Electric-field control of spin waves at room temperature in multiferroic BiFeO$_3$

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To face the challenges lying beyond current CMOS-based technology, new paradigms for information processing are required. Magnonic$^1$ proposes to use spin waves to carry and process information, in analogy with photonics that relies on light waves, with several advantageous features such as potential operation in the THz range and excellent coupling to spintronics$^2$. Several magnonic analog and digital logic devices$^3$ have been proposed, and some demonstrated$^4$. Just as for spintronics, a key issue for magnonics is the large power required to control/write information (conventionally achieved through magnetic fields applied by strip lines, or by spin transfer from large spin-polarized currents). Here we show that in BiFeO$_3$, a room-temperature magnetoelectric material$^5$, the spin wave frequency ($>$600 GHz) can be tuned electrically by over 30%, in a non-volatile way and with virtually no power dissipation. Theoretical calculations indicate that this effect originates from a linear magnetoelectric effect related to spin-orbit coupling induced by the applied electric field. We argue that these properties make BiFeO$_3$ a promising medium for spin wave generation, conversion and control in future magnonics architectures.

Magnetolectric multiferroics possess coexisting magnetic and ferroelectric phases, with cross-correlation effects between magnetic and electric degrees of freedom$^6$. As such, they can potentially be used to control spin-based properties by electric fields$^7$, with very low associated power dissipation. This feature appears promising not only for spintronics, in which information is encoded by the spin-polarization of the electrical current$^8$, but also for magnonics that use magnetic excitations (spin waves) for information processing$^9$. Indeed, just as coupling between magnetic and ferroelectric order parameters exists in multiferroics, coupled spin and lattice excitations termed electromagnons have also been demonstrated$^{10}$. Such mixed excitations exist at low temperature in multiferroic manganites$^{11}$ and are suspected at room temperature in BiFeO$_3$.$^{12}$ Although in the former systems, electromagnons have been shown to depend on magnetic fields$^{13}$, their predicted sensitivity to electric fields, at the heart of their potential applicative interest, remains to be demonstrated.$^{14}$

In this paper, we focus on BiFeO$_3$(BFO), a special case among multiferroic materials. Indeed, BFO has a very high ferroelectric polarization reaching 100 $\mu$C/cm$^2$.$^{12}$ below $T_C = 1143$ K and becomes an antiferromagnet below $T_N = 643$ K. The spins form a cycloid structure with a wavelength of $\lambda_0 = 62$ nm and an associated cycloid wavevector equal to $Q = 2\pi/\lambda_0$. The magnetic cycloid lies in the (-12-1) plane, formed by the ferroelectric polarization $\parallel$ [111] and the cycloid wavevector $Q \parallel [10 - 1]$ (Fig. 1a). An electric field can simultaneously induce the flop of the polarization and the cycloidal plane$^{16}$. The electrical switch of antiferromagnetic-ferroelectric domains in BFO has been observed$^{17,18}$ and controlled in a ferromagnet-multiferroic heterostructure$^{2}$. Here we report direct electric-field control of spin wave states in BFO at room temperature.$^1$

In BFO, inelastic light scattering reveals two species of spin wave excitation modes. These are observed in Raman spectra as two series of sharp peaks labelled cyclon ($\phi_n$) and extra cyclon modes ($\psi_n$) below 70 cm$^{-1}$, the frequency of the lowest phonon mode.$^{10,19,20}$ The cyclon $\phi_n$ and extra cyclon $\psi_n$ modes correspond respectively to the spin oscillations in and out of the cycloidal plane (Fig. 1b) and their Raman scattering signature are reported in Fig. 1c. These two species of magnons originate from the translational symmetry breaking$^{21}$ of the cycloidal ground state. The spin wave momentum is no more conserved, and can be increased or decreased by a multiple of the cycloid wavevector $Q$. This leads to magnon zone folding at the Brillouin zone center, where $\phi_n$ and $\psi_n$ correspond to magnon wavevector equal to $k = nQ$. 

\[ S_{\phi_n} = \frac{1}{4} \frac{\pi}{\lambda_0} \left( 2n - 1 \right) \]

\[ S_{\psi_n} = \frac{1}{4} \frac{\pi}{\lambda_0} \left( 2n + 1 \right) \]

\[ \lambda_n = \frac{\pi}{2} \frac{\lambda_0}{n} \]

\[ \Omega_n = \frac{\pi}{\lambda_0} n \]

\[ \phi_n \parallel (10 - 1) \]

\[ \psi_n \parallel (111) \]
The experimental set-up used to apply an electric field and to detect the optical excitations of spin waves is presented in Fig. 1. The device consists of bottom and top (transparent) electrodes that enable the application of an electric field along the [010] and [0−10] directions of a bulk BFO sample. The effect of the external electric field on the spin wave modes is tracked in Fig. 1c. An external electric field applied along the [010] direction induces a blue shift of the ψn modes (ψ2 and ψ3) and a red shift of the φn modes (φ2, φ3, and φ4). The promise of this electric-field control depends on our ability to selectively tune the spin wave states using the polarization hysteresis cycle and the switching of the polarization vector P.

Figures 2a,b show the frequency shift of the φ2 (cyclon) and ψ2 (extra-cyclon) modes as a function of the polarization cycle. This figure demonstrates that the spin wave modes are directly connected to the polarization hysteresis loop shown in Fig. 2c. With an initial polarization state $P_1 \parallel [111]$, decreasing the applied electric field ($E \parallel [010]$) induces an increase of the $\phi_2$ mode frequency (red diamond, Fig. 2b) following path 1 in the polarization cycle. Traveling along path 2 with a negative electric field ($E \parallel [0-10]$), the frequency of the $\phi_2$ mode (blue star) increases up to the flip of $P$ along the [1-11] direction ($P_2$) at critical electric field $E_c \approx −35$ kV/cm. Beyond $E_c$, $\phi_2$’s frequency decreases. The hysteresis cycle can be completed along paths 3 and 4 leading to frequency shifts that are symmetric to the ones along 1 and 2. The $\psi_2$ mode is also directly connected to the polarization loop, but exhibits an opposite behaviour with respect to the $\phi_2$ mode (Fig. 2c). The extra-cyclon mode $\psi_2$ presents a much stronger frequency shift under the effect of an electric field of 50 kV/cm, $\Delta \omega_{\psi_2} = (+2.1 \pm 0.1)$ cm$^{-1}$. Remarkably, the $\psi_2$ frequency is seen to increase by over 5 cm$^{-1}$ at maximum $E$ field, corresponding to a 30% shift of its natural frequency. This experiment clearly demonstrates the coupling between the spin waves and the ferroelectric character of the material and that a spin wave frequency hysteresis loop can be created and controlled at room temperature using the ferroelectric hysteresis loop.

There exists other methods for electric-field control of spin waves. Rado et al. detected a shift of the order of 3 × 10$^{-5}$ cm$^{-1}$ (relative shift of 0.01%) in lithium ferrite under the application of similar voltage. Recently, Vlaminck and Bailleul demonstrated a doppler shift of...
the order of $10^{-3}$ cm$^{-1}$ (0.3%) using electric currents. The present experiment shows that the coupling between magnetic and ferroelectric degrees of freedom provides a much more efficient method for electric-field control of spin waves, with frequency shifts over 5 cm$^{-1}$ (30%), several orders of magnitude larger than with previous methods.

The strong spin wave frequency shifts that we observe may be interpreted as resulting from a combination of magnetoelectric interactions. The component of $E$ along $P$ (denoted $E_z$) cannot play any role because of the competition with the internal electric field parallel to $\hat{z}$ produced by $P$. Hence we only consider interactions involving $E_\perp = (E_x, E_y)$. The Dzyaloshinskii-Moriya (DM) interaction that couples $E$ to $M \times L$ is allowed by the R3c crystal symmetry of BFO, and also induces a transition from the cycloidal to a homogeneous spin state at large $E_\perp$. The DM interaction produces spin wave shifts that are independent of $E$ at low electric field, at odds with the data, and that scale as $E_\perp^2$ at larger field. Another class of magnetoelectric interactions, the so-called flexoelectric interactions, can be interpreted using the Landau free energy model.

Here, we have found that the spin wave frequency shifts can be interpreted using the Landau free energy model based on an additional kind of magnetoelectric interactions induced by the external electric field. Indeed, the R3c symmetry of BFO allows the presence of two linear magnetoelectric interactions that couple the Néel order parameter $L$ directly with $E_\perp$.

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The calculated curves show that cyclon and extra cyclon mode frequencies converge to two fixed points at the critical electric field $E_{hs}$ required to destroy the cycloid. When $E > E_{hs}$, the spin ground state becomes homogeneous in space. The closed symbols are the experimental data obtained following path 1 (insert) in the polarization cycle using $E \parallel [010]$ from 0 to 125 kV/cm: $ψ_1$ (circle), $ψ_3$ (diamond), $ψ_4$ (down triangle), $ψ_2$ (star), $ψ_3$ (up triangle). $P$ is parallel to the [111] direction and no polarization flop occurs. Solid lines are explicit numerical calculations obtained from a dynamical Ginzburg-Landau theory based on the linear magnetoelectric interaction $F_2$.

**FIG. 3: Electric field dependence of the measured and calculated spin wave frequencies.** When the applied electric field is zero, the energy of the $φ_n$ and $ψ_n$ modes are $E_{φ_n} = n v_0 Q$ and $E_{ψ_n} = \sqrt{1+n^2} v_0 Q$ respectively, with index $n$ labelling the modes, $v_0 = 1.4 \times 10^5$ cm/s the fundamental cyclon spin wave velocity, and $Q$ the cyclon wavevector. The figure shows the spin wave mode energies normalized to $v_0 Q$ as a function of the ratio of the applied electric field $E$ divided by the electric field $E_{hs}$ required to destroy the cycloid. When $E > E_{hs}$, the spin ground state becomes homogeneous in space. The closed symbols are the experimental data obtained following path 1 (insert) in the polarization cycle using $E \parallel [010]$ from 0 to 125 kV/cm: $φ_1$ (circle), $φ_3$ (diamond), $φ_4$ (down triangle), $ψ_2$ (star), $ψ_3$ (up triangle). $P$ is parallel to the [111] direction and no polarization flop occurs. Solid lines are explicit numerical calculations obtained from a dynamical Ginzburg-Landau theory based on the linear magnetoelectric interaction $F_2$. 

with $κ_1$ and $κ_2$ phenomenological coupling constants. Physically, $F_1$ and $F_2$ model additional magnetic anisotropy energies induced by $E_\perp$. Hence their microscopic origin is related to spin-orbit coupling. The first interaction ($F_1$) produces a red shift for both $ψ_n$ and $φ_n$ modes when $E_\perp$ is increased. Thus, $F_1$ cannot explain the experimental observations at low $E_\perp$ (Fig. 3a,b). On the other hand, the interaction $F_2$ induces a blue shift for all $ψ_n$ modes, and a red shift for $φ_n$ modes with $n \geq 2$ as found experimentally, see Fig. 3. This interaction drives the system into a homogeneous state when $E_\perp$ becomes greater than a homogeneous critical field $E_{hs} \propto 1/κ_2$. The calculated curves show that cyclon and extra cyclon mode frequencies converge to two fixed points at the crit-
The spin wave velocities are equal, which further confirms it as a key multifunctional concept, providing a handle for the non-volatile, low-power technology. The demonstration of electrical control of spin wave states represents a significant step towards making new spin wave-based technologies. The cyclon spin wave dispersion as \( \omega_\psi = v_\psi \sqrt{k^2 + Q^2} \). For \( E = 0 \), the spin wave velocities are equal, \( v_\phi = v_\psi = v_0 = 1.4 \times 10^6 \text{ cm/s} \). However, under an electric field of 100 kV/cm the \( \phi \) and \( \psi \) spin wave velocities are tuned by \( \Delta v_\phi = -6 \times 10^4 \text{ cm/s} \), and \( \Delta v_\psi = +4 \times 10^4 \text{ cm/s} \) respectively. While the speed of electron spin precession in a magnetic field is generally fixed by intrinsic properties of the materials considered, our work shows that in a multiferroic the spin wave speed can be continuously adjusted and in a different way depending on the spin propagating mode by the applied electric fields.

We have demonstrated that the frequency of spin waves can be tuned electrically by over 30% at room temperature in multiferroic BiFeO\(_3\). This electric-field dependence mimics that of the ferroelectric polarization, providing a handle for the non-volatile, low-power control of spin waves. Thus, aside from its potential for spintronics\(^{29}\) and photonics\(^{30}\), BiFeO\(_3\) emerges as an exciting platform for testing novel magnonic device concepts, which further confirms it as a key multifunctional material for beyond-CMOS technology.

**Method**

**Experimental method**

BiFeO\(_3\) single crystals were grown in air using Bi\(_2\)O\(_3\)-Fe\(_2\)O\(_3\) flux in an alumina crucible as detailed in ref.\(^{13}\), and present a single ferroelectric and antiferromagnetic domain state. Polarized optical microscope images of the samples show that the crystal consists of one single ferroelectric domain\(^{22}\). Neutron measurements on the same samples have shown the presence of one antiferromagnetic domain\(^{16}\). A conducting Indium tin oxide (ITO) layer was grown by pulsed laser deposition on the top of the (010) sample surface to apply a uniform electric field. ITO has no Raman signal in the frequency range of interest. All the measurements were performed in vacuum at room temperature on several samples.

Raman scattering was performed on the (010) sample surface in backscattering geometry using the 647.1 nm laser line. Raman scattering is collected by a triple spectrometer Jobin Yvon T64000 equipped with a CCD. The spot size is about 100 \( \mu \text{m}^2 \) and the penetration depth is less than \( 10^{-5} \text{ cm} \). Reproducible Raman measurements have been performed on several points on the sample surfaces.

The \( \phi_n \) and \( \psi_n \) modes (\( n \) index labels the modes from their lowest to highest energy) were selectively observed using parallel and crossed polarizations in the (010) plane, respectively (see Supplementary Information). The polarizations are defined with respect to the projection of the cycloid wavevector \( Q \parallel [10-1] \) in the (010) plane (the direction of the wavevector \( Q \) is not directly accessible in the (010) plane). In order to show simultaneously several \( \phi_n \) and \( \psi_n \) modes, Fig.\(^{11}\) presents measurements without specific polarization.

**Theoretical method**

We consider a total free energy given by \( F = F_0 + F_1 + F_2 \), with \( F_0 \) the usual model free energy of multiferroic BFO\(^{21,25}\).

\[
F_0 = \frac{A}{2} L^2 + \frac{r}{2} M^2 + \frac{G}{4} L^4 + \frac{c}{2} \sum_{i=x,y,z} (\nabla L_i)^2 - \alpha_P P \cdot [L(\nabla \cdot L) + L \times (\nabla \times L)],
\]

and \( F_1, F_2 \) given by Eqs.\(^{11,24}\) respectively [we omit the purely ferroelectric contributions to Eq.\(^{11}\) because they play no role in the discussion below]. Here \( A, r, G, c, \) and \( \alpha_P \) are phenomenological constants. The ground state is determined by the condition \( \frac{\partial F}{\partial L} = 0 \); when \( E_L = 0 \) the ground state is a harmonic cycloid \( L_0 = L_0 \sin(Qx)\hat{x} + \cos(Qx)\hat{z} \) with wavevector \( Q = \frac{\alpha_P}{c} \) and amplitude \( L_0^2 = \frac{\sqrt{E_L}}{G} \). The effect of \( E_L \) is to reduce the ground state wavevector \( Q \) and to add additional anharmonic contributions to \( L_0 \) at odd multiples of \( Q \). When \( E_L \) is equal to a critical field \( E_{hs} = \frac{\alpha_P P}{\sqrt{G}} \), the cycloid wavevector \( Q \) becomes equal to zero, signaling a transition to a homogeneous state.

The spin wave excitation frequencies are determined from the Landau-Lifshitz equations of motion. After combining the equations of motion for the order parameters \( L \) and \( M \) we get

\[
\frac{\partial^2 L}{\partial \tau^2} = -r(\gamma L_0)^2 \left[ \frac{\delta F}{\delta L} - \left( \dot{L}_0 \cdot \frac{\delta F}{\delta \dot{L}_0} \right) \right], \tag{4}
\]

where \( \gamma \) is the gyromagnetic ratio. We find wave-like solutions by plugging in \( L = L_0 + (\delta L)e^{i\omega t} \) in Eq.\(^{11}\), with \( (\delta L) = \phi(x)\hat{D} + \psi(x)\hat{y} \). The unitary vector \( \hat{D} \) is tangential to \( L_0 \), i.e. it is orthogonal to \( L_0 \) but lies within the cycloid plane. Plugging \( \phi(x) = \sum_n \phi_n e^{i\omega x} \), and \( \psi(x) = \sum_n \psi_n e^{i\omega x} \) into Eq.\(^{11}\) leads to a matrix equation whose eigenvalues give the spin wave excitations at \( k = 0 \).
We want to underline that the free energy model for BFO Eq. 3 does not contain any magnetic anisotropy. Nevertheless, the present experiment shows that an external E field induces magnetic anisotropy linear in E, see Eq. 2. In other words, the electric field activates a latent anisotropy in the material, leading to a large effect in the case of Eq. 2.

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