

Probing multiferroicity and spin-spin interactions via angular dependent dielectric measurements on Y-doped HoMnO₃ in high magnetic fields

R. Vasic,^{a)} H. D. Zhou, J. S. Brooks, and C. R. Wiebe

Department of Physics, Florida State University, Tallahassee, Florida 32310 and National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32310

(Presented on 10 January 2007; received 31 October 2006; accepted 27 November 2006; published online 26 April 2007)

Dielectric measurements are used to characterize magnetic phase transitions in the doped ferroelectric oxides Ho_{1-x}Y_xMnO₃ ($x=0.4$). The focus of this experiment is on the effects of the magnetic field direction on the reentrant T - B - θ phase diagram below the Néel temperature. The Ho sublattice plays a major role in all magnetic phase transitions for Y doping ($x=0.4$), consistent with previous results ($x=0,0.6,0.8$). Two successive Mn spin rotations in the ab plane in the antiferromagnetic state are driven by the interaction with the Ho subsystem, although the Ho ordering peak in data is not pronounced. The dielectric response is a very sensitive probe for fine analysis of all aspects of spin-spin interactions in diluted Ho_{1-x}Y_xMnO₃. The magnetic field anisotropy study is an important step towards the understanding of magnetic and electric phase competition in the diluted $4f$ system by the nonmagnetic yttrium (Y) ion. © 2007 American Institute of Physics. [DOI: 10.1063/1.2710066]

I. INTRODUCTION

Multiferroics is one of the most challenging areas of frustrated spin systems in the transition metal oxides due to the coupling of ferroelectric, magnetic, and dielectric mechanisms. The starting point for understanding the rare earth (Ho) hexagonal compounds is YMnO₃, which has a ferroelectric transition at $T_C=900$ K.¹ At 70 K there is antiferromagnetic ordering in the ab plane due to the relief of highly frustrated Mn–Mn spin interactions via lattice distortions.² A more complex system is HoMnO₃, where the nonmagnetic Y³⁺ ions³ have been substituted by magnetic Ho³⁺. The ferroelectric transition temperature ($T_C=875$ K) is not significantly different, but there are other zero-field magnetic phase transitions at lower temperatures.³ The Mn³⁺ spins in the ab plane of hexagonal HoMnO₃ order antiferromagnetically at 76 K. Following the antiferromagnetic ordering of the Mn sublattice is a spin reorientation transition at around 40 K (T_{SR}). The magnetic symmetry is changing from $P6_3cm$ to $P6_3cm$, which is associated with forming a small magnetic moment at Ho site.^{4–8} The Ho sublattice orders completely at 5 K, where a second Mn spin reorientation takes place.⁹ The recent measurements of the magnetic structure have revealed that at T_N , the Mn spins are in a noncollinear 120° antiferromagnetic structure in each ab plane. At T_{SR} there is a 90° spin rotation accompanied by a partial ordering of Ho moments along the c direction. Finally, at T_{Ho} , there is a second spin rotation of Mn spins in the basal plane, with a complete antiferromagnetic ordering of the Ho moments.^{4,10} The emphasis of our study on diluted system Ho_{1-x}Y_xMnO₃ ($x=0.4$) is on the anisotropic properties of magnetic field induced phases.

II. EXPERIMENT

Dielectric measurements are a convenient method for characterization of multiferroics comparable to the susceptibility, heat capacity, and lattice constant studies. In this report we use angular dependent dielectric measurements to probe multiferroicity in doped transition metal oxides Ho_{1-x}Y_xMnO₃ ($x=0.4$) (Fig. 1). Single crystals of doped HoMnO₃ were grown by a traveling-solvent-floating zone (TSFZ) technique.¹¹ Samples were prepared, oriented, and polished for dielectric measurements with parallel plate silver electrodes normal to the c direction. A standard ac capacitance bridge method was employed at 1 kHz, where the rms electric field amplitude applied between plates in the c direction was 100 V/cm. The real (capacitive, C) and loss (dissipative, D) signals were measured at 1 kHz versus temperature in a low field superconducting magnet at the National High Magnetic Field Laboratory. A single axis rotator was used to measure the anisotropy of the dielectric response to the magnetic field direction. The samples were fixed on a copper holder of the rotation stage to avoid errors in temperature reading and movement in high magnetic fields.

III. RESULTS

Dielectric measurements have been previously used to map out the reentrant temperature–magnetic field phase transitions which involve in-plane Mn spin rotations in the antiferromagnetic state of HoMnO₃ below the Néel temperature.^{4,9} More recently, we have studied the magnetic field dependent phase diagram of the ferroelectric alloy materials Ho_{1-x}Y_xMnO₃ for $x=0, 0.6$, and 0.8 for fields directed along both the ab in-plane and c -axis basal plane directions.¹² The purpose of the present work has been to extend these studies to include angular dependent dielectric measurements on Ho_{1-x}Y_xMnO₃ (where $x=0.4$ in the present work).

^{a)}Electronic mail: vasic@magnet.fsu.edu

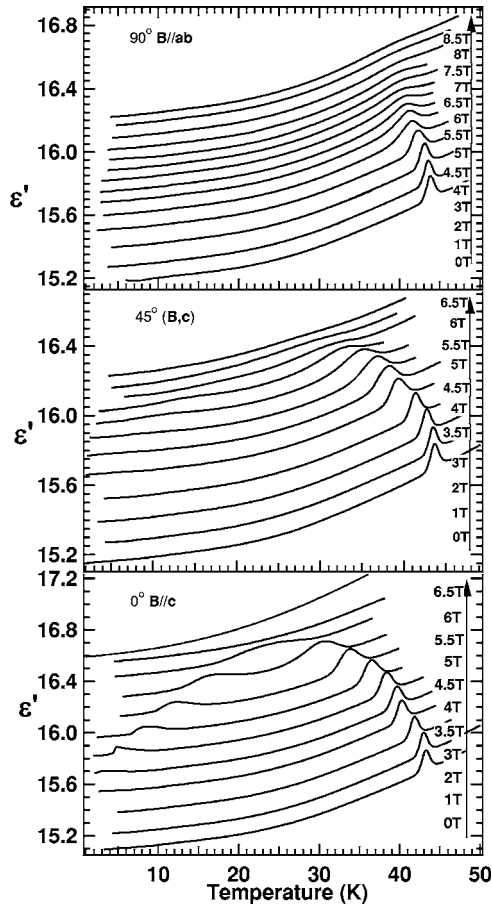


FIG. 1. Temperature dependence of the real part of dielectric constant for $\text{Ho}_{1-x}\text{Y}_x\text{MnO}_3$ ($x=0.4$) for different magnetic fields. For $B > 0$, the curves are offset for clarity. The upper and lower reentrant transitions are evident in the increase (peaks) in the dielectric response at the phase boundaries. (The angles between magnetic field and c axis are 0° , 45° , and 90° ; 0° is for $c \parallel B$; and 90° is for $c \perp B$.)

In our previous alloy study we showed that the Ho sublattice plays a major role in all transitions, and that the phase diagram for $\text{Ho}_{1-x}\text{Y}_x\text{MnO}_3$ ($x=0, 0.6, 0.8$) is dependent on magnetic field direction.¹² This behavior is a consequence of the interaction of the Ho sublattice spin system with the YMnO_3 antiferromagnetic triangular lattice. In the present work, we find (see Figs. 1–3) that the reentrant phase boundaries increase in both temperature and field with the increase of the angle θ (where $\theta=0^\circ$ refers to $B \parallel c$, and 90° refers to $B \parallel ab$). In Fig. 1 the temperature dependent dielectric response for different magnetic fields is presented for $\theta=0^\circ$, 45° , and 90° . The anisotropic effects are further illustrated in Fig. 2 for constant magnetic field: 5, 5.5, and 6 T, versus field direction for $\theta=0^\circ$, 10° , 20° , 30° , 45° , and 90° . In Fig. 3 the angular dependent phase diagrams are plotted, where, for clarity, we plot only the peak positions corresponding to the reentrant phase transitions. The anisotropic effects are weak up to 3 T for all orientations of magnetic field. The holmium ordering peak (T_{Ho}) is not pronounced for doping $x=0.4$ (yttrium). These data show agreement with the results of other authors for HoMnO_3 ($B \parallel c$).¹³ The slope dT_{SR}/dB (Fig. 3) is significantly less at higher angles and the spin reorientation (T_{SR}) occurs at higher fields. The lower transition (T_{SR}) is very pronounced up to 30° , while for 45° it is

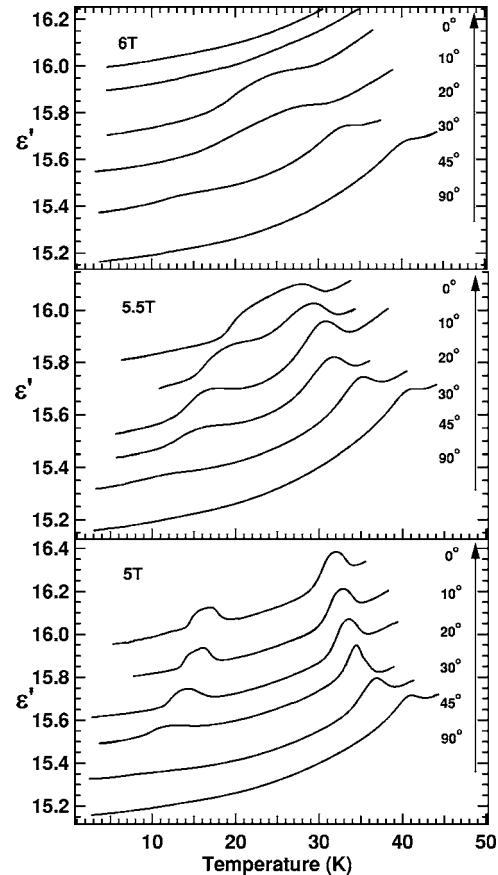


FIG. 2. Temperature dependence of the real part of dielectric constant for $\text{Ho}_{1-x}\text{Y}_x\text{MnO}_3$ ($x=0.4$) for different angles between magnetic field and c axis. For angles $< 90^\circ$ ($c \perp B$), the curves are offset for clarity. (Constant magnetic fields are 5, 5.5, and 6 T.)

weaker and expands the phase region of lower symmetry ($P6_3cm$). The reentrant phase boundary is gone for higher angles where we show, for clarity, just 90° ($B \parallel ab$ basal plane). The reentrant phase boundaries merge for 6 and 5.5 T (Fig. 2), but for 5 T, there are two distinct anomalies for all measured angles except 90° . We found that the ab component increases the transition at higher temperature (T_{SR}) and decreases the transition at lower temperature (T_{SR}), expanding the $P6_3cm$ phase region (Fig. 3). The reentry behavior emerges in the range of angles around 45° for diluted system $\text{Ho}_{1-x}\text{Y}_x\text{MnO}_3$ ($x=0.4$).

It is also important to notice that transition widths show dependence on the direction of the magnetic field, and for smaller angles, widths are smaller and peaks are more pronounced.

IV. DISCUSSION

Here we report our major findings for $\text{Ho}_{1-x}\text{Y}_x\text{MnO}_3$ ($x=0.4$): (1) in-plane magnetic field suppresses the second spin rotation transition in diluted system; (2) for increasing angle (larger than 30°), T_{SR} transition approaches T_N and the $P6_3cm$ phase expands in temperature and magnetic field range. At zero field, the lower T_{SR} is suppressed by larger dilution (with Y).¹² The angular effects are significant starting from 3 T, simultaneous with the increase of the component of the magnetic field in the ab basal plane ($B \perp c$). In order to suppress ordering, the maximum magnetic field in

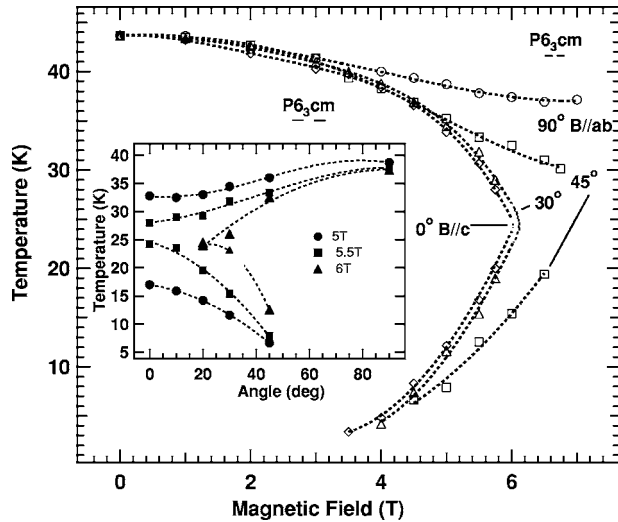


FIG. 3. Magnetic field-temperature phase diagrams for $\text{Ho}_{1-x}\text{Y}_x\text{MnO}_3$ ($x=0.4$) as a function of magnetic field and field direction. The open symbols represent temperature sweeps. All data are from temperature sweeps, and only the dielectric peak locations are indicated (phase boundaries are approximate because peaks represent intermediate phase between high symmetric $P6_3cm$ and lower symmetric $P6_3cm$). Open circles, 90° ; open squares, 45° ; open triangles, 30° ; and open rhomboids, 0° ; the angles are between the direction of magnetic field and c axis. (Dashed lines are guides for the eyes.) The intermediate phase boundary widths corresponding to the dielectric constant peak maxima are not indicated because of the small angular dependence up to 3 T. [Inset: angular-temperature phase diagrams for $\text{Ho}_{1-x}\text{Y}_x\text{MnO}_3$ ($x=0.4$) as a function of the angle between the direction of magnetic field and c axis. Temperature-magnetic field anisotropy is plotted at constant magnetic fields: solid circles, 5 T; solid squares, 5.5 T; and stars, 6 T.]

the c direction (0°) is 6 T, much larger than for pure HoMnO_3 (4 T).¹² The symmetry of Mn spin configuration is lower ($P6_3$) as the spins rotate from one configuration to the other.⁵ As we reported recently, the reduced holmium concentration increases the magnetic field, where the $P6_3cm$ configuration returns to the higher symmetry configuration $P6_3cm$.¹²

The magnetic field interaction with the holmium sublattice, coupled to the Mn spin system, drives the transitions. The Mn spins in the ab basal plane are highly frustrated, and the focus of this study was to identify subtle changes in dielectric anomalies due to the change of the ratio between in-plane ($B\parallel ab$) and the interplane field component ($B\parallel c$). A simple argument, confirmed in data trends, indicates that Ho ordering along the c direction is affected by magnetic field in the ab plane. Furthermore, the magnetic field component in the ab plane at some field induces antiferromagnetic polarization effects, i.e., spin flip, which suppresses reentrant behavior.

The reentrant magnetic phase appears in the range of angles around 45° in the case of $x=0.4$. For the magnetic field direction in this range, the low and high temperature phases (T_{SR}) merge. In the case of $\text{Ho}_{1-x}\text{Y}_x\text{MnO}_3$ ($x=4$), there is no signature of holmium ordering in dielectric data up to the magnetic fields of 9 T and down to a temperature of 2 K. The anisotropic effects are stronger in higher Y doping ($x=0.7$, to be published) and the sensitivity of angular data is higher. We suggest magnetic field anisotropic studies by other methods that can confirm our findings. The peak

quality represents degree of dilution and ordering, so we can see, for an angle of 45° , that there is a tendency for merging of two reentrant peaks. For larger angles, the $P6_3cm$ phase is expanded compared to the central symmetry ($P6_3cm$), which dominates in the case of zero angle. In brief, the angular measurements are efficient tool for probing holmium ordering on a subtle scale of meV.

V. SUMMARY

Due to the angular dependence of dielectric constant, we show a variety of subtle modifications in magnetic phase transitions in diluted $4f$ holmium magnetism by doping with nonmagnetic Y ion. Our angular dependent dielectric data from a superconducting magnet (0–9 T) reveal particular interactions in the hexagonal system between Ho–Y, Ho–Mn, and Y–Mn systems in the ab plane and c direction. From symmetry arguments, we generalize the effects of higher doping, angle, or magnetic field which expand the region of the $P6_3cm$ phase. In brief, relative effects should be analyzed in diluted system with focus on the highly sensitive anisotropic response of the system to the magnetic field. Our goal is to continue with dielectric studies of transition metal multiferroics via doping and angular dependent studies at high magnetic fields. For higher dilution, $x=0.5$ and more, the phase diagrams are still not closed in the range of 0–9 T.

ACKNOWLEDGMENTS

This research was sponsored by the National Nuclear Security Administration under the Stewardship Science Academic Alliances program through DOE Research Grant No DE-FG03-03NA00066 (E.J.) and NSF Grant Nos. DMR0203532 and DMR0602859 (J.S.B.). The NHMFL is supported by the contractual agreement between the National Science Foundation through NSF Grant No. DMR0449569 and the State of Florida.

- ¹F. Bertaut, P. Fang, and P. Forrat, C. R. Hebd. Seances Acad. Sci. **256**, 1958 (1963).
- ²Z. J. Huang, Y. Cao, Y. Y. Sun, Y. Y. Xue, and C. W. Chu, Phys. Rev. B **56**, 2623 (1997).
- ³P. Coeur, P. Guinet, J. C. Peuzin, G. Buisson, and E. F. Bertaut, in *Proceedings of the International Meeting on Ferroelectricity*, edited by V. Dvork, A. Fouskov, and P. Glogar (Institute of Physics of the Czechoslovak Academy of Science, Prague, 1966), Vol. 1, pp. 332–340.
- ⁴O. P. Vajk, M. Kenzelmann, J. W. Lynn, S. B. Kim, and S. W. Cheong, Phys. Rev. Lett. **94**, 087601 (2005).
- ⁵B. Lorenz, F. Yen, M. M. Gospodinov, and C. W. Chu, Phys. Rev. B **71**, 014438 (2005).
- ⁶A. Muoz, J. A. Alonso, M. J. Martinez-Lope, M. T. Casis, J. L. Martinez, and M. T. Fernández-Daz, Chem. Mater. **13**, 1497 (2001).
- ⁷Th. Lonkai, D. Hohlwein, J. Ihringer, and W. Prandl, Appl. Phys. A: Mater. Sci. Process. **74**, 843 (2002).
- ⁸M. Fiebig, D. Fröhlich, K. Kohn, St. Leute, Th. Lottermoser, V. V. Pavlov, and R. V. Pisarev, Phys. Rev. Lett. **84**, 5620 (2000).
- ⁹Th. Lottermoser, Th. Lonkai, U. Amann, D. Hohlwein, J. Ihringer, and M. Fiebig, Nature (London) **430**, 541 (2004).
- ¹⁰See, for example, M. Fiebig, T. Lottermoser, D. Fröhlich, A. V. Goitsev, and R. V. Pisarev, Nature (London) **419**, 818 (2002).
- ¹¹H. D. Zhou, J. C. Denyszyn, and J. B. Goodenough, Phys. Rev. B **72**, 224401 (2005).
- ¹²R. Vasic, H. D. Zhou, E. Jobilong, C. R. Wiebe, and J. S. Brooks, Phys. Rev. B **75**, 014436 (2007).
- ¹³B. Lorenz, A. P. Litvinchuk, M. M. Gospodinov, and C. W. Chu, Phys. Rev. Lett. **92**, 087204 (2004).