

## Magnetic and Magnetoelectric Excitations in $\text{TbMnO}_3$

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Magnetic and magnetoelectric excitations in the multiferroic  $\text{TbMnO}_3$  have been investigated at terahertz frequencies. Using different experimental geometries we can clearly separate the electroactive excitations (electromagnons) from the magnetoactive modes, i.e., antiferromagnetic resonances. Two antiferromagnetic resonances were found to coincide with electromagnons. This indicates that both excitations belong to the same mode and the electromagnons can be excited by a magnetic ac field as well. In spite of the  $90^\circ$  rotation of the magnetic cycloid in external magnetic fields, the electromagnons are observable for electric ac fields parallel to the  $a$  axis only.

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During recent years, materials with magnetoelectric (ME) coupling have attracted much interest especially due to their intriguing physical mechanisms and their potential for applications [1–5]. ME coupling is especially strong in multiferroics, i.e., materials which are simultaneously ferroelectric and ferromagnetic. The strength of ME effects in multiferroics is due to direct coupling of the magnetic and electric order parameters and partly due to the improper character of the ferroelectricity. This coupling allows, for example, switching of electric polarization in the sample in external magnetic fields [6,7]. One promising class of multiferroics is represented by frustrated magnets [3] in which magnetoelectricity is induced by complex spin arrangements like cycloidal or spiral antiferromagnetic structures.

Given the observation of the static magnetoelectric effects in susceptibilities and polarizations, the existence of dynamic effects can be expected from first principles. Indeed, strong magnetoelectric modes have been observed in multiferroic manganites  $\text{TbMnO}_3$  and  $\text{GdMnO}_3$  and termed electromagnons [8]. The electromagnons have been detected in the infrared spectra of  $\text{YMn}_2\text{O}_5$ ,  $\text{TbMn}_2\text{O}_5$  [9],  $(\text{Eu:Y})\text{MnO}_3$  [10,11], and  $\text{DyMnO}_3$  [12] using similar experimental techniques. Soft magnon modes observed in the inelastic neutron scattering data of  $\text{TbMnO}_3$  have been attributed to electromagnons as well [13,14]. Based on available experimental data and on existing theoretical models, electromagnons can be defined as spin modes which become excited by an electric field due to ME coupling [8,15]. The large spectral weight of the electromagnons distinguishes them [15] from seigneto-magnons in ME compounds, as predicted about 40 years ago by Baryachtar and Chupis [16,17].

In spite of the enormous progress in the field of ME effects the underlying microscopic mechanisms still remain under debate. In order to explain spin driven ferroelectricity and dynamical properties of frustrated magnets various

approaches like phenomenological analysis [18,19], Brillouin-zone folding [20], spin current model [21,22], inverse Dzyaloshinskii-Moriya (DM) interaction [23], and direct Heisenberg exchange [24,25] have been suggested. Recently it has been suspected that some of the excitations detected in far infrared and terahertz (THz) spectroscopy might be due to two-magnon scattering processes [12,26,27].

Among magnetoelectric manganites,  $\text{TbMnO}_3$  is probably one of the most intensively studied using spectroscopic techniques. In addition to results from dielectric [6,28] and optical [8,26] spectroscopies, the magnetic structure of this material is well known from neutron scattering [29–31] and x-ray [32,33] experiments. In addition, inelastic neutron scattering data are available for  $\text{TbMnO}_3$  [13,14,34] which allow us to compare characteristic frequencies of spin excitations and of electromagnons. At  $T_N = 42$  K  $\text{TbMnO}_3$  orders antiferromagnetically with the magnetic moments of manganese ions aligned along the  $b$  axis with an incommensurate sinusoidal modulation [29–31]. Upon cooling a second transition into a cycloidal (spiral) phase occurs at  $T_C = 28$  K with a slightly different modulation vector [31]. This low temperature phase is ferroelectric with spontaneous polarization parallel to the  $c$  axis [6]. Finally, a phase transition at about 9 K is attributed to the magnetic ordering of the Tb sublattice.

In this Letter we present investigations of magnetic and magnetoelectric excitations in  $\text{TbMnO}_3$  for different experimental geometries. The coincidence of the characteristic frequencies for pairs of these excitations indicates that electromagnons can be excited by magnetic ac field as well. Finally we prove that the  $c$  axis in  $\text{TbMnO}_3$  remains electrically silent independent of the orientation of the magnetic cycloid.

Single crystals of  $\text{TbMnO}_3$  have been grown using the floating-zone method with radiation heating. Samples characterization using x-ray, magnetic, and dielectric mea-

measurements showed an agreement with the published results [28]. The transmittance experiments at terahertz frequencies ( $3 \text{ cm}^{-1} < \nu < 40 \text{ cm}^{-1}$ ) were carried out in a Mach-Zehnder interferometer arrangement [35,36] which allows measurements of electrodynamic properties in a geometry with controlled polarization of the radiation.

Figure 1 shows three examples of the experimental transmittance of  $\text{TbMnO}_3$  for different geometries. The upper and middle panel of Fig. 1 have been obtained in geometries where magnetically excited modes are observed. We assign these modes to antiferromagnetic resonances in  $\text{TbMnO}_3$ . Because of the comparative weakness of these modes, the transmittance is not far from unity even close to the resonance and the Fabry-Pérot oscillations on the sample surfaces are clearly seen. On the contrary, the excitation observed in the lower panel of Fig. 1 reveals much stronger absorption, which is partly close to the sensitivity limit of our spectrometer. As has been discussed previously [8,15], these modes are excited by the electric field and are termed electromagnons.

As demonstrated in the lower panel of Fig. 1 the electromagnon mode splits into two excitations, which is most clearly seen in the spectra at the temperatures below 4 K.

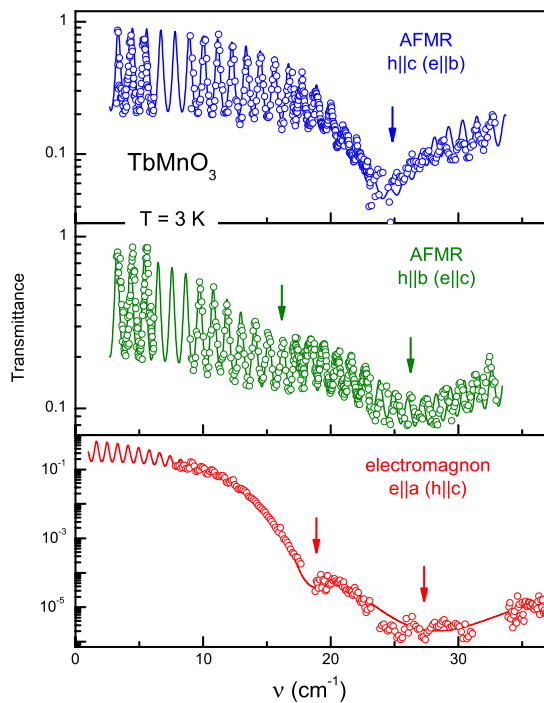


FIG. 1 (color online). Examples of terahertz transmittance spectra of  $\text{TbMnO}_3$  for different experimental geometries. Upper and middle panels: antiferromagnetic resonance modes with excitation conditions  $\tilde{h} \parallel c$  and  $\tilde{h} \parallel b$ , respectively. Lower panel: transmittance for a geometry  $\tilde{e} \parallel a$  with electromagnons at 18 and  $26 \text{ cm}^{-1}$ . Much lower transmittance in this case is due to stronger intensity of electromagnons compared with AFMR. Symbols: experiment; lines: fits using Lorentzian line shape. Specific geometry of each transmittance experiment is given in parentheses.

Using direct analysis of the transmittance spectra in combination with the temperature scans, the second weaker electromagnon at  $18 \text{ cm}^{-1}$  can be followed up to  $T = 20 \text{ K}$ , i.e., deep into the cycloidal phase. This allowed us to compare the terahertz data with the results by inelastic neutron scattering (INS) [13,14] where two magnon modes have been observed in the cycloidal phase.

The frequencies of various excitations in  $\text{TbMnO}_3$  are summarized in Fig. 2. In this figure two observed electromagnons are indicated by solid circles and squares. In the spin spiral phase the electromagnon energies correspond to the excitation energies of well-defined quasiparticles. In the collinear sinusoidal phase the electromagnons are seen as broad over damped modes [15]. The energies as plotted for  $T > 27 \text{ K}$  correspond to the line width of these modes indicating that the damping strongly increases towards the transitions into the paramagnetic phase.

The frequencies of the observed antiferromagnetic resonances in  $\text{TbMnO}_3$  are plotted in Fig. 2 as open symbols. A total of four such magnetic modes have been observed in the frequency range of our experiment. Remarkably, both antiferromagnetic resonances (AFMR) and electromagnons can still be observed in the paramagnetic phase. This effect has been previously observed for other multiferroics [15] and should probably be attributed to magnetic fluctuations.

One important result in Fig. 2 is the close coincidence of two AFMR modes with electromagnons. In analogy to electromagnons, these two modes are indicated by open circles (high frequency mode, excited by  $\tilde{h} \parallel b$  and  $\tilde{h} \parallel c$ ) and open squares (low frequency mode, excited by  $\tilde{h} \parallel b$ ).

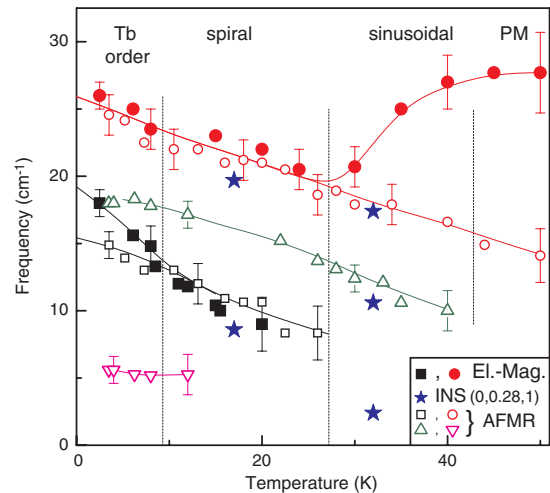


FIG. 2 (color online). Temperature dependence of the mode frequencies of various excitations in  $\text{TbMnO}_3$ . Solid symbols: electromagnons which are observed for  $\tilde{e} \parallel a$  only. In the sinusoidal phase ( $T > 27 \text{ K}$ ) the electromagnons frequencies are not well defined and the positions of the maxima in  $\epsilon_2$  are plotted. Stars indicate the results from inelastic neutron scattering experiments [13,14]. Open symbols: antiferromagnetic resonances with the following excitation conditions: circles  $\tilde{h} \parallel b$  and  $\tilde{h} \parallel c$ , squares  $\tilde{h} \parallel b$ , triangles  $\tilde{h} \parallel a$ . Lines are a guide to the eye.

Another AFMR mode at intermediate frequencies which is given by open triangles can be attributed to the phason mode of the magnetic  $bc$  cycloid. This agrees with the excitations conditions  $\tilde{h} \parallel a$  for this mode. The remaining magnetic mode around  $5 \text{ cm}^{-1}$  can be excited for  $\tilde{h} \parallel a$ . Based on the fact that this mode is observed mainly in the Tb-ordered phase, we attribute this mode to the excitation of the ordered Tb moments.

In Fig. 2 the modes seen with INS technique [13,14] are indicated by stars. Rough coincidence of both excitations suggests that both spectroscopic techniques probe the same mode. We recall, however, that the INS frequencies have been obtained at nonzero wave vector with  $k_0 \approx 0.28$ . On the contrary, in the optical spectroscopy the relevant wave vector equals to the wave vector of the photon and is always close to zero. Therefore, this region of the magnon branch cannot be excited directly and further mechanisms should play a role. In the present case the apparent wave-vector contradiction is resolved due to static modulation of the magnetic structure with the same wave vector  $k_m = k_0 \approx 0.28$ . In the presence of a periodic modulation the umklapp processes with  $k_m$  become allowed and the momentum conservation during the absorption of a photon with  $k_{ph} \approx 0$  can be fulfilled:  $k_{ph} = k_m - k_0 \approx 0$ .

The electromagnons have been classified as inhomogeneous spin modes which become electrically active due to ME coupling [15]. Because of magnetic origin of these modes it can be also expected that the same modes will be excited by magnetic ac field as well. This explains the observed coincidence of two electromagnons with the AFMR modes. Our preliminary theoretical analysis of the spin oscillations in the  $bc$  cycloidal phase shows the existence of spin modes of two different types. First, one expects the existence of the modes which can be excited both by magnetic field  $\tilde{h} \parallel b, c$  axes and by electric field  $\tilde{e} \parallel a$  axis. In the simple model without magnetic anisotropy within the  $bc$  plane, these modes are twice degenerated and in the real system correspond to the observed pair of high and low frequency magneto- and electroactive modes (Fig. 2). Second, one phason mode is expected for the oscillations of the antiferromagnetic vector within the  $bc$  plane. Without  $bc$ -plane anisotropy the frequency of this mode is zero (Goldstone mode). The phason mode corresponds to the AFMR with excitation condition  $\tilde{h} \parallel a$  which is similar to the  $F$  mode [36] in a canted antiferromagnet.

We discuss now the behavior of the electromagnons in  $\text{TbMnO}_3$  in external magnetic fields parallel to the crystallographic  $a$  and  $b$  axes. These results are represented in Fig. 3. Slight deviation of the shape of the modes from that published previously [8,15] is basically due to weak sample dependence of the spectra. We recall that according to the previous experiments, the external fields along the  $c$  axis suppress the electromagnons [8] and induce a canted antiferromagnetic structure [28,32]. External magnetic field along the  $a$  and  $b$  axes leads to the rotation of the magnetic cycloid from the  $bc$  plane to the  $ac$  plane.

Applying magnetic fields  $\mu_0 H > 5 \text{ T}$  along the  $b$  axis allows for complete rotation of the cycloid plane. Along the  $a$  axis only a tilting of the cycloid can be achieved using our magnet. In both cases and already for fields above  $\approx 2 \text{ T}$  substantial changes in the spectral structure of the electromagnons can be observed. For  $\mu_0 H \parallel a$  instead of initially two electromagnons we observe four new modes in the spectra. We attribute the appearance of these modes to the change of the excitation conditions of the magnetic cycloid due to tilting. For magnetic fields along the  $b$  axis and in low fields a redistribution of the spectral weight of electromagnons is seen. After the transition to the  $ab$  cycloid an additional mode appears at  $22 \text{ cm}^{-1}$ . Qualitatively similar complexity of the magnetic modes has been observed recently in neutron scattering experiments [34] and complicated excitation conditions have been determined. However, in our case all observed modes retain the excitation condition  $\tilde{e} \parallel a$ .

From the simple arguments the rotation of the magnetic cycloid from  $bc$  plane to the  $ac$  plane should simultaneously switch the excitation conditions for the electromagnons from  $\tilde{e} \parallel a$  to  $\tilde{e} \parallel c$ . In order to check this prediction, a series of transmittance experiments for ac-electric fields along the  $c$  axis has been carried out. Typical result of these experiments is shown in Fig. 4. The data are given in the representation  $n + i\kappa = \sqrt{\epsilon\mu}$  because electric and magnetic contributions are mixed in these experimental geometry. However, the main result can be stated already at this point: All changes detected along the  $c$  axis as function of magnetic field are extremely weak and electromagnons are not observed along the  $c$  axis. Indeed the measured changes in the refractive index at the magnetic

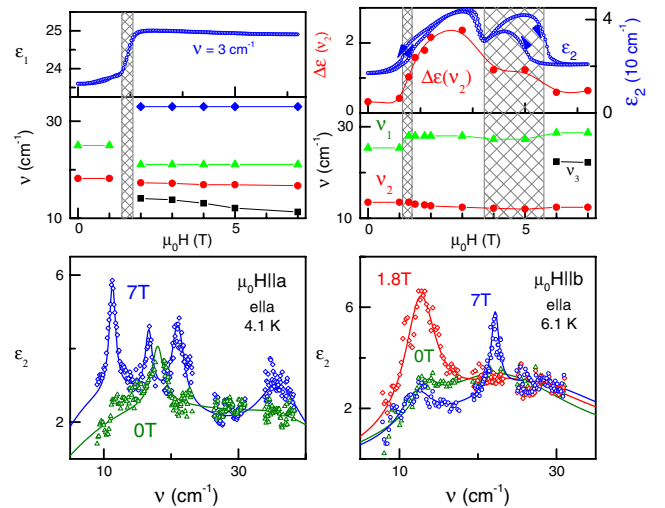


FIG. 3 (color online). Behavior of the electromagnons in  $\text{TbMnO}_3$  in external magnetic fields. Left panels:  $\mu_0 H \parallel a$ ; right panels:  $\mu_0 H \parallel b$ . Lower panels: examples of the absorption spectra. Lines are fits using Lorentzian line shape. Upper panels: field dependence of the mode frequencies and of the dielectric constant.  $\Delta\epsilon$  represents the dielectric contribution of the  $\nu_2$  mode. Lines are guides to the eye.



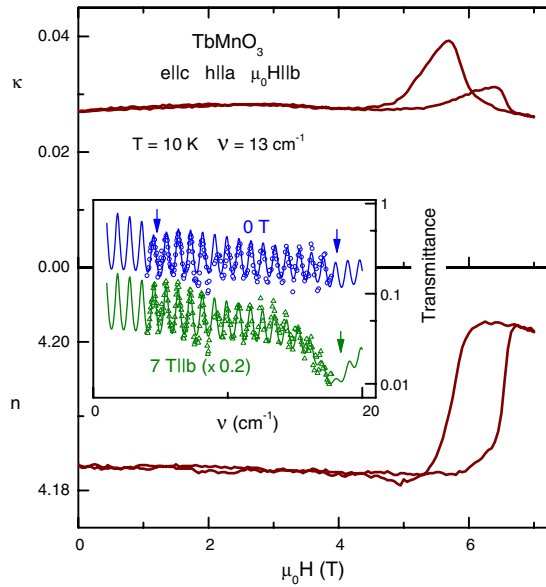


FIG. 4 (color online). Magnetic field dependence of the refractive index in  $\text{TbMnO}_3$  along the  $c$  axis demonstrating the absence of the electromagnons in  $c$  direction. Close to  $\mu_0 H = 6$  T the magnetic  $bc$  cycloid is switched to the  $ab$  cycloid. According to the simple arguments, the electromagnon contribution would be expected to rotate from  $a$  axis to the  $c$  axis (see text). The inset shows examples of transmittance spectra. Here the spectra for  $\mu_0 H = 7$  T have been shifted for clarity.

transition amount roughly 0.5%. This value should be compared with the dielectric strength of the electromagnons along the  $a$  axis which reaches  $\approx 5\%$ . However, even the observed small changes along the  $c$  axis are not due to magnetoelectric contribution but due to shifts of the AFMR frequencies, i.e., are of purely magnetic origin. The changes in the refractive index, shown in Fig. 4, can be well explained using increased intensity of the AFMR mode at  $\sim 18 \text{ cm}^{-1}$ , which is excited by  $\tilde{h} \parallel a$  in this experimental geometry (Fig. 1 and inset in Fig. 4). This result is challenging for the interpretation of the electromagnons as spin excitations of spiral structures. In addition to the above-mentioned two-magnon scenario an explanation on the basis of the DM coupling has been suggested recently [37]. Within this model structural peculiarities of perovskite manganites are responsible for exclusive  $\tilde{e} \parallel a$  excitation conditions for the electromagnons.

In conclusion, we have carried out terahertz experiments in multiferroic  $\text{TbMnO}_3$  in order to study magnetic and magnetoelectric excitations in this compound. Using different experimental geometries it was possible to separate magnetoelectric excitations (electromagnons) from antiferromagnetic resonances. The frequencies of two AFMR modes coincide with the electromagnon frequencies. This indicates that both excitations correspond to the same mode of the magnetic cycloid and the magnetoelectric excitations can be excited via magnetic as well as via electric fields. No electromagnon contribution can be de-

tected along the  $c$  axis even after the induced rotation of the magnetic cycloid from  $bc$  to  $ab$  plane. This clearly contradicts simple explanation of the electromagnons based on the magnetic cycloid.

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