Observation of electromagnon excitations in the BiFeO$_3$ spiral magnet

M. Cazayous, Y. Gallais, and A. Sacuto
Laboratoire Matériaux et Phénomènes Quantiques (UMR 7162 CNRS), Université Paris Diderot-Paris 7, 75205 Paris cedex 13, France
Laboratoire de Physique des Solides (UPR5 CNRS), Ecole Superieure de Physique et de Chimie Industrielle, 10 rue Vauquelin, 75231 Paris, France

R. de Sousa
Departement of Physics and Astronomy, University of Victoria, Victoria, B.C., Canada, V8W 3P6

D. Lebeugle and D. Colson
Service de Physique de l’Etat Condensé, DSM/DRECAM/SPEC, CEA Saclay, 91191 Gif-sur-Yvette, France

(Dated: February 2, 2008)

Recently, oxide multiferroics have attracted much attention due to their large magnetoelectric effect which allows the tuning of magnetic properties with electric field and vice versa and open new venues for future spintronic applications such as multiple-state memory devices with dual magnetic and electric control. BiFeO$_3$ (BFO) belongs to this new class of materials and shows both ferroelectric and antiferromagnetic orders at room temperature with a large electric polarization, associated with a cycloidal spiral magnetic ordering. The incommensurate magnetic order induces magnon zone folding and allows investigations by optical probes of unusual spin waves which couple to optical phonons, the so called ”electromagnons”. Here, we unravel for the first time the electromagnon spectra of BFO by means low energy inelastic light scattering technique. We show the existence of two species of electromagnons corresponding to spin wave excitations in and out of the cycloidal plane. The present observations present an unique opportunity to study the interplay between ferroelectric and magnetic orders.

Low-frequency magneto-optical resonances in the dielectric susceptibility of multiferroic compounds have attracted much attention the last few years. Optical measurements of magnetic and dynamical properties such as Raman spectroscopies are still in their infancy. In BFO, the intimate relationship between electrical polarization and spin wave excitations or magnons is directly related to the strong electromagnetic coupling detected at room temperature in BFO. A recent theory on spine dynamics in incommensurate multiferroic BFO predicted the observation of a series of electromagnon resonances by an optical probe.

Here we report a low-energy Raman scattering study on BFO single crystal where we observe for the first time two species of low-energy electromagnons with two well defined energy level structures. The level structures are linked to the magnon zone folding induced by the periodicity of the cycloid and their coupling with electrical polarization. We assign the two sets of energy levels to the electromagnon mode excitations in and out of the cycloid plane in BFO. In addition we show that the temperature dependence of the electromagnon modes drastically contrasts with the one of the optical phonons. The sudden increase of the intensity of the modes and the softening of their frequencies close to T= 140K reveal the occurrence of a spin reorientation phase transition in BiFeO$_3$ which confirms the magnetic nature of the electromagnon modes.

The BiFeO$_3$ single crystals studied were grown in air using a Bi$_2$O$_3$-Fe$_2$O$_3$ flux technique. They have a millimeter size and have the shape of a christmas tree with a large surface plane corresponding to the (010) face in the pseudo-cubic representation. The spontaneous electrical polarization has a magnitude between 50 and 100 $\mu$C/cm$^2$ along [111] direction and makes an angle of...
The equally and non equally spaced modes at low frequencies correspond respectively to $\Psi$ and $\Phi$ electromagnon modes selected using parallel (\(//\)) and crossed (\(\perp\)) polarizations as defined in Fig. 1.

54 degrees with the (010) face (Fig. 1h). It comes from a rhombohedral distorted perovskite structure below a high Curie temperature \((T_c\sim 1100\) K) above which the BFO structure is pseudo-cubic. From a magnetic point of view, BFO exhibits a G-type antiferromagnetic order below the Néel temperature \((T_N\sim 640\) K)\(^{28}\). The magnetic order is subjected to long range modulation associated with a cycloidal spiral with a period length of approximately 62 nm\(^{29}\). The spiral propagation is along [01-1] direction with a spin rotation within (-12-1) plane (Fig. 1a and b).

Raman measurements have been performed using the 647.09 nm (1.9 eV) excitation line from a Ar\(^+\)-Kr\(^+\) mixed gas laser. The Raman scattering spectra were recorded between 7 and 300 K using a triple spectrometer Jobin Yvon T64000 with the high rejection rate in order to measure at the lowest frequencies.

Figure 2 shows the low frequency Raman spectra of BFO single crystal. The incoming and outgoing light polarizations are in the (010) pseudo cubic plane which contains the cycloidal propagation wave vector. Although no phonons are expected under 50 cm\(^{-1}\)\(^{16,21}\) several peaks can be observed. Twelve peaks are detected with the first lying at 7.4$\pm$0.5 cm\(^{-1}\) very closed to the stray-light centered at zero energy and the last one at 59$\pm$0.5 cm\(^{-1}\). By choosing parallel (\(//\)) polarizations (see Fig. 1f) and crossed polarizations (\(\perp\)) in the (010) plane we have successfully selected two distinct sets of peaks. They are respectively denoted $\Psi$ and $\Phi$ and their energy is reported in Fig. 2. A first glance on Fig. 2 reveals that the peak locations of the $\Phi$ modes are equally spaced starting at zero frequency and remarkably correspond to an arithmetical sequence of ratio close to 7.4 cm\(^{-1}\) (the sixth and seventh modes are missing). By contrast the sequence of the $\Psi$ modes is not regularly spaced at low frequencies as it can be seen in Fig. 3 where the $\Phi$ and $\Psi$ modes frequencies are plotted as a function of the $n$ mode index. The $n$ index labels the modes from their lowest to highest energy.

To go further, we have interpreted our Raman spectra based on a recent theoretical work which predicts the possible observation of electromagnons in incommensurate BiFeO\(_3\) spiral magnet by optical spectroscopy\(^{18}\). This approach is based on the effective Ginzburg-Landau free energy which includes the coupling between the spin waves and the electrical polarization. This approach leads to two species of electromagnon excitations which lie in and out of the cycloidal plane, respectively the cyclon and the extra-cyclon modes, with distinctive dispersive energy curves that depend on their coupling to the electrical polarization. Crucially, the two sets of hybridized spin wave modes are expected to be detected by optical spectroscopies at small wavevectors \((k \approx 2\pi/5000\) Å\) such as Raman scattering thanks to the zone folding of the antiferromagnetic (AF) magnons induced by the incommensurability of the spiral magnet. The AF magnon zone folding leads to a very simple expression for the energy level structure of the cyclon mode which remains gapless as expected from the AF ordering. The extra-cyclon energy level structure however, is expected to acquire a gap due to the pinning of the cycloidal plane by the electrical polarization in full agreement with our observation\(^{18}\) (see Fig. 3). The energy levels sequences are respectively given by $E_c(n) = \epsilon_c(q)|n|$ and $E_{exc}(n) = \epsilon_c(q)\sqrt{n^2+1}$. $\epsilon_c(q)$ is the cyclon energy at the wavevector $q$ which is simply related to the AF magnon velocity $v$: $\epsilon_c(q) = \sqrt{q}\epsilon$. In this picture only one adjusting parameter, i.e. the cyclon energy (or equivalently the AF magnon velocity) is needed. It is therefore straightforward to compare our experimental data to the theory by plotting the $\Phi$ and $\Psi$ modes frequencies as a function of the mode index $n$ and fitting the data with respect to the cyclon and extra-cyclon energy levels equations.

The results are shown in Fig. 3. Our experimental data remarkably fit to the equations and we can unambiguously assigned the $\Phi$ sequence to the energy levels of the cyclon modes and the $\Psi$ sequence to the extra cyclon modes. The best agreement is obtained for a cyclon energy $\epsilon_c(q)$ equal to 7.5$\pm$0.2 cm\(^{-1}\). The estimated cyclon energy $\epsilon_c(q)$ calculated by de Sousa et al. is about 10$^{12}$ rad/s equivalent to 5.3 cm\(^{-1}\) and calculated in order to match the susceptibility measured on thin films. This is close to our experimental findings performed in bulk single crystal. The magnon velocity $v$ can be estimated...
FIG. 3: Energy levels of electromagnons. φ (blue squares) and Ψ (red full circles) mode frequencies as a function of the mode index \( n \). The expressions of the energy levels fit well the experimental data with a cyclon energy of \( \epsilon_c(q) = 7.5 \pm 0.2 \text{cm}^{-1} \).

FIG. 4: Magnetic signature of the electromagnons. a, Temperature dependence of the four electromagnon energies \( \Psi_2, \Phi_2, \Phi_4 \) and \( \Psi_4 \) and of one typical optical phonon mode. The decreasing slope of the electromagnon wavenumber presents an anomaly around 140 K. b, Integrated intensity (area under the Raman peaks) of the electromagnon and phonon excitation. The electromagnon intensity exhibits a maximum at 140 K unlike the phonon mode.

using the magnon wavevector \( q = 2\pi/62 \text{ nm} \) which gives a velocity of \( 1.4 \times 10^6 \text{ cm/s} \).

In Fig. 4a, is shown the evolution of the electromagnon energy levels as a function of temperature. The typical variation of an optical phonon is also reported in Fig. 4b. We can clearly see that the temperature dependence of the electromagnon energies reveals an anomaly close to \( T=140 \text{ K} \) whereas the optical phonon energy continuously decreases as a function of temperature. Interestingly the Raman integrated intensities of the electromagnon peaks exhibits a maximum at \( T=140 \text{ K} \) as shown in Fig. 4b, while the integrated intensity of the phonons remains featureless: the integrated intensity of a typical optical phonon is shown in Fig. 4b and slowly decreases as the temperature is raised with no abrupt change at 140 K.

Similar softening has already been observed in the magnon temperature dependence of rare-earth orthoferrites RFeO\(_3\) (R being a rare-earth atom)\(^{22,23}\) and assigned to spin reorientation phase transition of the ordered Fe\(^{3+}\) magnetic moments. At room temperature, the Fe\(^{3+}\) magnetic moments in BiFeO\(_3\) is confined in (-12-1) cycloidal plane (Fig. 1a). Our measurements suggest a small spin reorientation out of this plane.

Our study has revealed two species of electromagnons in BiFeO\(_3\): the cyclon and extra-cyclon. They present two well defined sequences of energy levels at \( k = 0 \): the cyclon sequence remains gapless while the extra-cyclon sequence is gapped by the pinning of the cycloid plane by the electrical polarization. The present experimental findings are made possible by the incommensurability of the spiral magnetic ordering of BFO and open new venues to study electromagnon excitations under magnetic and electric fields via optical probes. We hope they will reveal the intimate relationship between magnetic and ferroelectric magnetic orders in multiferroic materials.

Acknowledgements

The authors would like to thank R. Lobo and Ph. Monod for helpful discussions and for a critical reading of the manuscript.
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