Magnetodielectric Effects from Spin Fluctuations in Isostructural Ferromagnetic and Antiferromagnetic Systems

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We report on the effects of spin fluctuations, magnetic ordering, and external magnetic field on the dielectric constant of the ferromagnet $SeCuO_3$, and the antiferromagnet $TeCuO_3$. A model based on the coupling between uniform polarization and the q-dependent spin-spin correlation function is presented to explain the different behaviors for these isostructural compounds. The large magnetocapacitance near the transition temperature in the ferromagnet $SeCuO_3$ suggests routes to enhancing the magnetodielectric response for practical applications.

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The behavior of systems with strongly coupled magnetic and electronic degrees of freedom provides both challenges for many-body theory as well as new phenomena for possible applications. One manifestation of such coupling in the itinerant limit is the interplay between ferromagnetism and charge order in the colossal magnetoresistance manganites [1,2]. In the limit of localized charge, effects of strong coupling are more subtle, and manifested chiefly through a magnetocapacitive (MC) response, which can take several different forms [3–5]. After the first experimental realization of magnetoelectric coupling in Cr_2O_3 [6], similar effects have been observed in several other materials including Gd_2CuO_4 [7], $YMnO_3$ [8], $EuTiO_3$ [9], and $BiMnO_3$ [10]. The present strong interest in coupled magnetic dielectric properties is further motivated the search for so-called multiferroic materials — compounds possessing (anti)ferromagnetic, (anti)ferroelastic, and/or (anti)ferroelectric — which have been proposed for use in fabricating next-generation multifunctional devices [11,12].

In this Letter, we compare the magnetodielectric [13] (MD) response in a ferromagnetic insulator and an isostructural antiferromagnet. We investigate the effect of ferromagnetic (FM) and antiferromagnetic (AF) magnetic correlations on the dielectric constant, ε, by measuring the sample capacitance as a function of temperature and magnetic field. There are differences between the FM and AF samples in the temperature and magnetic field dependence of ε both in the paramagnetic and the magnetically ordered regimes. This range of observations is accounted for by developing a model which couples the dielectric response to the q-dependent spin-spin correlations.

The structure of $SeCuO_3$ and $TeCuO_3$ is that of a distorted perovskite with the small Se^{4+} or Te^{4+} ions on the A-cation sites producing a Cu-O-Cu bond angle of $\alpha_{\text{Cu-O}} = 121°$ (structure shown in the inset of Fig. 1) [14]. For $SeCuO_3$, the Cu^{2+} ions undergo a ferromagnetic (FM) phase transition at $T_c = 25$ K, with a saturation magnetization of $0.7\mu_B$ per Cu ion. Both the FM transition as well as the reduced moment have been understood to arise from the dependence of the superexchange interaction on $\alpha_{\text{Cu-O}} = 127.1°$, which for $SeCuO_3$ sits on the FM side of the Goodenough-Kanemori value ($\alpha_{\text{GK}} = 127.5°$). The isomorphic system $TeCuO_3$, on the other hand, exhibits

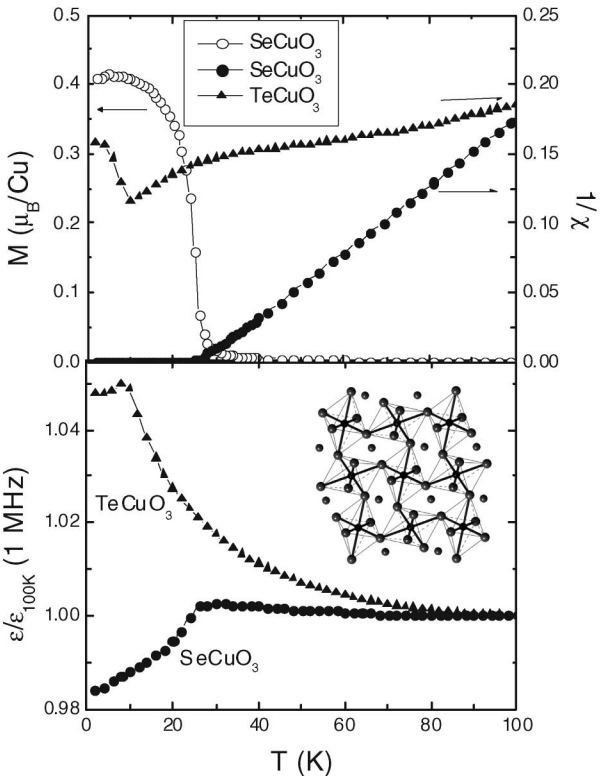

FIG. 1. Magnetization of $SeCuO_3$ and $TeCuO_3$ versus temperature in the 1 kOe field (upper) and dielectric constant of $SeCuO_3$ and of $TeCuO_3$ versus temperature in the zero applied field (lower). The inset shows the structure of $SeCuO_3$.

antiferromagnetism which is reflected in a value for $\alpha_{\text{Cu-O}} = 130.5°$, which sits just on the antiferromagnetic (AF) side of α_{GK} [14]. Both materials are good insulators, and this makes them uniquely well suited to study effects that depend on the sign of the superexchange interaction without complications brought about by differences in other material factors.

The samples used in the study were made by solid state reaction at 700 °C under 60 kbar pressure using high purity SeO_2, TeO_2, and CuO starting materials. The purity of the phases was checked by x-ray powder diffraction and the details were given elsewhere [14]. We measured the magnetization of $SeCuO_3$ and $TeCuO_3$ using a SQUID magnetometer. The inverse magnetization of these samples versus temperature and the magnetization of $SeCuO_3$ at an applied field of 1 kOe are shown as the upper plot in Fig. 1. The $SeCuO_3$ curves show the onset of a sharp ferromagnetic transition at $T_c = 25$ K, while the $TeCuO_3$ sample undergoes antiferromagnetic ordering at $T_N = 9$ K; both are consistent with earlier measurements [14]. We prepared the samples for capacitance measurements by polishing opposite parallel faces and then depositing ~80 nm thick Au layers onto these smooth surfaces to serve as electrodes. Pt wires were attached to the electrodes using silver epoxy. The samples were fixed to a glass plate on the probe using GE varnish to ensure mechanical stability. We measured the capacitance using an Agilent 4284A LCR meter. All dielectric measurements were done at a frequency of 1 MHz with an excitation of 1 V. Lower frequency measurements with different excitation voltages showed qualitatively similar behavior.

The dielectric response of these samples is shown in the lower plot of Fig. 1 as a function of temperature in the absence of an applied magnetic field. $SeCuO_3$ exhibits an almost temperature independent dielectric constant until just above T_c. $TeCuO_3$, on the other hand, shows a pronounced increase in ε as the sample is cooled. Both samples undergo a sharp drop in dielectric constant coincident with the onset of magnetic ordering, at 25 K for $SeCuO_3$ and 9 K for $TeCuO_3$. Qualitatively similar features were observed in both the antiferromagnet $EuTiO_3$, in which the shift is attributed to the softening of an optical phonon mode at the antiferromagnetic ordering transition [9], as well as in the insulating ferromagnet $BiMnO_3$ [10].

We have also investigated the dielectric response in $SeCuO_3$ as a function of temperature at fixed magnetic field (shown in Fig. 2) and in both $SeCuO_3$ and $TeCuO_3$ as a function of magnetic field at fixed temperatures close to the magnetic ordering transition (Fig. 3). These figures also include data on the magnetization of both the FM and AF samples taken under the same conditions as the dielectric measurements to investigate the effects of magnetic correlations on the dielectric constant.

The observations to be understood in Figs. 1–3 are as follows: (i) the temperature independence of ε_0 for both

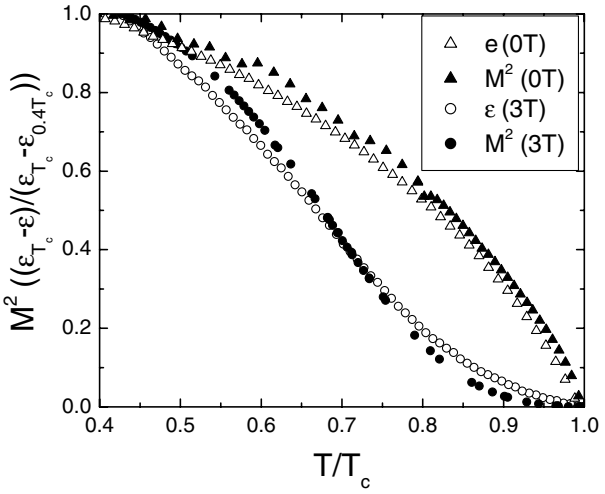

FIG. 2. Comparison of the shift in ε (scaled to the value at $T = 0.4T_c$) to M^2 (scaled in the same way) for $SeCuO_3$ below T_c.

$SeCuO_3$ and $TeCuO_3$ at high temperatures (Fig. 1); (ii) the rise in ε for $TeCuO_3$ (AF) as the temperature is decreased towards to the transition temperature T_N, while for $SeCuO_3$ (FM) ε remains almost constant as the temperature is reduced to T_c (Fig. 1); (iii) the larger drop in ε for $SeCuO_3$ (FM) in the ordered phase compared to that in $TeCuO_3$ (AF) (Figs. 1 and 2); (iv) the sharp magnetic field dependence of ε near the ferromagnetic transition, while for the AF transition the dependence on H is smooth (Fig. 3).

All these observations are explained by a simple phenomenological model for the coupling of the uniform electric polarization P to the magnetization M_q at wave

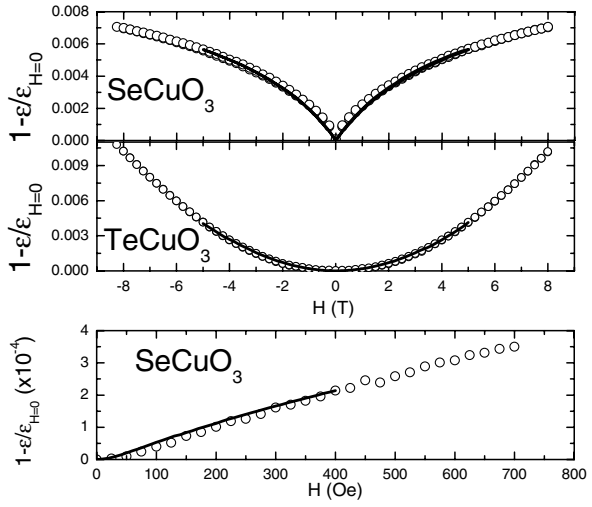

FIG. 3. Suppression of ε as a function of magnetic field at T_c (T_N) in $SeCuO_3$ ($TeCuO_3$). Note that the bottom plot showing $\varepsilon(H)$ for $SeCuO_3$ plots the magnetic field on a different scale than the upper two plots. The solid lines show the measured values of $M(H)^2$.

vector q. Explicitly taking into account the q dependence of the magnetization serves to keep the FM and AF magnetic ordering on equal footing, which is crucial for this comparative study. The lowest order free energy invariant considered is

$$F = \frac{P^2}{2\varepsilon_0} - PE + P^2 \sum_q g(q) \langle M_q M_{-q} \rangle (T). \quad (1)$$

This is the simplest term which couples the polarization and magnetization. Neglecting the q dependence of the magnetization, this term would simply be $P^2 M^2$, which has been discussed in other literature [10]. We explicitly include the q dependence of the spin-spin correlation function in order to extend the model to very general forms of magnetic order, including FM and AF transitions discussed in this present work. Here E is the applied electric field, ε_0 is the "bare" dielectric constant, $g(q)$ is the q-dependent coupling constant, and $\langle M_q M_{-q} \rangle$ is the thermal average of the instantaneous spin-spin correlation, which obeys the sum rule

$$\sum_q \langle M_q M_{-q} \rangle = N g^2 \mu_B^2 S(S+1). \quad (2)$$

In addition to the term discussed in Eq. (1), there can also be couplings of the form $\lambda_{ijk}(P_i M_j \nabla_j M_k)$, which may be relevant near domain walls. These couplings are unimportant in these polycrystalline samples examined here and are neglected.

Extremizing Eq. (1) with respect to the polarization P leads to

$$P = \frac{E}{\frac{1}{\varepsilon_0} + 2\sum_q g(q) \langle M_q M_{-q} \rangle} \equiv \varepsilon E, \quad (3)$$

so that the actual value of the dielectric constant ε is

$$\varepsilon = \frac{\varepsilon_0}{1 + 2\varepsilon_0 I(T)}, \qquad I(T) = \sum_q g(q) \langle M_q M_{-q} \rangle (T). \quad (4)$$

Given the sum rule of Eq. (2), it follows that the temperature dependence of ε depends on the relative q dependence of $g(q)$ and of $\langle M_q M_{-q} \rangle (T)$. At high temperatures where $\langle M_q M_{-q} \rangle$ is q and T independent, $\varepsilon/\varepsilon_0$ is temperature independent for both the incipient FM and the incipient AF. This immediately explains observation (i) above.

As T is decreased towards the magnetic ordering temperature, $\langle M_q M_{-q} \rangle$ develops q dependence, peaking near $q = 0$ for the FM case and near the magnetic Bragg vector at the zone boundary for the AF case. To determine the temperature dependence of ε, we will also need a microscopic theory for $g(q)$. The dielectric constant depends on the long wavelength longitudinal and transverse optic phonon frequencies through the Lyddane-Sachs relation. We suppose that the microscopic origin of $g(q)$, the coupling between the polarization and spin correlations in Eq. (1), arises from the coupling of magnetic fluctuations to the optic phonon frequencies. That is, the spin correlations perturb the optical phonon frequencies, which in turn shift the dielectric constant. We expand the exchange integral of neighboring spins on the distance between the atoms carrying the spins expanded in terms of the normal coordinates for these phonons, which is expressed as

$$\begin{aligned} H_{\text{ex}} &= \sum_{i<j} J_{ij} S_i S_j \\ &\approx \sum [J_{ij}(R_{ij}^0) + \vec{J}'(u_i - u_j) \\ &\quad + J''(u_i - u_j)^2 + \ldots](S_i S_j). \end{aligned} \quad (5)$$

The first term in Eq. (5), proportional to $(u_i - u_j)$, affects the phonon frequencies only to second order and is therefore related to four-spin couplings. This will be less important than the term proportional to $(u_i - u_j)^2$ which changes frequencies of transverse and longitudinal polarized phonons in leading order proportional to $\langle S_i S_j \rangle$. Expanding $(u_i - u_j)^2$ in terms of the phonon coordinates u_q and, keeping only the long wavelength modes relevant for determining the dielectric constant ($q \to 0$), we find the coupling has the form

$$J'' u_0^2 \sum_q (1 - \cos q \cdot R_{ij}^0) \langle S_q S_{-q} \rangle, \quad (6)$$

where R_{ij}^0 are the nearest neighbor coordinates. Then, using our assumption that the shift in dielectric constant can be cast solely in terms of a frequency shift in the optic phonons and formally comparing Eq. (6) to Eq. (4), we suggest that $g(q)$ in Eq. (3) is proportional to $(1 - \cos q \cdot R_{ij}^0)$. For ferromagnets, this coupling vanishes as q^2 in the long wavelength limit, where $\langle M_q M_{-q} \rangle$ develops a peak as T approaches T_c. For antiferromagnets, the coupling is a maximum for q near a zone boundary, where $\langle M_q M_{-q} \rangle$ develops a peak as T approaches T_N [15].

We can now qualitatively explain the observations (ii) to (iv) using Eq. (3) and such a form for $g(q)$. This type of problem has been examined for investigating the change in resistivity near a FM or AF transition [16,17] and the effects of AF fluctuations on s-wave superconductivity [18]. As T is decreased towards T_c, $\langle M_q M_{-q} \rangle$ develops a peak around $q = 0$ with a width proportional to the correlation length $\xi(T)$. In this region, the contribution to the integrand of $I(T)$ is suppressed by a factor of q^4. The major part of the integrand for $I(T)$ remains unchanged except very close to the transition where $R_{ij}^0/\xi \ll 1$, and a reduction (enhancement) in ε is expected from (4) for $J'' > 0$ ($J'' < 0$). Our experiments are not precise enough to reveal this critical region.

On the other hand, for the incipient AF, as T is decreased $\langle M_q M_{-q} \rangle$ develops an increasing peak in the region where $g(q)$ is nearly a constant. This is also the region of most of the phase space in the integral of $I(T)$. Therefore a larger effect in the AF is to be expect, as found. From the experiment, an increase in ε corresponds to $J'' < 0$. In the critical regime $\xi a \gg 1$, i.e., for $|T - T_N|/T_N \ll 1$, a peak in ε similar to the specific heat is to be

expected following the theory of Fisher and Langer [16]. Some hint of a peak may be found in Fig. 1.

We turn now to the region $T \ll T_c$ or T_N. For the AF, as well as the FM, in the classical approximation $\langle M_q M_{-q} \rangle \sim M^2$, where M is the staggered moment at $q = 2\pi/R_{ij}^0$ for the AF and at $q = 0$ for the FM. We see immediately using the derived form for $g(q)$ that $I(T) \to 0$ in this regime for the FM. With $J'' < 0$, this means that for the FM $\varepsilon \sim \varepsilon_0$ for $T \ll T_c$ which is lower than the asymptotic value for $T \gg T_c$. More generally, in ferromagnets exhibiting magnetodielectric behavior, the intrinsic dielectric constant ε_0 is measured only at low temperatures, where the magnetic fluctuations are frozen out. On the other hand, for the AF, there is essentially no change in $I(T)$ for $T \ll T_N$ compared to $T \sim T_N$ (excepting the critical regime). The contrasting behaviors in $\varepsilon(T)$ for the AF and FM are thus qualitatively explained. We can further test these ideas in the FM, where according to the argument above, the decrease in the dielectric constant for $T < T_c$ is simply proportional to the ordered M^2. This is shown in Fig. 2 at both zero field and at finite field.

Finally we discuss observation (iv) regarding the different magnetic field dependence for $T \sim T_c$ and for $T \sim T_N$. A sharp effect near $T \sim T_c$ is to be expected since, near T_c, M is a strongly nonlinear function of H due to the switching of domains. This is exhibited in Fig. 3 where the relative change in ε vs H is plotted together with the measured M^2. Only smooth behavior is to be expected for small H near T_N in the AF. For large fields, a uniform magnetization does develop in the AF, so effects similar in magnitude to that in the FM are to be expected as found in Fig. 3.

We have investigated the temperature and magnetic field dependence of the dielectric constant for both $SeCuO_3$ (FM) and $TeCuO_3$ (AF) and have developed a simple model for understanding how the q-dependent spin-spin correlations change the measured capacitance. By positing that the MD effect arises from long wavelength frequency shifts in the optical phonons induced by magnetic fluctuations, we find an expression for the microscopic q-dependent coupling between uniform polarization and the spin-spin correlation function. This model gives good qualitative agreement with the experimental measurements of ε — both the temperature dependence of the dielectric constant and the magnetocapacitance can be expressed simply in terms of the temperature and field variations of magnetic fluctuations and the uniform magnetization.

The practical interest in understanding magnetodielectric couplings arises from device applications. The analysis presented above, based on a comparison of the MD response of FM $SeCuO_3$ and AF $TeCuO_3$, suggests routes to materials with higher MD coefficients. The data and our model show that antiferromagnets might demonstrate the larger overall temperature effect on ε through the q dependence of $g(q)$, especially at temperatures just above T_N. However, for effective coupling to an external magnetic field, a ferromagnetic order parameter would be required. It is conceivable that these two ingredients could be engineered into a material using either thin film deposition or nanoscale synthesis techniques. Here, the FM and AF components should have spatial proximity and be strongly coupled. Since there are few insulating ferromagnets, such nanostructuring could also provide a way to ensure the composite material is an effective dielectric. If such a material were feasible, it would resemble a dielectric version of exchange coupling, which provides a basis for giant magnetoresistance.

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