We have investigated the dielectric anomalies associated with spin ordering transitions in the tetragonal spinel Mn$_3$O$_4$ using thermodynamic, magnetic, and dielectric measurements. We find that two of the three magnetic ordering transitions in Mn$_3$O$_4$ lead to decreases in the temperature dependent dielectric constant at zero applied field. Applying a magnetic field to the polycrystalline sample leaves these two dielectric anomalies practically unchanged, but leads to an increase in the dielectric constant at the intermediate spin-ordering transition. We discuss possible origins for this magnetodielectric behavior in terms of spin-phonon coupling. Band structure calculations suggest that in its ferrimagnetic state, Mn$_3$O$_4$ corresponds to a semiconductor with no orbital degeneracy due to strong Jahn-Teller distortion.

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I. INTRODUCTION

Magnetodielectrics can be described as materials in which magnetic ordering produces dielectric anomalies, or alternately, materials in which the low-frequency dielectric constant is sensitive to an external magnetic field. These materials have been studied for several decades, but the recent surge in activity in studying multiferroics has prompted renewed interest in understanding the origins of the spin-charge coupling in these systems. While multiferroics are also magnetodielectric, the converse is frequently not true. Nevertheless, characterizing the shifts in the dielectric constant induced by magnetic ordering offers crucial insights into possible spin-charge coupling mechanisms. Additionally, the recognition that substantial magnetodielectric coupling often arises in systems with non-collinear magnetic structures offers the possibility that dielectric spectroscopy may be a simple yet powerful tool for identifying phase transitions among complex magnetic structures.

Many magnetodielectric systems have been investigated in the past several years, including SeCuO$_3$, EuTiO$_3$, BiMnO$_3$, CoCr$_2$O$_4$, and TmFeO$_3$ in addition to a very large set of studies on magnetocapacitive coupling in multiferroics. Several models have been proposed for explaining the observed dependence of the low-frequency dielectric constant on spin structure and external magnetic field. The simplest of these postulates a dielectric response which varies as the square of the net magnetization. These models fail to account for the large dielectric shifts observed at antiferromagnetic transitions, which can be qualitatively understood by considering a coupling between the dielectric constant and the $q$-dependent spin-spin correlation function. It has recently been recognized that magnetoresistive contributions in inhomogeneous systems can also give rise to magnetocapacitive effects.

In the following, we discuss the synthesis and characterization of the magnetodielectric spinel Mn$_3$O$_4$ whose structure is displayed in figure. This system has been studied previously by Suzuki et al., who found that Mn$_3$O$_4$ displays a sharp drop in the dielectric constant at the ferrimagnetic $T_C = 42$ K. This feature was attributed to the orbital degree of freedom in this system. Since Mn$_3$O$_4$ is known to exhibit several complex low temperature spin states, we conducted more detailed measurements of the dielectric constant at each of the magnetic transitions in order to elucidate how specific spin structures yield different magnetocapacitive couplings. At the onset of long range magnetic order
in Mn$_3$O$_4$ below 42 K, the A-site Mn$^{2+}$ spins order ferromagnetically along [010], while the B-site Mn$^{3+}$ spins order along [001]. Below 39 K these B-site spins order in a spiral structure with an incommensurate propagation vector along [010] and at 33 K these Mn$^{3+}$ ions exhibit a more complex order with the 16 ions in the magnetic unit cell having a net moment antiparallel to the Mn$^{2+}$ spin direction.

II. EXPERIMENTAL AND COMPUTATIONAL DETAILS

Well-sintered, brown pellets of Mn$_3$O$_4$ were prepared from the oxalate MnC$_2$O$_4$·2H$_2$O by decomposing at 650°C for 1 h, pelletizing, and heating to 1200°C for 12 h following which the pellets were rapidly cooled to the room temperature. Rapid cooling was required in order to avoid producing Mn$_2$O$_3$ as an impurity phase. X-ray diffraction patterns were obtained using Cu-Kα radiation on a Philips XPert MPD diffractometer operated at $45$ kV and $40$ mA, and subject to Rietveld refinement using the XND Rietveld code.

The DC magnetization of Mn$_3$O$_4$ was measured on a Quantum Design SQUID magnetometer as a function of temperature and field. We measured the specific heat and AC susceptibility using standard options on a Quantum Design PPMS, which was also used to regulate temperature and magnetic field for dielectric measurements. For specific heat measurements, approximately 30 mg of the powder sample was cold pressed into a solid pellet, which was found to have a small internal thermal time constant. To measure the dielectric properties, we pressed a circular pellet from approximately 50 mg of sample, then fashioned parallel plate electrodes using conducting silver epoxy. The dielectric measurements were done at an excitation frequency of $30$ kHz with a drive of $1$ V. There was no significant frequency or bias dependence to the excitation frequency of $30$ kHz with a drive of $1$ V. There was no significant frequency or bias dependence to the measurements.

The electronic structure of Mn$_3$O$_4$ was calculated using density functional methods. For these calculations, we used the linear muffin tin orbital (LMTO) method within the generalized gradient approximation (GGA), as implemented in the STUTTGART TB-LMTO-ASA program. Starting structures for LMTO calculations were obtained from experimental Rietveld refinements. 262 irreducible k-points were employed within the irreducible part of the Brillouin zone.

III. RESULTS AND DISCUSSION

Mn$_3$O$_4$ is a tetragonally distorted spinel, as illustrated in figure with space group I4$_1$/amd (No. 141). The polycrystalline samples used in this study were monophasic as revealed by X-ray diffraction Rietveld analysis shown in figure. In this structure, Mn$^{2+}$ ions are located at the tetrahedral site at $(0, \frac{1}{4}, \frac{1}{4})$, and Mn$^{3+}$ ions at the octahedral site$(0, \frac{1}{4}, \frac{1}{4})$. O is at the general position $(0, y, z)$. More structural details are provided in the caption of figure. Suzuki et al. have suggested that the $e_g$ orbital at the Mn$^{3+}$ site is partially occupied, leading to an orbital degree of freedom. However, it is known that on cooling Mn$_3$O$_4$ undergoes a transition from a cubic spinel to Jahn-Teller distorted tetragonal structure at 1433 K. As a consequence of this Jahn-Teller structural distortion on Mn$^{3+}$, the electronic structure of tetragonal Mn$_3$O$_4$ as calculated here using density functional theory, and previously using Hartree-Fock theory suggests no orbital degeneracy. The LMTO-GGA density of states calculated for collinear ferrimagnetic Mn$_3$O$_4$, and projected on the different Mn atoms and on O are displayed in the panels of figure. The system is characterized by large exchange splitting: near 4 eV on the tetrahedral A site (occupied by Mn$^{2+}$) and near 3 eV on the octahedral B site (occupied by Mn$^{3+}$). Both sites are completely spin-polarized, with the crystal field configurations as indicated in the caption of the figure. The Jahn-Teller distortion on the octahedral B site manifests clearly in the majority spin channel, which is seen to comprise filled $t_{2g}$ states centered around $-2$ eV, separated from a filled $d_{5z}$ state just below $E = 0$. The empty majority $d_{x^2-y^2}$ states are found centered near 1 eV. The minority Mn $d$ states at the B site are all empty and found starting at 0 eV. The crystal field splitting on the B site is of the order of 4 eV. O $p$ states are found a little below the filled Mn $d$ states.
FIG. 3: Projected LMTO-GGA Densities of state of semiconducting, Néel-ferrimagnetic Mn$_3$O$_4$ plotted in the two spin directions. (a) Tetrahedral $d^3$ Mn$^{3+}$ on the A site showing filled minority $e$ and $t_2$ states, and empty majority $e$ and $t_2$ states. (b) Octahedral Mn$^{3+}$ on the B site with a Jahn-Teller distortion resulting in a gap within filled and empty $d$ states: majority $d_{z^2}$ is separated from majority $d_{x^2-y^2}$. All minority states are empty. (c) The O $p$ states. The origin on the energy axis is the top of the valence band.

which is not surprising given the position of Mn in the middle of the first transition metal series. As would be expected for a fully spin-polarized ferrimagnet, the calculated magnetic moment per Mn$_3$O$_4$ formula unit is precisely 3 $\mu_B$ corresponding to 8 spins from two octahedral Mn$^{3+}$ ions, compensated by 5 spins from the tetrahedral Mn$^{2+}$ ion.

In order to identify the numerous magnetic transitions in Mn$_3$O$_4$ we first measured the specific heat capacity of this sample, both at zero magnetic field and under the application of a field. These results are shown in panel (a) of figure[4]. There are three distinct peaks in heat capacity at $H=0$, corresponding to magnetic phase transitions at roughly $T = 34$ K, $T = 40$ K, and $T = 42$ K. Approximating the lattice background to specific heat as a constant 0.5 J mole$^{-1}$ K$^2$ over the small temperature range of the peak, we find a total spin entropy of approximately 1.2 $k_B$/Mn$_3$O$_4$. This is somewhat smaller than previously reported values but consistent with the suggestion that substantial geometrical frustration reduces the entropy change from the full value expected for complete spin order $\approx 5 k_B$/Mn$_3$O$_4$. These three peaks in Mn$_3$O$_4$ specific heat correspond to the development of complex spin structures investigated previously by neutron diffraction measurements. Applying a magnetic field produces substantial broadening in the 42 K peak, but does not significantly shift the transition.

FIG. 4: (a) Mn$_3$O$_4$ ac susceptibility measured at $\omega/2\pi = 10$ kHz and zero field. (b) Mn$_3$O$_4$ specific heat measured at $H = 0$, $H = 1$ T, and $H = 3$ T. For clarity, the $H = 0$ T and $H = 1$ T data have been offset by 0.2 and 0.1 J mole$^{-1}$ K$^2$ respectively.

We also see distinct features corresponding to these magnetic transitions in Mn$_3$O$_4$ in ac susceptibility measurements. The imaginary component of the complex susceptibility measured at 10 kHz is plotted in panel (b) of figure[4]. The three peaks in the magnetic loss signal correspond to the three magnetic phase transitions observed the specific heat data. There is a substantial increase in the magnetic loss at the onset of long-range magnetic order at 42 K, which remains high through the additional magnetic phase transitions at 40 K and 34 K. Small features are also observed in the real component of the complex magnetization (not shown), but these anomalies are more difficult to discern against the large signal from the 42 K transition. The upper panel of figure[5] plots the zero-field cooled and field cooled temperature dependent DC magnetization under a measuring field of 1000 Oe, and the temperature dependent magnetic hysteresis loops. The transition to long-range order at 42 K is clearly visible, as is a small anomaly at $T = 15$ K in the ZFC curve, but the two additional magnetic phase transitions at $T = 34$ K and $T = 40$ K give no signal. $M(H)$ loops plotted in the lower panel of figure[5] show a net saturation magnetization corresponding to a moment of $\approx 1.5 \mu_B$/formula unit, with significant coercivity developing only at temperatures below 34 K.

The temperature dependent dielectric constant of Mn$_3$O$_4$ close to these magnetic ordering transitions is shown in figure[6](a). At zero applied magnetic field, we
FIG. 5: (a) Zero field cooled (ZFC) and field cooled (FC) magnetization curves for Mn$_3$O$_4$ measured in a field of 1000 Oe. (b) Magnetic hysteresis loops measured at temperatures from $T = 4$ K (far left) to $T = 44$ K (far right).

FIG. 6: (Color online) (a) Temperature dependent dielectric constant of Mn$_3$O$_4$ at $H = 0$ (solid circles) and $H = 5$ kOe (open squares). The broken line is the scaled neutron intensity of the (120) reflection taken from reference 15. (b) Magnetic field dependence of the dielectric constant of Mn$_3$O$_4$ at different temperatures.

FIG. 7: (Color online) (a) Percentage change in Mn$_3$O$_4$ dielectric constant (relative to $H = 0$) as a function of increasing magnetic field at fixed temperatures of 30 K, 25 K, 15 K, and 10 K (upper trace to lower). (b) Solid curve: percentage change in Mn$_3$O$_4$ dielectric constant (relative to the minimum value). Dashed line: square of the net magnetization. Both are measured as a function of increasing magnetic field measured at 15 K. (c) Relative change and net magnetization measured as a function of decreasing magnetic field at 15 K.

see a sharp decrease in the dielectric constant at 42 K, coincident with the onset of long range magnetic order in Mn$_3$O$_4$. The dielectric constant decreases by approximately 0.2%, consistent with the magnitude of the drop observed previously in Mn$_3$O$_4$. In addition to the large drop in dielectric constant at 42 K, we observe a much smaller, but still distinct, negative shift of 0.015% in the dielectric constant at the 34 K magnetic transition. A hint of such behavior is also visible in previous studies on Mn$_3$O$_4$. While both the 42 K and 34 K magnetic transitions in Mn$_3$O$_4$ lead to clear dielectric anomalies at zero field, there is no suggestion of any magnetodielectric coupling associated with the 40 K transition. However, the application of a modest magnetic field substantially alters the dielectric response of Mn$_3$O$_4$. The negative magnetodielectric shifts associated with the 42 K and 34 K transitions remain relatively unchanged, but the 40 K magnetic transition now produces a significant increase in dielectric constant.

In order to probe the effects of an applied magnetic field on the dielectric response of Mn$_3$O$_4$ we measured the dielectric constant at fixed temperature as a function of applied field. These data are plotted in figure 6(b). In the paramagnetic phase, there is a very slight decrease in dielectric constant with magnetic field. Just below the onset of long-range magnetic order, the shift in dielectric constant with applied field remains negative, but with a
change in curvature. However, the development of the spiral magnetic structure below 40 K leads to positive magnetodielectric shifts at low magnetic fields, followed by smaller decreases at higher fields. The increase in dielectric constant saturates at approximately 0.06% in a field of 3 kOe.

We extended our measurements on the magnetic field dependence of the dielectric constant to lower temperatures, below the 34 K transition. As shown in figure IV, Mn$_3$O$_4$ develops magnetic hysteresis at low temperatures, with the coercive field reaching approximately 5 kOe by $T = 10$ K. Figure IV(a) plots the relative shift in dielectric constant as a function of increasing magnetic field, measured at fixed temperatures. At $T = 30$ K, there is a slight asymmetry in the curve; this asymmetry increases substantially as the temperature is reduced. We attribute this asymmetry to magnetic hysteresis in Mn$_3$O$_4$ at lower temperatures. Figures IV(b) and IV(c) plot the change in dielectric constant relative to the minimum value, together with the square of the magnetization at $T = 15$ K, separately for increasing and decreasing magnetic fields. While the relative change in dielectric constant does not simply follow the square of the magnetization, the minimum dielectric constant does occur at (approximately) the coercive field, where $M = 0$. As we will discuss in the following, we believe the dielectric shift in Mn$_3$O$_4$ is not determined by the net magnetization, but rather a more complex spin-spin correlation function for the magnetically ordered phase.

IV. DISCUSSION

While both positive and negative magnetodielectric couplings have been observed previously, it is unusual for both to be present in a single system. As such, Mn$_3$O$_4$ provides an important test system for understanding the mechanisms underlying magnetodielectric effects. Several factors have been suggested to contribute to magnetization-induced changes in dielectric constant, including spin-phonon coupling, electronic structure, and orbital degrees of freedom. Electron-magnon scattering has also been proposed to explain the increase in dielectric constant observed at certain magnetic transitions in multiferroics. In the following, we concentrate mainly on discussing our experimental results in the context of possible spin-phonon coupling.

It has been suggested that spin-structure induced shifts in phonon frequencies can produce changes in the dielectric constant through the Lydanne-Sachs-Teller relation. In this framework, the optic phonon frequencies, hence dielectric constant, are coupled to the spin-spin correlation function for the magnetic structure, so the dielectric constant should vary with the neutron peak intensity. The onset of long range order in Mn$_3$O$_4$, which produces a significant drop in the dielectric constant, is associated with the growth of the (120) neutron peak at 33 K. We have extracted the intensity of the (120) peak from reference and plotted this as a broken line in figure IV after correcting for a small difference in transition temperature. While the drop in dielectric constant in Mn$_3$O$_4$ is somewhat steeper than the increase in neutron intensity, the dielectric shift approximately follows the intensity in the (120) peak and, in particular, both level off below 35 K.

While the qualitative agreement between the (120) neutron intensity and drop in the Mn$_3$O$_4$ dielectric constant below 42 K are consistent with the spin-phonon model for magnetodielectric coupling, the detailed mechanism remains unclear. As a first step in developing a microscopic model it is necessary to identify which specific phonon modes couple to the complex spin structure. The deformation produced by the octahedral Jahn-Teller Mn$^{3+}$ ions gives rise to the tetragonal distortion to $I4_1/amd$ symmetry in Mn$_3$O$_4$. This distortion leads to 10 allowed Raman active modes, $\Gamma = 2A_{1g} + 3B_{1g} + 2B_{2g} + 3E_g$, rather than the 5 modes in cubic spinels with $Fd\bar{3}m$ symmetry. Experimentally, only 5 Raman modes are observed, including a large amplitude $A_{1g}$ mode at 660 cm$^{-1}$ attributed to the motion of oxygen ions inside the MnO$_6$ octahedra and associated with the cooperative Jahn-Teller distortion. Because magnetodielectric coupling is often associated with non-collinear magnetic structures, it is tempting to postulate that the dielectric anomaly in Mn$_3$O$_4$ below 42 K arises because of coupling between the complex spin structure exhibited by the B site Mn$^{3+}$ ions and vibrations of the MnO$_6$ octahedra. However, further temperature dependent Raman studies are needed to look for a shift or increase in intensity of the 660 cm$^{-1}$ peak at the 42 K transition to test this suggestion.

As the (120) neutron scattering intensity varies smoothly below 42 K, some additional spin-phonon coupling must be responsible for the dielectric anomaly observed at 35 K in zero field. Below 40 K, an additional neutron scattering reflection is observed at (1,1,+,0). The propagation vector $q = 1 - \tau$ increases monotonically with decreasing temperature. This peak locks in at $q = 1$ at the 34 K magnetic transition, which also produces a sharp increase in intensity. We suppose that this low temperature magnetic structure also couples to an optic phonon mode in Mn$_3$O$_4$, giving rise to the dielectric shift observed below 34 K. Between 34 K and 40 K, $\tau$ is non-zero and temperature dependent and the magnetic structure is incommensurate with the lattice structure. The spin-phonon coupling coefficient is predicted to vary with the overlap between the $q$-dependent spin structure and phonon mode. The incompatibility between spin and lattice structure could lead to a varying coupling coefficient, which averages to zero and gives no net magnetodielectric coupling. Only when the spin structure locks in at $q = 1$ at 33 K does the spin-phonon coupling constant become non-zero. We point out that incommensurate magnetic structures can lead to very dielectric anomalies associated with transitions into ferroelectrically ordered phases. This is distinctly different
from our observations in Mn$_3$O$_4$, which seem to suggest that incommensurate magnetic structures do not produce sizeable dielectric anomalies.

It is rather more difficult to motivate the positive shift in dielectric constant below 40 K in an applied magnetic field, and positive magnetocapacitance in this temperature range (see figure 6). One possibility is that even a modest magnetic field, below 3 kOe, is sufficient to lock-in some commensurate value for the propagation vector $q$ of the (110) structure, leading to non-zero magnetodielectric coupling. Because the low temperature dielectric constant shows hysteretic effects compatible with the magnetic hysteresis curves shown in figure 5, this (110) spin structure may also be expected to exhibit hysteresis. Alternatively, some additional mechanism for magnetodielectric coupling beyond the spin-phonon model considered here may be relevant. Additional studies of the magnetic field dependence of the Mn$_3$O$_4$ dielectric constant on single crystal samples may be required to clarify the origins of the positive magnetocapacitance observed between 34 K and 40 K at low fields.

In summary, we have investigated the dielectric properties of Mn$_3$O$_4$ in detail and found evidence for magnetodielectric coupling associated with specific magnetic structures. An incommensurate magnetic transition in Mn$_3$O$_4$ produces no dielectric anomaly at zero magnetic field, but applying modest fields produces an increase in dielectric constant at this transition. These magnetodielectric features can be qualitatively understood using a spin-phonon coupling model, although a more detailed understanding of the specific phonons involved in the coupling would be necessary to compare theory and experiment in detail.

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