Evidence for Electroactive Excitation of the Spin Cycloid in $TbMnO_3$

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Terahertz electromagnetic excitations in the multiferroic $TbMnO_3$ single crystals are investigated across the magnetic field induced rotation of the magnetic spin cycloid. In addition to the electromagnon along the *a* axis, the detailed polarization analysis of the experimental spectra suggests the existence of an electroactive excitation for *ac* electric fields of the electromagnetic wave along the crystallographic *c* axis. This excitation is possibly the electroactive eigenmode of the spin-cycloid in $TbMnO_3$, which has been predicted within the inverse Dzyaloshinskii-Moriya mechanism of magnetoelectric coupling.

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Multiferroics represent an intriguing class of materials in which magnetism and electricity are strongly coupled. This magnetoelectric coupling leads to a mutual influence of magnetic and electric ordering, which results in a rich new physics and in various possible applications [1–4]. Recently, a new class of multiferroics has attracted enormous interest because the ferroelectric polarization in these systems is induced by a cycloidal ordering of the magnetic moments [5–7]. The magnetic and electric order in these materials are accompanied by coupled spin-lattice vibrations [8] showing strong electric dipole activity and termed electromagnons [9,10]. Initially detected in $GdMnO_3$ and $TbMnO_3$ [11], the electromagnons appear to exist in cycloidal magnetic phases of many different multiferroics [12–19]. In most cases, the distinct structure of these excitations is seen which includes two or more separate modes. For example, in $TbMnO_3$ one can observe at least 3 excitations: two with the energy around $\simeq 2$ meV (10–20 cm^{-1}) and the third one at $\simeq 8$ meV (60 cm^{-1}).

Ferroelectric polarization in spiral magnets has been successfully explained on the basis of the inverse Dzyaloshinskii-Moriya (DM) coupling between the magnetic moments [20–23]. Within this model a spiral spin structure lowers the symmetry of the system leading to an effective magnetoelectric coupling term and an electrical polarization $\mathbf{P}$ in the form $\mathbf{P} \sim \mathbf{e}_{ij} \times (\mathbf{S}_i \times \mathbf{S}_j)$. Here $\mathbf{S}_i$ and $\mathbf{S}_j$ are the neighboring spins and $\mathbf{e}_{ij}$ is the lattice vector connecting them. Consequently, it was reasonable to assume the same mechanism to explain the existence of the electromagnons [24]. In this model the electromagnons are the eigenmodes of the spin cycloid which can be excited by the electric component of the electromagnetic wave [9]. However, after initial success of this explanation a number of experimental results contradicted the predictions of the model. The basic example can be given by $TbMnO_3$ at low temperatures: the DM model predicts that the excitation conditions for the electromagnon should be tied to the magnetic cycloid; i.e., for the *bc*-plane oriented cycloid the electric polarization must be parallel to the *c* axis ($P \parallel c$) and the electromagnons should be excited for *ac* electric fields of the incident electromagnetic wave parallel to the *a* axis ($\tilde{e} \parallel a$). Accordingly, for the *ab*-plane oriented cycloid the polarization $P \parallel a$ and electromagnons for $\tilde{e} \parallel c$ should be observed. This basically corresponds to the interchange of the *a* and *c* axes in the excitation conditions. Although the orientation of the static electric polarization has been confirmed in many experiments [5,25,26], the excitation conditions for the electromagnon contradicted the predictions of the model: the selection rules for the excitations remained the same (i.e., $\tilde{e} \parallel a$) independently of the orientation of the cycloid [11–19]. In order to account for this contradiction, a model based on Heisenberg exchange coupling between spins has been proposed recently [18,27,28]. According to this model, the structural peculiarities of orthorhombic multiferroic manganites lead to the selection rules $\tilde{e} \parallel a$ regardless of the orientation of the spin cycloid.

The Heisenberg exchange model assigns the high energy electromagnons observed between 60 and 80 cm^{-1} to the zone edge magnons [18,27–29], but the nature of the lower energy electromagnons close to 20 cm^{-1} remains uncertain. It seems reasonable to recall the statements of the DM model and to assume that the low-frequency electromagnons are somehow related to the excitations of the spin cycloid observed by inelastic neutron scattering (INS) [30–32] because the characteristic frequencies coincide closely [30,33]. This assumption is supported by a recent observation of the magnetic excitation channel for electromagnons [33] which can be also seen as antiferromagnetic resonances (AFMR) within certain excitation conditions. However, in order to prove this assumption, the predicted excitation conditions for the eigenmodes of the cycloid should be found experimentally. Most specifically, one should expect the excitation conditions along the *c* axis if the spin cycloid is oriented in the *ab* plane. Such excitation conditions were not observed up to now [27,33]. A possible reason for this fact is the weakness of the dielectric contribution of the spin modes within the DM mechanism. In order to resolve this experimental difficulty, $TbMnO_3$ seems to be an ideal candidate, because the magnetic cycloid can be rotated between the ab plane and the bc plane in external magnetic fields. Thus the ultimate experiment must record the c-axis response across the magnetic field induced rotation of the spin cycloid.

In this Letter we have carried out detailed polarization analysis of terahertz excitations in $TbMnO_3$. Special attention has been paid to the selection rules of different excitations upon the rotation of the spin cycloid from bc to ab plane in external magnetic field $B \parallel b$ axis. It was found that a new excitation arises in the high-field phase with excitation conditions $\tilde{e} \parallel c$ and $\tilde{h} \parallel a$, with $\tilde{e}$ and $\tilde{h}$ being the electric and magnetic fields of the incident electromagnetic wave. We argue that this excitation could not be explained by purely magnetic contribution but carries a substantial electric component.

The transmittance experiments at terahertz frequencies ($3\ \mathrm{cm}^{-1} < \nu < 30\ \mathrm{cm}^{-1}$) have been carried out in a Mach-Zehnder interferometer arrangement [34,35] which allows measurements of amplitude and phase shift in a geometry with controlled polarization of radiation. The experiments in external magnetic fields up to 8 T have been performed in a superconducting split-coil magnet with polypropylene windows. Single crystals of $TbMnO_3$ have been grown using the floating-zone method with radiation heating. The samples were characterized using x-ray, magnetic, dielectric, and optical measurements [9,36]. The results of these experiments including the magnetic phase diagram are closely similar to the published results [25].

The paramagnetic phase in $TbMnO_3$ above 40 K is followed by a sinusoidally modulated antiferromagnetic state which transforms below 28 K into the cycloidal spin structure oriented within the bc plane [37,38] (inset in Fig. 1). According to the symmetry analysis [6,22], static electric polarization along the c axis is allowed in the low-temperature phase. In external magnetic fields the spin cycloid rotates from the bc plane towards the ab plane [26,32]. Correspondingly, the electric polarization rotates from the $P \parallel c$ axis to the $P \parallel a$ axis [5,25,26].

Dynamic experiments on $TbMnO_3$ in external magnetic fields reveal that the c-axis properties are indeed sensitive to the orientation of the cycloid. The examples of such changes are shown in Fig. 1 which represents the terahertz properties of $TbMnO_3$ in external magnetic field $B \parallel b$ inducing the rotation from the bc-plane to the ab-plane oriented cycloid. The magnetic field scans in these experiments were made in the geometry with $\tilde{e} \parallel c$ and $\tilde{h} \parallel a$ and at $T = 10$ K. The data are represented as refractive index $n + i\kappa = \sqrt{\varepsilon\mu}$ as both electric and magnetic contributions could be mixed in this experimental geometry. Figure 1 contains already the first hints of the appearance of an additional absorption mode after the rotation from bc-plane to ab-plane spin cycloid as steplike changes in $n + i\kappa$ around $B = 6$ T.

In low external magnetic fields the refractive index only slightly decreases with increasing frequency. This behavior is quite typical for dielectrics with absorption. At the lowest frequency 4.7 cm^{-1} the field dependence of the optical parameters is influenced by a Tb mode around 5 cm^{-1} [33]. This mode is first shifted towards zero frequency in low external magnetic fields and disappears completely above $B = 6$ T. This leads to a substantial decrease of the absorption [$\kappa(4.7\ \mathrm{cm}^{-1})$] and reveals a complicated structure of the refractive index at 4.7 cm^{-1}. The changes observed at 4.7 cm^{-1} can be well understood assuming a suppression of a Lorentzian mode situated between 5 and 6 cm^{-1}.

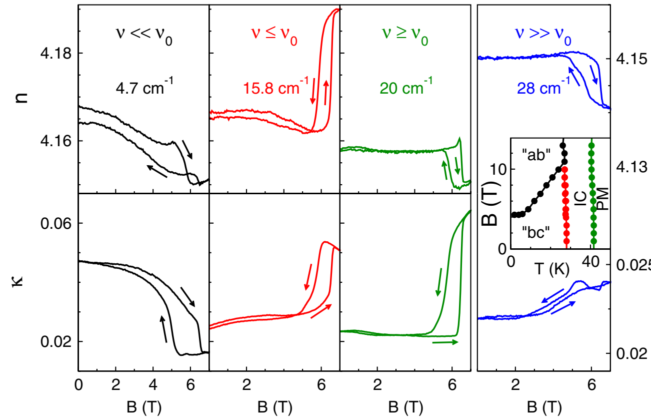

FIG. 1 (color online). Dependence of refractive index [$n = \mathrm{Re}(\sqrt{\varepsilon\mu})$, upper panels] and absorption coefficient [$\kappa = \mathrm{Im}(\sqrt{\varepsilon\mu})$, lower panels] in $TbMnO_3$ on magnetic field $B \parallel b$ axis on field induced rotation from the bc- to the ab-oriented magnetic cycloid. Polarization of incident wave is $\tilde{e} \parallel c$, $\tilde{h} \parallel a$, where $\tilde{e}$ and $\tilde{h}$ are electric and magnetic ac fields of the electromagnetic wave. Note different vertical scales of the right frames (28 cm^{-1}). The inset shows B-T phase diagram of $TbMnO_3$ for $B \parallel b$ [25]. "ab" and "bc" denote ab-plane and bc-plane oriented cycloids, respectively, PM—paramagnetic and IC—sinusoidal phases.

Three higher frequency scans (15.8, 20, and 28 cm^{-1}) in Fig. 1 reveal a systematic frequency dependence. In the low field phase with the bc cycloid the absorption is rather small and is roughly frequency independent. After the rotation to the ab spin cycloid above 6 T the absorption is the strongest at $\nu = 20\ \mathrm{cm}^{-1}$, which indicates the appearance of a new mode close to this frequency. Here especially the high-field values of $\kappa(28\ \mathrm{cm}^{-1})$ are substantially smaller indicating that this frequency is far above the resonance of the new mode. The changes in optical parameters at 28 cm^{-1} are quite small and could be only seen due to different vertical scales in the right frames. The behavior of the refractive index between 15.8 cm^{-1} and 28 cm^{-1} is consistent with the appearance of a new mode in the high-field phase. Indeed, assuming the growth of a Lorentzian close to 20 cm^{-1}, one would expect the increase of the refractive index at 15.8 cm^{-1} and a decrease for $\nu \geq 20\ \mathrm{cm}^{-1}$ in agreement with the observed results. However, a better understanding of the underlying processes can be obtained within a direct analysis of the spectra in the relevant frequency range as presented below.

Figure 2 shows the field dependent spectra for two different geometries of the experiment. The thicknesses of the samples are similar for both orientations: 1.24 mm (upper panel) and 1.33 mm (lower panel), respectively. The spectra in the lower panel with $\tilde{e} \parallel c$ and $\tilde{h} \parallel a$ correspond well to the known results [27,33] and show a mode at about 21 cm^{-1} which appears after the field induced reorientation of spin cycloid to the ab plane. Based on the weakness of this mode, both in Ref. [27] and in Ref. [33] it has been concluded that the mode around 21 cm^{-1} is of purely magnetic origin and represents an antiferromagnetic resonance of the magnetic cycloid for $\tilde{h} \parallel a$ axis. Indeed, the strength of this mode ($\Delta\varepsilon \sim 0.05$, assuming electric origin) is extremely weak compared to the electromagnon observed for $\tilde{e} \parallel a$ ($\Delta\varepsilon \sim 2$) [9,11]. The mode in Fig. 2 is observed for the ab-plane cycloid and within $\tilde{h} \parallel a$ excitation conditions. Tracing this mode back into the bc-oriented cycloid in zero external fields, it can be expected to originate from the excitation conditions $\tilde{h} \parallel c$. (This corresponds to the interchanging of the a and c axis). Indeed, an AFMR mode excited for $\tilde{h} \parallel c$ of the similar strength has been observed around 21 cm^{-1} in the phase with the bc-plane cycloid [33].

A careful comparison of both panels in Fig. 2 reveals interesting differences between two excitation conditions. The strength of the mode in the geometry where $\tilde{e} \parallel b$ is roughly the half of that where $\tilde{e} \parallel c$. This strongly suggests that for geometry in which $\tilde{e} \parallel c$ the electric dipole contribution is indeed measurable and represents the previously unobserved $\tilde{e} \parallel c$ counterpart of the electromagnon. These results agree well with the original explanation of the electromagnons as electrically active eigenmodes of the cycloidal structure [9,24].

In order to make the discussion quantitative, the experimental spectra in the upper panel of Fig. 2 were fitted with magnetic Lorentz oscillators. If we now take the parameters of the mode from the geometry with $\tilde{e} \parallel b$ and plot the expected transmittance spectra for the geometry $\tilde{e} \parallel c$ we obtain the absorption value which is too weak compared to the experiment (the "μ only" curve in the lower panel of Fig. 2). The only possible explanation is that this mode has distinct nonzero electric contribution along the c axis. The actual fit for this geometry was obtained by taking parameters of the magnetic oscillator from $\tilde{e} \parallel b$, $\tilde{h} \parallel a$ geometry and adding an electric oscillator with the same resonance frequency $\nu_0 = 20.7\ \mathrm{cm}^{-1}$ and line width $\gamma = 4.9\ \mathrm{cm}^{-1}$ as the magnetic one. The reasoning behind this assumption is that both contributions are electric and magnetic parts of the same eigenmode of the spin cycloid. The strengths of both components is given by $\Delta\mu = 0.0038$ and $\Delta\varepsilon = 0.05$, respectively.

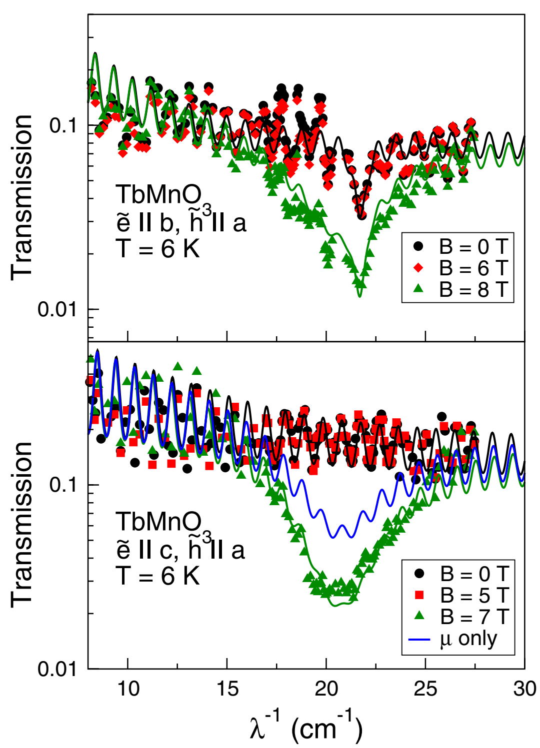

FIG. 2 (color online). Transmittance spectra of $TbMnO_3$ in external magnetic fields $B \parallel b$ for different experimental geometries. Symbols are experimental data and solid lines are fits with Lorentz oscillators as discussed in the text.

Figure 3 shows the linear absorption coefficients $\alpha = 4\pi\kappa\lambda^{-1}$ which allow direct comparison of different experimental geometries. Symbols were calculated from transmittance spectra T using the expression $T = (1-R)^2 \exp(-\alpha d)$, where $R = |(\sqrt{\varepsilon\mu}-1)/(\sqrt{\varepsilon\mu}+1)|^2$ is the reflectance on the boundary between the air and the sample, and d is the sample thickness. Solid lines are model calculations using the same parameters as in Fig. 2. One can see again that the mode at 21 cm^{-1} is stronger in the case of $\tilde{e} \parallel c$ and $\tilde{h} \parallel a$ excitation. (A weak narrow mode seen close to 22 cm^{-1} for $\tilde{e} \parallel b$, $\tilde{h} \parallel a$ geometry is possibly due to impurities in the sample. Including this mode in the fit lead to the model curve shown by the blue dashed line. The strength of this mode is at least an order of magnitude smaller than the strength of the broad mode and does not change the overall picture.)

The mode intensity for the "main" $\tilde{e} \parallel a$ electromagnon ($\Delta\varepsilon_a \simeq 2$ [11]) is about 40 times stronger than the electric contribution along the c axis ($\Delta\varepsilon_c \simeq 0.05$) observed in the present experiment. The large electromagnon absorption along the a axis was one of the challenging questions in explaining its origin. The relatively weak static electric polarization does not fit well with the large dielectric absorption of the electromagnon if both are caused by Dzyaloshinskii-Moriya interactions [27]. On the contrary, the Heisenberg exchange mechanism [18,27,28] seems to explain well the intensities of at least the high-frequency electromagnons above 50 cm^{-1}. In this model the edge-zone magnon couples to alternating orthorhombic distortions at oxygen sites via symmetric Heisenberg exchange interaction. This leads to the coupling of the zone edge magnon to homogeneous electric fields along the a axis. As

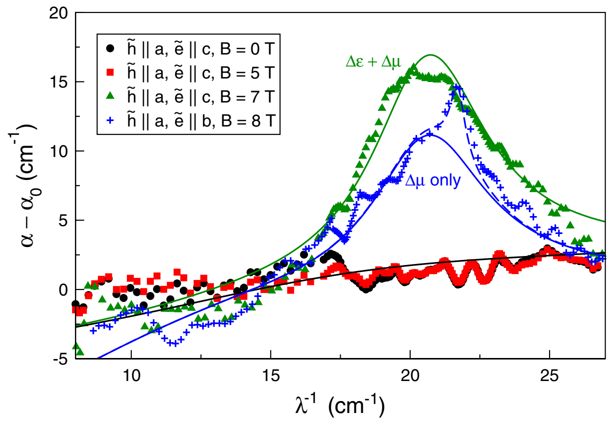

FIG. 3 (color online). Linear absorption coefficient $\alpha = 4\pi\kappa\lambda^{-1}$ in $TbMnO_3$ for different polarizations showing the emergence of an additional mode in the phase with the *ab* cycloid (green triangles and blue crosses). Symbols are experimental data calculated from transmittance spectra as described in the text. Solid lines are model calculations using Lorentz oscillators with the same parameters as in Fig. 2. The dashed line includes the weak impurity mode as described in the text. The data are shifted vertically to eliminate background absorption in different samples.

the symmetric interaction is much stronger than the relativistic DM coupling, the hybridized electromagnon has enough strength to explain the experimental intensities for $\tilde{e} \parallel a$. Much weaker [27] DM components cannot be seen in this experimental geometry because of the dominance of the intensity induced by the Heisenberg exchange coupling. On the contrary, rotating the magnetic cycloid towards the *ab* plane, both contributions can be well separated experimentally. The Heisenberg exchange part remains oriented along the *a* axis, as confirmed by different experimental groups [15,19,27,33]. The weak DM electromagnon rotates with the cycloid and can be clearly observed in the present experiment as an electric contribution along the *c* axis.

One question remains: why do we observe only one mode in the high-field phase? The probable reason is that one of two modes is too weak and is not seen in the spectra. This argument is supported by recent inelastic neutron scattering experiments [32]. In these experiments the modes of the *ab* plane spin cycloid have been investigated. Although this *ab*-plane orientation has been achieved using an external magnetic field along the *a* axis, the comparison to the present results is still very instructive. It has been observed that the excitations of the *ab* cycloid are dominated by a strong mode at 2.25 meV [32]. This frequency corresponds well to the excitation at 21 cm^{-1}, seen in Figs. 2 and 3.

In conclusion, we performed detailed polarization analysis of the electric and magnetic excitations in $TbMnO_3$ in the high-field phase where the spin cycloid rotates from the *bc* to the *ab* plane. The observed excitation at 21 cm^{-1} could not be described by purely magnetic contribution as was suggested previously. We argue that this excitation is the missing electroactive eigenmode of the spin cycloid. The weakness of this mode is in agreement with the Dzyaloshinskii-Moriya contribution to the dynamical magnetoelectric coupling in $TbMnO_3$, which represents a relativistic counterpart to the Heisenberg exchange mechanism.

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