Anomaly in Nonlinear Magnetoelectric Response of YbMnO$_3$

U. Adem, M. Mostovoy, N. Bellido, A. A. Nugroho, C. Simon, and T. T. M. Palstra

$^1$Zernike Institute for Advanced Materials, University of Groningen, 9747 AG Groningen, The Netherlands
$^2$Laboratoire CRISMAT, UMR CNRS ENSICAEN, 1450 Caen, France
$^3$Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung, Jl. Ganesha 10, Bandung 40132, Indonesia

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We observe a seemingly complex magnetic field dependence of dielectric constant of hexagonal YbMnO$_3$ near the spin ordering temperature. After rescaling, the data taken at different temperatures and magnetic fields collapse on a single curve describing the sharp anomaly in nonlinear magnetoelectric response at the magnetic transition. We show that this anomaly is a result of the competition between two magnetic phases. The scaling and the shape of the anomaly are explained using the phenomenological Landau description of the competing phases in hexagonal manganites.

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The recent interest in multiferroic materials was triggered by the discovery of the giant magnetocapacitance (MC) and magnetically-induced rotations of electric polarization in orthorhombic rare earth manganites $^{1,2,3}$. This multiferroic behavior is rooted in magnetic frustration, which gives rise to non-centrosymmetric spin orderings that induce electric polarization $^4$. Furthermore, the presence of competing spin states in these frustrated magnets results in a strong sensitivity of the magnetically-induced electric polarization to applied magnetic fields. In this respect multiferroics are similar to colossal magnetoresistance manganites and high-temperature superconductors $^5$.

In this Letter we study effects of critical magnetic fluctuations and the competition between different magnetic states on the non-linear magnetoelectric response of the hexagonal YbMnO$_3$ by measuring the magnetic field and temperature dependence of its dielectric constant. Ferroelectricity in hexagonal manganites $^{7}$ appears well above the magnetic transition and is of nonmagnetic origin: An electric dipole moment along the $c$ axis is spontaneously induced by tilts of manganese-oxygen bipyramids and buckling of rare earth-oxygen planes at $T_C > 600$K $^6$, while the ordering of Mn spins occurs at a much lower temperature $T_N < 120$K. However, the spin ordering in hexagonal manganites results in a surprisingly strong lattice relaxation, which affects the spontaneous electric polarization $^6$.

The Mn ions in hexagonal manganites form well-separated triangular layers parallel to the $ab$ plane and antiferromagnetic exchange interactions between nearest-neighbor spins $^{11}$, which makes the Mn spin subsystem low-dimensional and frustrated and results in enhanced spin fluctuations observed well above $T_N$ $^{12}$. Frustration and rare earth magnetism are responsible for a rich variety of magnetic phases observed at low temperatures and in applied magnetic fields $^{13}$. Due to magnetoelectric coupling each magnetic transition gives rise to a singularity of the dielectric constant $^{6,13,14,15}$, which is more pronounced than the corresponding singularity in magnetic susceptibility.

We find that close to the Néel temperature $T_N=81$K the MC of YbMnO$_3$ measured as a function of magnetic field and temperature obeys a scaling behavior and has a very sharp anomaly. The detailed comparison with results of model calculations led us to a conclusion that the effect of magnetic fluctuations is completely overshadowed by the magnetic field dependence originating from the competition between two antiferromagnetic states, one of which is weakly ferromagnetic. Using a mean field Landau expansion of free energy in powers of two competing order parameters, we reproduce the shape of the anomaly as well as the changes in the behavior of MC observed in the wide range of magnetic fields and temperatures.

Polycrystalline samples of YbMnO$_3$ were prepared by solid state synthesis. A single crystal was grown from this powder by the floating zone technique. Magnetization $M(T)$ of the samples was measured by a Squid magnetometer (MPMS7 Quantum Design) using a field of 0.5T. Field dependence of the magnetization was measured up to 5T. Capacitance of the samples was measured in an commercial system (PPMS Quantum Design) using a home-made insert and an Andeen-Hagerling 2500A capacitance bridge operating at a fixed measurement frequency of 1 kHz as well as using an Agilent 4284A LCR meter up to 1MHz. Electrical contacts were made using Ag epoxy.

The temperature dependence of the capacitance $C(T)$ proportional to the in-plane dielectric constant $\varepsilon_a$ is shown as an inset of Fig. 1a. Below the Néel temperature $T_N = 82$K, the capacitance is somewhat suppressed by the emergence of magnetic order $^{10}$. The MC, $\frac{\Delta C(T)}{C(0)}$, where $H$ is magnetic field along the $c$ axis, for a set of temperatures between 76.5K and 95K is shown in Fig. 1b. In this small temperature interval around $T_N$ the behavior changes dramatically: at 76.5K only a positive curvature is observed. With increasing temperature a high-field downturn appears, and at 80K only a negative curvature can be observed, which changes
back to positive above 90K.

This unusual behavior is a consequence of the fact that by varying temperature and magnetic field we force the system to pass through a magnetic transition. The critical behavior becomes apparent when we plot \( \frac{C(T) - C(0)}{C(0)} \) vs temperature [see Fig. 1(a)]. The procedure to evaluate \( \Delta C \) at fixed magnetic fields versus temperature i.e. replottedting the rescaled changes of dielectric constant in magnetic field versus temperature, effectively reveals the magnetic field dependence of \( C \). The strong temperature dependence of \( C \) masks the magnetic field dependence when \( C(T) \) is measured at fixed magnetic fields. The data taken at various \( T \) and \( H \) remarkably fall onto a single curve with a very sharp anomaly at \( T_N \) where the temperature derivative of \( MC \) becomes large and positive while its magnitude shows an almost discontinuous jump from a positive to a negative value. The observed scaling behavior of \( MC \) can be understood in terms of a different physics. Below we show that the shape and scaling behavior of \( MC \) can be explained within a mean field theory by the competition between antiferromagnetic and weakly ferromagnetic states.

The temperature dependence of capacitance is added as an inset. (b) Temperature dependence of \( MC \) at constant magnetic fields. The inset shows the shift of \( T_N \) in magnetic field obtained from magnetic susceptibility measurements. Electric field is parallel to the \( ab \) plane, while \( H \parallel c \).

**FIG. 2** (Color online) The self-energy diagrams of the first (a) and second (b) order in the coupling constant \( g \), describing contributions of magnetic fluctuations (wavy lines) to dielectric susceptibility.

**FIG. 1** (Color online) (a) Magnetic field dependence of \( MC \) of YbMnO\(_3\) single crystal at constant temperatures near \( T_N \). The temperature dependence of capacitance is added as an inset. (b) Temperature dependence of \( MC \) at constant magnetic fields. The inset shows the shift of \( T_N \) in magnetic field obtained from magnetic susceptibility measurements. Electric field is parallel to the \( ab \) plane, while \( H \parallel c \).

This may result from magnetic fluctuations that become critical close to Néel temperature. The two lowest-order self-energy diagrams describing contributions of magnetic fluctuations to dielectric susceptibility are shown in Fig. 2. The lowest-order term is given by \( \delta \chi^{(1)} = -g\chi_0^2 \langle L^2 \rangle \propto \tau^{-1-\alpha} \), where \( \alpha \) is the exponent describing the critical behavior of magnetic specific heat \( \chi_0^2 \). The corresponding singularity in MC \( \propto g\lambda \sigma_{\text{sign}}(\tau) |\tau|^{-\alpha} \), for \( \tau = \frac{T - T_N}{T_N} < 0 \), which accounts for the observed dielectric constant anomaly below \( T_N \) [see the inset of Fig. 1(a)]. The magnetic field dependence of Néel temperature, \( T_N \approx T_N(0) - \lambda H^2 \), gives rise to a discontinuity of \( MC \) at \( T_N \) and its anomalous behavior below \( T_N \), is roughly consistent with our data. However, the most prominent feature of the observed anomaly – the long negative tail for \( T > T_N \) [see Fig. 1(b)] – cannot be explained in this way.

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lateral $ab$ layers. These phases differ by orientation of the spins with respect to the crystallographic axes and spins in neighboring layers as well as by the ordering of rare earth spins. The magnetic phase diagram of YbMnO$_3$ studied by a variety of different experimental techniques includes the low-field B$_2$ phase (magnetic space group $P_{63}mcm$) and the high-field A$_2$-phase (magnetic space group $P6_{3}cm$). The symmetry of the latter state allows for a net magnetization in the $c$ direction (largely due to the rare earth spins and therefore small near the Mn spin-ordering temperature), which is why the A$_2$ phase is stabilized by $H\parallel c$.

The competition between the A$_2$ and B$_2$ phases was discussed in Ref. [24] using the phenomenological free energy expansion in two order parameters:

$$f = \sum_{\gamma=A,B} \left[ \frac{\alpha_{\gamma}}{2} T - T_{\gamma}^{(0)} - \lambda_{\gamma} H^2 \right] L_{\gamma}^2 + \frac{b_{\gamma} L_{\gamma}}{4}$$

$$+ \frac{d_{\gamma}}{2} L_{\gamma}^2 L_{\gamma}^2 - H \left( \phi_{L_{\gamma}} + \frac{\phi'}{3} L_{\gamma}^3 + \frac{\phi''}{2} L_{\gamma} L_{\gamma}^2 \right)$$  \hspace{1cm} (1)

where $L_A (L_B)$ is the order parameter describing the A$_2$ (B$_2$) phase and $H$ is magnetic field along the $c$ axis. The linear coupling of $L_A$ to $H$ corresponds to the spontaneous magnetization present in the A$_2$ phase.

The typical phase diagram for $T_B^{(0)} > T_A^{(0)}$ (when the $B_2$ phase is energetically more favorable than the $A_2$ phase at zero field) is shown in Fig. 3. Due to the linear coupling between $H$ and $L_A$, the latter order parameter is nonzero for an arbitrarily weak magnetic field, so that for $H \neq 0$ the transition occurs between the $A_2$ phase and the $B_2$ phase with some admixture of the $A_2$ phase.

The MC for this model, shown in Fig. 4(c), is calculated by adding to the free energy Eq. (1) the terms describing the coupling of the magnetic order parameters to the in-plane electric polarization and the dielectric response of the nonmagnetic state,

$$\Delta f = \frac{P^2}{2} \left( \sum_{\gamma=A,B} g_{\gamma} L_{\gamma}^2 + g_{A} L_{A} H \right) + \frac{P^2}{2\chi_0} - PE$$  \hspace{1cm} (2)

has the same shape as the one observed in YbMnO$_3$ and, for weak fields, obeys the observed scaling. This behavior can be understood by noting that the main contribution to the magnetic field dependence of the dielectric susceptibility comes from $L_A$, which is linearly coupled to $H$. This field-induced order parameter grows as $T$ approaches the $T_N$ from above [see Fig. 3(a)], which gives rise to the 'high-temperature' negative MC tail, with $\Delta \chi_e \propto -L_{A}^2$. In the weak-field regime $L_A \propto H$, so that $\Delta \chi_e \propto \chi_e(T,H)\propto \chi_e(T,0)$ is approximately field-independent, which explains the observed scaling.

As the magnetic field increases, the character of the transition in the two-parameter model changes: in low fields the transition is of second order (red dashed line in Fig. 3), while in high fields and low temperatures it becomes a first-order transition (blue line) [see also Figs. 3(a) and (b)]. The first- and second-order transition lines are separated by the critical point. This change in the nature of the transition is also clearly seen in the experiments by comparing the field-dependence of MC at low temperatures [see Fig. 3(a)] to that at high temperatures [see Fig. 1(a)]. At 2K the MC shows a distinct cusp at the first-order transition, which is well reproduced within our model [see Fig. 3(d)]. In YbMnO$_3$ the changes in the order of the transition are made more dramatic by the fact that at low temperatures and high mag-
nonlinear magnetoelectric response, although its shape, Thus many other systems should show an anomaly in 3 shows four competing states \[18\] and for Ni$_3$V$_2$Os \[27\]. Thus many other systems should show an anomaly in nonlinear magnetoelectric response, although its shape, which depends on parameters of the Landau free energy, may vary from material to material.

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