Polaronic Transport Induced by Competing Interfacial Magnetic Order in a $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3/\text{BiFeO}_3$ Heterostructure

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Using ultrafast optical spectroscopy, we show that polaronic behavior associated with interfacial antiferromagnetic order is likely the origin of tunable magnetotransport upon switching the ferroelectric polarity in a $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3/\text{BiFeO}_3$ (LCMO/BFO) heterostructure. This is revealed through the difference in dynamic spectral weight transfer between LCMO and LCMO/BFO at low temperatures, which indicates that transport in LCMO/BFO is polaronic in nature. This polaronic feature in LCMO/BFO decreases in relatively high magnetic fields due to the increased spin alignment, while no discernible change is found in the LCMO film at low temperatures. These results thus shed new light on the intrinsic mechanisms governing magnetoelectric coupling in this heterostructure, potentially offering a new route to enhancing multiferroic functionality.

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The quest to achieve strong magnetoelectric 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 [1–3]. 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 [4–8]. 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 magnetoelectric coupling [1–3,9–11].

Heterostructures consisting of manganite and multiferroic layers are particularly promising in this regard. The most extensively studied combination [2,3,9,10,12] consists of the colossal magnetoresistive manganite $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (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 BiFeO_3 (BFO), which has coexisting coupled AFM and FE phases in which the magnetization can be switched by an

applied electric (E) field [13]. The combination of these materials thus has great potential for exhibiting novel phenomena by coupling different FM, AFM, and FE phases across the interface. Indeed, a new interfacial state between LSMO and BFO has been discovered experimentally and discussed theoretically [2,14–16]. This state displays an exchange-bias field and magnetotransport that can be tuned by switching the FE polarization, increasing the potential for device control through interfacial coupling. However, a complete picture of the interplay between FM and AFM orders in this heterostructure has yet to be reached.

Current understanding of the exchange-bias field, which arises from the interaction between FM and G -type AFM [AFM(G)] orders at the interface, is based on spin canting or pinning in BFO, with the assumption of negligible canting in the manganite layer [14–16]. However, given that the spin interaction is mutual, it is not clear why FM spins in LSMO can induce AFM spins in BFO to cant, but the reverse has not been discussed. In fact, the interfacial spin-spin interaction $J_{\text{FM-AFM}(G)}$ could enable the use of effective “AFM staggered fields” to control FM spins in an alternating arrangement, which cannot be done using an applied magnetic (B) field. Furthermore, relatively little effort has been made to explain the E -field switchable magnetotransport in the manganite layer, which is arguably of equal importance.

One can shed light on these issues using ultrafast optical spectroscopy (UOS), which has been demonstrated to be a sensitive probe of the charge, spin, and orbital order in colossal magnetoresistive manganites [17–23]. In particular, much insight into the physics of these systems has been

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obtained from probing large photoinduced changes in the optical conductivity between low and high frequencies [known as dynamical spectral weight transfer (DSWT)] [17–20,24], which are strongly coupled to the magneto-transport properties [25].

Here, we use UOS to uncover the polaronic nature of carrier transport in a LCMO/BFO heterostructure, originating from spin canting in LCMO near the interface with AFM-ordered BFO. This is revealed through the difference in DSWT between a LCMO film and a LCMO/BFO heterostructure at low temperatures, and further supported by the observed increase in conductivity when a B field is used to increase the spin alignment. These results can thus provide a new avenue to engineering multiferroic functionality [2], since the AFM-ordered spins in BFO interact with FM spins in LCMO across the interface and are coupled to the FE polarization [13,16].

The samples studied here are a thin film of optimally doped LCMO (thickness $t = 10$ nm), which is a FM metal (FMM) below T_c and a paramagnetic insulator (PMI) above T_c (~ 260 K in the bulk, ~ 160 K in our film), and a LCMO (10 nm)/BFO (50 nm) bilayer heterostructure, both grown on (001) SrTiO₃ (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 [29]. The degenerate optical pump-probe

measurements use an amplified Ti:sapphire laser system producing pulses at a 250 kHz repetition rate with ~ 150 fs duration and energy ~ 4 μ J/pulse at a center wavelength of 780 nm (1.59 eV). The incident pump fluence is ~ 25 μ J/cm², creating a photoexcited carrier density of $\sim 7 \times 10^{18}$ cm⁻³ ($\sim 4 \times 10^{-4}$ per unit cell). The photoinduced initial increase in the lattice temperature is 2–4 K, calculated from the heat capacity, which should decrease with increasing equilibrium temperature. The B field-dependent measurements are performed in a ~ 5 T superconducting magnet.

To unravel quasiparticle dynamics in our LCMO/BFO heterostructure, it is essential to first understand the dynamics in our thin LCMO film. Previous UOS experiments on LCMO have shown that in thick films ($t > 75$ nm), the first time constant ($\tau_1 < 1$ ps) arises from electron-phonon coupling in both FMM and PMI phases. The second time constant originates from spin-lattice relaxation ($\tau_2 \sim 30$ –100 ps), slowing down near T_c due to an increase in the spin specific heat, and the third time constant τ_3 is due to heat diffusion ($\tau_3 > 1$ ns) [18,24,30]. In our 10 nm LCMO film, temperature-dependent measurements of the transient photoinduced change in reflectivity, $\Delta R/R$ [Fig. 1(a)], reveals that τ_2 and τ_3 are much faster than in thicker films. However, thickness-dependent measurements on a series of LCMO films (not shown) reveal that their origin is the same [31]. This is confirmed by a numerical simulation for 1 D thermal diffusion across an interface, which demonstrates that the faster decay times in thin films result from the strong influence of the substrate thermal diffusion on thermal transport, rather than diffusion

FIG. 1. 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 dashed and dash-dotted lines are numerical simulations of 1 D thermal diffusion across the LCMO/STO interface at 10 and 300 K, calculated as in Ref. [26]. Insets show the dynamics at early times. The spike-like feature in the data of (c) at 300 K at $t = 0$ is due to the coherent artifact [27]; its superposition with the transient reflectivity signal leads to the observed sub-ps oscillatory signal. (b) Schematic diagram of the optical conductivity versus energy (< 2.5 eV) for typical optimally doped manganites in both Drude-like (low-temperature) and polaron-like (high-temperature) phases (simplified illustration redrawn from data of Ref. [28]). The solid blue and dashed red lines illustrate the optical conductivity before and after laser excitation. The polaron peak is observed around ~ 1 –1.6 eV in various manganites.

in the films themselves [dashed and dash-dotted lines in Fig. 1(a)] [26]. Therefore, as in thicker films, the $\Delta R/R$ signals measured on our thin LCMO film originate from laser heating-induced DSWT [17,18]. Importantly, these signals, obtained in a noncontact manner, can indicate whether the equilibrium state of LCMO is metallic or insulating, as follows.

In optimally doped manganites, the time-integrated optical conductivity displays a Drude-like feature in the low-temperature FMM state [32,33] [blue solid line in upper panel of Fig. 1(b)]. This feature evolves into a higher-energy (~ 1 – 1.6 eV) peak as T increases [32,33] [blue solid line in 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, which trap electrons hopping from Mn^{3+} to Mn^{4+} sites, reducing the conductivity [25,32–36] (see Appendix C for more detail). The formation of this polaron peak is considered to be a signature of competition between the electron kinetic energy and the J-T lattice distortion [25]. However, this temperature-induced SWT can be reversed by an applied B field. The applied field enhances the spin alignment, increasing the conductivity, which reduces the polaronic peak and recovers the Drude-like feature [i.e., following the blue solid line from the lower to the upper panel in Fig. 1(b)] [25,36–41].

DSWT then occurs after femtosecond photoexcitation, which transfers energy from the electronic subsystem to the lattice within a few picoseconds, causing $\Delta R/R$ at ~ 1 – 1.6 eV to transiently reproduce the change in optical conductivity on this time scale [20,42]. Therefore, below T_c , $\Delta R/R > 0$ indicates a photoinduced increase in the lattice temperature, increasing the resistivity ρ of the metallic state [$d\rho/dT > 0$; the DSWT transiently redistributes the spectrum to higher energies [upper panel of Fig. 1(b)], so $dR/dT(1.59 \text{ eV}) > 0$]. Above T_c , $\Delta R/R < 0$ symbolizes a photoinduced increase in the conductivity of the insulating state by liberating polarons [$d\rho/dT < 0$; the DSWT transiently redistributes the spectrum to lower energies [lower panel of Fig. 1], so $dR/dT(1.59 \text{ eV}) < 0$]. Representative “resistive” ($T < T_c$) and “conductive” ($T > T_c$) transients are given by the 10 and 300 K traces in Fig. 1(a), respectively. For clarity, we emphasize 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 (due to polaronic transport). Finally, since an applied B field increases the conductivity, the conductive transient measured in the insulating state evolves towards a resistive transient as the field increases [18–20]. In this manner, we can use UOS to reveal whether LCMO is insulating or metallic in equilibrium (see Appendix A for more details on DSWT in manganites).

We can now use this detailed characterization of our thin LCMO films as a basis for understanding carrier transport

in the LCMO/BFO heterostructure. First, we note that the $\Delta R/R$ signal in LCMO/BFO must be due to photoinduced changes in the LCMO layer, since the band gap of BFO is greater than 2.6 eV, preventing it from being directly photoexcited with our 1.59 eV pump photons [43,44]. In addition, we expect that the temperature-dependent DSWT in optimally doped LCMO should stay the same when changing the material underneath, as long as no novel interface state is formed.

This is observed in LCMO/BFO above ~ 165 K [through comparing Figs. 1(a) and 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, implying 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 is more insulating when grown on BFO.

This is likely most significant near the LCMO/BFO interface, where the two materials can directly interact [2,3,14,16]. Our UOS measurements can sensitively probe this interface. Since our 10 nm LCMO film is much thinner than the laser absorption depth (~ 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 $\Delta R/R$ [45].

To gain more insight into the insulating nature of the LCMO/BFO interface, we perform low-temperature measurements in a B field up to 5 T directed along the surface normal, allowing us to directly rotate spins (and thus overcome interfacial spin pinning [16]). Figure 2 displays the measured $\Delta R/R$ signal for LCMO/BFO as a function of the B field at 10 K, where both samples were zero-field cooled. The inset shows the signal from the individual

FIG. 2. Photoinduced time-dependent reflectivity change in LCMO/BFO as a function of B field at 10 K. The inset shows the $\Delta R/R$ signal from a single LCMO film, taken under the same experimental conditions.

LCMO film, measured under the same conditions as LCMO/BFO, which reveals no discernible change since the magnetization is saturated in the low-temperature FMM state. 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

Overall, our femtosecond optical data suggest that interfacial LCMO/BFO is insulating in equilibrium, and that the application of a B field causes it to become more conductive. Because both samples are zero-field cooled, we can rule out the possibility of domains as the origin of this behavior in LCMO/BFO. Another possibility, charge transfer between LCMO and BFO, is prohibited in equilibrium, as Ref. [14] measured no change in the valence state of Fe^{3+} . Photostriction has previously been observed in BFO [46] but is unlikely to affect our results, since both our previous experiments [43] and time-resolved x-ray diffraction [44] on BFO measured no response upon ~ 1.5 eV excitation. Finally, the difference in thermal diffusion between BFO/STO and STO (a factor of ~ 5) is also unlikely to influence our results, since the high-temperature data (≥ 165 K) on both samples is very similar (Fig. 1), and thermal diffusion would not be affected by a B field. A more detailed exclusion of these effects is presented in Appendix B. Instead, the conductive transient observed at low temperatures and high B fields in LCMO/BFO suggests that polarons play a significant role in the observed phenomena [similar to the PMI phase of LCMO, Fig. 1(a)], likely by decreasing the charge kinetic energy near the LCMO/BFO interface. Such polaronic behavior could arise from AFM order, orbital order, or a lattice distortion that creates a trapping potential, all of which are likely coupled.

The most likely explanation for the observed polaronic behavior when LCMO is grown on BFO is an induced AFM order in LCMO (reducing the FM order). This can result from interfacial coupling to G -type BFO, with its alternating spin alignment of Fe^{3+} ions [14] at the interface, through the interfacial spin-spin interaction $J_{\text{FM-AFM}(G)}$ [Fig. 3(a)]. For more insight, we consider that in optimally doped manganites, transport is governed by the double exchange interaction, in which the charge kinetic energy H_k is determined by the hopping amplitude $t_{ij}(1 + \langle \mathbf{S}_i \mathbf{S}_j \rangle / S^2)^{1/2} = t_{ij} \cos(\theta_{ij}/2)$ [25], where $\mathbf{S}_i$, $\mathbf{S}_j$ are nearest-neighbor Mn t_{2g} spins and θ_{ij} is the angle between them [Fig. 3(a)]. In the general Hamiltonian for Mn e_g electrons, hopping is linked to phonons (H_{ph}) and the electron-phonon coupling ($H_{e\text{-ph}}$), both of which are related to the formation of polarons [25]. As H_k surpasses H_{ph} and $H_{e\text{-ph}}$, the spins become more ordered and the state becomes more metallic, i.e., with increased conductivity. In LCMO/BFO, the induced AFM order at the interface will increase θ_{ij} in LCMO [Fig. 3(a)], suppressing in-plane electron hopping. This results in a discernible difference between LCMO and LCMO/BFO in a high B field, which

FIG. 3. Schematic diagrams showing spin tuning through ferroelectric switching, where we only show the spin component perpendicular to the interface in bulk BFO [47]. The spin alignment is depicted in LCMO(FM)/BFO (G -type AFM) with FE polarization (a) towards the interface (darker gray with stronger interaction) and (b) away from the interface (lighter gray with weaker interaction). (c) The corresponding magneto-resistance R_s in states (a) and (b) as a function of gate voltage V_g , sketched from Ref. [2].

increases the alignment of the induced AFM spins [38,39] while keeping the ordered FM spins saturated. We note that neutron diffraction measurements on LSMO/BFO superlattices grown in the same system at LANL have revealed a reduced magnetization in the LSMO layers, supporting this hypothesis [48].

This picture, based on an induced interfacial AFM order in LCMO, can now be used to shed light on previous work in which the magnetotransport was tuned by switching the FE polarization [2,16]. In LCMO/BFO, the separation l between Fe^{3+} and $\text{Mn}^{3+/4+}$ ions across the interface affects the strength of $J_{\text{FM-AFM}(G)}$ and, therefore, θ_{ij} (i.e., $J_{\text{FM-AFM}(G)}$ exponentially decays as $\sim e^{-l/d}$ [49], where d is the atomic distance, $\sim 3\text{--}5$ Å). Thus, when the BFO film is electrically poled such that the polarization points to the interface [displacing Fe^{3+} ions towards the interface, Fig. 3(a)], the reduction in l enhances the effective AFM field (the magnitude of $J_{\text{FM-AFM}(G)}$ and θ_{ij} increase), decreasing 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 the two FE polarity states is $\gtrsim 0.7$ Å (the lower limit is estimated from as-grown, nonelectrically poled LSMO/BFO [50]), which is significant compared to d . Therefore, tunable magnetotransport can be observed when switching the FE polarization in BFO [2,3] [Fig. 3(c)].

Our results thus indicate that polarons originate from competing interfacial FM/AFM order in LCMO/BFO. 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 FM LCMO. The ionic distance

between these two transition metals can then be used to tune magnetotransport in these systems.

In summary, our UOS studies reveal a difference in the DSWT between single-layer LCMO and a LCMO/BFO heterostructure. This indicates that interfacial transport in LCMO/BFO is polaronic in nature and is modified in a magnetic field, while no change is observed in LCMO. In 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. Furthermore, 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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APPENDIX A: DYNAMIC SPECTRAL WEIGHT TRANSFER REVEALED BY DEGENERATE OPTICAL PUMP-PROBE SPECTROSCOPY

Colossal magnetoresistance in manganites originates from a giant change in the conductivity that is controlled by the spin alignment (either through applying an external magnetic field or going to low temperatures). This in turn dominates the optical properties from terahertz to visible frequencies through spectral weight transfer, as schematically depicted in Fig. 1(b). SWT is a well-established concept in manganites (described in more detail in Refs. [25,28,32–35,51]). At low temperatures, the optical conductivity in optimally doped manganites is dominated by a low-frequency Drude peak, which is a signature of the metallic state. As the temperature increases, the amplitude of the Drude peak diminishes as the conductivity decreases (due to decreasing spin alignment), and a peak in the near-to-mid-infrared concurrently increases, which has been widely attributed to the trapping of free carriers into polaronic states [25,32–35]. In the high-temperature insulating phase (above T_C), a strong external magnetic (B) field can induce SWT from the IR polaronic peak to the low-frequency Drude peak by orienting spins (and thus increasing the conductivity). In the low-temperature metallic phase, the B field will not increase the conductivity, since the spins are already well aligned.

Optical measurements can, therefore, be significantly influenced by the spin alignment through SWT. This can then be extended to nonequilibrium optical measurements, in which the femtosecond pump pulse introduces heat when the sample is at low temperatures (resulting in SWT to higher frequencies) and liberates carriers trapped in polaronic states when the sample is at high temperatures (initiating SWT to lower frequencies); this is the idea of dynamic spectral weight transfer [described in the paper and schematically depicted in Fig. 1(b)]. DSWT is a well-known concept that has been widely shown to dominate the response in ultrafast optical measurements on manganites [17–20,24].

Further support for this concept comes from previous work on similar samples: in Fig. 14 of Ref. [42], it was clearly shown that, for an LCMO film, the time constant associated with DSWT was nearly identical when probing at both 1.5 eV and THz frequencies. This is strong evidence that a 1.5 eV probe is sensitive to DSWT, even in the absence of complementary optical-pump, THz-probe measurements. Therefore, the degenerate 1.5 eV pump-probe measurements described here can clearly reveal the transition from Drude-like to polaronic behavior in LCMO through DSWT, since the origin of the photoinduced change in optical properties is the same.

Finally, we emphasize that the strongest evidence for the sensitivity of our ultrafast optical reflectivity measurements to the spin alignment is given by the field tuning experiment displayed in Fig. 3: while we saw significant field tuning in LCMO/BFO, we observed no change in LCMO, strongly supporting the field-induced increase in the conductivity of LCMO/BFO, while the conductivity of LCMO/STO was saturated as all the spins were already aligned at 10 K.

APPENDIX B: EXCLUSION OF OTHER POSSIBLE CONTRIBUTIONS TO OUR DATA

We considered the influence of lattice mismatch and/or modifications of the lattice properties due to the change in the layer underneath LCMO. Therefore, we performed temperature-dependent ultrafast optical measurements of LC(S)MO on MgO (on which manganites are relaxed, as measured with x-ray diffraction) and on STO (on which manganites are strained, also measured with x-ray diffraction). We find that the results are very similar for different substrates, indicating that simple lattice mismatch or random interfacial disorder should not influence the observed data. We also considered the effect of changes in the thermal diffusivity on our data. However, we can exclude this possibility, since our data on LCMO/BFO/STO and LCMO/STO are very similar at higher temperatures [Figs. 1(a) and 1(c)], despite the fact that the thermal conductivities of BFO (~ 2 W/m/K) and STO (11 W/m/K) and the heat capacities of BFO (~ 2 J/cm³/K) and STO (~ 2.2 J/cm³/K) at 300 K lead to a factor of ~ 5 difference

in the diffusivities of BFO ($\sim 0.01 \text{ cm}^2/\text{s}$) and STO ($\sim 0.05 \text{ cm}^2/\text{s}$). This should lead to a corresponding difference in the time constant associated with thermal decay in our data, but we observe no significant difference [traces at 300 K in Figs. 1(a) and 1(c)]. Furthermore, the difference in thermal diffusivity increases with decreasing temperature [52] while the specific heat of BFO varies little and that of STO decreases 30% between 165 and 300 K, but our LCMO/BFO/STO and LCMO/STO data remain quite similar down to ~ 165 K, making it very unlikely that this would significantly influence our results (particularly since the 50 nm BFO layer is much thinner than the STO substrate, which thus serves as a heat sink). Finally, because an AFM material has no response to an external B field of the magnitude used in our experiments, if the thermal diffusivity of BFO is the origin of the observed difference, then we would not expect to see the B -field dependence shown in Fig. 2.

It is also worth considering the possible influence of photostrictive effects on our data, as they have been previously observed in BFO [46]. In this context, it is important to emphasize that our optical pump pulses only photoexcite the LCMO layer, since the pump photon energy (1.59 eV) is much lower than the band gap (~ 2.6 eV) of BFO. We extensively studied both single-crystal BFO and thin films of BFO grown on STO, and we have never found an observable optical response with a 1.59 eV pump, even at much higher fluences when two-photon processes could play a role (we have tried fluences up to 2 orders of magnitude larger than we used here to pump BFO, with no observable optical response). Our detailed studies of ultrafast dynamics in single crystal BFO can be found in Ref. [43], and comparison of the dynamics between BFO single crystals and films is available in Ref. [53]. In addition, if a photostrictive effect arising from the BFO layer somehow influenced our data, we would expect to see a significant difference between the dynamics in LCMO/BFO/STO and LCMO/STO at all temperatures, which is not the case at high temperatures (Fig. 1). Therefore, within our experimental sensitivity, we conclude that BFO is not directly excited through either one-photon or multiphoton processes, and can, therefore, exclude the possibility of structural changes due to direct excitation of BFO. Additional support can be found in Ref. [44], where photoinduced changes in the lattice constants of a BFO film were discovered using time-resolved x-ray diffraction with above-gap excitation, but not observed when using a 1.55 eV pump.

Finally, we note that other methods used to unravel quasiparticle dynamics in oxides, such as time-resolved SHG and magneto-optical Kerr effect (MOKE), are not as suitable for studying polaronic behavior in LCMO/BFO. Our preliminary SHG measurements on LCMO/BFO indicate that BFO is the origin of the observed SHG signal, due to broken inversion symmetry from its FE order. This

is, therefore, insensitive to the interfacial spin order and conductivity of the LCMO layer. Furthermore, the MOKE signal would be influenced by both the signal from FM order throughout the LCMO layer as well as the induced FM order in the BFO layer, making it difficult to isolate the dynamics in the LCMO layer near the interface. Therefore, ultrafast optical reflection or transmission measurements, at an energy that is not sensitive to the optical properties of BFO, are actually more useful and straightforward to interpret in this case.

APPENDIX C: POLARON BINDING ENERGY

The optical conductivity schematically depicted in Fig. 1(b) (< 2.5 eV) is primarily dominated by electron hopping between Mn^{3+} and Mn^{4+} , i.e., without polarons below T_c (upper panel) and with polarons above T_c (lower panel). Below T_c , the optical transition in the metallic state can be regarded as an intraband transition. Above T_c , the peak originates from correlated $\text{Mn}^{3+} - \text{Mn}^{4+}$ transitions, i.e., $\text{Mn}^{3+}(\text{distorted}) + \text{Mn}^{4+}(\text{undistorted}) \rightarrow \text{Mn}^{4+}(\text{still distorted}) + \text{Mn}^{3+}(\text{undistorted})$. We note that the final state initially has the (now unfavorable) J-T distortion on the wrong site, since the phonon cannot respond to the new excited state within the pulse duration. This causes the polaron binding energy E_p to be half of the energy of the absorption peak (~ 750 meV).

More insight into the microscopic origin of E_p is given by expressing the phonon energy as

$$E = \frac{1}{2} kx^2 - fx, \quad (\text{C1})$$

where f is the magnitude of electron-phonon coupling, i.e., the extra force on the phonon when an electron occupies the site. It can then be shown that the energy of the absorbing transition is given by $E_{\text{final}} - E_{\text{initial}} = f^2/k$, and that the polaron binding energy is $E_p = (1/2)f^2/k$. We note that there is no oscillator whose energy $\hbar\omega = E_p$.

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