

Supporting Information

Polarization Control of the Interface Ferromagnetic to Antiferromagnetic Phase Transition in Co/Pb(Zr,Ti)O₃

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I. EFFECT OF THE CATION DISTRIBUTION ON THE ATOMIC STRUCTURE

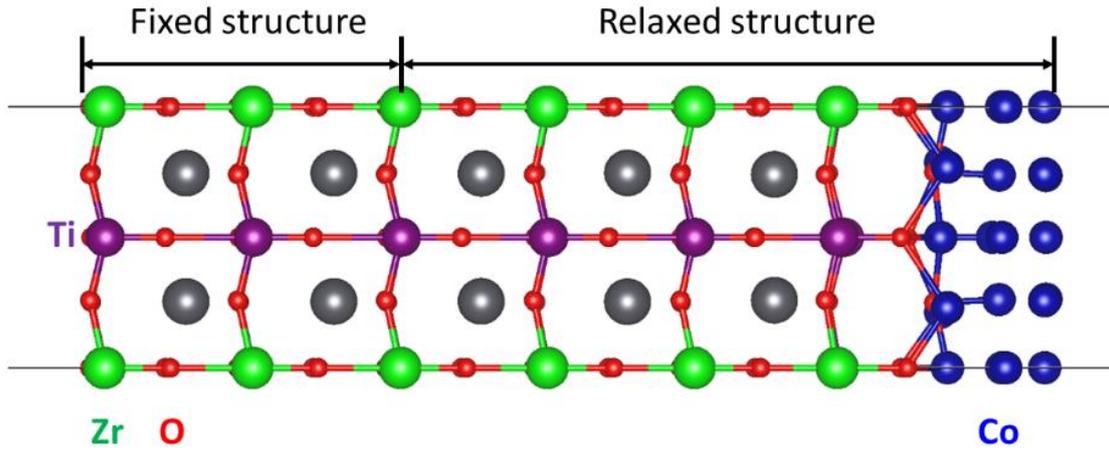


Figure S1: Slab used for Co(2MLs)/CoO/PZT(001) for a $P\uparrow$ state of the PZT polarization.

The modeling of $\text{PbZr}_{0.25}\text{Ti}_{0.75}\text{O}_3(001)$ (PZT) is performed using a $2\times 2\times 5.5$ asymmetric cell in which Zr (25%) and Ti (75%) atoms are homogeneously distributed. This leads to a ZrTi_3O_8 surface termination with 11 atomic layers in the (001) direction as shown in Fig. S1.

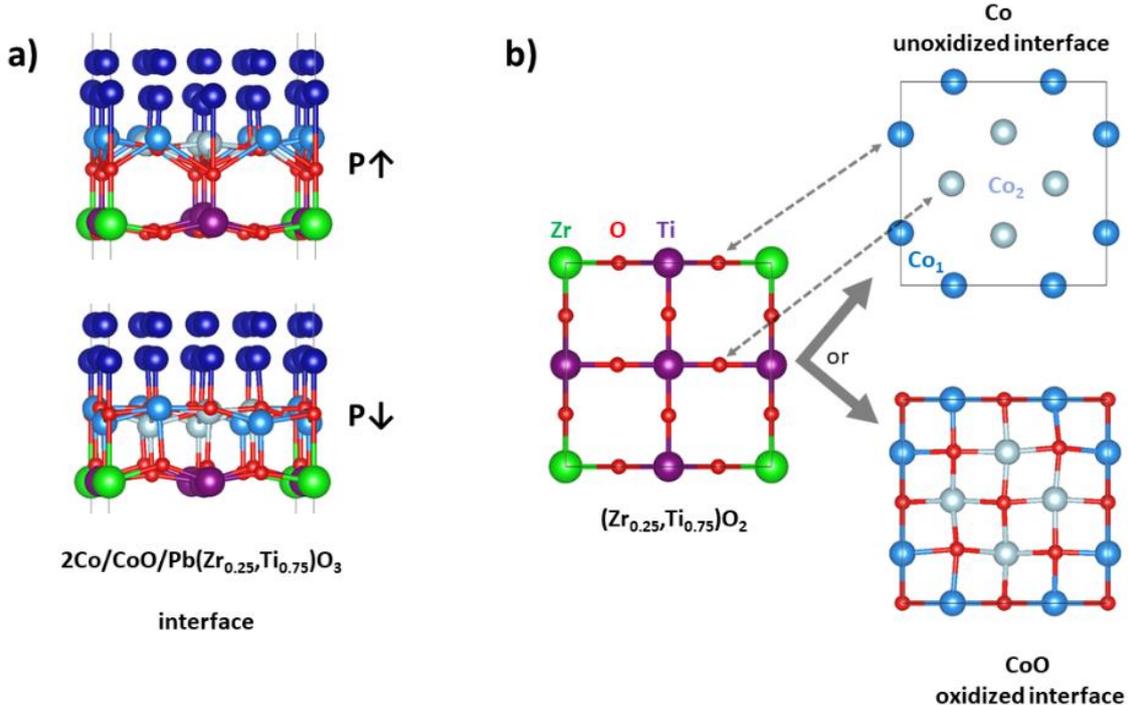


Figure S2: Distribution of non-equivalent Co atoms, Co_1 , and Co_2 in (a) oxidized-Co/PZT interfaces with a (100) view, and (b) with a (001) view for unoxidized and oxidized Co/PZT interfaces.

For sake of simplicity, all the results given in the manuscript body text are averaged for each (001) atomic monolayer (ML). It is however interesting to notice that we can distinguish two non-equivalent Co atoms (referred to as Co₁ and Co₂ in Fig. S2) depending on the local symmetry and the chemical environment of the oxygen atoms they are bonded to.

Co₁ correspond to the Co atoms in the Co or CoO interface (IF) layer which are bonded to an oxygen atom linked to a Ti and a Zr cation, while Co₂ represent the Co atoms linked to an oxygen atom surrounded by two Ti atoms (see Fig. S2).

Heterostructure		$d_{\text{Co-O}} (\text{\AA})$							
		$\text{P}\uparrow$				$\text{P}\downarrow$			
		Co ₁ (Ti-O-Zr)		Co ₂ (Ti-O-Ti)		Co ₁ (Ti-O-Zr)		Co ₂ (Ti-O-Ti)	
		IF Co	IF CoO	IF Co	IF CoO	IF Co	IF CoO	IF Co	IF CoO
IF	(1 ML)	2.79	2.90	2.02	2.09	1.86	1.97	1.91	1.95
IF+2Co	(3 ML)	2.09	3.64	2.02	3.36	1.88	2.04	1.87	2.00
IF+4Co	(5 ML)	2.09	3.46	2.02	3.50	1.89	2.03	1.88	2.04

Table S1: $d_{\text{Co-O}}$ interatomic distances between Co atoms of the interface layer (IF) and oxygen atoms of the (Zr,Ti)O₂-terminated PZT surface where the two nonequivalent Co sites (Co_{1,2}) are discriminated. These values are given for both unoxidized (IF = Co) and oxidized (IF = CoO) interfaces.

Supplementary table S1 displays the $d_{\text{Co-O}}$ distances in both unoxidized and oxidized-Co/PZT at different thicknesses for P \uparrow and P \downarrow in which the two non-equivalent Co₁ and Co₂ sites are considered. We observe that the (Zr,Ti) cation environment has a stronger impact at low Co thicknesses (< 2 MLs).

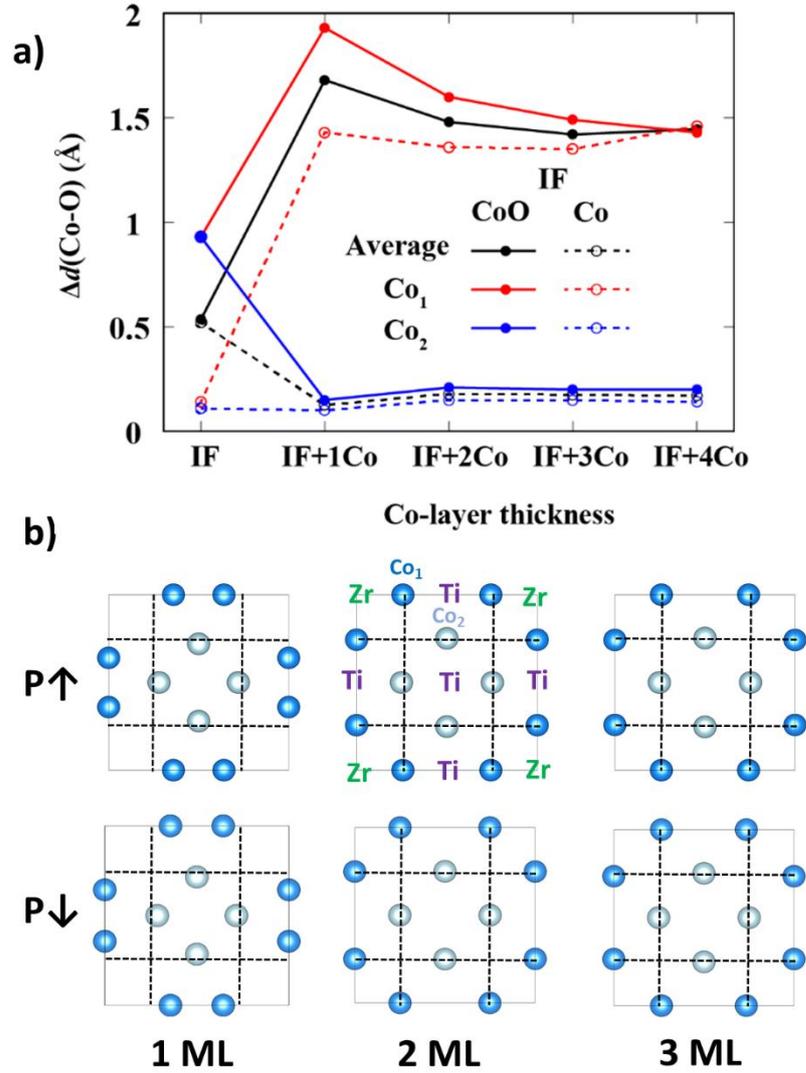


Figure S3: (a) Variations $\Delta d_{\text{Co-O}} = d(\text{P}\uparrow) - d(\text{P}\downarrow)$ of the interfacial interatomic distances between Co (IF) and O (IF-1) atoms. The black, red and blue curves represent, respectively, the averaged distance variations, and the variation of the two non-equivalent Co sites, Co₁ and Co₂. The polarization dependence of the (001) in-plane atomic structure of the unoxidized-Co/PZT interface is displayed at different Co thicknesses in panel (b).

Figure S3a shows the variation of the distance $\Delta d_{\text{Co-O}}$ between Co (IF) and oxygen atoms of the (Zr,Ti)O₂ layer (IF-1) when the PZT polarization is reversed. We observe that the difference between the interatomic distance for Co₁ and Co₂ decreases when the Co add-layer thickness increases, in a similar way as the averaged value of $d_{\text{Co-O}}$ (undiscriminated Co sites) given in the manuscript (Fig.1). Figure S3b displays the polarization-dependence of the in-plane atomic structures of the unoxidized-Co/PZT interface at different Co add-layer thicknesses. We observe for 1 ML of Co on PZT, corresponding to the interface layer only, in-plane distortions

with a displacement of the Co atoms away from the Zr, and toward the Ti atoms. Such distortion is likely related to the cation distribution and it does not change significantly when the polarization state is reversed (i.e., it does not affect Δd values). Concerning the evolution of $\Delta d_{\text{Co-O}}$, these distortions vanish starting from 2 ML of Co atoms (IF+1Co). The influence of the distribution of the (Zr,Ti) cations on the electronic and magnetic properties will also mostly affect the thinnest Co layers, partly because of the lattice distortions.

II. MAGNETIC ORDER

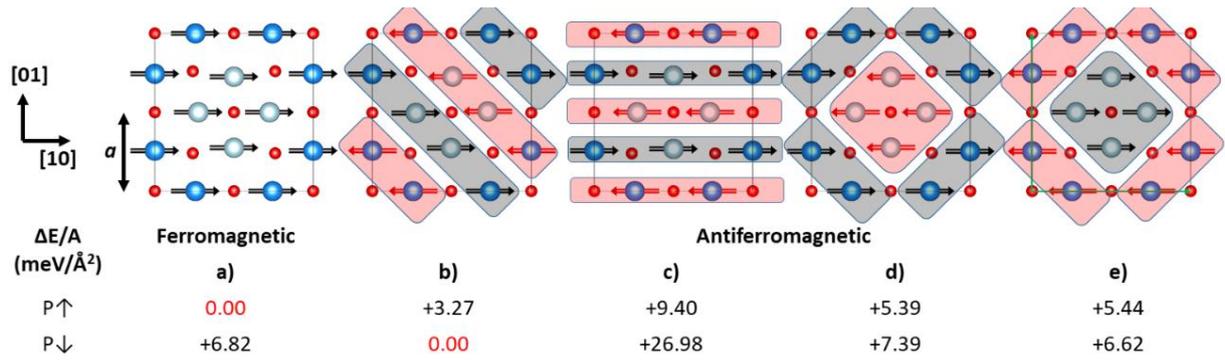


Figure S4: Representation of the 5 magnetic orders tested for the CoO/PZT bilayer. a) ferromagnetic (FM) order, b) antiferromagnetic (AFM) order in the [110] direction, c) AFM order in the [010] direction, d-e) AFM order which respects the symmetry imposed by the (Zr,Ti) cations distribution. The relative surface energy differences are given below each magnetic structure as a function of the electric polarization direction.

We consider in the following different antiferromagnetic configuration in CoO/PZT bilayers in order to find the energetically most stable state. The first antiferromagnetic order displayed in Fig.S4b shows alternating positive and negative magnetic moments along the [110] direction. The second configuration (Fig.S4c) contains alternated positive and negative magnetic moments in the [010] direction, while the two last configurations (Fig.S4d-e) follow the (Zr,Ti) cations distribution and the related Co₁ and Co₂ atoms carrying magnetic moments of opposite direction. The calculations show that at P↑, the most stable states are: the ferromagnetic order (Fig.S4a), followed by the antiferromagnetic state (Fig.S4b). When the PZT polarization is reversed to P↓, the antiferromagnetic state labeled (b) in Fig. S4 becomes the most stable. Even if this configuration does not follow the symmetry imposed by the

distribution of the cations, the antiferromagnetic order is found to be robust and stable when increasing the Co-layer thickness.

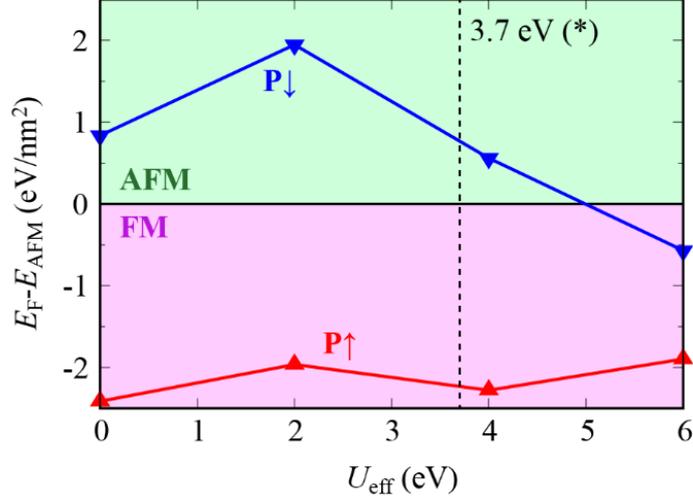


Figure S5: Energy difference between the ferromagnetic and antiferromagnetic order in the [110] direction as a function of U_{eff} . The dotted line labeled (*) corresponds to the CoO bulk reference value $U_{\text{eff}} = 3.7$ eV derived by Youmbi and Calvayrac.¹

Figure S5 demonstrates the robustness of the AFM to FM transition upon polarization reversal when varying the $U_{\text{eff}}(\text{Co},3\text{d})$ parameter entering in the expression of the so-called $+U$ correction in the exchange-correlation term.² At P_{\uparrow} , the energy difference between the FM and AFM states remains negative (i.e., AFM order stable) for U_{eff} ranging from 2 to 6 eV. When the PZT polarization is reversed to P_{\downarrow} , the energy difference between the FM and AFM states is positive (i.e., FM order stable) and it changes its sign around $U_{\text{eff}} \approx 5$ eV. Note that this value is far above the U_{eff} value proposed for CoO bulk.

III. MAGNETOCRYSTALLINE ANISOTROPY

In the body text of the manuscript, we focused mainly on the in-plane versus out-of-plane magnetic anisotropy. In the following, we discuss the existence of a purely in-plane anisotropy in Co/PZT bilayers due to the (Zr,Ti) cation distribution in the PZT substrate. Table S2 shows the magnetocrystalline anisotropies energy (MAE) values obtained in the film plane, along [100] and [110], as well as in the out-of-plane [001] direction. In fact, at P_{\uparrow} we observe that [100] and [110] in-plane magnetization directions are almost equivalent, while at P_{\downarrow} an in-plane anisotropy between [100] and [110] is observed, until a Co thickness of 3ML (2Co/1CoO/PZT). In 1CoO/PZT, we observe that the in-plane magnetization direction along

[110] is more stable than the [100] direction. In thicker films (1-2MLCo/CoO/PZT), the [100] in-plane direction is favored, while at around 3-4 MLs of Co/CoO/PZT, the magnetization becomes isotropic in the film plane. This result is explained by the stabilization of the atomic structure and the decrease of the lattice distortions in thick Co films (see, e.g., Fig.S3 and the related discussion).

	$\Delta E/A$ (mJ/m ²)					
	\mathbf{P}_{\uparrow}			\mathbf{P}_{\downarrow}		
Heterostructure	[100]	[110]	[001]	[100]	[110]	[001]
1CoO/PZT	0.0	0.023	3.072	0.186	0.0	2.000
1Co/1CoO/PZT	0.001	0.000	1.020	0.615	0.987	0.000
2Co/1CoO/PZT	0.003	0.000	1.698	0.000	0.344	0.476
3Co/1CoO/PZT	0.002	0.000	0.800	0.000	0.066	1.032
4Co/1CoO/PZT	0.003	0.000	1.718	0.0	0.026	1.084

Table S2: Magnetocrystalline anisotropies Energy (MAE) defined as the difference of energy per area unit between the most unstable and the most stable magnetic directions. The energy is calculated for different directions of the magnetization. The energy obtained for the most stable magnetization direction is taken as the origin and set to 0 for each polarization state and Co-layer thickness.

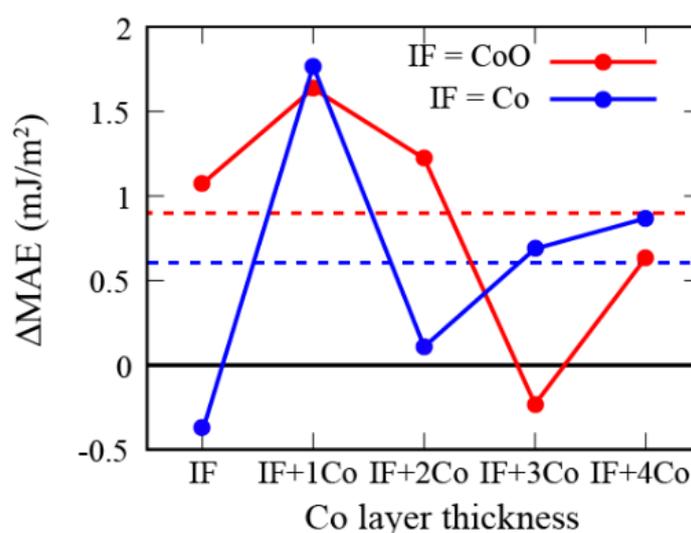


Figure S6: Variation of the MAE with the PZT polarization $\Delta MAE = MAE(\mathbf{P}_{\uparrow}) - MAE(\mathbf{P}_{\downarrow})$.

Figure S6 displays the variation of MAE when the PZT polarization is reversed. The polarization-dependent variation of the MAE shows oscillations as a function of the Co layer thickness. Comparison of the average oscillations in the two interface types shows that the oxidization slightly reinforces the in-plane anisotropy. The oscillations moreover present a different periodicity depending on the oxidation state of the Co/PZT interface.

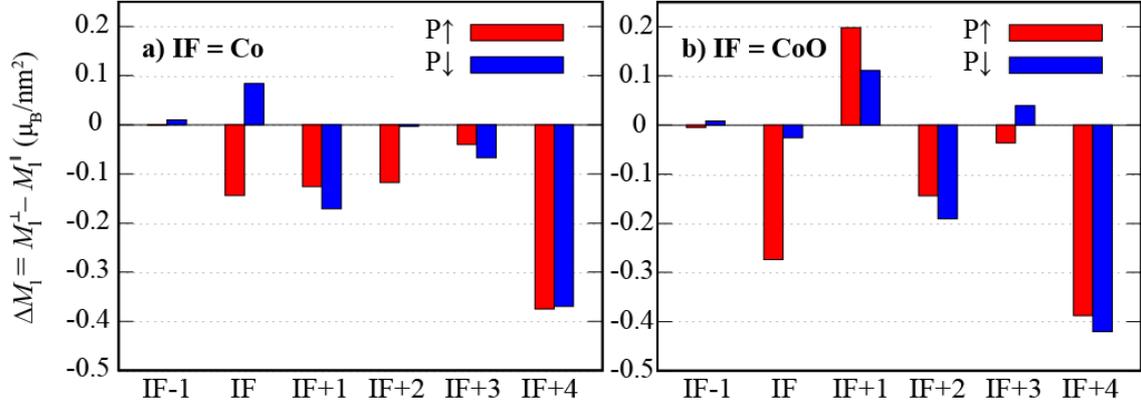


Figure S7: Orbital moment anisotropy $\Delta M_l = M_l^\perp - M_l^\parallel$ analyzed layer by layer in a Co(4ML)/IF/PZT with a) unoxidized-interface (IF = Co) and b) oxidized interface (IF = CoO). The polar state of PZT is represented by red (P^\uparrow) and blue (P^\downarrow) bars. According to our sign convention, a positive (negative) value corresponds to an out-of-plane (in-plane) magnetic anisotropy.

Figure S7 displays the orbital moment anisotropy $\Delta M_l = M_l^\perp - M_l^\parallel$. It corresponds to the difference between the orbital moments at two orthogonal orientations (\perp and \parallel). An overall negative sign of ΔM_l is observed for Co(5ML)/PZT, regardless of the oxidation state of interface. A $\Delta M_l < 0$ is characteristic of an in-plane anisotropy favored by the dominating surface contribution, as shown *e.g.*, in Co/SrTiO₃,³ a system that is known to exhibit comparable properties as Co/PZT interfaces. Nonetheless, we notice peculiar polarization-dependent effects at the interface region in Co(5ML)/PZT. An out-of-plane anisotropy ($\Delta M_l > 0$) is observed for P^\downarrow at IF=Co (Fig.S7a), and this magnetic state can be converted to in-plane anisotropy by reversing the PZT polarity to P^\uparrow . The oxidized interface IF=CoO (Fig.S7b) also shows an out-of-plane anisotropy at IF+1 (*i.e.*, shifted by 1 layer with respect to unoxidized-Co(5ML)/PZT) but the magnetic state is unaffected by polarization reversal in this case.

IV. EFFECT OF THE POLARIZATION STATE ON THE INTERFACE SPIN MOMENTS

$M_S (\mu_B)$								
	$P\uparrow$				$P\downarrow$			
	Co_1 (Ti-O-Zr)		Co_2 (Ti-O-Ti)		Co_1 (Ti-O-Zr)		Co_2 (Ti-O-Ti)	
Heterostructure	IF Co	IF CoO	IF Co	IF CoO	IF Co	IF CoO	IF Co	IF CoO
IF	1.77	1.56	1.87	2.16	2.05	-2.36 +2.32	2.05	-2.36 +2.28
IF+1Co	1.55	2.04	1.53	2.10	1.81	+1.17 +2.19	1.82	-2.11 +2.21
IF+2Co	1.61	2.02	1.59	2.06	1.81	-2.30 +2.15	1.84	-2.35 +2.09
IF+3Co	1.65	2.06	1.64	2.07	1.81	-2.21 +2.15	1.82	-2.34 +2.07
IF+4Co	1.62	2.03	1.61	2.05	1.83	-2.28 +2.17	1.84	-2.33 +2.12

Table S3: Variation of the interface (IF) spin magnetic moment M_S with the polarization state. The results obtained for both oxidized (IF=CoO) and unoxidized (IF=Co) interfaces at different Co add-layer thickness are provided for the two non-equivalent Co sites labeled Co_1 and Co_2 depending on the environment of the adjacent oxygen. At IF=CoO in the $P\downarrow$ state, two different values of the interface spin moment with opposite sign are displayed. These values correspond to the individual moments in the two sublattices of the antiferromagnetic system.

V. SUPPLEMENTARY REFERENCES

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- (2) Dudarev, S. L.; Botton, G. A.; Savrasov, S. Y.; Humphreys, C. J.; Sutton, A. P. Electron-Energy-Loss Spectra and the Structural Stability of Nickel Oxide: An LSDA+U Study. *Phys. Rev. B* **1998**, *57* (3), 1505–1509.
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- (4) Zhang, J.; Lukashev, P. V.; Jaswal, S. S.; Tsymbal, E. Y. Model of Orbital Populations for Voltage-Controlled Magnetic Anisotropy in Transition-Metal Thin Films. *Phys. Rev. B* **2017**, *96* (1), 014435.