Supplemental Material for

Small Co-doping induced magnetic and electrical transitions in single crystal $CaFe_{0.95}Co_{0.05}O_3$

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S1. HUBBARD U PARAMETER TEST

To verify the robustness of our conclusions regarding the insulating charge-disproportionated state, we tested different values of the Hubbard U parameter for Fe 3d electrons. Figure S1 shows the band structures of $CaFeO_3$ in the ferromagnetic (FM) configuration with U = 5, 6, and 7 eV.

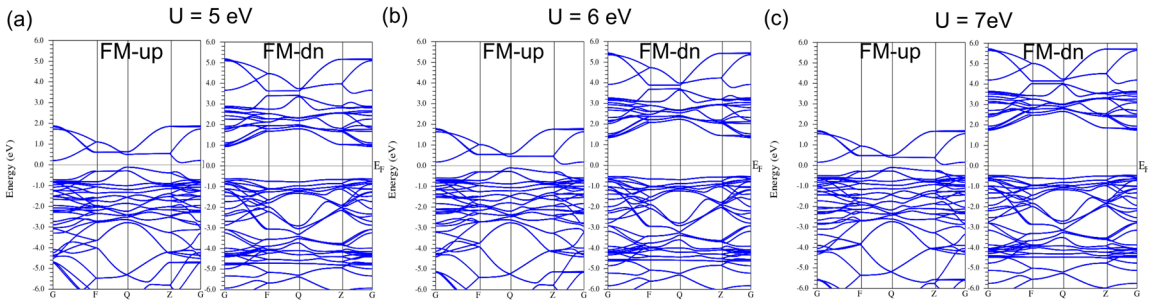

Figure S1. Band structures of $CaFeO_3$ in the FM configuration with different U values: (a) U = 5 eV, (b) U = 6 eV, and (c) U = 7 eV. The upper panels show the spin-up channels and the lower panels show the spin-down channels.

S2. Co SUBSTITUTION SITE PREFERENCE

To determine the thermodynamically preferred substitution site for Co in $CaFe_{0.95}Co_{0.05}O_3$, we calculated the total energies for Co substituting at Fe^{3+} and Fe^{5+} sites in different magnetic configurations. The supercell $Ca_{12}Fe_{11}Co_1O_{36}$ (corresponding to 8.33% Co doping) was used.

Table S1. Total energy comparison for Co substituting at Fe^{3+} and Fe^{5+} sites in $Ca_{12}Fe_{11}Co_1O_{36}$. Negative ΔE values indicate that the Fe^{5+} site is energetically preferred.

Magnetic Order	**Co at Fe^{3+} site (Ry)**	**Co at Fe^{5+} site (Ry)**	**ΔE (meV/f.u.)**	**Preferred Site**
FM	-52537.34177	-52537.34290	-1.3	Fe^{5+} (slight)
A-AFM	-52537.28572	-52537.32690	-46.7	Fe^{5+}
C-AFM	-52537.23411	-52537.25147	-19.7	Fe^{5+}
G-AFM	-52537.15445	-52537.02735	+144.1	Fe^{3+}

S3. MAGNETIC CONFIGURATION ENERGY COMPARISON

Table S2 summarizes the total energies of $CaFeO_3$ ($Ca_4Fe_4O_{12}$) calculated for different magnetic configurations at 15 K ($P2_1/n$ structure). The results show that the ferromagnetic (FM) configuration has the lowest energy, followed by the A-type antiferromagnetic (A-AFM) configuration. The G-type AFM configuration has the highest energy, with an energy difference of approximately 63.7 meV/f.u. relative to the FM state.

Table S2. Calculated total energies and magnetic moments of $CaFeO_3$ for different magnetic configurations at 15 K. PM denotes paramagnetic (non-spin-polarized) calculation.

Magnetic Configuration	**Total Energy (Ry)**	**Relative to FM (meV/f.u.)**	**Total Magnetic Moment (μB)**
FM	-17432.0096	0	16.00
A-AFM	-17431.9892	+18.4	~0
C-AFM	-17431.9729	+36.7	~0
G-AFM	-17431.9459	+63.7	4.00
PM	-17431.3140	-	-

S4. DENSITY OF STATES

Figure S2 shows the density of states for $Ca_{12}Fe_{11}Co_1O_{36}$ (8.33% Co doping) in both FM and A-type AFM configurations, with Co occupying either the Fe^{3+} or Fe^{5+} sites.

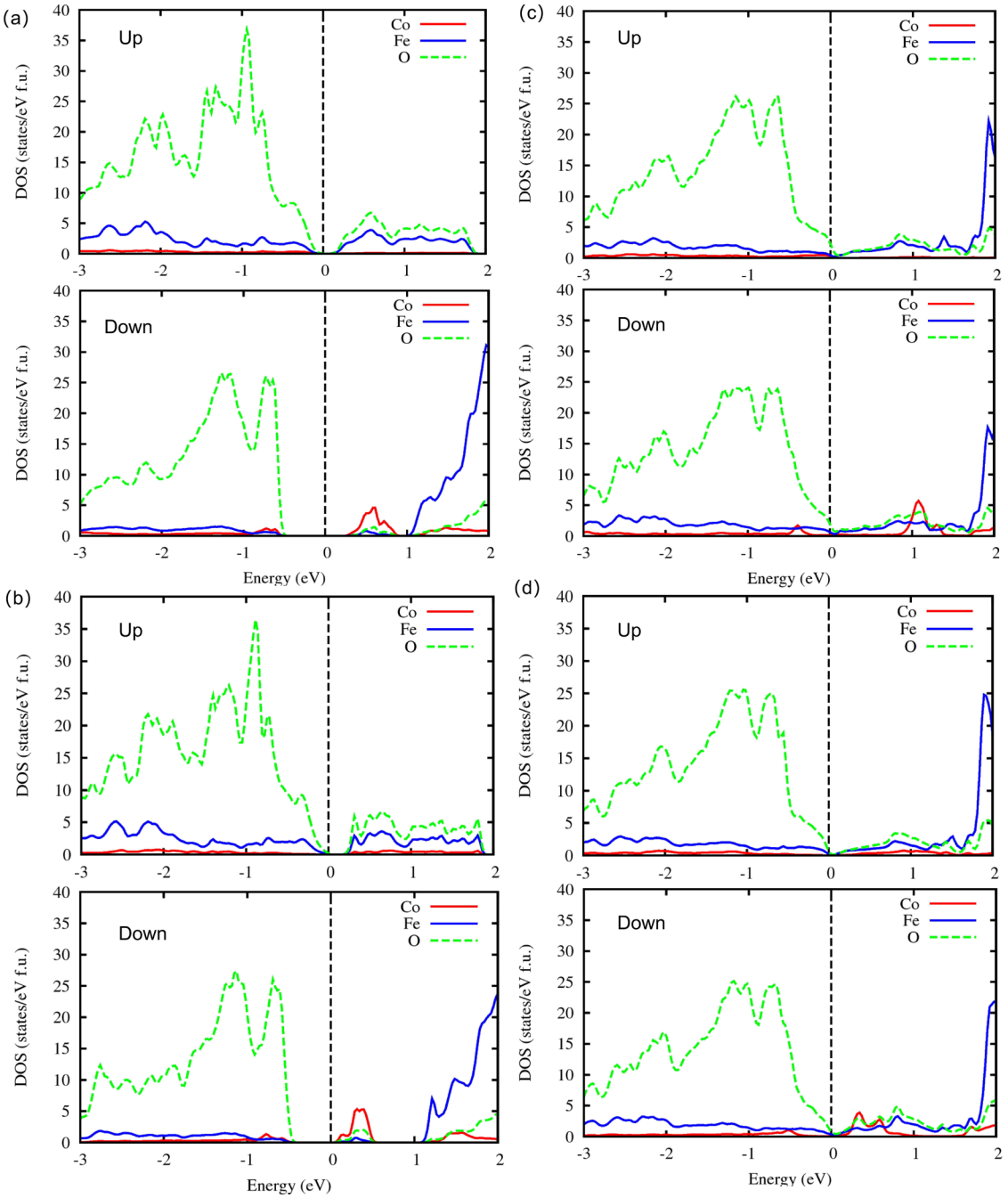

Figure S2. Density of states of $Ca_{12}Fe_{11}Co_1O_{36}$ for (a) FM configuration with Co at Fe^{3+} site, (b) FM configuration with Co at Fe^{5+} site, (c) A-type AFM with Co at Fe^{3+} site, and (d) A-type AFM with Co at Fe^{5+} site. The Fermi level is set to zero.