Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supporting Information

for

Crystal Structure Resolution of an Insulator Due to Cooperative Jahn-Teller through Bader's Theory: The Challenging Case of Cobaltite Oxide Y114

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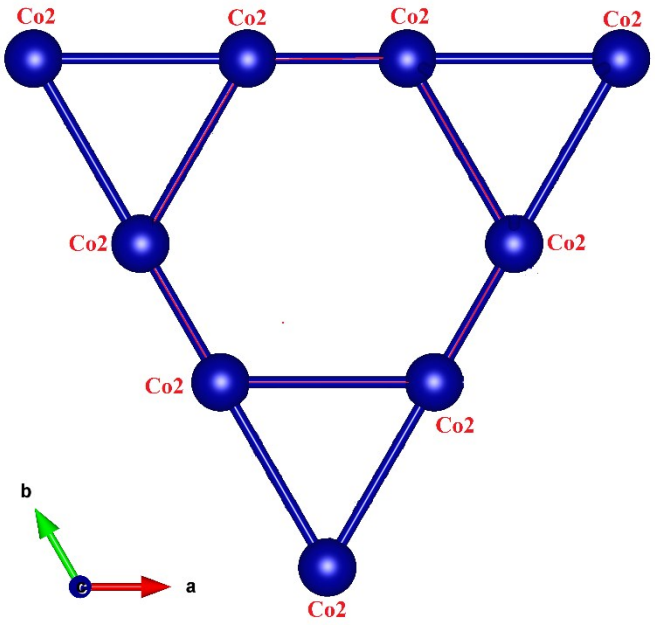
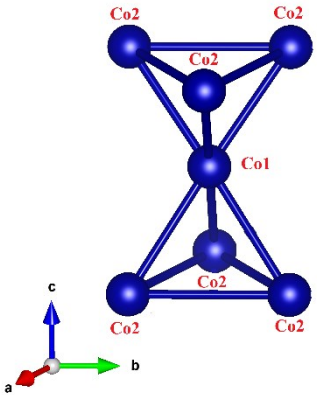
E.S.I.1 (a) Scheme of Kagome lattice adapted from study of Owerre *et al.* (2015)[1] to LDA+U full optimized hexagonal structure of Y114 seen from **c** lattice view. There are two different cobalt atoms indicated with Co1 and Co2, which both present within experimental structure tetrahedral coordination of different dimension. The red hexagon denotes the Brillouin zone with Γ = (0, 0); K = (2π/3, 0); M = (π/2, π/2$\sqrt{3}$). (b) Scheme of geometrical relationship between triangular and adjacent Kagome lattice adapted from study of Soda *et al.* (2006)[2] to LDA+U full optimized hexagonal structure of Y114 seen from **b** lattice view; the susceptibility measurements attributed +3 to Co1 and +2 to Co2 with the impossibility to attribute spin order.

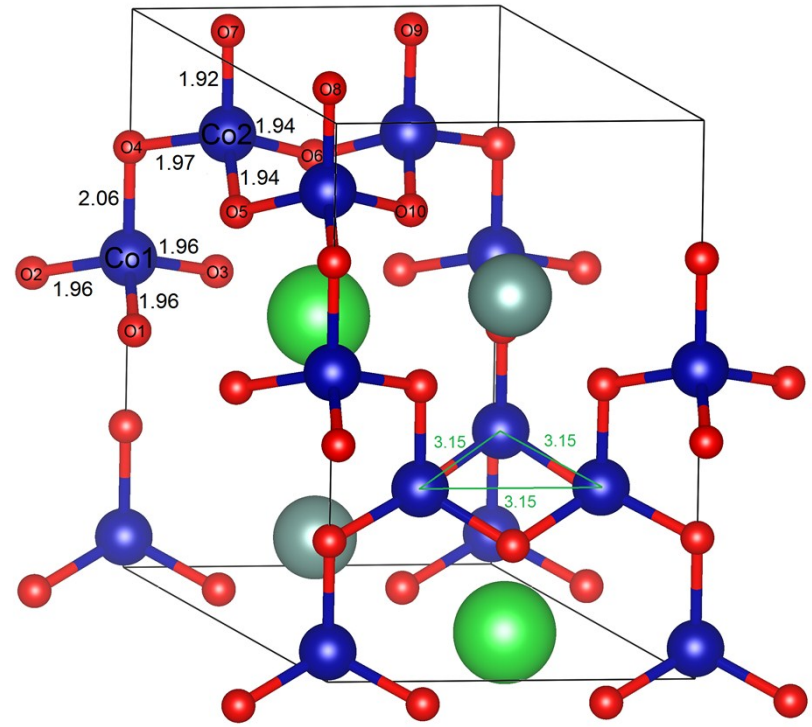


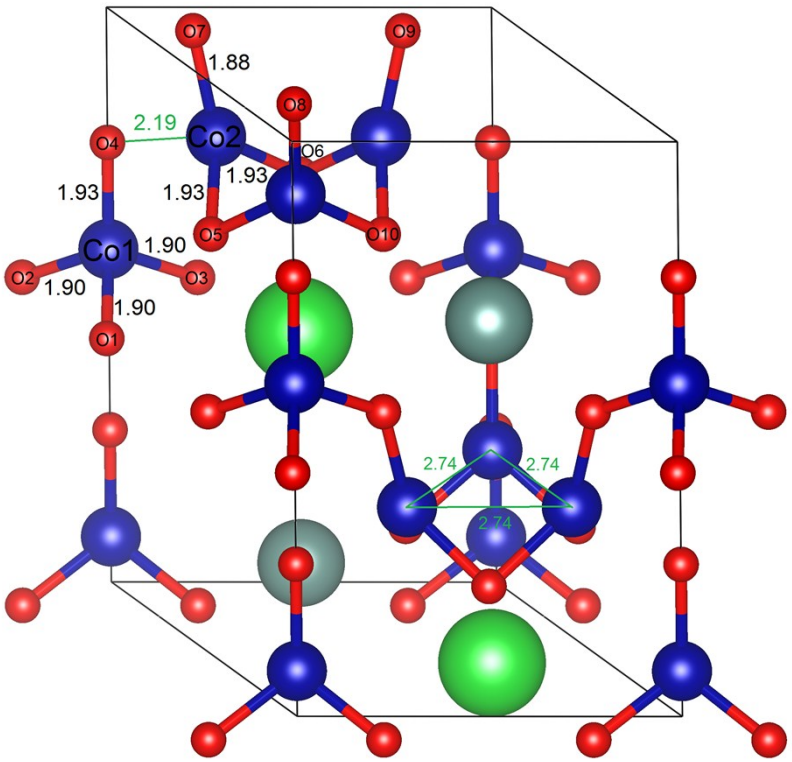
(a)



(b)

E.S.I.2 Comparison between the Y114 hexagonal crystal structure as from the experimental data[3] (upper) and after LDA+U DFT full optimisation (lower). The bond distances are in Angstrom. Legend of colours: Cobalt (blue), Oxygen (red), Barium (green), Yttrium (grey).





E.S.I.3 Bond distances for Y114 optimized at LDA+U DFT approximation with different Hubbard energies.

E_{Hub} / *eV*	Co1-O1	Co1-O2	Co1-O3	Co1-O4	Co2-O5	Co2-O6	Co2-O7
5	1.8983	1.8983	1.8983	1.9344	1.9325	1.9325	1.8752
8	1.8985	1.8985	1.8985	1.9344	1.9322	1.9322	1.8753
9	1.8985	1.8985	1.8985	1.9344	1.9322	1.9322	1.8753
10	1.8985	1.8985	1.8985	1.9344	1.9322	1.9322	1.8753

E.S.I.4 Bond angles for Y114 optimized at LDA+U DFT approximation with different Hubbard energies.

E_{Hub} / *eV*	O1-Co1-O2	O1-Co1-O3	O1-Co1-O4	O2-Co1-O3	O2-Co1-O4	O3-Co1-O4	O5-Co2-O6	O5-Co2-O7	O6-Co2-O7
5	100.1791	100.1790	117.6609	100.1790	117.6609	117.6609	95.4961	128.4969	128.4975
8	100.2128	100.1447	117.6628	100.1746	117.6628	117.6628	95.5203	128.4939	128.5036
9	100.1431	100.1961	117.6757	100.1930	117.6757	117.6757	95.5203	128.5120	128.5033
10	100.2073	100.1877	117.6628	100.1446	117.6628	117.6628	95.5202	128.4941	128.5034

E.S.I.5 Bond distances for Y114 and the substituted structures, optimized at LDA+U DFT approximation and according the standard LDA DFT method, respectively. For Y114 the experimental data[3] are also reported.

Bond distance (Å)	Y114		CA	ZC	ZA
M1 =	$Co1(Co^{3+})$		$Al(Al^{3+})$	$Co1(Co^{3+})$	$Al(Al^{3+})$
M2 =	$Co2(Co^{2+})$		$Co2(Co^{2+})$	$Zn(Zn^{2+})$	$Zn(Zn^{2+})$
	exp.[3]	*comp.**	*comp.***	*comp.***	*comp.***
M1-O1	1.9558	1.8983	1.8053	1.8432	1.7866
M1-O2	1.9558	1.8983	1.8195	1.8695	1.7866
M1-O3	1.9558	1.8983	1.7808	1.8695	1.7866
M1-O4	2.0642	1.9344	1.8357	1.9168	1.7965
M2-O5	1.9366	1.9325	1.8257	1.9789	1.9621
M2-O6	1.9366	1.9325	1.8372	1.9789	1.9621
M2-O7	1.9194	1.8752	2.0082	2.0483	2.0473

* LDA+U (PAW) DFT

** LDA (PAW) DFT

E.S.I.6 Bond angles for Y114 and the substituted structures, optimized at LDA+U DFT approximation and according the standard LDA DFT method, respectively. For Y114 the experimental data[3] are also reported.

Bond Angle		Y114		CA	ZC	ZA
	M1 =	Co1(Co^{3+})		Al(Al^{3+})	Co1(Co^{3+})	Al(Al^{3+})
	M2 =	Co2(Co^{2+})		Co2(Co^{2+})	Zn(Zn^{2+})	Zn(Zn^{2+})
		exp.[3]	*comp.**	*comp.***	*comp.***	*comp.***
O1-M1-O2		110.0378	100.1791	109.8638	99.8038	110.8137
O1-M1-O3		110.0379	100.1790	114.0992	115.1270	110.8041
O1-M1-O4		108.8985	117.6609	110.8468	107.3022	108.1160
O2-M1-O3		110.0378	100.1790	107.9586	122.8699	110.7886
O2-M1-O4		108.8985	117.6609	104.8740	108.7392	108.1056
O3-M1-O4		108.8985	117.6609	108.7528	102.3166	108.0957
O5-M2-O6		102.9688	95.4961	146.3278	112.9289	119.7858
O5-M2-O7		113.2331	128.4969	106.1294	112.8891	107.3178
O6-M2-O7		113.2333	128.4975	106.8129	107.6850	107.2011
O4-M2-O7		106.8699	91.8521	95.4783	107.9351	108.8004

* LDA+U (PAW) DFT

** LDA (PAW) DFT

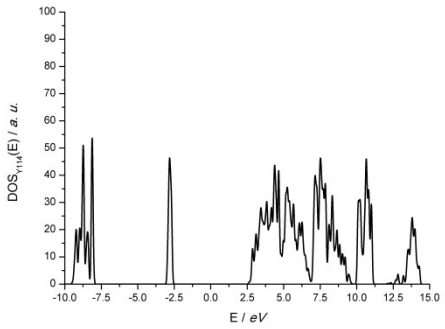
E.S.I.7 Atomic basin volumes and charges[4] for the fully optimized structures of Y114 and the substituted structures.

	Y114*		CA**		ZC**		ZA**	
M1 =	Co1(Co^{3+})		Al(Al^{3+})		Co1(Co^{3+})		Al(Al^{3+})	
M2 =	Co2(Co^{2+})		Co2(Co^{2+})		Zn(Zn^{2+})		Zn(Zn^{2+})	
SCF (*eV*)	-45121.20		-41822.63		-42790.70		-39468.13	
ATOM	Volume (*bohr³*)	Charge (*e*)	Volume (*bohr³*)	Charge (*e*)	Volume (*bohr³*)	Charge (*e*)	Volume (*bohr³*)	Charge (*e*)
Co1	75.10	0.50	-	-	67.16	1.40	-	-
Co2	78.13	0.30	76.48	1.15	-	-	-	-
Al1	-	-	3.44	2.92	-	-	3.43	2.92
Zn2	-	-	-	-	75.53	1.23	76.35	1.22
O1	94.99	-1.96	121.09	-1.61	97.26	-1.22	117.13	-1.62
O2	94.99	-1.96	118.44	-1.59	104.57	-1.24	117.14	-1.62
O3	94.99	-1.96	112.38	-1.56	104.57	-1.24	117.14	-1.62
O4	92.42	-1.85	108.91	-1.44	87.29	-1.20	98.95	-1.54
O5	96.17	-1.95	90.40	-1.22	99.13	-1.31	99.97	-1.32
O6	96.17	-1.95	93.44	-1.20	100.54	-1.32	99.97	-1.32
O7	94.99	-1.96	118.48	-1.59	97.27	-1.22	117.15	-1.62

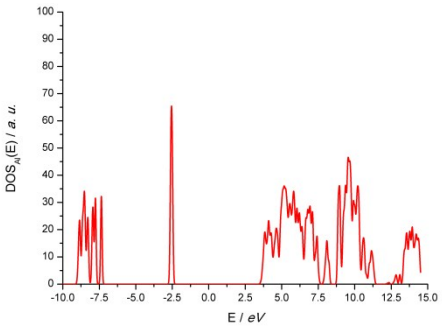
* LDA+U (PAW) DFT

** LDA (PAW) DFT

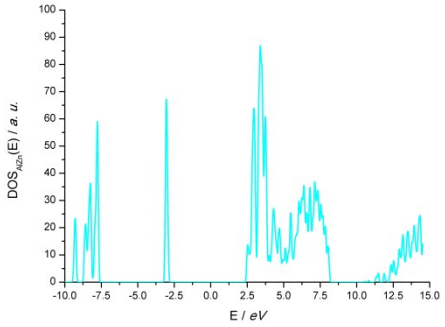
E.S.I.8 Plot of the DOS for the fully optimized structures of Y114 (black) and the substituted structures: CA (red), ZA (turquoise), and ZC (green). Please note that the same scales on the two axes were used to ease comparisons.



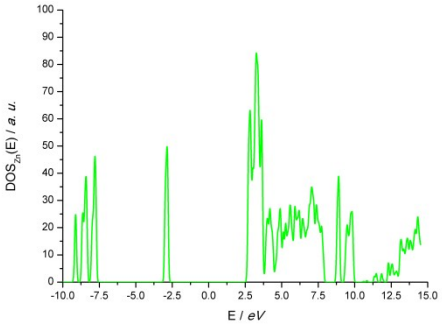
Y114*



CA**



ZA**

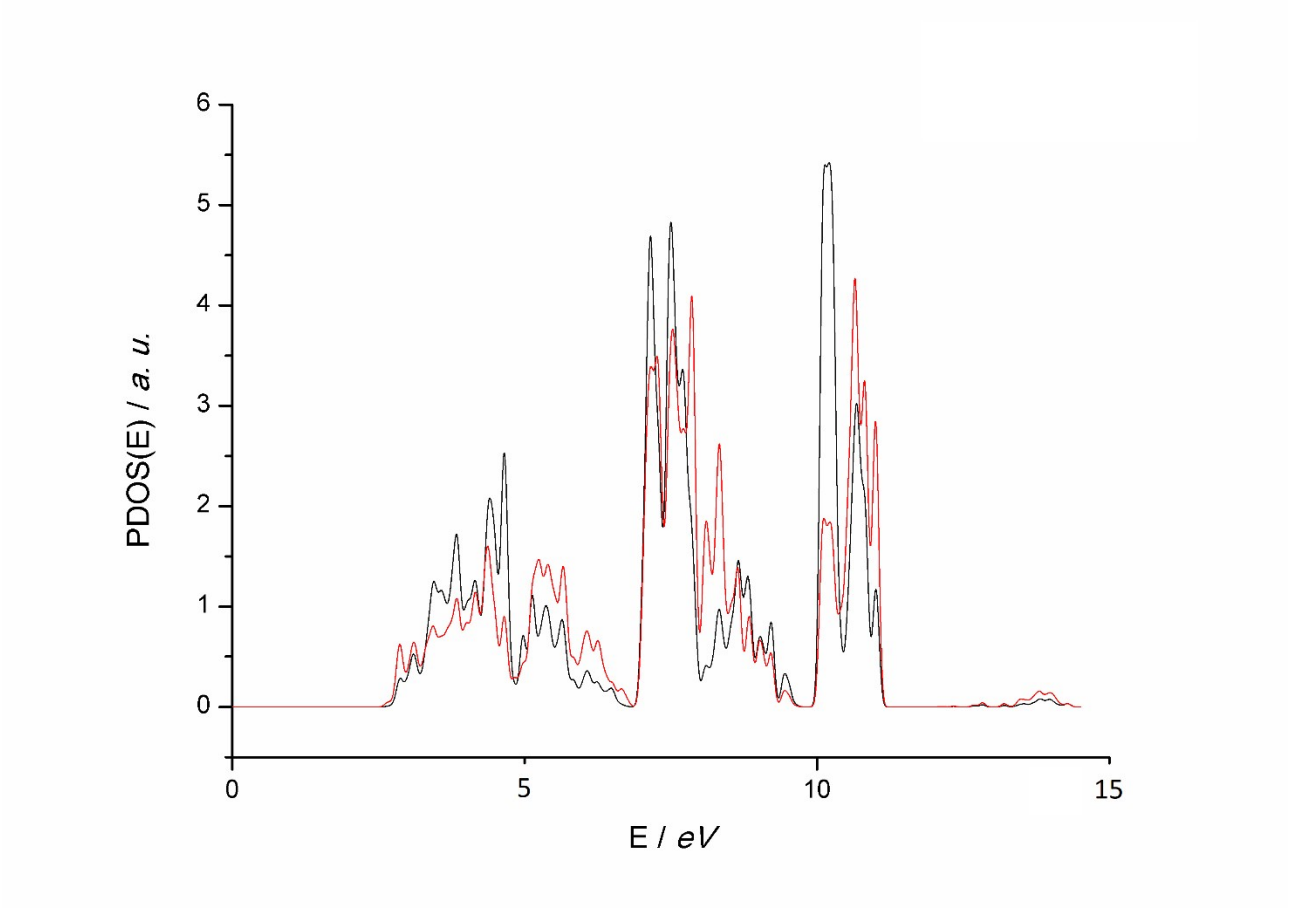


ZC**

* LDA+U (PAW) DFT

** LDA (PAW) DFT

E.S.I.9 Plots of *d*-PDOS for Co1 (black) and Co2 (red) atomic species into the full optimised crystal structure through LDA+U DFT calculation.



REFERENCES

1. S. A. Owerre, A. A. Burkov, R. G. Melko *Phys. Rev. B* 2016, **93**, 144402-144407.

2. M. Soda, Y. Yasui, T. Moyoshi, M. Sato, N. Igawa, K. Kakurai *J. Phys. Soc. Jap.*, 2006, **75**, 5, 054707-054713.

3. M. Valldor, M. Andersson *Sol. St. Sciences* 2002, **4**, 923–931.

4. M. Yu, D. Trinkle, *J. Chem. Phys.*, 2011, **134**, 064111