Coupling between magnetism and dielectric properties in quantum paraelectric $EuTiO_3$

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The dielectric constant of quantum paraelectric $EuTiO_3$, which contains Eu^{2+} with $S=7/2$ spin and Ti^{4+}, has been measured under a magnetic field. The dielectric constant shows a critical decrease at the antiferromagnetic ordering of the Eu spins at 5.5 K, as well as a substantial change under a magnetic field (by $\sim 7\%$ with 1.5 T), indicating a strong coupling between the Eu spins and dielectric properties. We show that the variation of the dielectric constant is dominated by the pair correlation of the nearest-neighbor Eu spins, likely via the variation of the soft-phonon-mode frequency.

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I. INTRODUCTION

The coupling between magnetism and electric conduction in metals gives rise to various interesting phenomena, such as colossal magnetoresistance in perovskite manganites.[1] In this class of compounds, itinerant carriers are strongly coupled with localized spins by Hund coupling (the order of eV), and the properties of itinerant carriers (the effective mass and the scattering rate) depend on the configuration of the localized spins. In such a situation, electric conduction can be controlled by a magnetic field via the coupling with localized spins, leading to large negative magnetoresistance. In a similar manner, the coupling between magnetism and dielectric properties in magnetic insulators would be possible where the dielectric properties depend on the configuration of localized spins and the dielectric constants can be controlled by a magnetic field via the coupling with localized spins. In most magnetic insulators, however, such a coupling is fairly weak and the dielectric constant barely changes under a magnetic field. The dielectric constant of insulators is usually dominated by a band gap between their valence band and conduction band with an energy scale of eV, and this is much larger than that of a magnetic interaction or magnetic field. Accordingly, magnetic ordering or a magnetic field least affects the dielectric constant of such insulators. To enhance the coupling between magnetism and dielectric properties, therefore, the energy scale dominating dielectric properties should be lowered and be comparable with that of magnetism. This can be realized if the material has a specific infrared-allowed optical phonon mode with low frequency, i.e., a soft phonon mode for the ferroelectric transition. In this case, the energy scale dominating the dielectric constant is that of the soft phonon, which is typically of the order of 10 meV, comparable with that of a magnetic interaction or magnetic field.

To explore such enhanced coupling between magnetism and dielectric properties, we chose perovskite $EuTiO_3$. It is known that tetravalent perovskite titanates $A\,TiO_3$ (A=Ba, Sr, Ca) show unique dielectric properties; i.e., $BaTiO_3$ is a ferroelectric (Ref. 2) and $SrTiO_3$ (Ref. 3) and $CaTiO_3$ (Ref. 4) are quantum paraelectrics. In these compounds, one T_{1u} phonon mode with cation motion opposing oxygen motion, as illustrated by the thin arrows in the lower panel of Fig. 1, shows a softening and is responsible for those dielectric properties.[5,6] $EuTiO_3$ (Ref. 7) also has a simple cubic perovskite structure with divalent Eu and tetravalent Ti, and thus similar dielectric properties caused by the soft T_{1u} mode are expected, though they have not been studied so far. A distinct feature of $EuTiO_3$ from other tetravalent perovskite titanates is the existence of localized $4f$ moments with $S=7/2$ on the

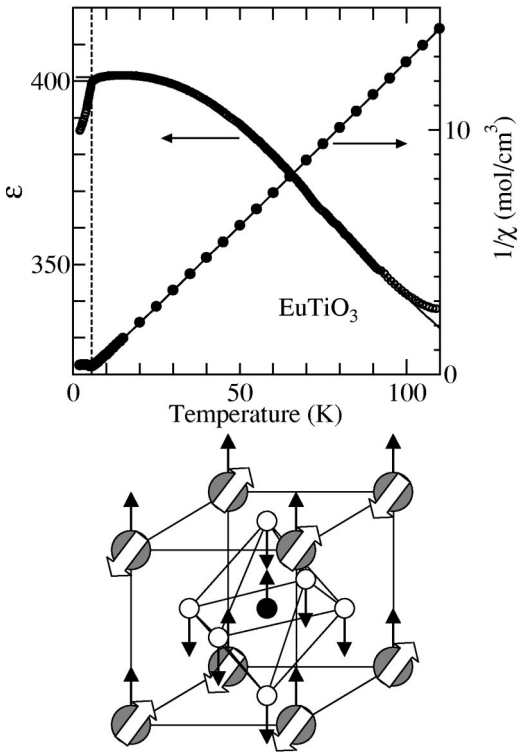

FIG. 1. Upper panel: temperature dependence of dielectric constants at 100 kHz (left axis) and inverse magnetic susceptibility (right axis) for $EuTiO_3$. The solid curve is the result of the fitting of dielectric constants to Barrett's formula (see text). The dotted line corresponds to the Néel temperature (5.5 K). Lower panel: crystal structure of $EuTiO_3$. Gray circles, white circles, and a black circle corresponds to Eu, O, and Ti, respectively. White thick arrows represent antiferromagnetic ordering of Eu spins. Thin arrows show the atomic motion of the soft-phonon mode with T_{1u} symmetry (see text).

Eu^{2+} sites, which order antiferromagnetically below 5.5 K (Ref. 7) with a spin structure as shown by the white arrows in the lower panel of Fig. 1. Because of the coexistence of a soft phonon and localized spins in this compound, one can expect enhanced coupling between the dielectric properties and magnetism. In an analogy with perovskite manganites, where itinerant carriers are coupled with localized spins and can be controlled by a magnetic field, it would be possible in $EuTiO_3$ that a soft phonon mode is coupled with localized spins and can be controlled by a magnetic field.

II. SAMPLES AND EXPERIMENTS

Pure $EuTiO_3$ and Ba-doped ($Eu_{1-x}Ba_xTiO_3$, $0 \leqslant x \leqslant 0.2$) samples were grown by the floating-zone technique.[8] X-ray powder diffraction measurements indicate that the crystal symmetry is cubic for $x \leqslant 0.2$ at room temperature and the lattice constant increases with increasing Ba concentration, i.e., 3.905 Å for $x=0$, 3.909 Å for $x=0.1$, and 3.925 Å for $x=0.2$. Dielectric constants were measured by a LCR meter (1–100 kHz) and capacitance bridge (1 kHz) under various magnetic fields up to 5 T. The crystals were cut into a disk shape, and indium was soldered on both sides as electrodes. Typical sample size was 10 mm^2 area and 1 mm thickness. A magnetic field was applied parallel to the electric field. The magnetization was measured by using superconducting quantum interference device (SQUID) magnetometer.

III. RESULTS OF $EuTiO_3$

In Fig. 1, the dielectric constant (ϵ) at 100 kHz and the inverse magnetic susceptibility ($1/\chi$) of $EuTiO_3$ are plotted as a function of temperature. The dielectric constant increases with decreasing temperature, and is saturated around 30 K with the value of ~ 400, which is anomalously high as a normal insular. It is found that there is least frequency dependence of ϵ between 1 and 100 kHz and the dielectric loss is zero within the experimental error below 70 K. These features indicate that $EuTiO_3$ is in a quantum paraelectric state at low temperatures. We have fitted the data to the Barrett's formula[9]

$$\epsilon = A + \frac{C}{(T_1/2)\coth(T_1/2T) - T_0}, \tag{1}$$

where T_0 equals the Curie-Weis temperature in the classical limit. The best-fit values are $A=181$, $C=2.34\times10^4$ K^{-1}, $T_1=162$ K, and $T_0=-25$ K, as shown by the solid line in Fig. 1. The negative value of T_0 indicates an antiferroelectric interaction in $EuTiO_3$. The dielectric constant, however, shows a sharp decrease below 5.5 K. This temperature coincides with a Néel temperature (T_N) as exemplified by the cusp of magnetic susceptibility shown in the same figure, and as reported earlier based on Mössbauer spectroscopy.[7] The change of the dielectric constant with antiferromagnetic ordering amounts to 3.5%.

The Eu^{2+} ion takes the $4f^7$ electron configuration and has a $S=7/2$ spin with a Heisenberg character and least magnetic anisotropy. If the magnetic field is applied to such antiferromagnetically ordered Heisenberg spins, they are immediately flipped perpendicular to the magnetic field and then are gradually changed into a ferromagnetic arrangement with increasing magnetic field. In fact, the magnetization of $EuTiO_3$ at 2 K increases almost linearly with increasing magnetic field and is saturated around 1.5 T with the value of the fully polarized Eu spins ($7\mu_B$ per Eu).[10] Since the spin state can be controlled from the antiferromagnetic to ferromagnetic by the magnetic field, we can expect a large magnetic field effect on the dielectric constant of $EuTiO_3$. In Fig. 2(a) the dielectric constants and in Fig. 2(b) magnetization vs temperature under several magnetic fields are plotted. With increasing magnetic field, low-temperature dielectric constants gradually increase and finally the cusp disappears. This behavior of the dielectric constants resembles that of magnetization, where the cusp disappears and the value reaches $7\mu_B$/Eu under a high magnetic field. As shown in the inset of Fig. 2, where $\epsilon(H)/\epsilon(0)$ vs magnetic field is plotted, the change of the dielectric constant reaches 7% at 1.5 T.

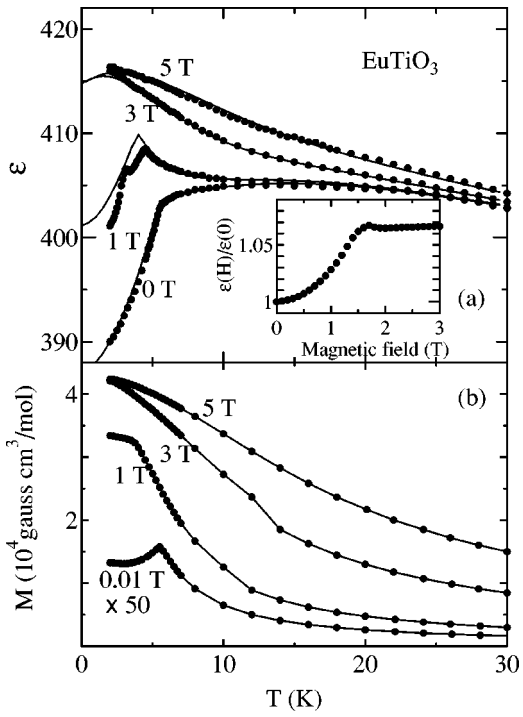

FIG. 2. (a) Dielectric constants at 1 kHz and (b) magnetization as a function of temperature under several magnetic fields for $EuTiO_3$. Solid lines in (a) are the fittings curves by Eq. (2) with $\alpha=2.74\times10^{-3}$. The inset shows the magnetic field dependence of the dielectric constant (normalized to the value at zero field) at 2 K.

IV. CALCULATION AND DISCUSSIONS

Which parameter is the most relevant to the change of dielectric constants? The dielectric constant decreases with the antiferromagnetic ordering of Eu spins whereas it increases with their ferromagnetic arrangement under a magnetic field. From this, it is natural to consider that the dielec-

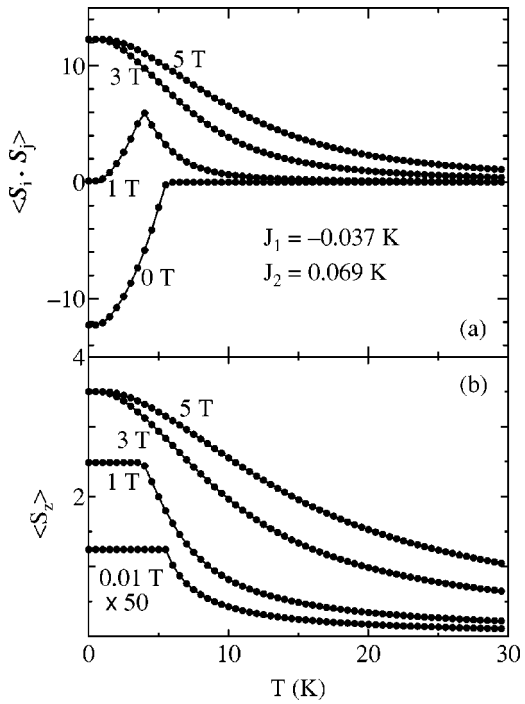

FIG. 3. (a) Spin pair correlation between nearest-neighbor sites $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ and (b) the z component (parallel to the magnetic field) of the total magnetization $\langle \mathbf{S}_z \rangle$ for the system with $S=7/2$ on the cubic lattice by a mean-field calculation. The nearest-neighbor interaction J_1 is -0.037 K and the next-nearest-neighbor interaction J_2 is 0.069 K.

tric constant is dominated by the pair correlation of the Eu spins, $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$, where i and j refer to the Eu sites next to each other. To verify this idea, we have made a mean-field calculation of the spin system with $S=7/2$ on the cubic lattice with a Hamiltonian $H=-\frac{1}{2}J_{ij}\Sigma \mathbf{S}_i \cdot \mathbf{S}_j$. Here, we assume both the nearest-neighbor interaction $J_1=-0.037$ K and the next-nearest-neighbor interaction $J_2=0.069$ K, to reproduce $T_N=5.5$ K and a positive Curie-Weiss temperature $\theta=3.17$ K. Note that the next-nearest-neighbor interaction (via oxygen) is ferromagnetic and its absolute value is larger than that of the antiferromagnetic nearest-neighbor interaction.[7] In the mean-field approximation, $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ is simply given by the product of $\langle \mathbf{S} \rangle$ on two sublattices. We show the calculated values of $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ as well as the z component (parallel to the magnetic field) of the total spin moment, $\langle S_z \rangle$, under several magnetic fields in Fig. 3. One can see good agreement between the behaviors of the dielectric constants and the calculated $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$, as well as between those of magnetization and the calculated $\langle S_z \rangle$. On the basis of this calculation, we have fitted the experimental data of $\epsilon(T)$ by the following formula:

$$\epsilon(T,H)=\epsilon_0(T)(1+\alpha\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle), \tag{2}$$

where $\epsilon_0(T)$ is the dielectric constant in the absence of a spin correlation, which has been estimated by fitting the experimental curve of $\epsilon(T)$ under 0 T above T_N. It should be noted that except for $\epsilon_0(T)$, the only fitting parameter for all the data is α, the coupling constant between spin correlation

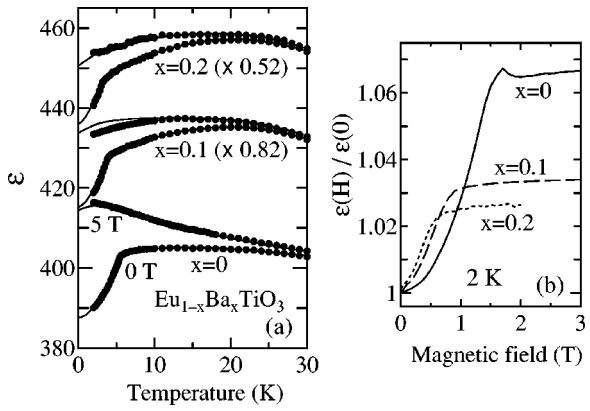

FIG. 4. (a) Dielectric constants of $Eu_{1-x}Ba_xTiO_3$ with $x=0$, 0.1, and 0.2 at 1 kHz as a function of temperature. They are multiplied by 0.82 for $x=0.1$ and by 0.52 for $x=0.2$ for clarity. Solid lines are the fitting curves (see text) with $\alpha=2.74\times10^{-3}$ for $x=0$, $\alpha=2.20\times10^{-3}$ for $x=0.1$, and $\alpha=2.11\times10^{-3}$ for $x=0.2$. (b) Magnetic field dependence of the dielectric constants (normalized to the values at zero field) at 2 K for $Eu_{1-x}Ba_xTiO_3$ with $x=0$ (the solid line), 0.1 (the dashed line), and 0.2 (the dotted line).

and dielectric constants, in Eq. (2). The best-fit value of α is 2.74×10^{-3} and the fitting curves are shown by solid lines in Fig. 1(a).

Now, it becomes clear that the dielectric constant is related to the pair correlation of neighboring Eu spins. Then, how do the Eu spins affect the dielectric constant? The main contribution to the large dielectric constant of this compound is a soft T_{1u} phonon mode as discussed above, and thus it is likely that this soft-phonon mode is modified by the Eu spins. We speculate that the hybridization between the Eu orbitals and the O $2p$ orbital is varied depending on the configuration of the Eu spins, which then modifies the frequency of the T_{1u} mode that contains Eu-O stretching motion (in the lower panel of Fig. 1). The magnitude of the phonon-frequency change with magnetic field can be estimated from that of the dielectric-constant change. The dielectric constant associated with one optical phonon is given by the following formula:

$$\epsilon(\omega)=\epsilon_1(\omega)-i\epsilon_2(\omega)=\epsilon_\infty+\frac{4\pi Ne^{*2}/\mu}{(\omega_0^2-\omega^2)+i\Gamma\omega}, \tag{3}$$

where N is the number of unit cells per volume, e^* the effective charge of ions, μ the effective mass of ions, ω_0 the phonon frequency, and Γ the scattering rate of the phonon. We assume that the change of the magnetic state of the Eu spins only affect ω_0 but neither e^* nor μ. Since ϵ_1 is proportional to $1/\omega_0^2$ in the dc limit of Eq. (3), the increase of ϵ_1 by 7% under a magnetic field means a decrease of ω_0 by 3.5%. This implies that the ferromagnetic arrangement of the Eu spins (positive $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$) softens the T_{1u} phonon mode. It also should be pointed out that if we assume $\hbar\omega_0/k_B$ as the order of ~ 100 K in $EuTiO_3$,[11] then its decrease is ~ 3.5 K, which is the order T_N, a typical energy scale of magnetism

in this compound. This rough estimate is consistent with our idea that the soft-phonon frequency is modified by the magnetism of the Eu spins.

V. Ba DOPING

To confirm the validity of Eq. (2) as well as to pursue a further enhanced coupling constant α, $Eu_{1-x}Ba_xTiO_3$ has been synthesized and the same measurements have been done on those samples. Since $BaTiO_3$ is a ferroelectric compound, it is expected that the absolute value of the dielectric constant increases with Ba doping. As seen in Fig. 4(a), the absolute value of the dielectric constant really increases with Ba doping. Equation (2) can satisfactory fit the magnetic field dependence of the dielectric constant also for the Ba-doped samples, as shown by solid lines in Fig. 4(a).[12] However, the change of the dielectric constant with magnetic field looks reduced with Ba doping, as more clearly seen in Fig. 4(b). This is partly because the magnetic Eu ions are diluted by nonmagnetic Ba ions. Taking account of such a dilution effect, α in Eq. (2) should be replaced by $(1-x)^2\alpha$. It is found that the α value still decreases with Ba doping ($\alpha = 2.74\times10^{-3}$ for $x=0$, 2.20×10^{-3} for $x=0.1$, and 2.11×10^{-3} for $x=0.2$), indicating that Ba doping intrinsically reduces the coupling between magnetism and dielectric constants. It is known that quantum paraelectric states are fragile against disorder and easily change into ferroelectric states or relaxors.[13] Such (local) ferroelectric ordering due to disorder seems to be occurring in $Eu_{1-x}Ba_xTiO_3$ with finite x, as suggested by the decreasing dielectric constants below 20 K. We speculate that in $Eu_{1-x}Ba_xTiO_3$ with finite x, the soft-phonon mode is partially frozen and produces a quasistatic lattice distortion, whereas the weight of the dynamical part contributing to the coupling between dielectric constants and magnetism is reduced. It should be noted, however, that the initial slope of ϵ against magnetic field rather increases with Ba doping in spite of the decrease of α, as seen in Fig. 4(b), because of the faster increase of magnetization with magnetic field for the Ba-doped samples.[10]

VI. SUMMARY

In summary, the dielectric constant of quantum paraelectric $EuTiO_3$ shows critical changes with magnetic ordering of Eu spins as well as under a magnetic field by $\sim 7\%$. We found that the change of the dielectric constant is dominated by the pair correlation of the Eu spins between nearest-neighbor sites, suggesting that the configuration of the Eu spins varies the frequency of a soft-phonon mode in $EuTiO_3$. The observed behaviors provide a clear demonstration of the possible magnetic field control of the dielectric constants in oxide materials.

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