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## **Supporting Information**

## Magnetic Domain-wall induced ferroelectric polarization in rare-earth orthoferrites AFeO<sub>3</sub> (A = Lu, Y, Gd): First-principles calculations

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(S1) The detailed magnetic moment direction of the of  $AFeO_3$  (A = Lu, Y, Gd) was shown below. The bulk magnetic ground state of G-AFM order was adopted as the intradomain magnetic structure. The configurations have checkerboard-like planes of up and down magnetic moments within the a-b planes, which are then stacked either AFM (within a domain) or FM (across the domain wall) along the c direction



FIG. S1. Side view of the magnetic domain structure with spin direction, blue and black arrows indicate spin up and spin down, respectively. Fe<sup>1</sup> and Fe<sup>11</sup> represent Fe ions in different magnetic domain regions, respectively

(S2) In order to more clearly observe the trend of the octahedral rotation angle at the domain wall, we calculate the octahedral rotation angle of the structure of L4-6 and L5-5 by the formula  $(90-\Omega)/2$  for LuFeO3, where  $\Omega$  is the angle among three oxygen ions between two corner-shared oxygen octahedral in the ab plane, <sup>1</sup> as shown in Figure S2. We found that the octahedral rotation angle has been reduced at domain wall, but its variation is very small, which is less than 0.2°. In addition, the octahedral rotation cancels the displacement of the two oxygen ions on the diagonal in the plane, while this does not cause a net displacement, as shown in the insert picture of the Figure S2.



FIG. S2. The octahedral rotation angle for LuFeO3. Insert: the octahedral rotation cancels the

displacement of the two oxygen ions on the diagonal in the plane.

(S3) We find that the contribution of the electrons is always 1~2 orders of magnitude larger than the ions, which indicates that in our structures, the electron term plays a greater role than the ion term. Therefore, in Eq. (1) part, we ignore the contribution of ions for simplicity in order to easier clarify the physically microscopic mechanism. What's more, the contribution of the ions is also part of the final polarization value, so it is also necessary to analyze the contribution of ions to polarization by considering the displacement and bond angle

Table S2. The energy (*E*, in eV/f.u. units) and polarization (*P*, in  $\mu$ C/cm<sup>2</sup> units) parameters of the orthorhombic AFeO<sub>3</sub> (A = Lu, Y, Gd). The polarizations are only along the *b* axis direction. *P*<sub>ion</sub> and *P*<sub>elc</sub> are represent the contribution of ions and electrons to polarization, respectively.

Configurations		LuFeO₃	YFeO <sub>3</sub>	GdFeO₃
L2-2	P <sub>ion</sub>	-0.003	-0.022	-0.007
	$P_{\rm elc}$	-0.089	-0.059	-0.069
L2-4	Pion	-0.001	-0.003	-0.005
	P <sub>elc</sub>	-0.053	-0.039	-0.043
L3-3	<b>P</b> ion	0.000	0.000	0.000
	$P_{\rm elc}$	0.000	0.000	0.000
L4-4	Pion	-0.001	-0.003	-0.003
	$P_{\rm elc}$	-0.041	-0.030	-0.032
L3-5	Pion	0.000	0.000	0.000
	$P_{\rm elc}$	0.000	0.000	0.000
L4-6	<b>P</b> ion	-0.001	-0.005	-0.003
	$P_{\rm elc}$	-0.031	-0.024	-0.027
L3-5	Pion	0.000	0.000	0.000
	P <sub>elc</sub>	0.000	0.000	0.000

(S4) From the perspective of the mechanism of multiferroic behavior, type II multiferroics can be separated into two groups: one is ferroelectricity induced by a specific type of magnetic canted structure where a relativistic quantum effect spin orbit coupling involved and another is induced by collinear magnetic structures where no relativistic quantum effect involved.<sup>2</sup>Therefore, all magnetic moments arranged along a specific axis for the latter without the necessity to take the spin-orbit interactions into account. By taking this consideration, we use the unified polarization model to make a detailed analysis of the physical mechanism of the magnetic domain polarization in AFeO<sub>3</sub> (A = Lu, Y, Gd) in the last part of the paper.

(S5) It has been reported that there may be conductivity on the AFM domain wall, such as the electrical insulator polycrystalline AFM compound Nd<sub>2</sub>Ir<sub>2</sub>O<sub>7</sub>. <sup>3</sup> The screening effect caused by the itinerant electrons will partially counteract the ferroelectric polarization, which is disadvantageous to the induction of ferroelectric polarization based on domain walls. Therefore, we calculated the band structure of AFeO<sub>3</sub> in different configuration containing domain wall structure. The results show that they have a distinct band gap in the range of 1.7 to 1.8 eV, showing the significant insulative character. This indicates that the magnetic domain wall ferroelectric polarization is experimentally measurable.



FIG.S3. Electronic band structure of  $AFeO_3$  with the *L2-2* configuration, the Fermi energy is indicated by the horizontal dashed lines.

## References

1 He J.; Borisevich A.; Kalinin S V. Control of octahedral tilts and magnetic properties of perovskite oxide heterostructures by substrate symmetry. *Physical review letters* 2010, 105(22): 227203.

2 Daniel Khomskii, Physics 2, 20 (2009).

3 E. Y. Ma; Y. T. Cui; K Ueda; S. Tang; K. Chen; N Tamura; P. M. Wu; J Fujioka; Y Tokura; and Z. X. Shen. *Science* **350** (6260), 538 (2015).