Electronic Supplementary Information (ESI)

Spin Rotation Driven Ferroelectric Polarization 180º Flop in Double-Perovskite Lu_2CoMnO_6

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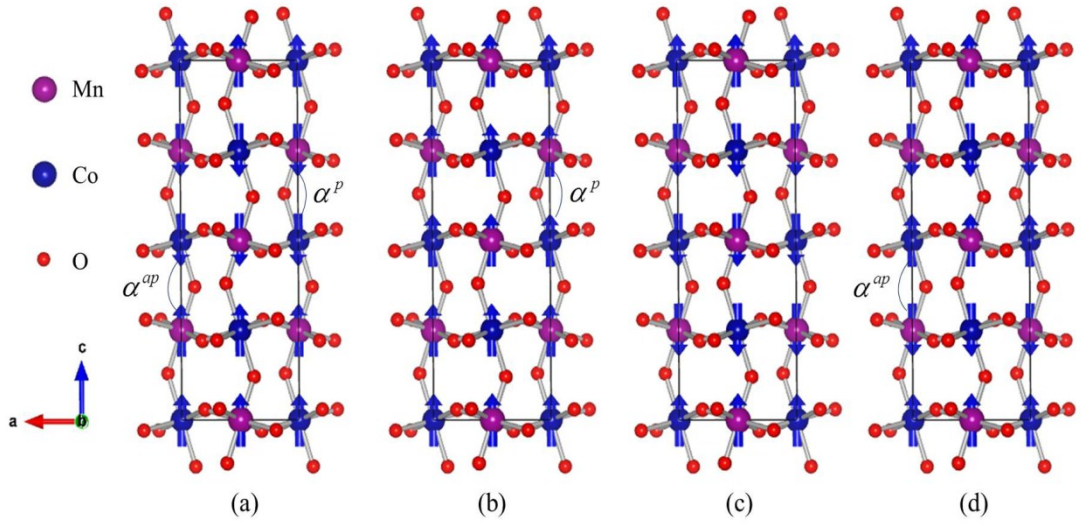

FIG. ESI1. Schematic diagram of the four collinear structures, (a) antiferromagnetic ↑↑↓↓, (b) ferromagnetic ↑↑↑↑, (c) ferrimagnetic ↑↓↓↓, (d) A-type antiferromagnetic ↑↓↑↓ spin configuration. Blue arrows denote the direction of spins, α^p and α^{ap} indicate Co-O-Mn angle (in degrees) for parallel and antiparallel Co, Mn spins.

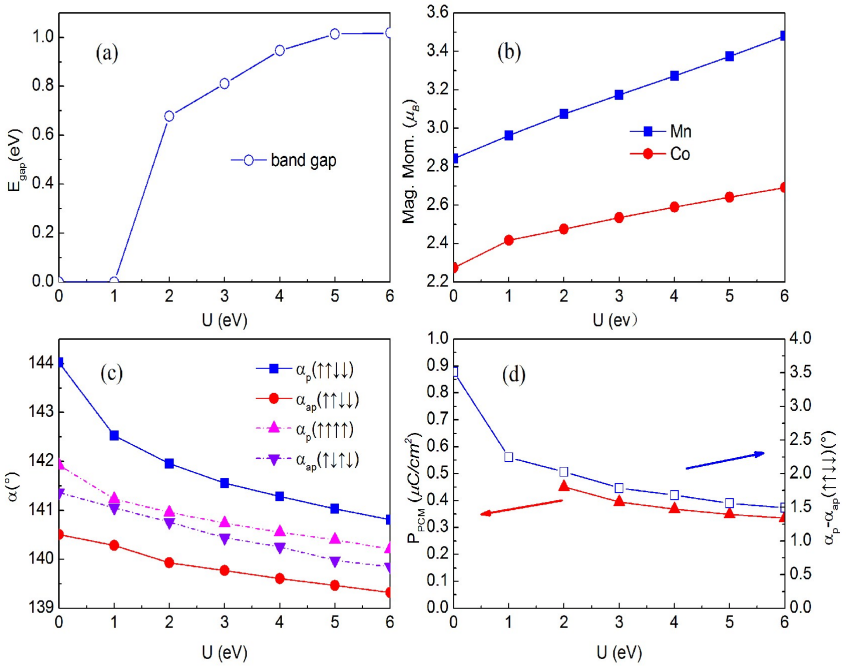

FIG. ESI2. The key electronic and structural parameters dependent on U for bulk Lu_2CoMnO_6. (a) Band gap. (b) Magnetic moments. (c) Co-O-Mn angles (in the unit of degrees) α^p and α^{ap} as defined in Fig. ESI1. (d) P_{PCM} and $\alpha^p - \alpha^{ap}$ within AFM-↑↑↓↓ spin configuration.

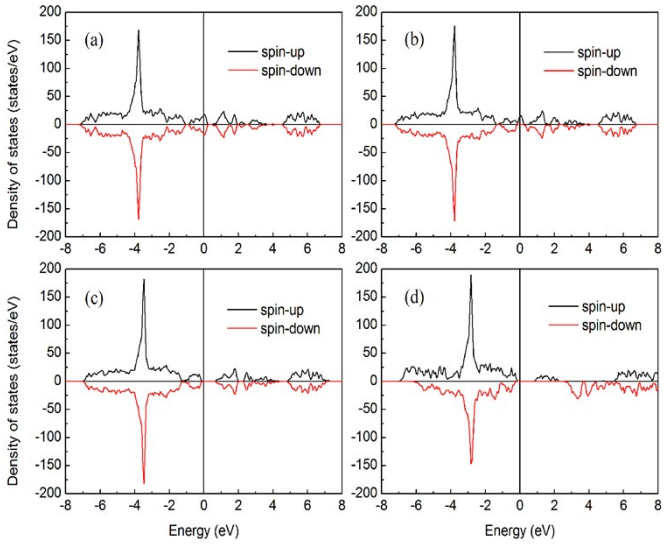

FIG. ESI3. Representative results for the electronic total density of states (DOS) close to the Fermi energy for bulk Lu_2CoMnO_6 and various U values. (a) $U_{Co} = U_{Mn} = 0$ eV for ↑↓↑↓-type magnetic structure. (b) $U_{Co} = U_{Mn} = 1$ eV for ↑↓↑↓-type magnetic structure. (c) $U_{Co} = U_{Mn} = 2$ eV for ↑↑↓↓-type magnetic structure. (d) $U_{Co} = U_{Mn} = 5$ eV for ↑↑↑↑-type magnetic structure.

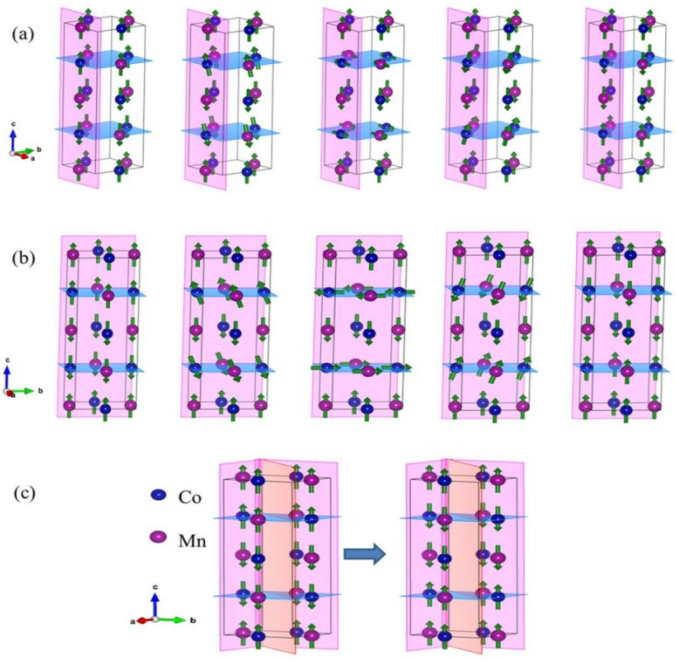

FIG. ESI4. (a) Spin rotation along *ac*-plane. (b) Spin rotation along *bc*-plane. (c) Any of the plane which through the *c*-axis. Green arrows denote the direction of spins, blue regions denote the layers of spin rotation, pink regions denote the planes of spin rotation, and the red regions denote the plane which through the *c*-axis.

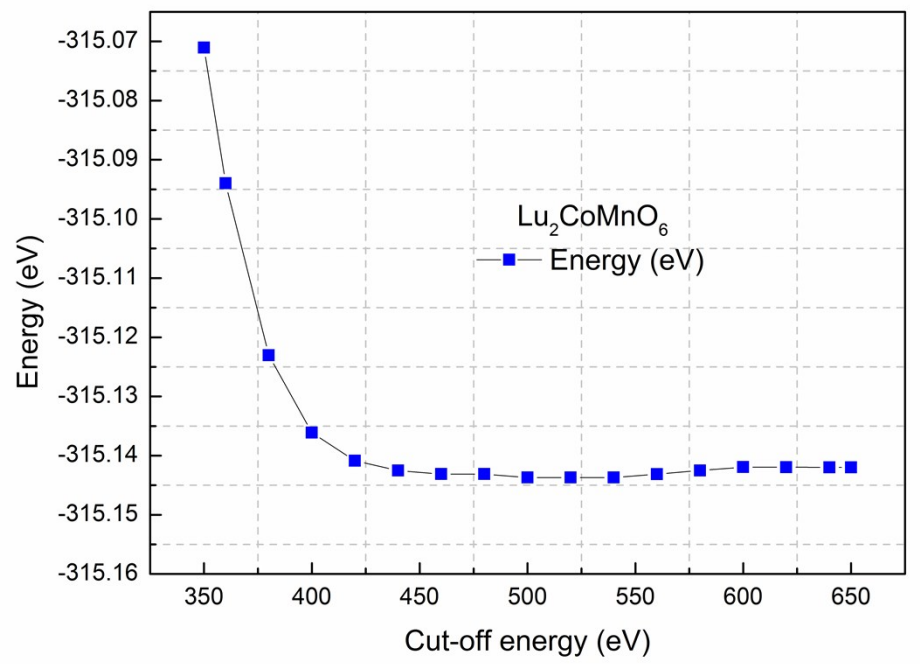

FIG. ESI5. Total energy as a function of cut-off energy for Lu_2CoMnO_6.

Table ESI1. Relative total energies achieved by the GGA+*U* calculation for four different spin configurations of double-perovskite Lu_2CoMnO_6. U_{Mn} and U_{Co} are the on-site repulsions for the atoms of Mn and Co, respectively. The energies of the ↑↑↓↓ magnetic configuration are set to zero as the reference energy.

Magnetic ordering	Relative total energy (meV)						
	U_{Mn}=U_{Co}=0	U_{Mn}=U_{Co}=1	U_{Mn}=U_{Co}=2	U_{Mn}=U_{Co}=3	U_{Mn}=U_{Co}=4	U_{Mn}=U_{Co}=5	U_{Mn}=U_{Co}=6
↑↑↓↓	0	0	0	0	0	0	0
↑↑↑↑	-14.42	79.49	18.48	5.02	-26.47	-46.36	-26.47
↑↓↓↓	-96.88	298.61	40.29	6.65	25.05	30.11	25.053
↑↓↑↓	-142.29	-29.04	7.47	38.34	63.49	83.98	25.053

Table ESI2. Comparison of atom positions of Lu_2CoMnO_6 for our calculations and the experimental taken from Ref. 9. $P2_1/n$ and $P2_1$ are the high- and low-symmetry structure, respectively.

	GGA+U($P2_1$)			GGA($P2_1/n$)			Expt.($P2_1/n$)[a]		
Ion	x	y	z	x	y	z	x	y	z
Lu1	0.5243	0.5776	0.2511	0.5261	0.5773	0.2513	0.5208	0.5787	0.2499
Lu2	0.4762	0.4222	0.3746						
Co1	0.0008	0.4994	-0.0007	0	0.5	0	0	0.5	0
Co2	0.4992	-0.0006	0.5014						
Mn1	0.4998	-0.0002	-0.0003	0.5	0	0	0.5	0	0
Mn2	0.0002	0.4998	0.5006						
O1	0.3821	0.9589	0.2438	0.3895	0.9653	0.2502	0.3841	0.9585	0.2411
O2	0.1181	0.4589	0.2562						
O3	0.1964	0.1843	-0.0556	0.1851	0.1981	-0.0558	0.1971	0.1957	-0.0575
O4	0.3036	0.6843	0.5556						
O5	0.3224	0.7044	-0.0617	0.3136	0.6916	-0.0524	0.3228	0.6953	-0.0593
O6	0.6218	0.0429	0.7568						

Table ESI3. The calculated structural parameters compared to experimental data. FM is the structures of spin configurations ↑↑↑↑ in Fig. ESI1b.

	GGAP+U ($P2_1/n$)			Expt ($P2_1/n$)		
	a=5.1566, b=5.5339, c=7.4354			a=5.1638, b=5.5467, c=7.4153		
Lu	0.5235	0.5763	0.2514	0.5208	0.5787	0.2499
Co	0	0.5	0	0	0.5	0
Mn	0.5	0	0	0.5	0	0
O1	0.3797	0.9564	0.2431	0.3841	0.9585	0.2411
O2	0.1970	0.1857	-0.0563	0.1971	0.1957	-0.0575
O3	0.3209	0.7042	-0.0631	0.3228	0.6953	-0.0593

Table ESI4. Diagonal elements of the Born effective charges tensor for ↑↑↓↓-antiferromagnetic Lu_2CoMnO_6 in the ferroelectric $P2_1$ phase.

Ion	Nominal ionic	Z*(*e*)		
	Charge (*e*)	Z_{xx}	Z_{yy}	Z_{zz}
Lu1	+3	3.91	4.01	3.82
Lu1	+3	4.01	4.02	3.71
Co1	+2	2.02	2.53	2.15
Co2	+2	2.23	2.43	2.31
Mn1	+4	3.71	4.03	3.92
Mn2	+4	3.76	4.06	3.92
O1	-2	-2.10	-1.81	-2.65
O2	-2	-2.11	-1.81	-2.55
O3	-2	-2.72	-2.29	-1.91
O4	-2	-2.73	-2.32	-1.96
O5	-2	-2.01	-3.14	-1.87
O6	-2	-1.98	-3.14	-1.91

The nature of bonding can further be correlated with the Born effective change (BECs *Z**). To calculate the BECs, we use density functional perturbation theory of the linear response formalism.[S1] Previous studies on many perovskite ferroelectrics show anomalously large BECs for some of the ions which are often explained as a manifestation of the strong covalent character of the bonds between the specific ions.[S2, S3] Table ESI4 summarizes the results of BECs of each ion along with their nominal charges. We observe that the Co/Mn ions have elements of BECs close to its nominal ionic charge, and the Z* of Lu and O atoms are significantly anomalously large. We conclude that the bonds between Co/Mn and surrounding O ions are primarily ionic.

[S1] S. Baroni, S. de. Gironcoli, A. D. Corso, and P. Giannozzi, Rev. Mod. Phys. **73**, 515 (2001).

[S2] P. Ghosez, X. Gonze, P. Lambin, and J. P. Michenaud, Phys. Rev. B **51**, 6765 (1995).

[S3] A. Roy, R. Prasad, S. Auluck, and A. Garg, J. Phys.: Condens. Matter**. 22**, 165902 (2010).

Table ESI5. The detailed description of PAW potential used in our calculations, including version, ENMAX, ENMIN and valence electron for Lu, Co, Mn and O, respectively.

Ions	Versions	ENMAX (eV)	ENMIN (eV)	Valence electron (n)
Lu	standard	255.788	191.841	$4f^{14}5s^{2}5p^{6}5d^{1}6s^{2}$ (25)
Co	standard	267.969	200.977	$3d^{7}4s^{2}$ (9)
Mn	Mn_pv	269.865	202.399	$3p^{6}3d^{5}4s^{2}$ (13)
O	O_s	282.841	212.131	$2s^{2}2p^{4}$ (6)