.6190(1)	0.8336(1), 0.9576(1), 0.1743(1)	0.1319(1), 0.7834(1), 0.8336(1)
O5	0.7306(1), 0.25, 0.3982(1)	0.3340(1), 0.7937(1), 0.1636(1)	0.9574(1), 0.6301(1), 0.3340(1)
O6	0.6977(1), 0.25, 0.8766(1)	0.3237(1), 0.9595(1), 0.6660(1)	0.6252(1), 0.2934(1), 0.3237(1)
O7	0.3019(1), 0.25, 0.1773(1)	0.1502(1), 0.0407(1), 0.3210(1)	0.3616(1), -0.2803(1), 0.1502(1)
O8	0.2672(1), 0.25, 0.5822(1)	0.1662(1), 0.2069(1), 0.3340(1)	0.5409(1), -0.1271(1), 0.1662(1)
O9		0.5430(1), 0.12094(1), 0.5115(1)	0.6324(1), -0.3905(1), 0.5430(1)
O10		0.0448(1), 0.1265(1), 0.5802(1)	0.7067(1), -0.4537(1), 0.0448(1)

O11		0.9868(1), 0.8740(1), 0.0074(1)	0.8813(1), 0.8666(1), 0.9868(1)
O12		0.6023(1), 0.8663(1), 0.0673(1)	0.9335(1), 0.7990(1), 0.6023(1)
R factor	$R_{wp}=0.085$, $R_p=0.061$ (X-ray) $R_{wp}=0.089$, $R_p=0.067$ (Neutron)	$R_{wp}=0.074$, $R_p=0.055$ (X-ray) $R_{wp}=0.077$, $R_p=0.061$ (Neutron)	$R_{wp}=0.074$, $R_p=0.055$ (X-ray) $R_{wp}=0.077$, $R_p=0.061$ (Neutron)

^aThese sites are for mixed Cu and Zn atoms.

Figure S3 Rietveld plot of the X-ray powder diffraction pattern for $\text{La}_4\text{Cu}_2\text{ZnMoO}_{12}$ using model A in the Table S4. The weak reflections marked by * in figure cannot be indexed in the monoclinic cell of the Model A.

Figure S4 Rietveld plot of the neutron diffraction pattern collected at room temperature for $\text{La}_4\text{Cu}_2\text{ZnMoO}_{12}$ using model B or C in the Table S4.

6 Rietveld plot and refinement details for $\text{La}_4\text{Cu}_2\text{ZnMoO}_{12}$ at 50K

Figure S5 Rietveld Plot of the neutron diffraction data collected at 50K for $\text{La}_4\text{Cu}_2\text{ZnMoO}_{12}$

Table S5 Rietveld refinement details of the neutron diffraction data collected at 50K for $\text{La}_4\text{Cu}_2\text{ZnMoO}_{12}$ ^a

La1	0, 0, 0	O2	0.1241(1), 0.7919(1), 0.3351(1)
La2	0, 0, 0.5	O3	0.9657(1), 0.6207(1), 0.8230(1)
La3	0.5, 0.5, 0	O4	0.1315(1), 0.7877(1), 0.8370(1)
La4	0.5, 0.5, 0.5	O5	0.9567(1), 0.6303(1), 0.3247(1)
La5	0.2559(1), 0.2445(1), 0.0012(1)	O6	0.6242(1), 0.2953(1), 0.3215(1)
La6	0.7486(1), -0.2510(1), 0.4969(1)	O7	0.3670(1), -0.2818(1), 0.1498(1)
Mo	0.9731(1), -0.7182(1), 0.1411(1)	O8	0.5415(1), -0.1283(1), 0.1669(1)
T1 ^b	0.4357(1), -0.1904(1), 0.6339(1)	O9	0.6307(1), -0.3853(1), 0.5392(1)
T2 ^b	0.9133(1), -0.6645(1), 0.6552(1)	O10	0.6876(1), -0.4547(1), 0.0233(1)
T3 ^b	0.4647(1), -0.2125(1), 0.1674(1)	O11	0.8942(1), 0.8482(1), 0.9856(1)
O1	0.4566(1), 0.1198(1), 0.3302(1)	O12	0.9174(1), 0.8237(1), 0.5908(1)
$R_{wp}=0.063$, $R_p=0.049$			

^aSpace group $P-1$ with $a=11.6843(15)$, $b=11.6782(16)$, $c=7.9294(15)$ Å, $\alpha=80.25(2)^\circ$, $\beta=99.81(2)^\circ$, $\gamma=39.67(2)^\circ$, $V=597.91(2)$ (Å³)

^bThese sites are for mixed Cu and Zn atoms

7 Rietveld plot and refinement details for $\text{La}_4\text{Cu}_2\text{ZnMoO}_{12}$ at 10K without and with magnetic contribution

Figure S6 Rietveld Plot of the neutron diffraction data collected at 10K for $\text{La}_4\text{Cu}_2\text{ZnMoO}_{12}$ without the magnetic contribution.

Figure S7 Rietveld Plot of the neutron diffraction data collected at 10K for $\text{La}_4\text{Cu}_2\text{ZnMoO}_{12}$ with the magnetic contribution.

Table S6 Rietveld refinement details of the neutron diffraction data collected at 10K for $\text{La}_4\text{Cu}_2\text{ZnMoO}_{12}$ without and with the magnetic contribution^a

	Without the magnetic contribution	With the magnetic contribution
La1	0, 0, 0	0, 0, 0
La2	0, 0, 0.5	0, 0, 0.5
La3	0.5, 0.5, 0	0.5, 0.5, 0
La4	0.5, 0.5, 0.5	0.5, 0.5, 0.5
La5	0.2549(1), 0.2451(1), 0.0001(1)	0.2549(1), 0.2451(1), 0.0001(1)
La6	0.7501(1), -0.2518(1), 0.4976(1)	0.7501(1), -0.2518(1), 0.4976(1)
Mo	0.9727(1), -0.7181(1), 0.1421(1)	0.9727(1), -0.7181(1), 0.1421(1)
T1 ^b	0.4371(1), -0.1915(1), 0.6368(1)	0.4371(1), -0.1915(1), 0.6368(1)
T2 ^b	0.9100(1), -0.6606(1), 0.6507(1)	0.9100(1), -0.6606(1), 0.6507(1)
T3 ^b	0.4647(1), -0.2137(1), 0.1702(1)	0.4647(1), -0.2137(1), 0.1702(1)
O1	0.4589(1), 0.1198(1), 0.3292(1)	0.4589(1), 0.1198(1), 0.3292(1)
O2	0.1282(1), 0.7884(1), 0.3359(1)	0.1282(1), 0.7884(1), 0.3359(1)
O3	0.9657(1), 0.6207(1), 0.8230(1)	0.9657(1), 0.6207(1), 0.8230(1)
O4	0.1315(1), 0.7877(1), 0.8370(1)	0.1315(1), 0.7877(1), 0.8370(1)
O5	0.9521(1), 0.6336(1), 0.3232(1)	0.9521(1), 0.6336(1), 0.3232(1)
O6	0.6262(1), 0.2941(1), 0.3226(1)	0.6262(1), 0.2941(1), 0.3226(1)
O7	0.3628(1), -0.2799(1), 0.1479(1)	0.3628(1), -0.2799(1), 0.1479(1)
O8	0.5411(1), -0.1297(1), 0.1671(1)	0.5411(1), -0.1297(1), 0.1671(1)
O9	0.6347(1), -0.3846(1), 0.5357(1)	0.6347(1), -0.3846(1), 0.5357(1)
O10	0.6876(1), -0.4548(1), 0.0233(1)	0.6876(1), -0.4548(1), 0.0233(1)
O11	0.8942(1), 0.8482(1), 0.9856(1)	0.8942(1), 0.8482(1), 0.9856(1)
O12	0.9174(1), 0.8237(1), 0.05908(1)	0.9174(1), 0.8237(1), 0.05908(1)
M ^c		0.6032, 0.6442, 0.4872
R factor	R _{exp} =0.068, R _p =0.053	R _{exp} =0.067, R _p =0.052

^aSpace group $P-1$ with $a=11.6678(8)$, $b=11.6843(8)$, $c=7.9273(11)$ Å, $\alpha=80.18(2)^\circ$, $\beta=99.76(2)^\circ$,

$\gamma=39.68(1)^\circ$, $V=597.23(3) \text{ (\AA}^3\text{)}$

^bThese sites are for mixed Cu and Zn atoms

^cThe magnetic moment is assumed to sit at the center of the three copper atoms, no position deviation for it. The magnetic moment is (-0.452, 1.718, -0.132), which is corresponding to $1.78\mu_B$ (see section 8 for details)

8 Some discussions on the ferromagnetic moment and the neutron diffraction data

There are no contributions from magnetic diffraction in the neutron diffraction data obtained at 300K and 50K for the magnetic moments sitting randomly. The data obtained at 10K is very similar to the data for 300K and 50K as shown in figure S8 without extra peaks but the relative intensity of some peaks are different (for example, the first peak becomes stronger marked by *)—this indicates that the ordering of the magnetic moments are ferromagnetic instead of anti-ferromagnetic. Using the software GSAS, the magnetic structure of $\text{La}_4\text{Cu}_2\text{ZnMoO}_{12}$ at 10K is obtained, which is shown in Figure S9 (During such a fitting, the magnetic moment is assumed to sit at the center of the three copper atoms shown as the red balls in the figure S9 The occupation is 0.666 corresponding to the fact that 1/3 atoms are zinc. Other details are listed in Table S6). The magnetic moment for Cu is $1.78\mu_B$, which agrees well with the theoretical value $1.73 \mu_B$. For clarity, the fitting with and without the magnetic diffraction contribution are present in Figure S10 for neutron diffraction data of $\text{La}_4\text{Cu}_2\text{ZnMoO}_{12}$ at 10K. It is reasonable to believe that there are really some contributions from magnetic diffraction in the neutron diffraction data of $\text{La}_4\text{Cu}_2\text{ZnMoO}_{12}$ at 10K.

Figure S8 Selected area of the GSAS fit to the neutron diffraction data of $\text{La}_4\text{Cu}_2\text{ZnMoO}_{12}$ at 300K, 50K and 10K as marked.

Figure S9 Magnetic structure for $\text{La}_4\text{Cu}_2\text{ZnMoO}_{12}$ at 10K. The red ball is the center of Cu_3^{II} cluster. Unit cell is shown by the black lines.

Figure S10 The neutron diffraction data fitted with and without magnetic structure.

9 Some discussions about the “Random model” and “Separate cluster model” of Cu and Zn in the Kagomé lattice

The Zinc and Copper in SS2 form the Kagomé lattice. The molybdenum has a unique site and makes no contribution to the magnetic interaction as shown by the parent compound $\text{La}_4\text{Cu}_3\text{MoO}_{12}$. The Zn atoms and Cu atoms are sited at the same crystalline site. It is the usual case that Zn atoms may randomly mix with Cu atoms. Then there are four kinds of trimer, the first one is that with three copper atoms (referred as $[\text{Cu}^{\text{II}}_3]$), the second with two copper atoms and one zinc atoms (referred as $[\text{Zn}^{\text{II}}\text{Cu}^{\text{II}}_2]$), the third with one copper atom and two zinc atoms ($[\text{Zn}^{\text{II}}_2\text{Cu}^{\text{II}}]$), the fourth with three zinc atoms ($[\text{Zn}^{\text{II}}_3]$), referred as the “Random model”. If the intratrimer antiferromagnetic interaction are strong enough, these four trimers are classed into two groups, one group with $s=1/2$ spin including $[\text{Cu}^{\text{II}}_3]$ and $[\text{Zn}^{\text{II}}_2\text{Cu}^{\text{II}}]$, the other group with $s=0$ spin including $[\text{Zn}^{\text{II}}\text{Cu}^{\text{II}}_2]$ and $[\text{Zn}^{\text{II}}_3]$. At this case, the free electrons per formula, n , can be expressed as following:

$$n = (1 - y)^3 + 3(1 - y)y^2 \quad (1)$$

Here, y is the ratio of $\text{Zn}/(\text{Cu}+\text{Zn})$.

The other extreme is that Cu atoms form trimer themselves and Zn atoms also form trimer themselves, referred as “Separate cluster model”. At this case, when the intratrimer antiferromagnetic interactions are strong enough, the free electrons per formula, n , can be expressed as following:

$$n = 1 - y \quad (2)$$

Here, y is the ratio of $\text{Zn}/(\text{Cu}+\text{Zn})$. As shown in Figure 9 (in the text), the equation (2) fits the data well.

Of course, there should be some other models to give the same result as equation (2). Let us try to find them all. As we known, for 1 molar $\text{La}_4\text{Cu}_{3-x}\text{Zn}_x\text{MoO}_{12}$, there are $3-x$ molar Cu and x molar Zn. If we suppose that there are z molar $[\text{Zn}^{\text{II}}\text{Cu}^{\text{II}}_2]$ and w molar $[\text{Zn}^{\text{II}}_2\text{Cu}^{\text{II}}]$, there should be $(3-x-2z-w)/3$ molar $[\text{Cu}^{\text{II}}_3]$ and $(x-2w-z)/3$ molar $[\text{Zn}^{\text{II}}_3]$. Therefore, the free electrons per formula, n , can be expressed as following:

$$n = (3-x-2z-w)/3 + w \quad (3)$$

If the rule of “one electron per $[\text{Cu}^{\text{II}}_3]$ cluster” is followed, then

$$[(3-x-2z-w)/3+w]/[(3-x)/3]=1 \quad (4)$$

That is,

$$(2z-2w)/x=0 \quad (5)$$

For the special case $x=0$, there are no $[\text{Zn}^{\text{II}}\text{Cu}^{\text{II}}_2]$ and $[\text{Zn}^{\text{II}}_2\text{Cu}^{\text{II}}]$ in $\text{La}_4\text{Cu}_3\text{MoO}_{12}$. Then, $z=w=0$.

For the general case, $x \neq 0$, we get $z=w$.

Therefore, if the rule of “one electron per 3Cu ” should be followed, there should be $(3-x-3z)/3$ molar $[\text{Cu}^{\text{II}}_3]$, z molar $[\text{Zn}^{\text{II}}\text{Cu}^{\text{II}}_2]$, z molar $[\text{Zn}^{\text{II}}_2\text{Cu}^{\text{II}}]$ and $(x-3z)/3$ molar $[\text{Zn}^{\text{II}}_3]$ in 1 molar $\text{La}_4\text{Cu}_{3-x}\text{Zn}_x\text{MoO}_{12}$. Here z is a free variable, but it should not be negative and should less than the smaller of $x/3$ and $(1-x/3)$ to ensure all values are positive.

So there is a large number of models for the rule of “one electron per $[\text{Cu}^{\text{II}}_3]$ cluster”. It is difficult to choose. However, in the general case where $z \neq 0$, we should answer the question - why the amount of “ $[\text{Zn}^{\text{II}}\text{Cu}^{\text{II}}_2]$ ” is equal to that of “ $[\text{Zn}^{\text{II}}_2\text{Cu}^{\text{II}}]$ ”? And we also should answer the

question if there are any rules on the ratio of $[\text{Zn}^{\text{II}}_2\text{Cu}^{\text{II}}]$ to $[\text{Zn}^{\text{II}}_3]$ or $[\text{Cu}^{\text{II}}_3]$. But for the very special case where $z=0$, only $[\text{Cu}^{\text{II}}_3]$ and $[\text{Zn}^{\text{II}}_3]$ clusters are present, which is just the Separate cluster model. The explanation for it may be that the Cu^{II} and Zn^{II} ions tend to form clusters separately. This is also simple and may be acceptable.

In summary, the Separate cluster model is specially mentioned just because it is the simplest one but not the only one.