Dynamic investigations of multiferroics: terahertz and beyond

D Talbayev1, A D LaForge2, N Hur3, T Kimura4, S A Trugman1, A V Balatsky1, D N Basov2, A J Taylor1, R D Averitt5

1 Center for Integrated Nanotechnologies, MS K771, Los Alamos National Laboratory, Los Alamos, NM 87545, USA
2 Department of Physics University of California San Diego, 9500 Gilman Drive, La Jolla, CA 92093, USA
3 Department of Physics, Inha University, Incheon 402-751, Korea
4 Division of Materials Physics, Graduate School of Engineering Science, Osaka University Toyonaka, Osaka 560-8531, Japan
5 Department of Physics, Boston University, 590 Commonwealth Avenue, Boston, MA 02215, USA

E-mail: raveritt@physics.bu.edu or diyar@lanl.gov

Abstract. We overview our recent studies of the electrodynamic response of multiferroic compounds. We report results of magnetic dynamics in multiferroic hexagonal manganite HoMnO3 by far-infrared spectroscopy in a magnetic field. Our results provide insight into the ferromagnetic nature of the rare-earth/Mn exchange that enables the electric-field control of magnetism in HoMnO3. In the multiferroic Ba0.6Sr1.4Zn2Fe12O22 we have observed a magnetic resonance using time domain pump-probe reflectance spectroscopy revealing the importance of the dynamic magnetoelectric effect which is a modulation of the dielectric tensor by magnetization precession. Our results highlight that magneto-electric dynamics manifest from the far-infrared through the visible and that both time-integrated and time-resolved spectroscopy are important tools in elucidating the microscopic properties of multiferroics.

1. Introduction

In magnetoelectric (ME) materials, or multiferroics, it is possible to modify the magnetization with an applied electric field or vice versa [1-4]. Recent experiments have demonstrated magnetic switching of electric polarization and switching of magnetization by an electric field, thereby opening remarkable opportunities in spintronics and magnetic recording [5-8]. The dynamical properties of multiferroics are determined by magnetic and lattice vibrations and by the hybridization between them [9], which can result in electric-dipole active magnons [10,11] as observed in far-infrared studies. The role of superexchange in multiferroics is also important and mediates ME coupling in multiferroics.

To date, very few multiferroics have been extensively investigated using optical spectroscopy. There are however, important results which indicate the utility of optical techniques to further our understanding of magnetoelectric phenomena. This includes nonlinear optical imaging studies of MF where the unique selection rules enabled the unambiguous identification of coupled antiferromagnetic and ferroelectric domains [12], the observation of electromagnons (i.e. electric dipole generation of spin waves) using far-infrared spectroscopy [10], and the observation of novel magneto-dielectric responses at optical frequencies [13].
In the following, we present the results of our recent studies in the far-infrared and visible in \text{HoMnO}_3 \text{ and } \text{Ba}_{0.6}\text{Sr}_{1.4}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}. Our results provide insight into the ferromagnetic nature of the rare-earth/Mn exchange that enables the electric-field control of magnetism in \text{HoMnO}_3. In the multiferroic \text{Ba}_{0.6}\text{Sr}_{1.4}\text{Zn}_2\text{Fe}_{12}\text{O}_{22} we have observed a magnetic resonance using time domain pump-probe reflectance spectroscopy revealing the importance of the dynamic magnetoelectric effect which is a modulation of the material dielectric tensor by magnetization precession that can be observed even in non-Kerr experimental configurations.

2. THz response of HoMnO$_3$

\text{HoMnO}_3 (HMO) crystallizes in a hexagonal lattice, space group P6$_3$cm. The crystal structure consists of layers of corner-sharing trigonal MnO$_5$ bipyramids separated by layers of Ho$^{3+}$ ions. Ferroelectricity sets in at T$_{FE} = 875$ K with the polarization along the hexagonal c axis and results from electrostatic and size effects that lead to the buckling of MnO$_5$ bipyramids and the displacement of the Ho$^{3+}$ ions out of the a-b plane. The magnetic structure of HMO is formed by Mn$^{3+}$ ions in a two-dimensional triangular network in the a-b plane coupled by antiferromagnetic (AF) exchange and also by Ho$^{3+}$ ions. The AF exchange between Mn$^{3+}$ magnetic moments leads to their 120° ordering at T$_N = 72$ K, and easy plane anisotropy confines the Mn spins to the a-b plane. Two in-plane spin reorientation transitions occur at temperatures T$_{SR1} \sim 38$ K and T$_{SR2} \sim 5$ K. The spin reorientation at T$_{SR2}$ is accompanied by antiferromagnetic ordering of the Ho$^{3+}$ ions. Several manifestations of ME coupling in HMO have been documented, one of the most prominent being the presence of the reentrant phase with a strong magnetodielectric response [7,14-17].

The HMO single crystals were grown using an optical floating zone furnace and characterized by static magnetization, electric polarization and dielectric constant measurements [18]. Polarized far-IR transmission of a 0.4 mm thick, (110) oriented crystal was measured as a function of temperature and applied magnetic field using a Bruker 66 Fourier-transform spectrometer coupled to an 8 Tesla split-coil superconducting magnet [19]. Static magnetic field B was applied both parallel and perpendicular to the c axis.

![Fig 1: Transmission spectra of HoMnO$_3$ with polarized far-IR light incident along the [110] direction at T=10 K. Arrows indicate magnetic absorption lines. The dotted line illustrates the simulation of the transmission spectrum with magnetic resonances that are centered at 27.5, 43.5, and 52.1 cm$^{-1}$.](image-url)

Figure 1 shows far-IR transmission spectra of the HMO crystal at low temperatures and zero magnetic field for two polarizations of the light incident along the [110] direction - the magnetic h-field of the lightwave parallel (h||c) and perpendicular (h⊥c) to the c axis. The spectra in Fig. 1 are normalized to the transmission through an empty aperture of the same size as the sample. The fringes with the period of $\sim 3$cm$^{-1}$ are due to multiple reflections of light within the sample. The transmission
minima indicated by arrows correspond to magnetic resonance frequencies. The broad absorption in both polarizations at frequencies above 70 cm\(^{-1}\) is of non-magnetic origin, as it exhibits no magnetic field dependence. The dotted line in Fig. 1 shows the simulated transmission, assuming that the magnetic and dielectric response of HMO consists of a collection of Lorentzian oscillators. This analysis shows that there are three magnetic resonances centered at 27.5, 43.5, and 52.1 cm\(^{-1}\).

This is further verified by magnetic field dependent studies in Figure 2. Color-coded transmission maps illustrate the magnetic field dependence of the resonance frequencies at T=10 K. To create the maps, we recorded the transmission spectra in 1 T steps between 0 and 8 T. The darker color in Fig. 2 indicates lower transmission and the white color indicates where the transmission is the highest; the symbols specify the positions of magnetic resonances extracted from the numerical simulation of the far-IR transmission.

We have performed a detailed analysis of the magnetic field dependence of the spectra, but in the following we focus on the 43 cm\(^{-1}\) mode. The sharp absorption line at 43.4 cm\(^{-1}\) in the (h \(\perp\) c) polarization to the antiferromagnetic resonance (AFMR) of the triangular lattice of Mn magnetic moments (transition 2 in Figs. 1, 2). This assignment is supported by the observation of the triangular AFMR at the same frequency (~43 cm\(^{-1}\)) and light polarization in hexagonal YMnO\(_3\) [20], a related compound with the same Mn magnetic structure and similar exchange and anisotropy parameters [21]. The AFMR corresponds to the gapped k = 0 magnon detected by inelastic neutron scattering at 47 cm\(^{-1}\) in HMO [22]. The similarity between the k = 0 magnon frequency and the position of the AFMR in our data further supports the assignment of the resonance.

A quantitative analysis of the magnetic field dependence indicates that the magnitude of the splitting in the B||c and cannot be understood unless we include exchange effects between the Ho ions and the Mn ions (this is not an important effect in YMnO\(_3\) as the Y ions are nonmagnetic) [23]. This ferromagnetic Ho-Mn exchange causes the electric-field induced ferromagnetic ordering of Ho magnetic moments along the c axis reported by Lottermoser et al [7]. The Ho-Mn interaction may also be responsible for the multitude of low-temperature (T< 8 K) magnetic phases and the two Mn spin reorientation transitions in HMO [22]. We believe that the rare earth-Mn interaction plays a significant role in all aspects of the physics of multiferroic hexagonal manganites. Our measurement of the
ferromagnetic HM exchange provides an important contribution to the modeling of the interplay between magnetism and ferroelectricity in hexagonal manganites with magnetic rare earth ions.

3. Coherent magnons in Ba$_{2-x}$Sr$_x$Zn$_2$Fe$_{12}$O$_{22}$ (BSZFO)

Ba$_{2-x}$Sr$_x$Zn$_2$Fe$_{12}$O$_{22}$ is a compound with a large ME response [24]. Single crystals of BSZFO with $x=1.4$ were grown from Na$_2$O-Fe$_2$O$_3$ flux following Momozawa et al [25]. BSZFO crystallizes in a hexagonal structure and shows magnetic ordering below $T_N=325$ K. The magnetic ground state exhibits a helimagnetic structure with the propagation vector along the c axis [24,26,27]. A magnetic field applied perpendicular to the c axis induces a series of magnetic phases ranging from a slightly modified helimagnet to a collinear ferromagnet [26,27]. BSZFO exhibits magnetic-field-induced electric polarization switching that is compatible with the variation of magnetic structures [24].

The setup for ultrafast measurements uses a 250-kHz repetition rate Ti:sapphire regenerative amplifier producing 6-$\mu$J, 80-fs pulses at 800 nm. The amplifier output is converted to 400-nm pump pulses by second harmonic generation. The pump fluence is in the 100–500 $\mu$J/cm$^2$ range. The onset of electronic absorption in BSZFO is around 600 nm as determined by room temperature ellipsometry. This dictates the choice of the pump wavelength, since the negligible absorption at long wavelengths prevents the detection of pump-induced reflectance changes. The BSZFO sample is mounted on the cold finger of a helium-flow cryostat in the center of a split-coil superconducting magnet.

Figure 3 shows the pump-probe reflectance spectra at 10 K, well below $T_N$. In zero magnetic field, the spectrum consists of a ~10-ps rise followed by a slowly-decaying plateau attributed to the initial electronic transfer between the 3d states of neighboring Fe ion [28] and the subsequent thermalization of electronic, lattice, and spin systems. Upon application of a field of 0.1 T, a distinct oscillatory response appears. Further increase of the field leads to an increase in the oscillation period. At 2.5 T, in the collinear ferrimagnetic phase, the oscillatory response disappears. We experimentally rule out coherent acoustic phonons because the oscillation frequency does not depend on the probe wavelength (not shown), and further, acoustic attenuation experiments are not consistent with strong variation of the coherent response in Figure 3. The observed response originates from the excitation of coherent magnons. The measured reflectivity oscillation results from the modulation of the refractive index $n$ by the motion of Fe spins. The dynamic modulation of $n$ by the precessing magnetization is similar to the modulation of $n$ by a static magnetic field found in several complex materials [13].

Precession is triggered when the sublattice equilibrium position is modified through picosecond heating of the crystalline lattice from energy relaxation of an initial optically excited electron distribution. This results in a rapid modification of the exchange coupling between sublattices...
resulting in coherent magnon generation. We detect the precessing magnetic moment as an oscillation of the reflectance. This sharply contrasts with conventional detection schemes that employ Kerr or Faraday rotation [29,30]. The modulation of the reflectance results from a strong ME response, i.e., the dependence of the dielectric constant $\varepsilon(\lambda)$ at optical wavelengths on the magnetic state that is modified by the precessing magnetization. This cross coupling between a magnetic precession mode and an electronic excitation is a manifestation of the ME coupling, a dynamic ME effect [31].

Acknowledgements: We would like to thank Darryl Smith for illuminating theoretical discussions and Jonathan Gigax for the numerical simulation of the Ho crystal field eigenstates. We would like to thank Elbert Chia for his help with reflectivity measurements and Andrew Dattelbaum for his assistance with ellipsometry measurements. We also thank Izabela Stroe, Jonathan Betts, and Albert Migliori for their assistance with resonant ultrasound measurements. The work at Los Alamos National Laboratory was supported by the LDRD program and the Center for Integrated Nanotechnologies.

References
[1] Fiebig M 2005 J. Phys. D 38 R123
[2] Eerenstein W, Mathur N D and Scott J F, 2006 Nature 442 759
[3] Cheong S-W and Mostovoy M 2007 Nature Mater. 6 13
[4] Ramesh R and Spaldin N 2007 Nature Mater. 6, 21
[5] Kimura T et al. 2003 Nature 426 55
[6] Hur N et al. 2004 Nature 429 392
[7] Lottermoser T et al. 2004 Nature 430 541
[8] Zavaliche F et al. 2005 Nano Lett. 5 1793
[9] Katsura H et al. 2007 Phys. Rev. Lett. 98 027203
[10] Pimenov A et al. 2006 Nature Phys. 2 97
[11] Sushkov A B et al. 2007 Phys. Rev. Lett. 98 027202
[12] Fiebig M et al., 2002 Nature 419 818
[13] Rai R C et al. 2006 Phys. Rev. B 74 235101; Rai R C et al. 2006 Phys. Rev. B 73 075112
[14] Lottermoser T and Fiebig M 2004 Phys. Rev. B 70 220407
[15] Lorenz B et al. 2004 Phys. Rev. Lett. 92 87204
[16] dela Cruz C et al. 2005 Phys. Rev. B 71 60407
[17] Yen F et al. 2005 Phys. Rev. B 71 180407
[18] Hur N et al. 2008 cond-mat:0805.3289
[19] Padilla W J et al. 2004 Rev. Sci. Instr. 75 4710
[20] Penney T Berger P and Kritiyakirana K 1969 J. Appl. Phys. 40 1234
[21] Sato T et al., 2003 Phys. Rev. B 68 14432
[22] Vajk O P et al. 2005 Phys. Rev. Lett. 94 87601
[23] Talbayev D et al. Phys. Rev. Lett. in press
[24] Kimura T et al. 2005 Phys. Rev. Lett. 94 137201
[25] Momozawa N et al. 1987 J. Cryst. Growth 83 403
[26] Momozawa N et al. 1985 J. Phys. Soc. Jpn. 54 771
[27] Momozawa N and Yamaguchi Y 1993 J. Phys. Soc. Jpn. 62 1292
[28] Kni'zek K Nova'k P and Kupferling M 2006 Phys. Rev. B 73 153103
[29] van Kampen M et al. 2002 Phys. Rev. Lett. 88 227201
[30] Kimel A V et al. 2007 J. Phys. Condens. Matter 19 043201
[31] Talbayev D et al. 2008 Phys. Rev. Lett. 101 097603