Supporting Information for

Enhanced Magnetization and Modulated Orbital Hybridization in Epitaxially Constrained BiFeO₃ Thin Films with Rhombohedral Symmetry

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*Transition from a spatially modulated spin state to a homogeneous spin state

According to the study of Bai et al. [S1], an epitaxial constraint induces the destruction of a spatially modulated cycloidal spin structure, releasing a latent antiferromagnetic component locked within the cycloid. This leads to a phase transition from the incommensurately modulated cycloidal spin state with a long wavelength $\lambda$ of $\sim 600\text{Å}$ [S2] to the homogeneous spin state. Considering the Ginzburg gradient energy as the difference in the free energy per unit volume between the spatially modulated spin state of the unconstrained film and the homogeneous spin state induced by a strong epitaxial constraint, one can obtain the following relation with the help of the previous analysis based on the Landau-Ginzburg theory [S1]:

$$\Delta F_{GZ} = F_{\text{cycloid}} - F_{\text{homo}} = -\frac{1}{4A}\left(\gamma P_o\right)^2 - \frac{1}{2}K_u + \frac{1}{4}\chi (\beta P_o)^2 + \frac{1}{2}K_{Rh}$$

(1)
where $P_o$ is the spontaneous polarization, $A$ is the stiffness constant in the inhomogeneous exchange interaction,$[^{33}]$ $\gamma$ is the inhomogeneous magnetoelectric (ME) constant in the Lifshitz invariant (actually denoted by $\alpha$ in Ref. [S3]). On the other hand, $\beta$ is the homogeneous ME constant appeared in the ME-like Dzyaloshinsky-Moria interaction.$[^{33}]$ $\chi_\perp$ is the susceptibility in the direction perpendicular to the antiferromagnetic vector.$[^{31}]$ In the above derivation, the effective uniaxial magnetic anisotropy constant,$[^{31}]$ $K'_u$, is decomposed into two terms: $K'_u = K_u - K_{Rh}$, where $K_{Rh}$ denotes a rhombic perturbation to $K_u$.$[^{31}]$

The term, $yP_o$, appeared in Eq. (1) can be equated with $2Aq$ with $q = 2\pi/\lambda$, where $q$ is the wave vector for the cycloidal spin modulation.$[^{31}]$ Then, using Eq. (1) one can immediately establish the following criterion for a spontaneous transition from the cycloidal spin state to the homogeneous spin state:

$$K_{Rh} \geq 2Aq^2 + K_u - \frac{\chi_\perp}{2}(\beta P_o)^2$$  \hspace{1cm} (2)

The above criterion can be satisfied by the two different contributions. As the misfit strain increases, the positive contribution to $K_{Rh}$ from the cycloidal spin modulation ($2Aq^2$ with $A>0$) disappears as $q \to 0$ or $\lambda \to \infty$, satisfying the criterion given in Eq. (2). On the other hand, the negative contribution to $K_{Rh}$ from the ME coupling energy of the homogenous spin state [i.e., $-(\chi_\perp/2)(\beta P_o)^2$] increases as the misfit strain increases. Both effects contribute to the above criterion of a spontaneous transition from the spin cycloidal state to the homogeneous spin state.
As shown in Figure 5b of the main manuscript, the inverse magnetic susceptibility increases suddenly as the misfit strain becomes smaller than a certain critical value (~0.08 %). This observation can be understood in terms of the phase transition from the cycloidal spin state to the homogeneous spin state with the onset value around 150 nm. Thus, the in-plane constrained epitaxial BFO films with R3c symmetry maintain their cycloidal spin state down to ~150 nm but undergo a spontaneous transition to the homogeneous spin state below this critical thickness (or above the critical value of the in-plane misfit strain). This transition then releases a latent antiferromagnetic component locked within the spin cycloid,\[^{[S1]}\] leading to an abrupt change in the slope of the plot of \(1/\chi_m\) vs. misfit strain at ~150 nm (Fig. 5b).

\* References

