The quest to achieve strong magnetoelectric (ME) coupling has driven the surge in research on multiferroic materials over the past decade. However, this has been quite difficult to accomplish using bulk materials, motivating researchers to explore other approaches, most notably the use of transition metal oxide heterostructures. In these novel systems, different degrees of freedom (DOFs) (e.g., charge, spin, and orbital) are coupled at a single interface between two different oxide layers to form a new state that displays properties dramatically different from those of the individual layers. Particular attention has been given to the coupling between ferromagnetic (FM), antiferromagnetic (AFM), and ferroelectric (FE) orders, as this could reveal new routes to realizing strong ME coupling.

Heterostructures consisting of manganite and multiferroic layers are particularly promising in this regard. The most extensively studied combination consists of the colossal magnetoresistive (CMR) manganite \( \text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 \) (LSMO) (or the similar compound \( \text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 \) (LCMO)), which is ferromagnetic below a critical temperature \( T_c \), and the canonical multiferroic \( \text{BiFeO}_3 \) (BFO), which has coexisting coupled AFM spins in an alternating arrangement, which can not be done using an applied magnetic (B) field. Furthermore, little effort has been made to explain the switchable magnetotransport in the manganite layer, which is arguably of equal importance, particularly due to its rich history in CMR manganites.

One can gain insight into these issues using ultrafast optical spectroscopy (UOS), which has been demonstrated to be a sensitive probe of the charge, spin and orbital order in CMR manganites. In particular, much insight has been obtained from probing large photoinduced changes in the optical conductivity from low to high frequencies (known as ‘dynamical spectral weight transfer’ (DSWT)). Which have been shown to be strongly coupled to the magnetotransport properties.

Here, we used UOS to observe a difference in DSWT between a thin LCMO film and a LCMO/BFO heterostructure at low temperatures. This is due to the polaronic nature of carrier transport in LCMO, originating from spin canting near the interface with AFM ordered BFO. This is supported by the observed increase in conductivity when a B field is applied, increasing the spin alignment. These results can thus provide a new avenue to engineering multiferroic functionality, since the AFM order is coupled to the FE polarization in multiferroics such as BFO.

The samples studied here are a thin film of optimally doped LCMO (thickness \( t=10 \) nm) and a LCMO(10 nm)/BFO(50 nm) heterostructure, both grown on (001)
SrTiO$_3$ (STO) substrates by pulsed laser (KrF) deposition. The heterostructure (LCMO/BFO) is deposited by switching the target without breaking the vacuum. The substrate temperature during film growth is initially optimized and maintained. The oxygen pressure during deposition is 100 mTorr. The samples are cooled to room temperature in pure oxygen (350 Torr) by turning off the power supply to the heater without further thermal treatment \cite{23}. The degenerate optical pump-probe measurements use an amplified Ti:sapphire laser system producing pulses at a 250 kHz repetition rate with $\sim$150 fs duration and energy $\sim$4 $\mu$J/pulse at a center wavelength of 780 nm (1.59 eV). The absorbed pump fluence is $\sim$5 $\mu$J/cm$^2$, creating a photoexcited carrier density of $\sim$10$^{18}$-10$^{19}$ cm$^{-3}$(10$^{-4}$-10$^{-3}$ per unit cell). The laser-induced heating in the samples is $<1$ K. The B-field-dependent measurements are performed in a $\sim$6 T superconducting magnet.

Our initial focus was to understand quasiparticle dynamics in our thin LCMO films without the influence of the BFO layer. Therefore, we measured the photoinduced change in reflectivity, $\Delta R/R$, as a function of the time delay between the pump and probe pulses at various temperatures (Fig. 1(a)). Optimally doped LCMO is a FM metal (FMM) below $T_c$ and a paramagnetic insulator (PMI) above $T_c$. After photoexcitation, there are three decay processes below $T_c$ and two above $T_c$ ($\sim$260 K in the bulk, $\sim$160 K in our film). We note that these measurements on our thin 10 nm film differ significantly from previous measurements on thick films \cite{19, 23, 24}. In thick films ($t > 75$ nm), for both FMM and PMI phases, the first time constant ($\tau_1 = \tau_{e-p} < 1$ ps) arises from electron-phonon coupling (corresponding to the initial negative $\Delta R/R$ signal and sub-ps recovery (negative upward signals) observed for all $T$). The second time constant, which depends strongly on $T$ near $T_c$, is the spin-lattice relaxation time ($\tau_2 = \tau_{s-l} \sim$30-200 ps in thicker films), which slows down near $T_c$ due to an increase in the spin specific heat. The third time constant, $\tau_3$, is from heat diffusion ($\tau_3 > 1$ ns in thicker films and bulks \cite{19, 23, 24}). In contrast, the relaxation processes measured here in our 10 nm film are much faster than in previous reports on thicker films (except for $\tau_{e-p}$), calling their origin into question.

For more insight into this, we performed the same measurements on LCMO films with different thicknesses grown under the same conditions (data not shown here). We observed similar temperature dependence for thicker films ($t > 100$ nm) as in the literature \cite{19, 23, 24}; however, $\tau_3$ strongly depended on the thickness for $t \sim$10-100 nm. To address this, we performed a numerical simulation modeling 1D thermal diffusion across an interface \cite{27}, using the acoustic mismatch model for the interface thermal resistance \cite{28} and including the laser absorption depth in LCMO ($\sim$100 nm). The simulation indicates that for thick LCMO films ($t > 50$ nm), thermal transport is dominated by the slow diffusivity of bulk LCMO, while for $t < 30$ nm it is governed by heat dissipation through diffusion in the substrate. This leads to a much faster decay in thin films than in thick films, since the substrate diffusivity is nearly an order of magnitude higher than that of bulk LCMO. By using the bulk val-

FIG. 1: (color online) Photoinduced change in optical reflectivity as a function of time delay at various temperatures, measured at 1.59 eV in (a) a LCMO film and (c) a LCMO/BFO heterostructure. In LCMO, $T_c \sim$160 K, consistent with that obtained through magnetotransport measurements. The dash and dash-dot lines are numerical simulations of 1D thermal diffusion across the LCMO/STO interface at 10 K and 300 K. Insets show the dynamics at early times. (b) Schematic diagram of the optical conductivity versus energy ($<2$ eV) for typical optimally doped manganites in both Drude-like (low temperature) and polaron-like (high temperature) phases. The solid blue and dashed red lines illustrate the optical conductivity before and after laser excitation. The polaron peak is $\sim$1-1.6 eV in various manganites.
ues for thermal parameters at 10 K and above $T_c$, we are able to reproduce the thermal relaxation process in the 10 nm thin film (Fig. 1(a)), and the observed change in the long decay time is due to different thermal dissipation mechanisms in the two samples, without being influenced by other size effects that could affect ultra thin films (a few atomic layers thick).

The $\Delta R/R$ signals discussed above originate from laser heating-induced DSWT, which transiently changes the optical conductivity in LCMO [18, 19]. In optimally doped manganites, the time-integrated optical conductivity displays a Drude-like feature at low temperatures [29, 30], as illustrated by the blue line in the upper panel of Fig. 1(b). This peak-like feature evolves from low to high ($\sim$1-1.5 eV) energies as $T$ increases [29, 30], as depicted by the blue line in the lower panel of Fig. 1(b). This SWT dominates the low energy physics ($<3$ eV) in manganites, and has been attributed to the appearance of Jahn-Teller (J-T) polarons as $T$ approaches $T_c$ from below that trap electrons hopping from Mn$^{3+}$ to Mn$^{4+}$ sites [24, 29, 30]. The formation of this polaron peak is generally considered to be a signature of competition between the electron kinetic energy and the J-T lattice distortion [24].

Similarly, after femtosecond photoexcitation, energy is rapidly transferred from the electronic subsystem to the lattice within a ps, driving DSWT, which causes $\Delta R/R$ at $\sim$1-1.6 eV to transiently reproduce the change in optical conductivity on this timescale [34]. Therefore, below $T_c$, $\Delta R/R > 0$ indicates a photoinduced increase in the resistivity of the metallic state ($d\rho/dT > 0$); the DSWT transiently redistributes the spectrum to higher energies (upper panel of Fig. 1(b)), so $dR/dT(1.5 \text{ eV}) > 0$). Above $T_c$, $\Delta R/R < 0$ symbolizes a photoinduced increase in the conductivity of the insulating state ($dp/dT < 0$); the DSWT transiently redistributes the spectrum to lower energies (lower panel of Fig. 1(b)), so $dR/dT(1.5 \text{ eV}) < 0$). Representative 'resistive' ($T < T_c$) and 'conductive' ($T > T_c$) transients are given by the 10 K and 300 K traces in Fig. 1(a), respectively. For clarity, we note that a 'resistive' $\Delta R/R$ transient indicates that the equilibrium state is metallic, while a 'conductive' transient indicates that the equilibrium state is insulating.

We can now use this detailed characterization of our thin LCMO films as a basis for understanding quasiparticle dynamics in the LCMO/BFO heterostructure. The temperature-dependent DSWT in optimally doped LCMO should stay the same when changing the material underneath (assuming similar thermal diffusivity), as long as no novel interface state is formed. This is observed in LCMO/BFO above 165 K in Fig. 1(c), indicating that the relaxation mechanisms remain the same at high temperatures. However, at low temperatures ($T < 100$ K) the resistive transient observed in LCMO alone is replaced by a conductive transient in LCMO/BFO.

This signal is due to photoinduced changes in the LCMO layer, since, in addition to the similarity of this signal to that observed in LCMO alone for $T > 165$ K, the band gap of BFO is greater than 2.6 eV for $T < 100$ K, preventing it from being directly photoexcited with our 1.59 eV pump photons [35]. Therefore, the difference in DSWT between the two samples at low temperatures implies a change in the magnetic and/or metallic properties of LCMO when grown on BFO. In particular, the observed conductive transient at low $T$, similar to that observed at high $T$ in LCMO alone, suggests that LCMO becomes more insulating when grown on BFO.

This is likely most significant near the LCMO/BFO interface, where the two materials can directly interact. Our UOS measurements can sensitively probe this interface. Since our 10 nm LCMO film is much thinner than the laser absorption depth ($\sim$100 nm), a substantial portion of the 1.59 eV photons reach the LCMO/BFO interface, such that any photoinduced changes in the interfacial states could significantly influence $\Delta R/R$.

To gain more insight into the insulating nature of the LCMO/BFO interface, we performed low temperature measurements in a B field up to 5 Tesla (T) directed along the surface normal, allowing us to directly rotate spins (and thus overcome interfacial spin pinning [16]). Fig. 2 displays the measured $\Delta R/R$ signal for LCMO/BFO as a function of $B$ field at 10 K, where both samples were zero-field cooled. The inset shows the signal from the individual LCMO film, measured under the same conditions as LCMO/BFO, which reveals no discernible change since the magnetization is saturated at low temperatures. However, in the heterostructure, we find a large field-tunable DSWT. As the B field increases, the
conductive transient looks more and more resistive, suggesting growth of the metallic state [24, 36].

Because both samples are zero-field cooled, we can rule out the possibility of domains as the origin of this behavior in LCMO/BFO. Instead, the conductive transient observed at low temperatures and low B fields in LCMO/BFO suggests that polarons play a significant role in the observed phenomena. More specifically, femtosecond photoexcitation causes electrons to hop from Mn$^{3+}$ to Mn$^{4+}$, after which the photoinduced energy is transferred to the lattice. This increases the lattice temperature, which in LCMO/BFO corresponds to excitation of the formation of J-T polaron pairs, causing the spectral weight near 1.5 eV [29, 30] to decrease, increasing the hopping amplitude. When the FE polarity is switched, the increase in $l$ (Fig. 3(b)) causes the magnitude of $J_{\text{FM-AFM(G)}}$ to decrease, increasing the hopping amplitude. The change in $l$ between two FE polarity states is $>\sim$3-5 Å (the lower limit is estimated from as- grown, non-electrically poled LSMO/BFO in Ref. [39]), which is significant compared to 3-5 Å. Therefore, tunable magnetotransport can be observed when switching the FE polarization in BFO [2, 3] (Fig. 3(c)). We thus suggest that polarons are the result of competing interfacial FM/AFM order in LCMO/BFO (by inducing AFM order in LCMO), and the ionic distance between two transition metals is a method of tuning magnetotransport in these systems. This mutual spin interaction results in a measurable magnetic moment in the Fe ion of G-type BFO [14] and an induced AFM order in the Mn ion of ferromagnetic LCMO.

In summary, our UOS studies reveal a difference in the DSWT between single layer LCMO and a LCMO/BFO heterostructure. From comparing the DSWT between the two samples, we find a low temperature polaronic feature in LCMO/BFO, which is reduced in a magnetic field, while no change is observed in LCMO. From the framework of the double exchange interaction, we suggest that an interfacial AFM order in LCMO is induced by an effective ‘AFM field’ arising from G-type antiferromagnetic ordered BFO, which reduces in-plane electron hopping. By switching the FE polarity in BFO, one can...
change the coupling strength by tuning the separation between Fe-Mn, providing a new avenue for achieving tunable magnetotransport [2, 3, 16].

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