Observation of Uniaxial Strain Tuned Spin Cycloid in a Freestanding BiFeO₃ Film

Zhe Ding, Yumeng Sun, Ningchong Zheng, Xingyue Ma, Mengqi Wang, Yipeng Zang, Pei Yu, Zhouzheng Chen, Pengfei Wang, Ya Wang, Yurong Yang,* Yuefeng Nie,* Fazhan Shi, and Jiangfeng Du*

Bismuth ferrite (BiFeO₃) possesses a non-collinear spin order while the ferroelectric order breaks space inversion symmetry. This allows efficient electric-field control of magnetism and makes it a promising candidate for applications in low-power spintronic devices. Epitaxial strain effects have been intensively studied and exhibit significant modulation of the magnetic order in bismuthBiFeO₃, but tuning its spin structure with continuously varied uniaxial strain is still lacking at this moment. Herein, in situ uniaxial tensile strain is applied to a freestanding BiFeO₃ film by mechanically stretching an organic substrate. A scanning nitrogen-vacancy (NV) microscopy is applied to image the nanoscale magnetic order in real space. The strain is continuously increased from 0% to 1.5% and four images under different strains are acquired during this period. The images show that the spin cycloid tilts by ≈12.6° when strain approaches 1.5%. A first principle calculation is processed to show that the tilting is energetically favorable under such strain. The in situ strain applying method in combination with scanning NV microscope real-space imaging ability paves a new way in studying the coupling between magnetic order and strain in BiFeO₃ films.

1. Introduction

Super-fast spin dynamics, substantial magneto-transport effects, and resistance to external magnetic field disturbance are all characteristics of antiferromagnetic materials. Owing to the advantages listed above, antiferromagnetic materials have significant applications in spintronics and other magnetism-based technologies.[3] Although being a promising material, because of its anti-parallel spin configuration which leads to zero stray-field, antiferromagnetic material cannot be well studied by conventional near-field imaging techniques.[2] Bismuth ferrite (BiFeO₃, BFO), a non-collinear antiferromagnetic perovskite compound possesses magneto-electric multiferroic properties under room temperature. Since the non-collinear spin cycloid breaks the spatial inversion symmetry, it can be controlled by an external electric field and thus costs much less energy than ordinary ferromagnetic devices.[2–6] BFO owns spin cycloids because of the Dzyaloshinskii–Moriya interaction (DMI). Such cycloids induce a net magnetization that is too weak to be observed with conventional methods such as magnetic force microscopy[7] and photoemission electron microscopy.[8] At the same time, since BFO has ≈2.7eV bandgap,[9] spin-polarized scanning tunneling microscopy cannot perform imaging either. Scanning Nitrogen-Vacancy microscopy (SNVM) is an emerging real-space scanning method with nanoscale spatial resolution and μT / Hz magnetic sensitivity.[10,11] It has been used to study the magnetic structure of BFO epitaxial films at the nanoscale.[2,12,13]

BFO is a perovskite compound that fulfills the noncentrosymmetric rhombohedral R3c space group.[14] The structure of BFO is shown in Figure 1c, for the sake of brevity, we adopt a pseudo-cubic unit cell. Each unit cell contains eight bismuth atoms at corners, while the iron atom is contained by an oxygen octahedron at the center. The BFO has a ferroelectric Curie temperature of 1103 K,[15,16] below which the ferroelectric polarization is as high as 100 μC cm⁻² in high quality grown films.[17,18] The antiferromagnetic order of BFO is characterized as G-type, with a Néel temperature TN = 683 K.[19] 3d electrons of Fe³⁺ are the origin of the magnetism of BFO, while ferroelectricity and...
antiferrodistortive break the spatial inversion symmetry which gives rise to a DMI. This interaction leads to a small canting angle between neighbor spins and this produces an effective spin density of $0.02 \mu_B$ per unit cell.\cite{2,20} Under certain conditions, the spin distribution will turn into cycloids, which has been confirmed in BFO thin films.\cite{2,12,21,22} A cycloid order can be described by a wave vector $k$, as shown in Figure 1c. The magnetic order of BFO is decided by external fields, strain, temperature, size, and more factors, while the effect of strain has been intensively studied.\cite{12,23–27} Previous works utilized different substrates to adjust the epitaxial strain in BFO and found two types of cycloid order.\cite{12,23} Despite these researches providing the phase diagram of BFO magnetic order with respect to epitaxial strain, most of the works focus on biaxial strain while real-space imaging of magnetic structure under uniaxial strain has not yet been performed. Furthermore, it is not easy to impose continuously adjustable strain to BFO in situ, which leaves the mechanism of BFO magnetic transformation at the critical point an open question.\cite{12,14,23} In recent years, several progresses on continuously tuning strains of perovskite oxide films have been made. Deng et al. reported a method to continuously tune epitaxial strain by varying the thickness of the buffer layer\cite{28–30} while freestanding films could be tuned by bending\cite{34} or stretching flexible organic substrates.\cite{32,33} In this work, we adopt molecular beam epitaxy (MBE) to prepare the freestanding BFO film.\cite{18,35} The 75-unit-cell-thick BFO (001) film is grown and transferred to the organic substrate Polyethylenenaphthalate (PEN) while the epoxy is used as the glue to conduct strain to the BFO film. During experiments, uniaxial, continuous and in situ tensile strain is imposed on the BFO film by means of mechanically stretching the PEN substrate.\cite{32,33} In principle, this method is able to impose arbitrary in-plane tensile strain on the film, while in this work the strain principal axis deviates from [110] by $\approx 4.7^\circ$. Such strain breaks the intrinsic $R3$c symmetry of BFO and provides a way to tune the spin cycloid’s direction continuously. A home-built SNVM is used to perform nanoscale magnetic imaging of its stray field. By using this method, we...
find that the direction of the cycloid order is modulated by the uniaxial strain which is confirmed by a first principle calculation. This phenomenon may help people understand the transition mechanism of magnetic order under strain[14,23] whilst the freestanding-film-based method can be used in strain-based spintronics, new heterostructure devices and other new multifunctional devices.[18,32,33] Our new freestanding-film-based method in combination with SNVM real-space imaging ability paves a new way to study strain-magnetism coupling in antiferromagnetic materials.

2. Results and Discussion

2.1. Real Space Imaging with SNVM

SNVM has been widely used in condensed matter physics,[36–41] here we apply SNVM to the freestanding BFO film to acquire stray field distribution near the surface. The structure of our SNVM setup is demonstrated in Figure 1a. The Nitrogen-Vacancy color center (NV center) in diamond is a point defect shown in the inset. It is formed by a nitrogen atom (orange ball in the inset) and an adjacent vacancy (blue ball in the inset) in a diamond lattice.[42] As shown in Figure 1b, the NV center is pumped from the ground state ($^3A_2$) into the phonon side-band by 532 nm green laser (green arrows) and relaxes into the excited state ($^3E$) with angular momentum conserved (grey arrows). $|m_s = 0\rangle$ emits photons (wavy red arrow) during the transition to ground state and the photons are finally detected by a single photon detector. $|m_s = \pm 1\rangle$ evolves into the ground state through meta-stable states ($^1A_1$, $^1E$) with no detectable photon emitted (black dotted line arrows). The degeneracy of $|m_s = \pm 1\rangle$ is lifted by Zeeman splitting generated by an external magnetic field ($\gamma_0 B_p$) and resonant microwave (MW, orange circled arrow) is applied by a copper micro-antenna to selectively excite one of the spin states. By using the photon count rate’s difference between $|m_s = 0\rangle$ and $|m_s = \pm 1\rangle$, it is straightforward to readout the NV center’s spin state.

In our experiment, by applying green laser and MW simultaneously while readout the photon counts, we utilize the Continuous Wave Optically Detected Magnetic Resonance (CW-ODMR) spectrum. To accelerate the imaging speed, we adopt the dual-isos-B protocol shown in Figure 1d.[2] Applying this protocol, by sampling at two MW frequencies, we can calculate the projection of the stray field to the NV axis.[34] By scanning across a magnetic film edge, we determine that the distance from the NV center to sample surfaces is 78.5 ± 1.8 nm (with 95% confidence).[34,43,44]

2.2. Sample Preparation and Characterization

To acquire the freestanding film for SNVM experiments, as shown in Figure 2a, BFO was grown by MBE on a single-crystalline (001) SrTiO$_3$ (STO) substrate with a thin layer of water-soluble Sr$_3$Al$_2$O$_6$ (SAO) on top.[18] The epitaxial film was then coated with epoxy and covered with an organic PEN substrate. After the epoxy layer was cured, the multi-layer assembly was soaked in water for about one week before the SAO layer was dissolved and the freestanding BFO film was separated from the PEN substrate.[32] As shown in the last step of Figure 2a, after the freestanding BFO sample was separated from the STO substrate, a piezoelectric force microscope (PFM) is utilized to form a capacitive contact actuator which is used to electrically polarize an area of the BFO film to [111].[34] During SNVM experiments, the NV probe was aligned to the center of the polarized domain so that the ferroelectric order parameter was kept uniform in the SNVM scanning area. The sample was then installed to the scanning stage equipped with a strain-applying actuator with which a uniaxial tensile strain is applied to the BFO film via the PEN substrate. It has been shown that strain distributes homogeneously on the sample in this kind of layout.[32] As shown in Section S4 (Supporting Information), by employing X-ray diffraction (XRD) after SNVM experiments, we
can calibrate strains under which the images are acquired.\textsuperscript{[34]} XRD data show that the sample is under compressive biaxial strain before the tensile uniaxial strain is applied. This compressive strain is the epitaxial strain induced by the STO substrate during MBE growing and remains in the sample as a background.\textsuperscript{[32]}

### 2.3. SNVM Results

SNVM imaging is implemented under four different strains: $\varepsilon = 0.0\%$, $0.7\%$, $1.3\%$, $1.5\%$, the results are shown in Figure 3. The principal axis of strain deviates from the high symmetry direction $[1\overline{1}0]$ by $4.7^\circ$, which breaks $R3c$ symmetry and leads to tilted cycloids. From the real-space imaging one can find that although the coherence length is relatively small, the sample does possess local cycloid order, which is modulated by the increasing uniaxial strain. Despite the relatively small coherence length, the spin cycloid’s variation during the increasing strain is rather distinct. We calculate the direction of the cycloid wave vector by minimizing variances on segments parallel to different directions and apply the region growing algorithm to the results to acquire the wave vector direction domain image plotted in Figure 3f–i. It is evident that during the application of strain, the wave vector tilts away from $[1\overline{1}0]$. The small coherence length in Figure 3a–d is attributed to the strain fluctuation which was first observed in freestanding graphene\textsuperscript{[46,47]} and other freestanding perovskite films\textsuperscript{[32,46–48]}. From the first principle calculation in Section 2.4, the strain direction determines the orientation of the cycloid wave vector energetically. Therefore, the strain fluctuation induces the variation of local strain direction which further causes a local variation of cycloid directions.

Note that such variation could be modulated by the applied strain, there are plural non-trivial local transitions while the applied strain increases. For example, by retracing with respect to tomography markers and magnetic patterns, we are able to determine that the areas highlighted with yellow boxes in Figure 3 are at the same spot.\textsuperscript{[45]} Two different ordered areas at this spot merge into one when strain approaches $1.5\%$. This phenomenon indicates that two uncorrelated cycloids under strain fluctuations are regulated into one because the magnetic energy barrier between these areas is flattened by the stronger anisotropic energy provided by the external uniaxial strain.

We have acquired a qualitative result that during the application of strain, the wave vector tilts away from $[1\overline{1}0]$. In order to obtain quantitative relation between the tilting angle and strain, we apply Fourier transformation (FT) to the initial and final real-space scanning results to obtain the wave vector distribution in reciprocal space, which is shown in Figure 4a,b. It is distinctive that the wave vector tilts away from $[1\overline{1}0]$ while the strain increases, this confirms our qualitative result from the real-space imaging. We divide $180^\circ$ into 40 bins and count the average FT amplitude in each bin to plot the angular distribution of cycloid wave vectors, the result is displayed in Figure 4e. One can find that, while the strain increases, the wave vector tilts by $\approx 12.6^\circ$. 

![Figure 3. Spin cycloid variation in real space during strain increasing. a–d) Images of stray field $B_p$ under different strains. The white scale bar corresponds to 500 nm, a reference of crystal orientation $[1\overline{1}0]$ and $[1\overline{1}0]$ is displayed to the right. Yellow boxes highlight a local transition of the spin cycloid, a limited alignment accuracy is responsible for the mismatches among (a–d).\textsuperscript{[45]} (e) The sketch of applied strain corresponding to the stray field images above. f–i) Wave vector direction in real space under different strains. The white scale bar corresponds to 500 nm. The fan-shaped color bar demonstrates the wave vector direction under the frame displayed by green and red arrows below.](image-url)
In order to explain the wave vector’s tilting under strain, first-principle-based simulations are performed using magnetic exchange interaction coefficients evaluated from the four-state mapping approach.\[50\]

The uniaxial strain is modeled by stretching the cell along the direction that slightly deviates from the pseudo-cubic [110] direction by 4.7°. The strain is chosen to be 1.5% according to XRD calibration, and an estimated Poisson’s ratio of about 0.24 calculated via XRD data is also considered.\[34\] Note that due to the symmetry broken caused by strain, the symmetry of the system is reduced from space group R3c to P1, and all the sixfold-degenerate pair in the R3c structure\[49\] are no longer degenerate. The calculated exchange coefficients are shown in Supporting Information.\[34\]

Parallel Tempering Monte Carlo (PTMC) simulations\[51,52\] are performed to solve the magnetic effective Hamiltonian. A large supercell of \(\sqrt{2a}a \times \sqrt{2b}b \times c (n = 2, 3, \ldots, 300)\) is used study the cycloid phase, where \(a\) is along the pseudo-cubic [110] direction, \(b\) is along the pseudo-cubic [100] direction, and \(c\) is along the pseudo-cubic [001] direction. To study the stable period of the cycloid phase, energy per Fe atom is calculated as a function of the cycloid period, as shown in Figure 5. This energy-versus-period curve shows a minimum at 119 nm, which is similar to that in the R3c phase.\[49\]

To study cycloid which deviates the [110] direction, several oblique supercells are constructed. The supercells slightly tilting about \(c\) direction were used. The angle between the lattice vector \(a\) and the pseudo-cubic [110] direction is used to define the oblique angle of the cycloid. For example, one of the oblique supercells used in this work is defined by \(a = 211a_0 - 165b_0\), \(b = 7a_0 + 9b_0\), \(c = c_0\) where \(a_0\), \(b_0\) and \(c_0\) are the vectors we used to define our relaxed R3c BFO lattices which are close to the pseudo-cubic [100], [010] and [001] direction, respectively. The oblique angle of such cell is then the angle between the \(a\) and \(a - b\), that is approximately 7°. Figure 5 shows the calculated energy of supercells with different oblique angles as functions of the cycloid period. The energies of supercells with non-zero oblique angles are lower than that of supercells without oblique angles, indicating that oblique supercells are more energetically favorable. Moreover, with the increasing of the oblique angle from 0°, the energy shows a nonmonotonic behavior with respect to the oblique angle, with a minimum around 18°. Such value is consistent with the measured value 12.6° (refer to Figure 4e).
To confirm the cycloids in the rotated supercells do propagate along a direction that deviates from [110], FT is also performed to the PTMC simulation results. Figure 4d shows the spectrum of one supercell with oblique angle 18° after the FT, showing a peak away from the pseudo-cubic [110] direction by 18°. On the other hand, Figure 4c shows such spectrum on a supercell without the oblique angle of a non-stretched cell (R3c phase as in Ref. [49]), showing a peak exactly along the pseudo-cubic [110] direction. The deviation of such peak from pseudo-cubic [110] direction definitely confirms that the cycloids in oblique cells do propagate along a direction that deviates from [110]. We thus conclude that such deviation of the cycloid is energetically more favorable than without deviation.

Note that we also performed the analysis above on BFO at the tensile strain of 0.5% along exactly the pseudo-cubic [110] direction without oblique angle, and found the cycloid propagates along the pseudo-cubic [110] (i.e., with oblique angle 0°) is the most energetically favored phase. This fact indicates that the deviation of the cycloid propagation originates from the symmetry broken caused by the uniaxial strain colored with an oblique angle.

3. Conclusion

In summary, we apply continuous in situ uniaxial strain to freestanding BFO films and scan the magnetic stray field near the surface with SNVM. A modulation of the direction of the magnetic order is found and a first principle calculation is conducted. The first principle calculation result confirms that the strain-induced magnetic effective Hamiltonian evolution is responsible for the rotation of magnetic order.

From our results, it is observed that the magnetic order of a freestanding film is more complex than as-grown films. Without the clamping effect from a solid substrate, thermal fluctuations, and other environmental factors will influence the sample. Since the magnetic free energy is much lower than other terms, this influence makes the magnetic order rather unstable. However, this result is still helpful for people to understand the mechanism of magnetic order transformation under strains.

Besides, our freestanding-film-based in situ strain-applying method paves a new way to study the coupling between strain and magnetism in antiferromagnetic freestanding films. This method possesses a high degree of freedom. People could apply much higher strain to freestanding films than normal as-grown films. It has been reported that strains as high as 8% have been applied to a freestanding La$_{0.7}$Ca$_{0.3}$MnO$_3$ membrane, while the strain applied to as-grown films is normally lower than 2%. Moreover, the direction and strength of the strain applied to a freestanding film can also be continuously tuned, providing new knobs to engineer the lattice symmetry and strain states with unprecedented degrees of freedom. Because of the merits above, we can study the film under conditions impossible to realize in as-grown films and find more novel phenomena.

Incidentally, since we can synthesize freestanding BFO films approaching the 2D limit, it is also interesting to study the intriguing magnetic and transport properties in the 2D limit in these strongly correlated oxides. Though beyond the scope of this work, it is another important goal we are trying to pursue.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

BFO, freestanding, spin cycloids, tensile strains

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