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Negative magnetodielectric effect in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$

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Real part of complex relative dielectric value is relatively decreased as large as $\sim 5\%$ from 50 K to 200 K in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, by applying a 6-T static magnetic field. $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ is thus implied primarily by the negative magnetodielectric effect, as a unified dielectric system in which 1-D finite dipole chains of B-site titanium ions, coexist with a collective of polaron-like 3d-electrons of A-site copper ions: the dipole chains are thermally activated for lattice ionic polarization above 50 K, and suppressed by the short-range hop of these quasi-particles, while their long-range movement are for bulk electronic polarization above 151 K. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4851815>]

I. INTRODUCTION

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) has attracted a great deal of scientific and practical attention due to its extraordinary dielectric response^{1–3}—almost 1000-fold reduction of the real part of complex relative dielectric value $\sim 10^4$ around 150 K without long-range structural transition, and giant permittivity at frequencies up to 1 MHz over a wide temperature range. Decades after the resurgence of interest and the intense investigations,^{1–34} to uncover physics picture is still a challenge.

Compared with “traditional” giant dielectric systems, BaTiO_3 or SrTiO_3 , the centrosymmetric $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (space group $Im\bar{3}$) demonstrates two additional distinct features: 1-D limitedly correlated off-center displacements of titanium ions⁷ and the antiferromagnetic spin order of copper ions below the Néel temperature $T_N = 25$ K.²¹ The off-center displacement of individual titanium ion along the $\langle 001 \rangle$ directions ~ 0.04 Å is comparable to that of classic ferroelectric BaTiO_3 ~ 0.10 Å in the cubic-to-tetragonal ferroelectric phase transition. Notably, these off-center displacements are only correlated along the individual $\langle 001 \rangle$ column, and the correlation length is ~ 5 – 10 unit cells, as estimated from the width of the $\mathbf{G} \pm \{001\}^*$ diffuse scattering. Thus results in 1-D finite dipole chain of Ti^{4+} ions, and the dipole chains are independent on each other, for the off-center displacements are not correlated from one such column to the next in the transverse direction, and never lock-in to form a long range ordered ferroelectric state. The inversion symmetry indicates that the dipole chains are antiparallel in thousands of crystalline unit cells, and once an a.c. voltage is applied, the electrical disturbance could induce a parallel-dipole-orientation branch³⁴ and the resultant net polarization is

non-zero, for the local crystal fields around them are different and their delays with respect to the a.c. electrical field are not same. The induced net polarization is ionic but not dipolar, because the off-center displacement of Ti^{4+} ion of single dipole in the dipole chain, not only the displacement direction but also the displacement magnitude, does the response to the applied a.c. electrical field, while the dipolar polarization is the change of dipolar orientation with the applied a.c. electrical field and the dipolar magnitude remains constant. Further, the spin arises from unpaired 3d electron at d_{xy} , d_{yz} , or d_{zx} orbital of Cu^{2+} ions, and below T_N superexchange interaction among them is concluded to stabilize the antiferromagnetic order against the thermal disruption.²¹ Such 3d electron, being a charged particle, corresponds to a quasi-particle like polaron, for it carries with it a cloud of correlated electronic polarization.³⁵ The orbital and electronic excitations,^{16,26} and the electron-transfer in the photo-oxidation⁸ indicate that the 3d electrons may be excited by thermal or photonic energy to hop from partly filled d orbitals of copper ions, via empty d orbitals of the nearest neighboring titanium ions, to those of the next neighboring copper ions, while utilizing the density-functional theory to consider that the running-wave functions of 3d electrons at d orbitals of copper ions overlap those of the bridging titanium ions, the narrow band gap is ~ 200 meV, the valence band is derived primarily from the partly filled d orbitals from copper ions, and the conduction band is made up primarily of empty d orbitals from titanium ions.¹⁸ When the long-range motion of polaron-like 3d electrons of copper ions is pinned at grain surfaces for bulk electronic polarization, and 1-D finite dipole chains of titanium ions are involved in lattice ionic polarization, and their dynamical response to an applied a.c. electric field, $\epsilon'(\omega, T)$, without or under a static magnetic field (SMF), is a many body issue, and can be detected below MHz,³⁶ where $\epsilon'(\omega, T)$ is the real part of complex relative dielectric function, T is the absolute temperature (K), and ω the frequency (Hz).

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A possible way to distinguish the ionic polarization from the electronic one is the negative magnetodielectric effect, which is the frequency- or temperature-dependent decrease of real part of complex relative dielectric value under a SMF. Negative magnetodielectric effect has revealed the fundamental spin-lattice coupling and so on. When the frequency of applied a.c. voltage is below 1 MHz, the ionic polarization contributes to both the dielectric relaxation and the complex relative dielectric value, while the electronic polarization only does to the complex relative dielectric value. Also the ionic polarization and the electronic one are thermally activated at various temperatures. For the electronic polarization, the polaron-like electrons may have a net spin and their dielectric response is affected by a static magnetic field, and $\epsilon'(\omega, T)$ at different static magnetic fields can indicate whether it originates from grain boundaries while the material is polycrystalline.

II. EXPERIMENT

The fabrication of bulk polycrystalline (ceramics) has been described in our previous work.^{22,23} The samples were of the same single-phase type and no twin boundaries were found.^{2,13} The magneto-dielectric spectra were obtained

using a Hewlett-Packard Impedance/Gain-Phase Analyzer, model 4294 (Agilent Co., USA) and a Physical Property Measurement System (PPMS, Quantum Design Co., USA). An applied voltage of 10 mV was used over the 100 Hz–1 MHz range from 10 K to room temperature. Before electrical measurement, the samples were polished to a thickness of 0.4 mm and then Ag electrodes were sputtered onto the surface. The a.c. electric field was applied perpendicular to the sample surface. The magnetic data were measured using a vibrating-sample magnetometer (VSM EV7, ADE Co., USA). Piezoresponse force microscopy was performed using a commercial atomic force microscope (Cypher, Asylum Research). Pt-coated Si conductive probes were used (Olympus AC240TM, force constant ~ 2 N/m and tip radius ~ 28 nm). The polished sample was polarized as a simple chessboard by using ± 40 V_{DC}. The topographic image was acquired by applying an ac voltage of 4 V at a frequency of 10 kHz (out of plane).

III. RESULTS AND DISCUSSION

Figure 1 presents the temperature- or frequency-dependent dielectric spectroscopy, and the magnetodielectric effect,

FIG. 1. (a) Dielectric plot. (b) Relative change with applied frequency from 50 to 200 K. (c) Temperature-dependent of the loss tangent peak. (d) The Arrhenius fitting.

while a 6-T SMF is applied perpendicular to the sample surface. The measured DC-conductivity of our $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ samples does not exceed $(10^9 \Omega\text{cm})^{-1}$, suggesting that CCTO is inherently an insulator.² However, the value of its optical band gap is in the energy range of semiconductor bandgaps.^{3,8,26} We conclude that the response of CCTO to dc and ac excitations is dominated by collective mode dynamics²³ with single-particle effects occurring only at optical frequencies. A characteristic dielectric response of CCTO is shown in Figure 1(a).

The relative change in the real part of complex relative dielectric value, $\Delta\epsilon'$, is defined as $\Delta\epsilon' = \{\epsilon'(\omega, T, H = 6\text{ T}) - \epsilon'(\omega, T, H = 0\text{ T})\} / \epsilon'(\omega, T, H = 0\text{ T})$. By applying a static magnetic field $H = 6\text{ T}$, a small but quite reproducible relative change as large as $\sim -5\%$ is observed from 50 to 200 K (Fig. 1(b)). It is, however, in the range from -1% to 1% below 50 K and above 200 K. The absolute value of ϵ' at 100 kHz is decreased by 80.8 at 126 K. The value of relative change of ϵ' is reasonably smaller than a $\sim -15\%$ capacitance difference between the sample under SMF $\sim 9\text{ T}$ at 100 K and that without a SMF at 300 K.²⁴

The accuracy of temperature control in PPMS indicates that the aforementioned polarization is a possible origin.³⁵ With increasing frequency, the temperature range of valley in $\Delta\epsilon'$ increases (Fig. 1(b)), which indicates that large thermal energy conserves the oscillations of the dipole chains. The loss-tangent profile under the SMF is changed by less than 1%. All temperatures of the loss-tangent peaks at different frequencies are increased by $\sim 14\text{ K}$, as shown in Fig. 1(c), suggesting a Debye-like relaxation character with a characteristic single relaxation time τ_0 . The departure of dielectric response from the Debye one, further indicates the collective nature of dielectric relaxation. In our previous work, we used a tentative relaxation time function to describe the response

of one dipole of a dipole chain to a.c. electrical field, and the Cole-Cole model to reveal its glassy nature of physics.²³ Here, these 1-D finite dipole chains are independent on each other, and an Arrhenius Law is fitted to their temperature-dependent behavior of the same τ_0 , as shown in Fig. 1(d), assuming the relaxation timescale $\tau = \tau_0 \exp(U/kT)$, where τ is the relaxation time, τ_0 the characteristic relaxation time, U is the activation energy, and k the Boltzmann constant. The activation energy $U(H = 0\text{ T}) \sim 88\text{ meV}$ is increased to $U(H = 6\text{ T}) \sim 116\text{ meV}$, which indicates an enhancement in barrier height for the off-center displacements of the titanium ions. The characteristic relaxation time $\tau_0(H = 0\text{ T}) \sim 44\text{ ns}$ is decreased to $\tau_0(H = 6\text{ T}) \sim 15\text{ ns}$.

Figures 2(a) and 2(b) present the paramagnetic state of the pristine CCTO and the ferromagnetic state of 6-T-Magnetized CCTO. A linear M-H loop at 77 K shows these samples are in a paramagnetic state, and excludes the possibility of magnetic impurity ions (Fig. 2(a)). The same samples were then magnetized at room temperature using a 6-T SMF. The applied direction of the SMF was perpendicular to the sample surface, and then the SMF was removed. The same samples show the “S”-shape loops along the surface normal (Fig. 2(b)), implying that the spins rotate and their components align along the surface normal. Previous first-principles work suggests that there is a metastable ferromagnetic (FM) state in CCTO, which is energetically lower than the paramagnetic (PM) state, but higher than the antiferromagnetic (AFM) state.²⁰ In magnetized CCTO, the PM-FM transition is induced by applying a strong SMF. The metastable FM state remains from 77 K to 200 K, in accordance with the FM-PM transition $\sim 400\text{ meV}$ (4638 K)/unit cell. Given that indirect superexchange interactions take priority over other direct interactions, and are responsible for crystallographic and antiferromagnetic structures,³¹ superexchange

FIG. 2. (a) Linear loop of pristine $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ at 77 K. (b) “S”-shape loops of 6-T-magnetized $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ at several temperatures. (c) Magnetodielectric plots in complex plane plots of ϵ' and ϵ'' . (d) Bulk and local potential wells for charge carriers. The inset is surface polarization topography at room temperature.

interaction is concluded to stabilize the parallel component of spin order against thermal fluctuation, even when the temperature is above the Néel temperature.

The superexchange interaction is mostly promoted via titanium ions rather than oxygen ions, and two superexchange interactions pass through one titanium ion,²¹ and their total strength ~ 28 meV is as many as the increment of the activation energy in the magnetodielectric effect. We conclude that superexchange interactions tie up the titanium ion by increasing its barrier height of double potential well, and suppress the contribution of its off-center displacement to single dipole moment, and, as a result, the dielectric polarization of a dipole chain and the part of ϵ' are decreased. Given that superexchange interactions arise from 3d electrons,³³ we conclude that 3d electrons are thermally activated to hop between the d orbitals of two nearest neighboring copper ions via those of the bridging titanium ion, and modify the crystal field around the titanium ion. In other words, 3d electrons locate at d_{xy} , d_{yz} , or d_{zx} orbitals of copper ions as initial or final state, and with “real” thermal excitation, they short-range hop $7.052 \text{ \AA}$ (double Ti-Cu distance) in 15 ns or longer, via one of empty d orbitals of the bridging titanium ion.³¹

Figure 2(c) presents the complex plot of ϵ' and ϵ'' of the magnetodielectric response, where $\epsilon''(\omega, T)$ is the imaginary part of complex relative dielectric function. The dielectric relaxation is a thermally activated process.³⁶ Below 50 K, non-zero interception at ϵ' axis indicates that 1-D finite dipole chains of titanium ions are “frozen,” and the inherent lattice mode contributes to $\epsilon' \sim 100$, and it is hardly affected by the SMF, and then the relative change of ϵ' is minor. With increasing temperature, the dipole chains are gradually and thermally activated with energy dissipation, and the corresponding dielectric spectroscopy changes from a short line (black) to an arc (cyan). At 151 K, the dielectric response of

the dipole chains dominates approximately as a semicircle, and its interception at ϵ' axis shows that the dipole chains contribute to ϵ' as large as $\sim 10^4$. The squeezed shape of arc indicates that the dipole chains are under the influence of superexchange interaction, e.g., short-range hop of polaron-like 3d electrons of copper ions.

Above 151 K, the appearance of the second arc indicates that the other larger polarization process is thermally activated. The alignment of spins on neighboring sites, usually favors electronic motion, and maximizes itinerant energy of electrons at high temperature. The overlap of d orbitals of two copper ions via their mixing of d orbitals of bridging titanium ion, allows the 3d electrons of copper ions to be delocalized.³⁵ Activated by large thermal energy above 151 K, polaron-like 3d electrons change from short-range hop to long range motion, and gradually move through copper-titanium sublattice via the electronic mixing pathway, such as $d_{zx}^{Cu2} \rightarrow t_{2g}^{Ti} \rightarrow d_{xy}^{Cu1}$, for the running-wave functions of d_{zx}^{Cu2} , t_{2g}^{Ti} , and d_{xy}^{Cu1} orbitals overlap each other. These quasi-particles behave as polarons, and induce the distortion of copper-titanium sublattice, which has been verified by the atomic pair distribution function (PDF) analysis.¹³ Without other observable defects, twin boundaries and so on, surface polarization topography at room temperature (the inset of Fig. 3) indicates that they are pinned at grain surface, and the induced sublattice distortion contributes to bulk electronic polarization. The bulk electronic polarization is also indicated by the observation of the piezoelectric effect²⁵ and the pyroelectric effect²⁶ at room temperature. From energy view, herein lies also the importance of bulk electronic polarization, for superexchange interactions ~ 28 meV are competitive to Coulomb interaction ~ 88 meV, while the $U(T, H = 0 \text{ T})$ mostly originates from interatomic Coulomb forces within TiO_6 octahedron.³³ At 230 K, the dielectric response of these quasi-particles appears apparent

FIG. 3. (a) Magnetic-field dependence of relative change shown for 1 kHz at 100 K. (b) Same as for 1 MHz at 150 K. (c) Frequency dependence of ϵ' for several temperatures in the negative magnetodielectric plots. The theoretical lines agree well with the experimental dots.

and contributes to $\epsilon' \sim 10^4$, when that of the dipole chains remains (Figure 2(c)). The excitation of polaron-like 3d electrons for dielectric response is also suggested by the room-temperature experiments that the enhancement of dielectric value is achieved by applying a strong optical field.³⁰ Then the “saturated” state of bulk electronic polarization is responsible for almost unchanged ϵ' above 151 K. The resultant bulk polarization, acting as a pinning potential well for charge carriers, and the local potential well within TiO_6 octahedron, result in two activation energies of charge carriers ~ 430 meV and ~ 62 meV, respectively (Fig. 2(d)).

Figure 3 presents the static-magnetic-field dependence of ϵ' (a and b), and the temperature dependence of ϵ' and ϵ'' (c and d) at several frequencies in the negative magnetodielectric effect. At the temperature with the largest $\Delta_{\epsilon'}$, we observe the SMF-dependent $\Delta_{\epsilon'}$, and show two loops $\Delta_{\epsilon'} = \{\epsilon'(\omega = 1 \text{ kHz}, T = 100 \text{ K}, H) - \epsilon'(\omega = 1 \text{ kHz}, T = 100 \text{ K}, H = 0 \text{ T})\} / \epsilon'(\omega = 1 \text{ kHz}, T = 100 \text{ K}, H = 0 \text{ T})$ at 100 K, and $\Delta_{\epsilon'} = \{\epsilon'(\omega = 1 \text{ MHz}, T = 150 \text{ K}, H) - \epsilon'(\omega = 1 \text{ MHz}, T = 150 \text{ K}, H = 0 \text{ T})\} / \epsilon'(\omega = 1 \text{ MHz}, T = 150 \text{ K}, H = 0 \text{ T})$ at 150 K for example. The “butterfly-like” shape rules out that the magnetodielectric response arises from a combination between the Maxwell-Wagner relaxation and the magnetoresistance effect, i.e., spin-polarized tunneling across grain boundaries.³⁷ The smaller SMF drives the less 3d electrons to parallel their spins, and the less titanium ions are affected by the superexchange interactions, and thus the contribution of their off-center displacements is less attenuated to the dipoles, the dipole chain, the polarization and ϵ' . Only with the nearest interactions, we can map the negative magnetodielectric process onto an effective system using the Ising model analysis of dielectric polarization (a finite chain) with the Hamiltonian^{38,39}

$$H = U - J s_j^z (s_{j+1}^z + s_{j-1}^z),$$

where the states of j -th dipole $s_j^z = \pm 1$ are the upward or downward dipole of off-center displacements of j -th Ti^{4+} ions in $[001]$ or $[00\bar{1}]$ column, and J is the exchange interaction between two nearest dipoles in one column. The corresponding complex relative dielectric functions are as follow is:

$$\epsilon'_n(\omega) = 1 - 2\gamma'\omega\tau\{F(\omega\tau)A(\omega\tau) - E(\omega\tau)B(\omega\tau)\} / \{E^2(\omega\tau) - F^2(\omega\tau)\},$$

$$\epsilon''_n(\omega) = 2\gamma'\omega\tau\{E(\omega\tau)A(\omega\tau) + F(\omega\tau)B(\omega\tau)\} / \{E^2(\omega\tau) + F^2(\omega\tau)\},$$

where $n, \gamma', A(\omega\tau), B(\omega\tau), E(\omega\tau)$, and $F(\omega\tau)$ are cited from Ref. 38. By using the resultant dielectric function, the experimental results (Figures 3(c) and 3(d)) are well fitted and there is an improvement over a simple Debye-type fitting of the experimental data. The induced exchange interaction in the LSDA + U method has shown a positive effect on the electronic structure in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$.⁸

The byproduct that the polaron-like 3d electrons thermally move in Cu-Ti sublattice above 150 K, is partly the

charge transfer between the A-site Cu ions and the B-site Ti ions, with valence changes cycles ($\text{Cu}^{2+} - e^- \leftrightarrow \text{Cu}^{3+}$, $\text{Ti}^{4+} + e^- \leftrightarrow \text{Ti}^{3+}$, $\text{Cu}^{2+} + e^- \leftrightarrow \text{Cu}^{1+}$), which is indicated by the photo-oxidation⁸ and the fabrication-process-related presence of Cu^{1+} , Ti^{3+} cations, and oxygen vacancies¹⁵ at room temperature. The A–B intersite charge transfer was also observed in another A-site-ordered double perovskite $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$.⁴⁰ These polaron-like electrons move among d_{xy} , d_{yz} , or d_{zx} orbitals of different Cu ions, and can anisotropically enlarge their electronic clouds of planar CuO_4 square, which presses CaO_{12} icosahedra at specific directions. The changed spatial symmetry of Ca^{2+} and Cu^{2+} electronic clouds, may be observed as Ca-Cu disorder.^{6,13} On the other hand, polaron-like 3d electrons are pinned at grain surfaces and could act as the depletion barrier, Schottky barrier,³³ which can explain the metal-contact-dependent dielectric measurements.²⁷

IV. CONCLUSION

In summary, the negative magnetodielectric effect as large as -5% is observed from 50 K to 200 K in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, which is attributed to the lattice ionic polarization of 1-D finite dipole chains of titanium ions is suppressed by the superexchange interaction, i.e., the short-range hop of polaron-like 3d electrons between d orbitals of the nearest neighboring copper ions via those of bridging titanium ion. Above 151 K, these quasi-particles are thermally activated and pinned at grain surfaces for bulk electronic polarization. The “frozen” state of lattice ionic polarization and the “saturate” state of bulk electronic polarization are then responsible for the minor negative effect observed below 50 K and above 200 K, respectively. $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ is thus implied as a unified system, which self-consistent explains the observable electrical and photo-related phenomena.

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