Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for

Unraveling the effect of B-site antisite defects on the electronic and magnetic properties in quadruple perovskite $CaCu_3Fe_2Nb_2O_{12}$

Hongping Li,[a] Quan Zhang,[a] Zhipeng Zhu,[a] Zhizhong Ge,[a] Changsheng Li,[a] Jian Meng[b] and Yi Tian[c,*]

[a]*Institute for Advanced Materials, School of Materials Science and Engineering, Jiangsu University, Zhenjiang, 212013, P. R. China*

[b]*State Key Laboratory of Rare Earth Resources Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, P. R. China*

[c]*Institute for Energy Research, Jiangsu University, Zhenjiang, 212013, P. R. China*

*Corresponding Authors: chmtyi@nus.edu.sg (Y. T.)

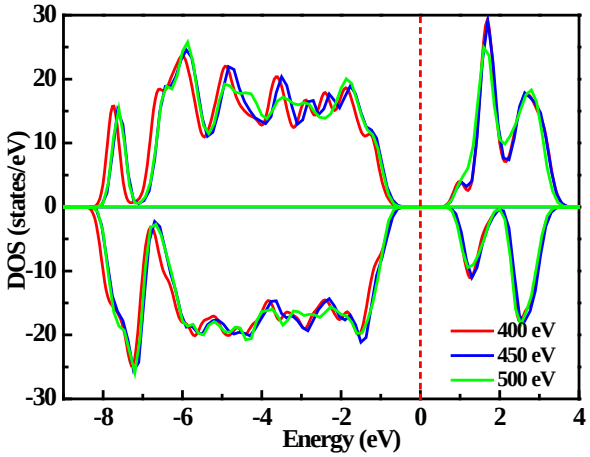
Cut-off energy

To validate the plane wave cut-off energy, we tested three different plane-wave cut-off energy of 400, 450 and 500 eV for the B-site ordered structure. The relaxed lattice parameters are listed in Supplementary Table s1. It is clear that the optimized lattice constant obtained with 400 eV is more consistent with the experimental data. Further, we compared the electronic structures (shown in Supplementary Fig. s1) and found no significant difference. Especially the band gap is independent of the plane wave cut-off energy, therefore, 400 eV was chosen in our calculations.

Supplementary Table s1 Experiment (EXP.) and optimized lattice constant and selected bond distances of order quadruple perovskite $CaCu_3Fe_2Nb_2O_{12}$.

[Å]	EXP.	400	450	500
a	7.504	7.496	7.547	7.566
Ca-O	2.634	2.641	2.658	2.665
Cu-O	1.980	1.946	1.960	1.965
Nb-O	1.977	2.029	2.015	2.019
Fe-O	2.017	2.005	2.023	2.029

Supplementary Fig. s1 Total DOSs of FIM configuration for order $CaCu_3Fe_2Nb_2O_{12}$ calculated with different cut-off energy.



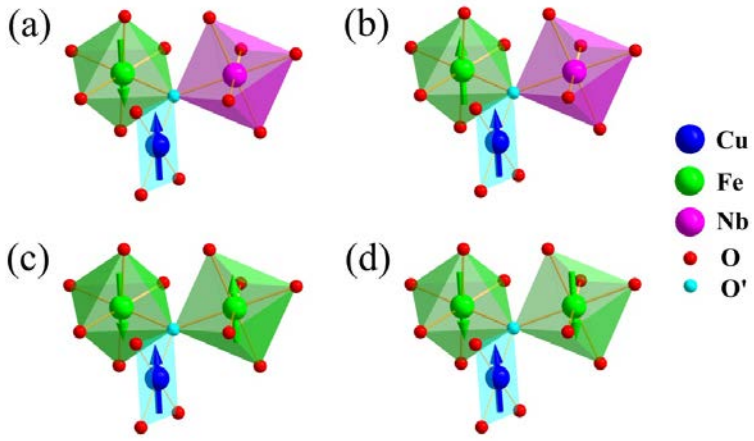
Supplementary Table S2 Calculated total energy differences of FIM relative to FM configuration (ΔE), band gap at the spin-up channel (E_{g+}) and the spin-down channel (E_{g-}), magnetic moments (M) for ordered $CaCu_3Fe_2Nb_2O_{12}$ obtained within GGA + U calculations.

				M (μ_B)		
U_{Cu}/U_{Fe} (eV)	ΔE (eV/fu)	E_{g+} (eV)	E_{g-} (eV)	Cu	Fe	total
			FM			
0.0/0.0		0.00	0.00	0.16	1.81	4.74
2.0/1.0		0.00	0.00	0.46	3.70	10.34
3.0/2.0		2.70	1.25	0.62	4.14	12.55
4.0/3.0		2.87	1.47	0.64	4.21	12.64
5.0/4.0		3.00	1.65	0.68	4.28	12.70
6.0/4.0		3.06	1.78	0.69	4.28	12.72
7.0/4.0		3.12	1.92	0.71	4.28	12.73
6.0/5.0		3.12	1.84	0.68	4.35	12.77
7.0/5.0		3.17	1.98	0.71	4.35	12.78
			FIM			
0.0/0.0	0.300	0.00	0.00	0.39	-3.67	-6.64
2.0/1.0	-2.162	0.66	0.62	0.52	-3.97	-6.85
3.0/2.0	-0.798	1.03	0.99	0.54	-4.07	-6.89
4.0/3.0	-0.455	1.33	1.32	0.58	-4.16	-6.92
5.0/4.0	-0.589	1.62	1.65	0.61	-4.25	-6.96
6.0/4.0	-0.550	1.74	1.78	0.64	-4.25	-6.94
7.0/4.0	-0.486	1.85	1.94	0.68	-4.25	-6.93
6.0/5.0	-0.466	1.86	1.94	0.65	-4.33	-7.00
7.0/5.0	-0.432	1.96	2.08	0.68	-4.33	-6.98

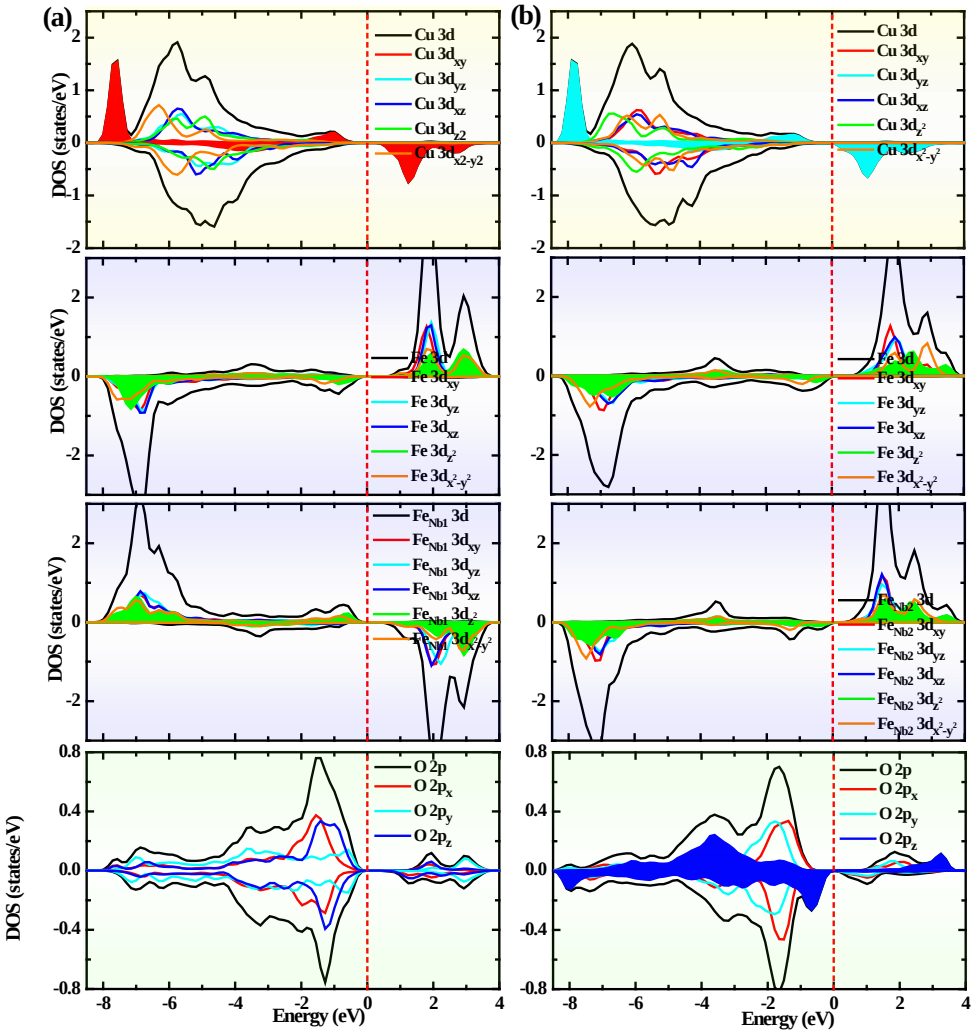
Supplementary S3 Relative Energy (ΔE) and total magnetic moments (M_{total}) of the possible magnetic configurations with both nonequivalent Cu and Fe spins for the disordered structures.

configuration	Cu	Fe	Fe_{Nb1}	Fe_{Nb2}	ΔE (meV/f.u.)	M_{total} (μ_B/f.u.)
	↑ ↑ ↑ ↑ ↑ ↑	↓ ↓ ↓	↑		0	2.01
ASI-1	↑ ↓ ↑ ↓ ↑ ↓	↓ ↓ ↓	↓		419	9.80
ASI-2	↑ ↑ ↓ ↓ ↓ ↑	↓ ↓ ↓	↓		418	9.80
ASI-3	↑ ↓ ↓ ↓ ↑ ↑	↓ ↓ ↓	↓		423	9.80
ASI-4	↑ ↓ ↑ ↓ ↑ ↓	↓ ↓ ↓	↑		88	4.91
ASI-5	↑ ↑ ↓ ↓ ↓ ↑	↓ ↓ ↓	↑		89	4.91
ASI-6	↑ ↓ ↓ ↓ ↑ ↑	↓ ↓ ↓	↑		92	4.91
	↑ ↑ ↑ ↑ ↑ ↑	↓ ↓	↑	↓	0	2.01
ASII-1	↑ ↓ ↑ ↓ ↑ ↓	↓ ↓	↓	↓	400	9.79
ASII-2	↑ ↑ ↓ ↓ ↓ ↑	↓ ↓	↓	↓	403	9.79
ASII-3	↑ ↓ ↓ ↓ ↑ ↑	↓ ↓	↓	↓	399	9.79
ASII-4	↑ ↓ ↑ ↓ ↑ ↓	↓ ↓	↑	↓	69	4.90
ASII-5	↑ ↑ ↓ ↓ ↓ ↑	↓ ↓	↑	↓	69	4.90
ASII-6	↑ ↓ ↓ ↓ ↑ ↑	↓ ↓	↑	↓	75	4.90
ASII-7	↑ ↓ ↑ ↓ ↑ ↓	↓ ↓	↓	↑	231	4.90
ASII-8	↑ ↑ ↓ ↓ ↓ ↑	↓ ↓	↓	↑	232	4.90
ASII-9	↑ ↓ ↓ ↓ ↑ ↑	↓ ↓	↓	↑	233	4.90
ASII-10	↑ ↓ ↑ ↓ ↑ ↓	↓ ↓	↑	↑	-76	0.00
ASII-11	↑ ↑ ↓ ↓ ↓ ↑	↓ ↓	↑	↑	-77	0.00
ASII-12	↑ ↓ ↓ ↓ ↑ ↑	↓ ↓	↑	↑	-79	0.00

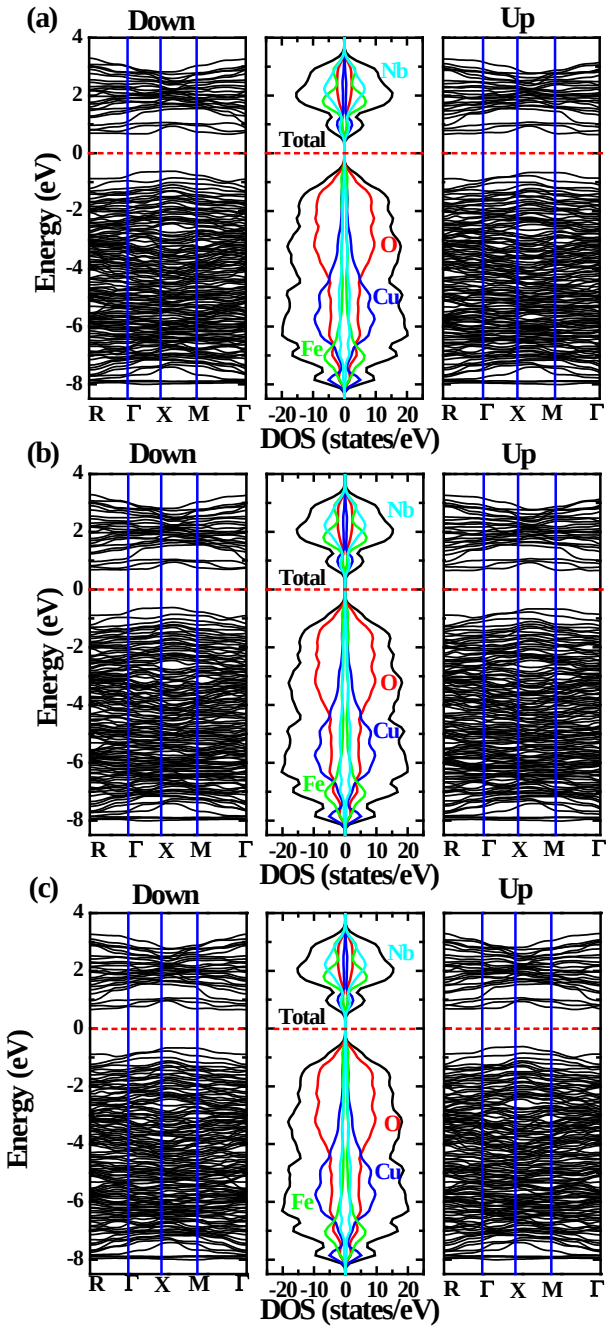
Supplementary Fig. S2 The possible magnetic interaction units in B-site disordered structures.



Supplementary Fig. S3 PDOSs of Cu 3d, Fe 3d and O 2p orbitals of (a) ASI-2 and (b) ASII-2 magnetic configuration listed in Table 3 for disorder $CaCu_3Fe_2Nb_2O_{12}$. The Fermi level is aligned to zero and indicated by a vertical dashed line.



Supplementary Fig. S4 Band structures and DOSs of the most stable magnetic configuration listed in Supplementary Table S3 for disorder $CaCu_3Fe_2Nb_2O_{12}$ (a) ASII-10, (b) ASII-11 and (c) ASII-12. The Fermi level is aligned to zero and indicated by a horizontal dashed line.



Supplementary Fig. S5 PDOSs of Cu 3d, Fe 3d and O 2p orbitals of ASII-12 magnetic configuration listed in Supplementary Table S3 for disorder $CaCu_3Fe_2Nb_2O_{12}$. The Fermi level is aligned to zero and indicated by a vertical dashed line.