Supporting Information for

Interfacial Magnetic Anisotropy of Iron-Adsorbed Ferroelectric Perovskites: First-Principles and Machine Learning Study

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FIG. S1. Effect of external electric field \mathcal{E} on MAE. (a) Local potential and electric field of ABO₃ about the z-axis. The inset structure is ABO₃ ferroelectric phase. By differentiating the average macroscopic potential (black line) obtained from the planar average Potential (gray line), we get the effective field \mathcal{E} (red line). (b) MAE of Fe-monolayer as a function of the external field. We set the $\Delta \eta$ to zero at $\mathcal{E} = 0$.

S1. ORIGIN OF THE ABRUPT CHANGE IN MAE

In the ABO₃/Fe slab, two major factors affect the MAE of the Fe layer. The first is the electric field caused by the spontaneous polarization of ABO₃. To calculate the field created by the spontaneous polarization of ferroelectric ABO₃, a 7-layer ABO₃ slab was made, and the local potential was calculated. In Fig. S1(a), gray is the Planar Average Potential of the entire slab, and black is the Macroscopic Average Potential^{S1,S2}. The red line is the electric field ($\mathcal{E} = |\mathbf{E}|$) obtained from the Macroscopic Average Potential. Between 8Å and 16Å of the slab, there is a section in which the electric field is flat. The value of this section is the electric field created by the spontaneous polarization of ABO₃, and the largest value among the systems we calculated is 0.13 V/Å. On the other hand, the MAE of the Fe monolayer reacts to the electric field, as shown in Fig. S1(b). Even at $\mathcal{E} = 0.20 \text{ V/Å}$, $\Delta \eta(\mathcal{E}) = \eta(\mathcal{E}) - \eta(0)$ only changes by 5 μ eV. Therefore, the influence of the electric field caused by the spontaneous polarization of the ferroelectric perovskite ABO₃ on the MAE of the Fe layer is small.

The second is the interface effect of atomic displacement accompanied by spontaneous



FIG. S2. The distance between Fe and B, the distance between B and O_{II}, and magnetic moment of the B for (a) Fe/CTO, (b) Fe/CZO, and (c) Fe/CHO.

polarization. As a function of the scaling factor ξ , The distance between Fe and B, the distance between B and O_{II} , and the magnetic moment of B are shown in Fig. S2. The three properties are expressed as increasing/decreasing amounts based on when ξ is 0. For the distance, + means moving away from each other, and - means getting closer. In the case of magnetic moment, + means to increase, and - means to decrease. As Fe and B move away from each other, B and O_{II} get closer, and the magnetic moment of B decreases. Also, as shown in Fig. 3 in the main text, the magnetic moment of B decreases rapidly when the magnetic moment of O_{II} is induced.

S2. ADDITIONAL ANALYSIS OF ELECTRONIC STRUCTURE CHANGES UN-DER POLARIZATION



FIG. S3. The Projected density of states (PDOS) for Fe 3d, O 2p, and Ti 3d orbitals under different polarization states ($\xi = +1$, 0, -1) for Fe adsorbed on CTO and BTO substrates. (a)–(d) show the PDOS of Fe 3d, O 2p (TiO₂ layer), O_{II} 2p, and Ti 3d in Fe/CTO, respectively, while (e)–(h) show the corresponding data for Fe/BTO. In CTO, the Fe 3d states exhibit noticeable polarizationdependent changes near the Fermi level, indicating strong hybridization sensitivity to polarization. In contrast, the Fe 3d state in BTO remains relatively stable across different polarization states. These results support that the polarization-driven modification of Fe orbital anisotropy, mediated by interfacial hybridization with the substrate, is a key factor underlying the observed MAE behavior.

To further explore the influence of polarization on the electronic structure, we analyzed the projected density of states (PDOS) for Fe 3d, O 2p, and Ti 3d orbitals under different polarization states ($\xi = +1, 0, -1$) in both CTO and BTO systems, as shown in Fig. S3. In the CTO system, the Fe 3d PDOS shows noticeable polarization-dependent variations, indicating changes in orbital occupation and hybridization. The O 2p and Ti 3d states also exhibit polarization-sensitive features, suggesting that the local bonding environment involving Fe is affected by the direction of polarization. In contrast, the Fe 3d PDOS in BTO remains relatively stable across different polarization states, with only subtle shifts. The O 2p and Ti 3d PDOS also show minimal changes. This contrast between CTO and BTO systems implies that the degree of polarization-induced electronic structure modulation varies with substrate, which may contribute to the presence or absence of a discrete MAE jump.

S3. VALIDATION OF MAE TRENDS ACROSS EXCHANGE-CORRELATION FUNCTIONALS

TABLE S1. Calculated magnetic moment given in μ_B of bulk Fe using different exchange-correlation methods (LDA, GGA, Hybrid) and Hubbard U values, compared with the GW reference value. The LDA results closely match the experimental value (2.13 μ_B), supporting its use in the present study for MAE calculations.

U (eV)	LDA	GGA	Hybrid	GW
0	2.141	2.243	2.869	2.31^{S3}
1	2.411	2.589		
2	2.634	2.710		
3	2.751	2.818		

To verify the robustness of the trends observed in our MAE calculations, we conducted additional computations using the GGA+U method with U = 1 - 3 eV. Fig. S4 shows the variation of the MAE as a function of polarization (ξ) for Fe adsorbed on CTO and BTO substrates under various U values. In the CTO system, the discrete jump in MAE associated with polarization switching is consistently observed across all U values. Although the absolute MAE values vary with increasing U value, the critical feature, which is the sudden upturn of MAE at negative ξ remains robust. In the BTO system, the MAE changes smoothly with polarization for all U values. A small jump is observed within the spontaneous polarization range when using GGA+U, unlike the LDA results, where no such jump is present within the spontaneous range. This difference arises because GGA tends to exaggerate the tetragonality of ferroelectric materials^{S4}, leading to an overestimated spontaneous



FIG. S4. Variation of MAE as a function of normalized polarization (ξ) for Fe adsorbates on CTO and BTO substrates, calculated using GGA and GGA+U methods. (a)–(d) show the results for Fe/CTO under GGA, GGA+U (1 eV), GGA+U (2 eV), and GGA+U (3 eV), respectively. (e)–(h) show the corresponding results for Fe/BTO. While the absolute MAE values vary with different Uparameters, the key trends which is the presence of a discrete MAE jump in CTO and the absence of such a jump in BTO are robust.

polarization (0.45 C/m² for BTO) compared to the LDA-calculated value (0.32 C/m²) and the experimental value (0.26 C/m²)^{S5}. As a result, polarization-induced atomic displacements of Ti and O are larger under GGA, effectively shifting the regime where the MAE jump occurs into the spontaneous polarization range. These results confirm that while the quantitative values of MAE are sensitive to the choice of U, the key qualitative trends, which are the presence or absence of a discrete MAE jump are robust and not dependent on the specific exchange-correlation treatment. Thus, our main conclusions remain valid even when accounting for possible correlation effects through GGA+U.

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