

Excitations across the Equilibrium and Photoinduced “Hidden” States of Magnetoresistive Manganites

Shiyu Fan^{1,*}, Feng Jin^{2,3}, Taehun Kim,¹ Umesh Kumar^{4,12}, Zixun Zhang,² Vivek Bhartiya¹, Jiemin Li,¹ Brandon Yalin¹, Yanhong Gu¹, Mingqiang Gu,⁵ Wen Hu,¹ Claudio Mazzoli¹, G. Lawrence Carr,¹ Osor S. Barišić⁶, Andrey S. Mishchenko^{6,7}, Valentina Bisogni¹, Sobhit Singh^{8,9}, Wenbin Wu,^{2,10,11} and Jonathan Pellicciari^{1,†}

¹*National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, New York 11973, USA*

²*Anhui Key Laboratory of Condensed Matter at Extreme Conditions, High Magnetic Field Laboratory, and Hefei National Research Center for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026, China*

³*School of Physics, Hefei University of Technology, Hefei, Anhui 230009, China*

⁴*Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854, USA*

⁵*Department of Physics, Southern University of Science and Technology, Shenzhen 518055, China*

⁶*Department for Research of Materials under Extreme Conditions, Institute of Physics, 10000 Zagreb, Croatia*

⁷*RIKEN Center for Emergent Matter Science (CEMS), 2-1 Hirosawa, Wako, Saitama, 351-0198 Japan*

⁸*Department of Mechanical Engineering, University of Rochester, Rochester, New York 14627, USA*

⁹*Materials Science Program, University of Rochester, Rochester, New York 14627, USA*

¹⁰*Institute of Physical Science and Information Technology, Anhui University, Hefei 230601, China*

¹¹*Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, China*

¹²*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*



(Received 10 July 2025; revised 30 December 2025; accepted 23 March 2026; published 23 April 2026; corrected 10 July 2026)

“Hidden” phases, generated using ultrafast laser pulses (few hundred femtoseconds), with distinct properties than at the thermodynamic equilibrium, are appealing for technologies, as they can be long-lived, with a lifetime of hours or weeks, and reversible with temperature sweeping or extra pulses. In this regard, $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ (LCMO) stands out due to its tunability through epitaxial strain, which can drive the bulk ferromagnetic metal into an antiferromagnetic insulator (AFI), and its susceptibility to photoinduced transitions. Indeed, AFI LCMO displays a long-lived photoinduced transition into a putative hidden phase whose exact nature and excitations are still largely unknown. Here, we combine ultrafast photoexcitation in the near infrared with *in situ* transport, x-ray absorption, and resonant inelastic x-ray scattering (RIXS) to investigate the excitations (polarons, phonons, and orbital) of the photoexcited phase of LCMO and contrast them with the thermodynamic phases achieved through strain and temperature. In the thermodynamic regime, we establish the correlation between polarons and transport placing them in the “strong coupling” regime of the Holstein model. Upon photoexcitation of LCMO-AFI, we uncover a long-lived phase characterized by the softening of the polaron excitations, the partial suppression of the Jahn-Teller distortion, and nearly unchanged phonons, showing the emergence of a photoexcited state absent in the equilibrium phase diagram. Finally, by varying temperature, epitaxial strain, and photoexcitation fluence, we construct a polaron phase diagram and identify the key spectroscopic signatures of each phase. Our laser-RIXS approach establishes a versatile platform for exploring photoinduced hidden phases in quantum materials in nonstroboscopic conditions.

DOI: [10.1103/24wn-q427](https://doi.org/10.1103/24wn-q427)

Subject Areas: Condensed Matter Physics,
Strongly Correlated Materials

*Contact author: sfan1@bnl.gov

†Contact author: pellicciari@bnl.gov

Published by the American Physical Society under the terms of the [Creative Commons Attribution 4.0 International](https://creativecommons.org/licenses/by/4.0/) license. Further distribution of this work must maintain attribution to the author(s) and the published article's title, journal citation, and DOI.

I. INTRODUCTION

Ultrafast laser pulses provide a powerful route to coherently excite materials into a nonequilibrium state, enabling phenomena such as metal-to-insulator transitions, multiferroicity, and enhanced superconductivity [1–10]. While most of these excited states are transient, lasting only few femto- to picoseconds [11–13], long-lived phases

can be created if the ultrafast laser pulse provides sufficient energy to cross or modify the free-energy barrier, driving the system into a metastable local minimum in the free-energy landscape [4,5,14,15]. These “hidden” phases are thermodynamically inaccessible and can persist for hours or longer due to the energy barrier that prevents relaxation to the ground state [2,4,5,16]. Importantly, such states can often be erased and recovered using additional external stimuli, such as temperature, magnetic field, or laser pulses at different wavelengths, and are, therefore, amenable for device applications [4,5]. Indeed, the ability to switch between pristine and photoinduced states on demand holds strong potential for ultrafast memory, logic, and quantum information applications based on dynamic control of material properties [17].

Quantum materials are susceptible to the emergence of photoinduced long-lived phases due to the interplay of the spin, lattice, charge, and orbital degrees of freedom and proximity of multiple ground states and order parameters [6,18–20]. One exemplar case is the colossal magnetoresistive $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ (LCMO), where multiple phases compete due to their close energy scales and intertwined degrees of freedom, offering the opportunity to switch them through static or dynamic perturbations [1,4,21,22].

Bulk LCMO displays a low-temperature ferromagnetic metal (FMM) phase that morphs into a paramagnetic insulating (PMI) phase at room temperature. Epitaxial tensile strain along the b axis induces an antiferromagnetic insulator (AFI) phase at low temperature that transitions into the same PMI of the bulk phase above a critical temperature [21,22]. Key ingredients to the understanding of the electronic transport in these phases are the Jahn-Teller distortion, the formation of polarons, and electron-phonon coupling [23–27]. Moreover, the tendency of LCMO toward phase transitions is highlighted by its switching through photoexcitation, leading the AFI phase into a long-lived nonergodic phase with distinct electronic and magnetic properties [1,4]. Previous studies have shown that ultrafast excitation can melt the AFI phase and stabilize the FMM state, often interpreted as a collapse of charge or orbital ordering [1,4,5,11]. While the macroscopic switching of resistance and magnetism has been reported in photoexcited epitaxially strained LCMO films [1,4], the main spectral features and, therefore, the microscopic character of the photoinduced state still remain poorly investigated.

Resonant inelastic x-ray scattering (RIXS) is a photon-in, photon-out scattering technique with sensitivity to all the electronic degrees of freedom (spin, charge, orbital, and their coupling to the lattice) [7,16,28]. In recent years, progress on the energy resolution and the coupling with other *in situ* stimuli led to significant advances in the field of condensed matter physics [16,29]. One of the latest development has been the coupling of RIXS with lasers, enabling the study of photoinduced phenomena [7,16,30,31]. While a significant effort has been put into the

development of time-resolved schemes [7,30,31], no reports are available at this time on the study of photoinduced transition in nonstroboscopic mode targeting metastable phases.

In this work, we combined near-infrared femtosecond laser (1030 nm, 1.2 eV, 250 fs) switching with *in situ* transport, x-ray absorption (XAS), and high-resolution RIXS to study the long-lived transition of LCMO. This multipronged approach enables simultaneous access to the transport, the Jahn-Teller distortion, low-energy collective modes, and higher-energy orbital excitations in photoexcited phases. Our central result is that the 1.2 eV photoexcitation on the AFI phase reshapes the Jahn-Teller distortion and polaronic excitations, inducing a long-lived hidden phase microscopically distinct from the equilibrium AFI, FMM, and PMI phases. This state is characterized by (i) a metastable reduction of the resistivity; (ii) partial suppression of the Jahn-Teller distortion; (iii) a substantial softening of the polaronic excitation; and (iv) almost unchanged Jahn-Teller-active phonons. These observations coherently point to a partially melted Jahn-Teller polaronic state rather than a direct photoinduced transition to the metallic FMM state.

This evidence is complemented by data collected by tuning temperature, strain, and excitation fluence, which enable us to construct a manganite polaronic phase diagram and identify an exponential correlation between the polaron excitations and electrical resistivity. This reveals that the polaron excitations of LCMO—FMM, AFI, PMI, and photoinduced phase—consistently fall within the strongly coupled Holstein regime. Our results highlight the polaron excitations as a microscopic parameter for tuning electric transport. Within this framework, the photoinduced phase occupies a nonequilibrium region of the polaronic phase diagram that cannot be accessed along the equilibrium axes of temperature or strain. More generally, our work proves a novel capability to investigate long-lived photoinduced phases in correlated materials using a high-end scattering technique like RIXS.

This manuscript is divided in the following sections. First, we characterize the electrical transport of LCMO under ultrafast laser switching and identify a long-lived insulating metastable phase stabilized after photoexcitation (Secs. II and III). We then compare the microscopic Jahn-Teller distortions, as well as the polaron and phonon signatures, of this photoinduced phase with those of the equilibrium FMM, AFI, and PMI phases (Secs. IV–VII). In these sections, we extract the polaron energies across the equilibrium and photoinduced phases, analyze their relation to the electrical resistivity within a strongly coupled Holstein framework, and establish how the polaronic renormalization controls transport (Sec. VIII). Afterward, we discuss that the long-lived photoinduced state corresponds to a distinct Jahn-Teller-polaronic configuration that cannot be reached by temperature or strain alone, and we

place these results in the broader context of metastable phases in manganites (Sec. IX). Finally, we summarize the main results in Sec. X.

II. EVOLUTION OF ELECTRIC TRANSPORT IN LCMO DRIVEN BY ULTRAFAST PHOTOEXCITATION

LCMO thin films in the FMM and AFI phases were grown on NdGaO₃ (NGO) substrates. The films thicknesses are 24 nm. The FMM and AFI phases are characterized by resistivity and magnetization measurements (see Supplemental Material [32], Fig. S1). The FMM film is weakly strained and nearly identical to the bulk. The AFI phase is achieved through annealing and exhibits approximately 0.8% epitaxial tensile strain along the *b* axis [21]. The penetration depth of the x-ray and 1030 nm

femtosecond laser exceed the film thickness [20,39], ensuring that the entire probed volume is fully excited by the laser [Fig. 1(a)].

To investigate the photoinduced state, we measured the resistance of an LCMO-AFI/NGO (100) film under near-infrared (1030 nm, 250 fs) laser excitation by depositing electrodes on the film surface [Fig. 1(b)]. Figure 1(c) shows the relative resistance change over time following laser exposure. The laser was operated at a repetition rate of 1 kHz with a maximum fluence of 34.9 mJ/cm² for 30 s. Upon illumination, the resistance changes by approximately −47% compared to the pristine state, suggesting that photoexcitation drives the system toward a more conductive state. After the laser is turned off, the resistance partially recovers but stabilizes at a value approximately 7%–8% lower than the initial state [Fig. 1(c)]. Notably, this persistent state remains unchanged even 30 min after the

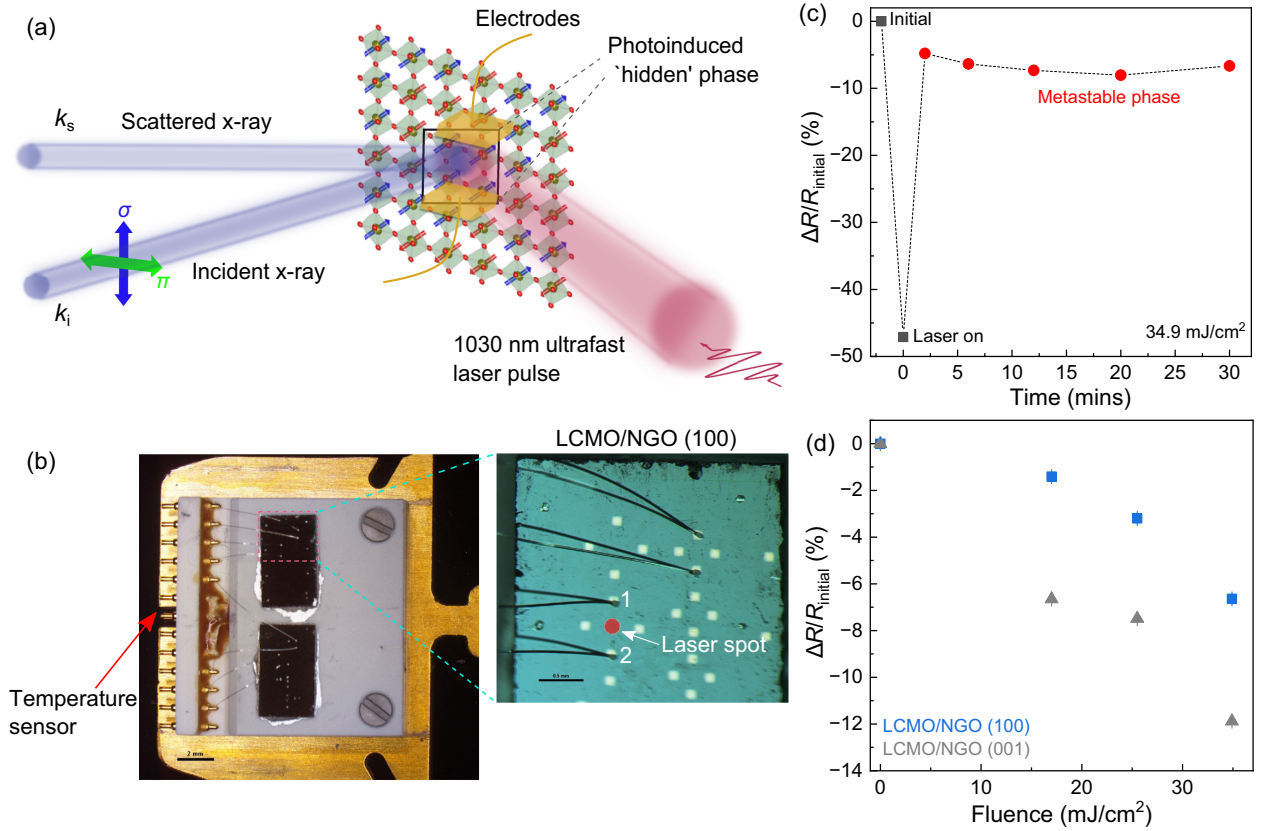


FIG. 1. (a) Schematic view of the *in situ* laser-transport-RIXS experimental setup. The laser pulses are 250 fs and 1030 nm center wavelength. The wave vector of the incident x-ray (k_i) is perpendicular to the ultrafast laser beam. σ and π refer to the polarization of the incident x-ray as perpendicular or parallel to the scattering plane, respectively. All RIXS spectra are taken with the σ polarization. The laser polarization is linearly horizontal, parallel to the scattering plane defined by k_i and k_s . The laser beam has an approximately 40° incident angle with respect to the film surface. The RIXS data are collected after photoexcitation in a “nonstroboscopic” manner. (b) Sample holder for the laser-transport-RIXS measurement. The top and bottom films correspond to the AFI LCMO/NGO (100) and LCMO/NGO (001), respectively. A temperature sensor is mounted next to the films to monitor temperature change upon laser irradiation. On the right, there is a close-up view of the electrodes deposited on the LCMO/NGO (100) film. The laser spot size is about 120 μm , and the distance between electrodes is 500 μm . (c) Relative resistance change with respect to the resistance of the initial AFI state (R_{initial}) at different recovering times. ΔR is defined as the resistance difference between the photoinduced and the initial AFI phase. (d) $\Delta R/R_{\text{initial}}$ as a function of laser fluence of the LCMO-AFI (100) and LCMO-AFI (001) films.

laser is turned off, confirming the formation of a long-lived metastable phase whose resistance is distinct from the equilibrium AFI and FMM phases. Heating effects can be ruled out, as all resistance values are measured long after laser exposure. Moreover, given that the laser-irradiated area spans only about one-fourth of the electrode spacing [Fig. 1(b)], the actual change in resistivity would be larger than what is reflected in the measured resistance. These results demonstrate that, although photoexcitation at 1030 nm moderately increases conductivity, the photo-induced metastable state still remains within a nonmetallic regime. For comparison, we also measured the laser-induced transport in another LCMO/NGO(001) film. A qualitatively similar photoinduced insulating metastable state is observed as well, although the absolute resistance is lower than in LCMO/NGO(100) due to the reduced epitaxial strain [Fig. 1(d)].

In our conditions, the photoinduced metastable phase appears at a laser fluence of approximately 34.9 mJ/cm², which differs from the reported fluence threshold at around 8–12 mJ/cm² (800 nm) [1,4,5]. While we cannot pinpoint the source of this discrepancy to a single factor, it is possible that it arises from a combination of differences in photoexcitation wavelength, laser pulse duration, and laser pumping protocol (pulse-picked vs quasicontinuous 1-kHz excitation within a 30-s window) which is discussed in later sections.

III. ULTRAFAST PHOTOEXCITATION MECHANISM IN LCMO

To obtain a more complete view of the multiplet electronic structure of LCMO and better understand the laser-pumping mechanism, we perform RIXS on the LCMO-AFI film at the Mn L_3 edge, which is highly

sensitive to Mn multiplets and orbital excitations [28,40]. Figure 2(a) showcases the RIXS spectra of the LCMO-AFI (100) film at 100 K. We can identify a broad series of peaks ascribable to the multiplets manifold of Mn ions. The peak at 1200 meV correspond to multiplets from Mn³⁺ dd excitations [40] which are localized, as they are connected to the electronic configuration of Mn and its local geometry. This localization is further evidenced from the RIXS intensity map at the Mn L_3 edge, where the 1200 meV excitation shows Raman-like behavior as the incident x-ray energy increases (see Supplemental Material [32], Sec. III). The peak at 1600 meV is attributed to an intersite Mn³⁺ to Mn⁴⁺ charge transfer excitation, consistent with optical spectroscopy [4]. The peak below 1 eV can be assigned to a polaron excitation which is discussed later together with O-K edge RIXS data. Our laser wavelength at 1030 nm (1.2 eV) lies well within the energy window of the Mn e_g manifold, matching the energy of the Jahn-Teller-active Mn³⁺ $d_{3z^2-r^2} \rightarrow d_{x^2-y^2}$ on-site excitation [40] and overlapping with the lower edge of the Mn³⁺ $\rightarrow$ Mn⁴⁺ intersite charge-transfer channel [Fig. 2(b)]. While the on-site transition is typically dipole forbidden in optical absorption, it becomes active under symmetry-breaking conditions such as O $2p$ –Mn $3d$ orbital hybridization or local lattice distortions. Consequently, both excitation pathways may contribute to the laser-induced transitions within the Mn e_g manifold [Fig. 2(b)].

IV. JAHN-TELLER EFFECTS IN THE FMM, AFI, AND PHOTOINDUCED PHASES

The transport properties of LCMO are affected by the Jahn-Teller distortion, specifically the Q_2 mode, where the Mn–O bond length in the basal plane exhibits

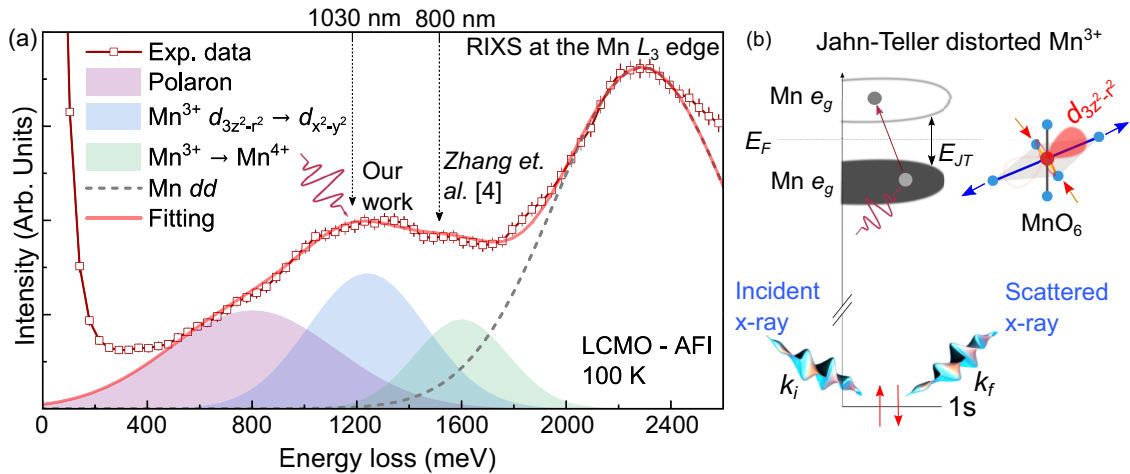


FIG. 2. (a) RIXS spectrum of the AFI phase of LCMO/NGO (100) at the Mn L_3 edge ($E_i = 643.2$ eV). We indicate the pump photon energies used here (1030 nm, 1.2 eV) and in Refs. [1,4] (800 nm, 1.55 eV). (b) Schematic view of a possible photoexcitation mechanism. While the laser wavelength is on resonance to the Mn³⁺ on-site d - d excitation, the 1.2–1.6 eV energy window also overlaps with the Mn³⁺ $\rightarrow$ Mn⁴⁺ intersite charge-transfer (CT) channel.

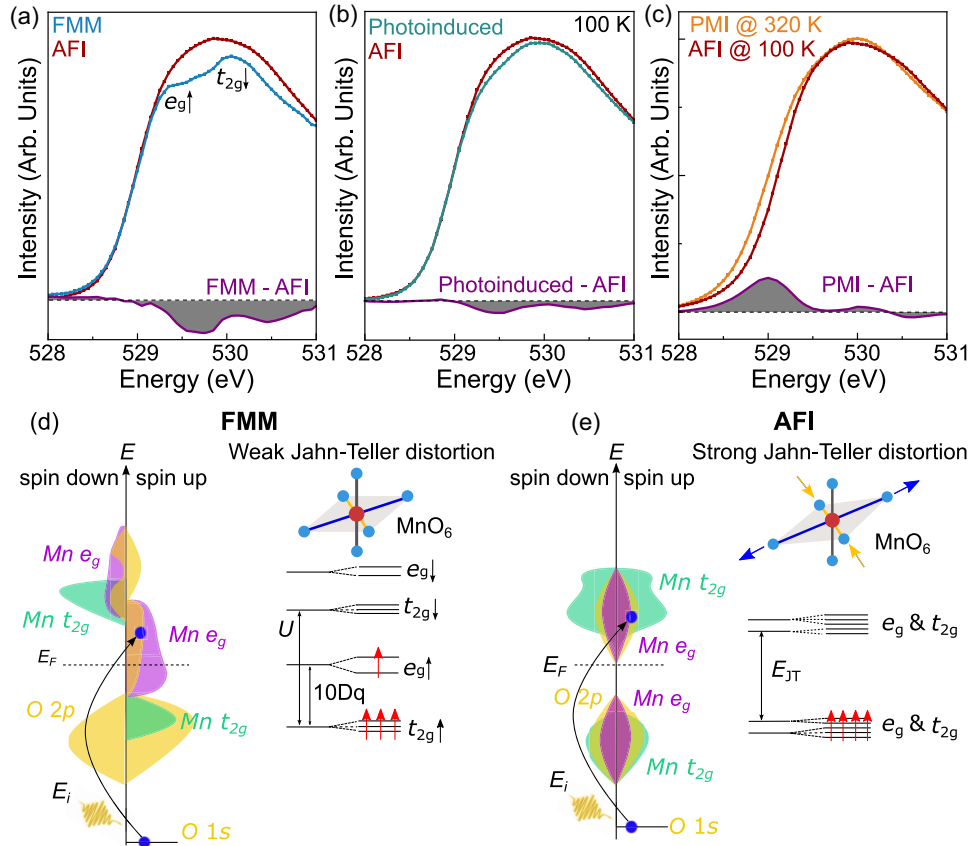


FIG. 3. (a) O - K edge XAS of the FMM and AFI phases at 100 K. The peaks between 528 and 531 eV are related to the Mn $3d$ and O $2p$ hybridization. (b) O - K edge XAS of the AFI and photoinduced phases at 100 K. (c) O - K edge XAS of the AFI phase at 100 K and the PMI phase at 320 K. Purple curves in (a)–(c): XAS difference plots of the FMM-AFI, photoinduced-AFI, and PMI-AFI phases, respectively. (d),(e) Schematic view of the spin-projected partial density of states (DOS) of the FMM and AFI phases, respectively, along with the O - K XAS process. The DOS of O $2p$, Mn e_g , and Mn t_{2g} states are filled with yellow, purple, and green colors, respectively. E_i refers to the incident x-ray energy. The view of the Mn $3d$ orbital splitting based on the DOS is included for better visualization of the weak and strong Q_2 Jahn-Teller distortion for the FMM and AFI phases, respectively. The DOS of the AFI phase is calculated based on a CE-type antiferromagnetic structure [44]. The CE-type refers to an antiferromagnetic structure that consists of zigzag chains of manganese ions in the ab -plane.

out-of-phase displacement [Fig. 2(b)] [1,41]. We identify the Jahn-Teller effects of the FMM, AFI, and photoinduced phases of LCMO/NGO (100) through their XAS responses. Figure 3(a) compares XAS at the O - K edge of the FMM and AFI phases at 100 K. A pre-edge peak at approximately 530 eV is associated to the hybridization between the Mn $3d$ and O $2p$ orbitals [42,43]. In the FMM phase, we observe a doublet splitting of the Mn-O hybridized peak, while only one broad feature is present in the AFI phase. Since XAS is primarily related to the unoccupied density of states (DOS), we can qualitatively discern the XAS line shape from *ab initio* calculations of the DOS (Supplemental Material [32], Fig. S13). In the FMM phase, the Fermi level is mainly occupied by spin-up Mn e_g itinerant electrons [Fig. 3(d)]. This is due to a weak Jahn-Teller distortion and gives rise to the half-metallic nature of the FMM phase. The Mn t_{2g} spin-down states are located in the higher conduction band and partially overlaps with the e_g states [Fig. 3(e)]. Their energy is higher than the Mn e_g spin-up

states, as the on-site Coulomb energy U is stronger than the crystal field splitting $10Dq$. Consequently, in the FMM phase, the two well-defined peaks in XAS are associated with the Mn e_g spin-up and t_{2g} spin-down [Fig. 3(a)]. In the AFI phase, epitaxial tensile strain enhances the Q_2 Jahn-Teller distortion, splitting the broad Mn e_g states at the Fermi level and opening up a band gap. This distortion renormalizes the DOS and leads to a significant overlap of the Mn e_g and Mn t_{2g} levels [Fig. 3(e)]. As a result, it gives rise to a broad Mn $3d$ manifolds [Fig. 3(e)]. Therefore, the broadening of the XAS linewidth and the absence of the e_g - t_{2g} doublet, as shown in Fig. 3(a), are distinctive signatures of the strong Q_2 Jahn-Teller distortion in the AFI phase.

Figure 3(b) presents the XAS of the AFI phase before and after photoexcitation. The sample was excited using a 1030 nm (1.2 eV) femtosecond laser with a 1-kHz repetition rate, 250-fs pulse duration, and a fluence of 34.9 mJ/cm² for 30 s—identical to the conditions for the

laser-transport measurements. The ultrafast laser is off during the XAS measurement. The spectral weight of the XAS between 529 and 530 eV is noticeably suppressed, whereas it is nearly unaffected around 530 eV. The largest spectral weight suppression is at the e_g peak [approximately 529.5 eV shown in Fig. 3(a)], indicating that the photoexcitation mainly renormalizes the Mn e_g states while barely affecting the Mn t_{2g} conduction bands [Figs. 3(d) and 3(e)]. This increases the e_g - t_{2g} splitting. Indeed, the XAS difference [purple curve in Fig. 3(b)] between the photoinduced and AFI phases closely resembles the line shape of the XAS difference plot shown in Fig. 3(a). However, the overall effects are weaker compared to the difference between the AFI and FMM phases achieved through epitaxial strain engineering. This indicates that the photoexcitation partially suppresses the Q_2 Jahn-Teller distortion as schematized in Fig. 2(b).

Figure 3(c) compares the XAS of the AFI (100 K) and PMI phases (320 K). The XAS of the PMI phase is broader than the AFI as evident by the increasing spectral weight below 529.5 eV. The XAS difference curve displays a distinct line shape compared to Figs. 3(a) and 3(b). Above

529.5 eV, where the e_g and t_{2g} peaks are observed [Fig. 3(a)], the XAS is almost identical for the two phases. The different line shapes of the XAS difference for the phases at low and high temperatures indicate that the photoinduced and PMI phases are distinct.

V. STRAIN, PHOTOEXCITATION, AND TEMPERATURE EFFECTS ON POLARON EXCITATIONS

Figure 4(a) shows the O- K edge RIXS of the FMM phase as a function of energy loss and incident x-ray energy. At this edge, RIXS probes the excitations of the Mn $3d$ manifolds owing to the strong hybridization between the O $2p$ and Mn $3d$ bands [Figs. 3(d) and 3(e)] [45,46]. The RIXS map exhibits three main features: a Raman-like phonon around 60 meV, a pronounced peak at approximately 500 meV, and weaker fluorescencelike features above 1 eV. The high-energy features above 1 eV are better observed at the t_{2g} resonance [Fig. 4(b)] and are consistent with the excitations of the strongly hybridized Mn $3d$ – O $2p$ manifold, with mixed on-site dd and intersite charge-transfer-like character, consistent with Mn L_3 -edge RIXS

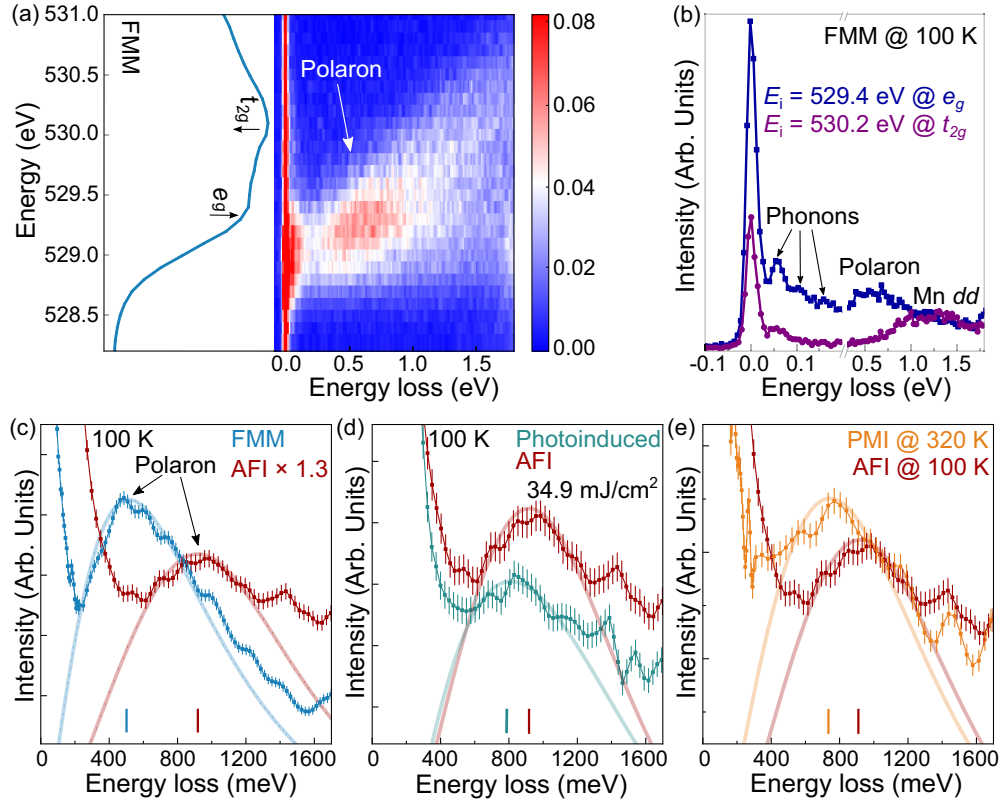


FIG. 4. (a) RIXS intensity map of the FMM phase as a function of incident photon energy and energy loss. The XAS of FMM at 100 K is included on the left. (b) RIXS spectra of the FMM phase at two incident energies: 529.4 and 530.2 eV. The peaks assigned to phonon, polaron, and Mn dd excitations are labeled. (c) RIXS spectra of the FMM and AFI phases at 100 K. The intensity of the RIXS spectra of the AFI phase is enlarged by 1.3 times for better visualization. (d) RIXS spectra of the AFI and photoinduced phases at 100 K. The spectrum of the photoinduced phase is offset along the vertical axis for better visualization. (e) RIXS spectra of the AFI and PMI phase at 100 and 320 K, respectively. Solid lines in (c)–(e): fitting of the polaron peak. Vertical lines at the bottom of each figure indicate the polaron energies. All RIXS spectra in (c)–(e) are taken with $E_i = 529.4$ eV.

and optical conductivity measurements [47–49]. The approximately 500 meV mode matches with a polaron response reported in the midinfrared optical studies on LCMO [24,48,50] and was also observed in $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ [46]. We attribute this feature to the excitation of localized carriers interacting with lattice vibrations—a hallmark of polarons induced by strong electron-phonon coupling [50–52]. In our RIXS spectra, the “polaron” refers to an excitation arising from the dynamic charge susceptibility associated with locally trapped carriers. The corresponding polaron energy represents an effective energy scale to excite such a trapped carrier into the $\text{Mn}^{3+} e_g$ conduction manifold and is, therefore, influenced by the Jahn-Teller distortion and electron-phonon coupling. The resonant enhancement of both phonon and polaron intensity at the Mn e_g site [Fig. 4(b)] highlights the dominant role of Mn e_g electrons in mediating the electron-phonon interaction. Additionally, weak peaks between 100 and 400 meV are observed at the e_g resonance and are ascribed to higher-order phonon harmonics [46].

Figure 4(c) displays a closer view of the RIXS spectra of the FMM and AFI phases at the Mn e_g resonance (529.4 eV). A spectral weight shift from high-to-low energy loss is uncovered across the epitaxial strain-induced insulator-to-metal transition (IMT). The polaron of the FMM phase is more intense and centered at approximately 450 meV, whereas that of the AFI phase is located at approximately 950 meV. To quantify the key features of these polarons, we fit the RIXS data. Since the polaron line shape is highly asymmetric for the FMM phase, we fit the RIXS spectra with an antisymmetric Lorentz function and use the same approach for the AFI [46]. The detailed fitting procedure is discussed in Supplemental Material [32].

Figure 4(d) showcases RIXS spectra of the AFI phase before and after photoexcitation. We tune the incident x-ray energy to the e_g resonance where the XAS shows the largest difference [Fig. 3(b)]. After photoexcitation, the polaron energy shifts from approximately 960 to 790 meV. While the photoinduced spectral weight redistribution resembles that observed in the epitaxial strain-driven transition [Fig. 4(c)], the polaron energy remains approximately 300 meV higher than that of the FMM phase. This suggests that the electron-phonon coupling in the photoinduced phase is stronger than in the pristine FMM phase, which is consistent with its more insulating character observed in the laser-transport measurements [Figs. 1(c) and 1(d)]. These findings support that the photoinduced phase is not a transition into the metallic FMM phase.

To investigate the polaron across the phase diagram of LCMO as a function of epitaxial strain and temperature, we collected RIXS spectra in the high-temperature PMI phase at 320 K ($T_C = 220$ K). Figure 4(e) compares the RIXS spectra of the AFI and PMI phases. The polaron energy shifts from approximately 960 to 750 meV across the

AFI-to-PMI transition. Even though the energy shift of the polaron is comparable for the PMI and the photoinduced phases [Fig. 4(d)], the photoinduced effects cannot be attributed to thermal heating, as the laser was off when collecting RIXS (the acquisition time of a RIXS spectrum is about 3 h). Furthermore, the photoinduced phase partially melts the Jahn-Teller distortion [Fig. 3(b)], whereas the PMI phase reflects thermal broadening and disorder but retains the Jahn-Teller distortion as corroborated by XAS [Fig. 3(c)]. This behavior is consistent with the well-known persistence of dynamic Jahn-Teller distortion in magnetoresistive manganites at high temperature [4,23–25].

VI. PHONONS OF THE FMM, AFI, PMI, AND PHOTOINDUCED PHASES

Owing to the high resolution of RIXS, we can measure phonons in LCMO as a function of temperature, epitaxial strain, and laser fluence. Phonons change dramatically across the epitaxial strain-induced IMT. Figure 5(a) compares the RIXS spectra below 200 meV for the FMM and AFI phases at 100 K. The phonon at approximately 60 meV is a Jahn-Teller active Mn-O stretching mode [24,46]. The FMM phase has a suppression of the phonon intensity, accompanied with about 10 meV redshift of the phonon energy. As the RIXS phonon intensity is proportional to the electron-phonon coupling strength [46,53], this suppression and the phonon softening reflect a reduction in coupling due to electronic screening in the metallic phase, consistent with its weak Jahn-Teller distortion and softened polaron energy [Fig. 4(c)].

Figure 5(b) depicts the evolution of the Mn-O stretching mode before and after photoexcitation. In contrast to the prominent softening of the polaron peak [Fig. 4(d)], the phonon exhibits only a minor redshift and negligible change in intensity compared to the unpumped AFI state. This suggests that the Jahn-Teller distortion is only partially relaxed, consistent with the reduced e_g-t_{2g} splitting in the XAS of the photoinduced phase [Fig. 3(b)]. Collectively, the photoinduced effects from XAS (Jahn-Teller distortion), RIXS (polaron and phonon), and transport are markedly different from those observed across the epitaxial strain-induced IMT [Figs. 4(c) and 5(a)]. This reinforces the conclusion that the photoinduced and FMM phases are distinct. Within our laser-pumping conditions, our observation contrasts with previous studies using 800 nm laser excitation, where the photoinduced state was sometimes interpreted as resembling the FMM phase [1,4].

The RIXS spectra of the high-temperature PMI phase exhibit a stronger elastic peak, attributed to thermal diffuse scattering, along with suppressed phonon intensity and higher phonon energy compared to the AFI phase. The phonon hardening is more significant near T_C (220 K), which is consistent with the dynamic Jahn-Teller model that links electron-phonon interaction with a double

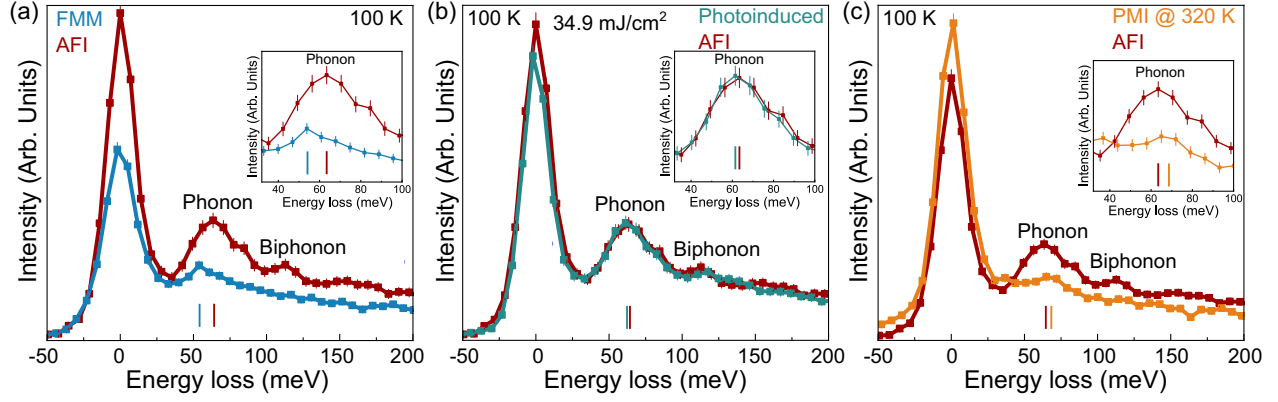


FIG. 5. (a) Low-energy RIXS spectra of the FMM and AFI (100) phases at 100 K. (b) Low-energy RIXS spectra of the AFI and photoinduced phases at 100 K. (c) Low-energy RIXS spectra of the AFI and the PMI phases at 100 and 320 K, respectively. The phonon and biphonon are labeled in each figure. The insets show the phonon at approximately 60 meV. Vertical lines at the bottom of each figure indicate the phonon energies. All RIXS spectra are taken with $E_i = 529.4$ eV.

exchange mechanism (see Supplemental Material [32], Fig. S11) [23,24]. This trend is opposite to the phonon softening seen in the FMM state [Fig. 5(a)], where the Jahn-Teller distortion is weakened. This reveals that the Q_2 Jahn-Teller distortion remains unrelaxed in the PMI phase. The different phonon behavior in the photoinduced and high-temperature PMI phases confirms that the photoinduced effects [Figs. 3(b) and 4(d)] do not arise from thermal heating, which would otherwise concurrently affect both the phonon and polaron excitations.

VII. FLUENCE DEPENDENCE OF PHONONS AND POLARON EXCITATIONS

To systematically characterize the evolution of the photoinduced phase, we measured the polaron and phonon responses at various laser fluence. Figure 6(a) shows RIXS spectra of the AFI (100) film as a function of fluence. Using a single-peak fit to the spectral feature between 400 and 1000 meV, the effective polaron energy decreases by about

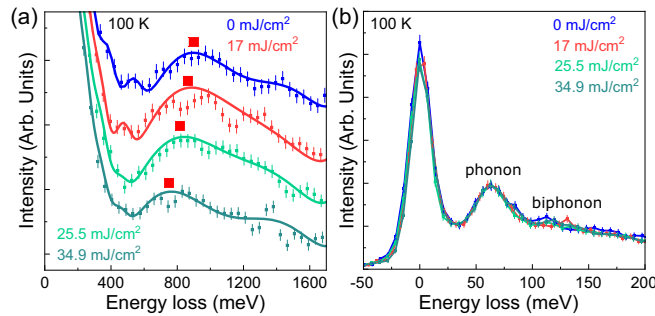


FIG. 6. (a) RIXS spectra of LCMO-AFI (100) at energy loss ~ 100 –1800 meV at different laser fluence. The data are vertically offset for better visualization. (b) RIXS spectra of LCMO-AFI (100) at energy loss from -50 to 200 meV at different laser fluence. The phonon and biphonon are labeled. All spectra are taken at $E_i = 529.4$ eV.

60–180 meV compared to that of the AFI phase as the laser fluence increases. The photoinduced phases at each fluence are long-lived, consistent with the laser-transport data [Fig. 1(d)]. Remarkably, the 60 meV Mn-O stretching phonon remains nearly unchanged across fluences.

The noticeable softening of the polaron excitations and constancy of the phonons to photoexcitation indicate that the photoinduced state differs from the FMM. However, with only a micron-scale spatial resolution, the spatial distribution of the photoinduced phase remains unknown with the possibility of phase separation and noncomplete switching between the AFI and the photoinduced phases. To better understand this issue, we have prepared another 24 nm LCMO/NGO (100) film which naturally exhibits mixed phase at the equilibrium (see Supplemental Material [32], Fig. S2). Unlike the photoinduced phase, this equilibrium mixed-phase sample shows a clear polaron spectral weight enhancement together with a significantly suppressed phonon intensity. Within our spatial and energy resolution, we do not observe a clear two-peak structure of the polaron features in the photoinduced RIXS spectra. Therefore, this difference highlights that the photoinduced state is unlikely to be composed by a mixed phase of AFI and FMM (see Supplemental Material [32], Fig. S2).

VIII. LINKING ELECTRIC TRANSPORT TO POLARONS

To relate the polaron excitations to the resistivity and clarify their connection, we measure the evolution of the polaron as a function of temperature. Figures 7(a) and 7(b) display RIXS spectra of the AFI and FMM (100) films at various temperatures. For the FMM film, the polaron excitations show a spectral weight suppression across the FMM-to-PMI transition at 220 K. The polaron energy has a nonmonotonic behavior as the temperature increases: It

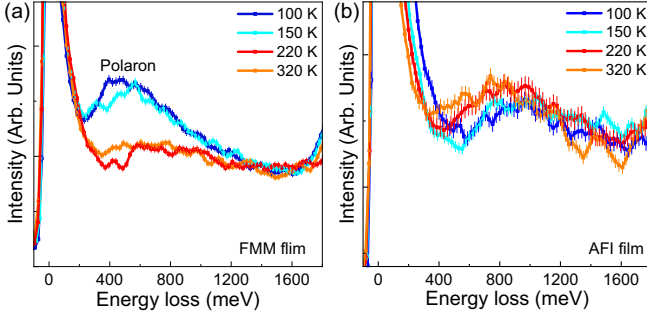


FIG. 7. (a,b) RIXS spectra of the FMM and AFI at different temperatures, respectively.

increases with temperature below T_C (220 K) and decreases with temperature above T_C . On the contrary, in the AFI, the polaron energy systematically decreases as the temperature increases, where its spectral weight is less sensitive to the temperature than that of the FMM film.

We quantify the polaronic excitations energy from fitting of the RIXS data. Figure 8(a) shows the extracted polaron energy as a function of temperature for both FMM and AFI. The resistivity changes more than 4 orders of magnitude with temperature [Fig. 8(b)], whereas the polaron energy changes within one order of magnitude. Therefore, a linear change in polaron energy is connected to an exponential change in resistivity. To explain this, we use the strong coupling limit of the Holstein polaron model [54]. In the “strongly coupled” small polaron regime ($\lambda_{e-ph} \gg 1$) of the Holstein polaron, the carrier mobility as a function of temperature [$\mu(T)$] is described by [55]

$$\mu(T) = \frac{1}{T^k} \exp\left(-\frac{E_p/4 - t'}{T}\right), \quad (1)$$

where E_p is the polaron energy. For a Holstein-type polaron, $E_p = 2E_b$, where E_b is the polaron binding energy. t' is the hopping amplitude, and $k = 1$ (1.5) for the adiabatic (nonadiabatic) case. The resistivity $\rho(T)$ is the inverse of the conductivity $\sigma(T) = n\mu(T)$, where we assume for simplicity that the carrier concentration is temperature independent. While this expression originates from a one-dimensional formulation, it captures the essential physics of small polaron tunneling between localized lattice sites and has been shown to be broadly applicable across different dimensionalities. Specifically, the functional form of the temperature-dependent mobility is governed primarily by the electron-phonon coupling strength and the spatial extent of the lattice deformation rather than the dimensionality *per se*. This behavior has been confirmed experimentally in two-dimensional manganite thin films [56] and through numerous experimental and theoretical studies showing consistent polaron dynamics across 1D and 3D systems [55,57,58]. Thus, Eq. (1) provides a reliable and physically meaningful framework for extracting transport-relevant parameters in the strongly coupled small polaronic regime of LCMO.

Figure 8(a) displays the calculated resistivity as a function of temperature. By fitting the temperature dependence of the polaron energy using Eq. (1), we determine $k = 1.1$ and $t' = 1260$ and 1650 K for the FMM and AFI phases, respectively. These t' values are physically reasonable when interpreted as effective hopping parameters

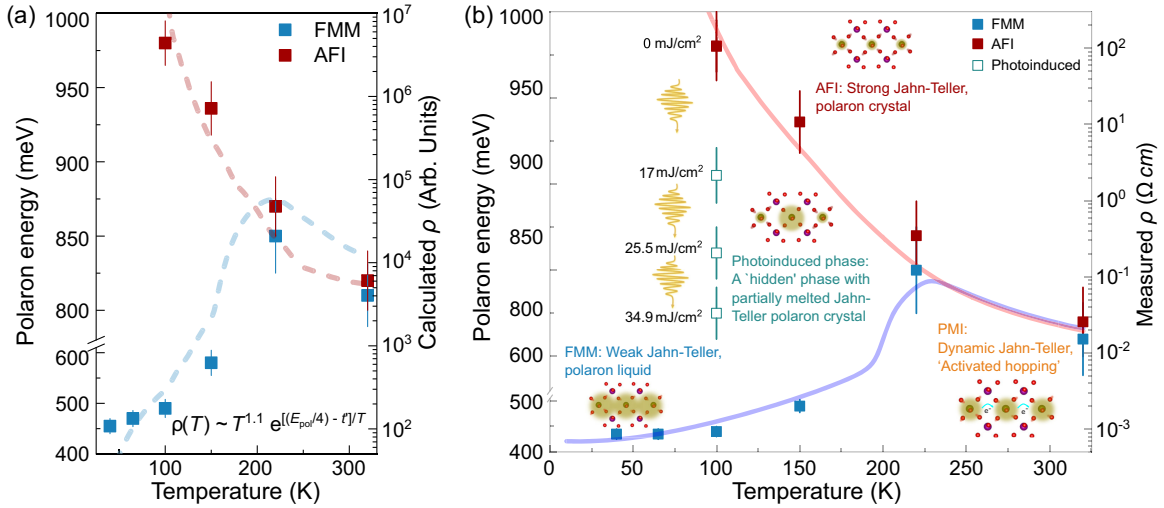


FIG. 8. (a) Polaron excitation energy of the FMM (blue squares) and AFI (red squares) as a function of temperature from fitting the RIXS spectra using an antisymmetric Lorentz function. Error bars are estimated from multiple fittings. The dashed lines are the calculated electric resistivity using Eq. (1). We find $t' = 1260$ and 1650 K for the FMM and AFI phases, respectively. (b) Polaron excitation energy of the FMM (red squares) and AFI (blue squares) samples as a function of temperature, along with the polaron energy of the photoinduced hidden phase at different laser fluence (green squares). The solid lines are the measured resistivity vs temperature curves of the pristine LCMO-FMM and LCMO-AFI films. The cartoons illustrate the different Jahn-Teller polaronic states corresponding to the AFI, FMM, photoinduced, and PMI phases, respectively.

within the strongly coupled Holstein polaron framework, which are distinct from the bare electronic hopping amplitudes. In the “strong-coupling” regime, the electron hopping is renormalized by the lattice distortion and the polaronic mass enhancement, and, thus, t' reflects the strong thermally activated mobility of dressed quasiparticles rather than bandlike transport [55]. We note that the extracted hopping amplitudes t' (1260 and 1650 K) correspond to polaron activation energies on the order of 110–140 meV, which is consistent with the values reported in optical and transport studies of manganites [26,52,56].

The calculated resistivity curve aligns with the experimental temperature trend of the polaron in all equilibrium phases, demonstrating that the polaron excitations of the FMM, AFI, and PMI phases are all in the strongly coupled regime [55]. For the photoinduced phase, the polaron also resides in the strong-coupling limit, as its energy falls between those of the FMM and AFI phases, while the phonon energy closely resembles that of the AFI phase. According to Eq. (1), the electric resistivity for a Holstein polaron in the strongly coupled regime depends solely on the polaron excitation energy E_p and the hopping amplitude t' . However, since E_p does not explicitly include any temperature-dependent terms [55], the strong temperature dependence of E_p observed in Fig. 8 arises from changes in the electron-phonon Hamiltonian parameters caused by the T -dependent reconstruction of LCMO. Our XAS and RIXS data on phonons indicate that the electron-phonon coupling strength in LCMO is sensitive to the local Jahn-Teller distortion. This suggests that the observed temperature dependence of E_p is strongly associated with the strength of the Q_2 Jahn-Teller distortion.

IX. DISCUSSION

Figure 8(b) summarizes the polaronic states for the AFI, FMM, PMI, and photoinduced phases under epitaxial strain, temperature, and photoexcitation. Even though the polarons in all phases are in the strongly coupled regime, their origins are distinct as their energies are influenced by the strength of the Q_2 Jahn-Teller distortion and the amplitude of “activated hopping” [55]. From theoretical work [55], the activated-hopping regime occurs when the thermal energy exceeds a quarter of the phonon frequency, resulting in a positive steepness of the polaron mobility ($d\mu/dT > 0$) [55]. As the polaron mobility is directly proportional to its excitation energy and the strength of electron-phonon coupling [55], we can classify different polaronic states of LCMO from the polaron temperature dependence measured by RIXS. The AFI phase has the largest $\lambda_{\text{e-ph}}$ as the Q_2 Jahn-Teller distortion is enhanced by b -axis tensile strain. This cooperative Jahn-Teller distortion (AFI phase) also stabilizes a putative charge- and orbital-ordered structure [4,5,21,44]. Therefore, the polaron of the AFI phase corresponds to an ordered array of the localized

Jahn-Teller clusters, namely, a “polaron-crystal” state [26]. This dramatically suppresses the electron hopping between the Mn sites, consistent with its robust insulating behavior (see Supplemental Material [32], Fig. S1). For the FMM phase, the polaronic excitation energy is about 500 meV lower than that of the AFI referring to a smaller $\lambda_{\text{e-ph}}$ due to the weaker Q_2 Jahn-Teller distortion. Furthermore, the polaron energy and resistivity increases with temperature when below 220 K, proving a negative steepness of the polaron mobility ($d\mu/dT < 0$) [Fig. 7(a)]. These behaviors indicate that the polaron of the FMM phase is not in the activated-hopping regime (when $d\mu/dT > 0$), as it would require a sizable phonon population unattainable at 100 K. The weak metallicity and strongly coupled polaron suggest that the polaronic state of the FMM phase aligns likely with a “polaron liquid” phase, where the polaron mobility lies between that of a coherent metal and an ordered polaron-crystal insulator [46]. In the photoinduced phase, the polaron excitation energy systematically softens from the initial AFI phase as the fluence increases. The polaron excitation energy falls between those of the AFI and FMM phases, while the phonon shows minimal changes, indicating the emergence of a new state induced by the partial melting of the Jahn-Teller polaron-crystal state [Figs. 3(b) and 5(b)]. The high-temperature PMI phase exhibits a polaron excitation energy similar to the photoinduced phase. However, the origin of the polaronic state differs, as the Q_2 Jahn-Teller distortion remains unrelaxed in the PMI phase [Figs. 3(c) and 5(c)]. On the other hand, the polaron excitation energy and resistivity decrease with temperature when above 220 K [Figs. 7(a) and 7(b)], consistent with an activated-hopping mechanism ($d\mu/dT > 0$) [55]. The different polaronic states of the FMM, AFI, PMI, and photoinduced phases are pictorially summarized in Fig. 8(b).

Another factor to explain the photoinduced phase is the role of orbital order. In perovskite manganites such as $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, the long-lived photoinduced states have been associated with glassy dynamics in the coupled charge-orbital-Jahn-Teller sector, with ultrafast melting of charge or orbital order followed by a slow, domain-limited recovery [59,60]. The AFI ground state of our LCMO films is likewise stabilized by cooperative Jahn-Teller distortions and possibly orbital order (see Supplemental Material [32], Fig. S13). In the photoinduced state, however, we find a substantial softening of the effective polaron excitation energy with fluence, while the 60 meV Jahn-Teller active phonon intensity and energy are only weakly modified and remain less suppressed than in an equilibrium mixed-phase film (Fig. 6 and see Supplemental Material [32], Fig. S2). The 60 meV mode is primarily sensitive to the *local* Jahn-Teller distortion amplitude, whereas the polaron excitation energy depends on a combination of factors from both charge and lattice degrees of freedom, including the long-range pattern of the

occupied e_g orbitals (orbital order), charge order, and the electronic hopping amplitudes and bandwidth. A photo-induced state in which long-range orbital or charge order is strongly disrupted (shorter correlation length, increased domain walls, and/or orbital disorder), whereas the average local Jahn-Teller distortion is only partially reduced, naturally produces a relatively overall unchanged phonon but a much larger shift of the polaron binding energy. This places the photoinduced state between the AFI and FMM phases and is qualitatively consistent with an intermediate orbital configuration that may be more disordered or glassy than in the AFI ground state [59,60]. At the same time, because our O K -edge RIXS measurements do not directly resolve orbital-order superlattice peaks and provide only volume-averaged information, we cannot distinguish unambiguously between a homogeneous phase with reduced orbital order and a more glassy, phase-separated configuration. A definitive characterization of the role of orbital order involved in the photoinduced transition will require future time-resolved resonant x-ray diffraction at the Mn L edge with sensitivity to orbital-order superstructures.

We next comment on the possible microscopic laser-switching mechanism of the photoinduced hidden phase, based on electric transport, phonons, polarons, and the evolution of the e_g - t_{2g} splitting associated with Jahn-Teller distortion. According to our density-functional theory (DFT) calculations, the CE-type AFI phase is charge and orbital ordered with the Jahn-Teller active Mn^{3+} and the Jahn-Teller inactive Mn^{4+} sites (see Supplemental Material [32], Fig. S13). The Mn^{3+} has a single electron occupying the $d_{3z^2-r^2}$ orbital which aligns along one of the in-plane diagonal direction of the MnO_6 octahedra [Fig. 2(b)] [21,41,61]. This orbital occupancy elongates the Mn—O bond along the direction in the Mn—O basal plane, as shown in Fig. 2(b). Consequently, epitaxial uniaxial tensile strain along the b axis enhances the Q_2 Jahn-Teller distortion, stabilizing the AFI phase over the FMM phase without altering the doping level.

Previous studies using an 800-nm pump [1,4], resonant with an optically allowed $\text{Mn}^{3+} \rightarrow \text{Mn}^{4+}$ charge-transfer excitation, reported a dramatic resistivity drop by several orders of magnitude [4]. The resulting photoinduced phase was interpreted to be similar in character to the bulk FMM phase. In contrast, our results using a 1030-nm pump suggest a different photoinduced long-lived state, raising the question of whether the excitation mechanism differs. Two possibilities can account for this difference: (i) The 1030-nm laser excites the low-energy tail of the same charge-transfer transition observed at 800 nm but has a higher fluence threshold; or (ii) the 1030-nm excitation primarily drives an on-site Mn dd orbital transition, specifically from $d_{3z^2-r^2}$ to $d_{x^2-y^2}$ based on our Mn L -edge measurements and DFT calculations (Fig. 2). While this on-site excitation is nominally dipole forbidden, it can

become optically active through vibronic coupling and O $2p$ —Mn $3d$ hybridization (Fig. 3). These two channels likely coexist within the 1.2–1.6 eV energy window, consistent with our RIXS analysis [Figs. 2(a) and 2(b)].

In addition to the wavelength, other laser parameters including pulse duration and repetition rate play a role. Our pulses (approximately 250 fs) are substantially longer than the 35–50 fs single-shot pulses used in Refs. [1,4]. The longer duration might allow for partial relaxation after the photoexcitation, lowering the transient electronic temperature and thereby increasing the fluence threshold required to cross the nonthermal phase boundary. This may also stabilize a distinct metastable phase which alters the relaxation pathway within the free-energy landscape [14,62]. Similar pulse-duration-dependent selection of driven quantum states has been demonstrated in Floquet and superconducting systems [63,64]. Furthermore, our quasicontinuous 1 kHz operation (approximately 3×10^4 pulses during a 30-s exposure window) differs from pulse-picked single-shot protocols reported in Refs. [4,5]. In this configuration, each pulse can interact with the sample that is still slightly out of equilibrium before fully relaxing to its equilibrium state. Therefore, the successive pulses can partially repopulate or relax preexisting photoexcited domains, effectively “annealing” the lattice into a higher-entropy configuration by partially melting the orbital order and Jahn-Teller distortion. This could naturally lead to a weaker or modified hidden phase and result in a higher fluence threshold compared to single-shot optical studies [1,4,5]. Single-shot measurements have revealed phases that can be obscured or modified under high-rep-rate, multipulse conditions, and related sensitivity of the selected metastable phase to excitation protocol has been reported in 1T-TaS₂ and Ta₂NiSe₅ [65–67], underscoring the importance of excitation protocol in determining the observed phase and threshold.

Our results show that the nature of the photoinduced phase in LCMO is very sensitive to all these parameters, which opens the possibility for studies based on different excitation protocols. Future laser-RIXS experiments with tunable wavelength, adjustable pulse duration, and capability of pulse picking as well as potential time-resolved RIXS measurement will be crucial to separate these effects and understand how different laser conditions reshape the free-energy landscape of manganites.

X. SUMMARY

In summary, our findings report on the emergence of a photoinduced hidden phase in LCMO and reveal the evolution of the elementary excitations across different electronic phases. We demonstrate that distinct polaronic states can be stabilized through the tuning of epitaxial strain, temperature, and orbital-selective photoexcitation and reveal the connection of the electronic transport with the polaronic excitations of each individual phase. Overall,

our experimental approach combining ultrafast optical photoexcitation and high-resolution RIXS offers direct spectroscopic access to orbital, phononic, and charge excitations and establishes a framework for exploring the coupling between multiple degrees of freedom in metastable laser-driven phases. These results pave the way for extending this methodology to other strongly correlated systems, enabling controlled manipulation of quantum matter beyond equilibrium.

XI. METHODS

A. Film preparation and characterization

The LCMO thin films were grown on the NdGaO_3 substrates with the [100] or [001] crystallographic direction normal to the surface. Using a KrF excimer laser with a wavelength of 248 nm, LCMO films were deposited via a customized pulsed laser deposition system at an energy density of approximately 2 J/cm^2 and a repetition rate of 5 Hz. The sample-to-target distance was fixed to 5.5 cm. During deposition, the substrate temperature and oxygen pressure were kept at 735°C and 40 Pa, respectively. Before cooling down to room temperature, all LCMO films were *in situ* annealed for 15 min and exhibit the ferromagnetic metallic ground state, which are labeled as the as-grown film. Then, some of LCMO films were *ex situ* annealed at 800°C in flowing O_2 gas for 30 h and show the anti-ferromagnetic insulating ground state, which are denoted as the annealed film. The LCMO films were structurally characterized with 2θ - ω linear scans by x-ray diffraction using $\text{Cu K}\alpha 1$ radiation (Panalytical X'pert) (see Supplemental Material [32], Fig. S1). The surface morphology was characterized using an atomic force microscopy (Veeco, MultiMode V). The magnetization measurements were performed using a Quantum Design magnetic property measurement system (MPMS3). The resistivity was determined by standard four-point-probe method in a temperature range of 10–300 K using a Quantum Design physical property measurement system. The x-ray diffraction, electric resistivity, and magnetization data are in Supplemental Material [32].

B. Laser-transport measurements in LCMO-AFI films

We deposited a series of electrodes on our LCMO/NGO (100/001) films with 500 or 300 μm separation distance. The voltage between the top (labeled as 1) and bottom (labeled as 2) electrodes shown in Fig. 1(b) is measured at the fixed current $I = 10 \text{ nA}$. The low applied current is to minimize Joule heating. The resistance is calculated using Ohm's law. The ultrafast laser spot is focused to roughly 120 μm and is guided to the center between the electrodes, which can be visualized by an infrared camera. In this case, the resistance between electrodes 1 and 2 will be a combination of the unswitched and switched areas, since the separation distance is much bigger than the laser spot

size. We, therefore, focus on only the percentage of changes in resistance rather than resistivity, since the precise resistivity change after photoexcitation depends on how domains are reformed and connected.

C. Ultrafast laser setup and laser beam characterization

We have developed an experimental setup where an ultrafast laser beam is introduced into the experimental RIXS sample chamber [see Supplemental Material [32], Fig. S12(a)]. Specifically, we use an ultrafast (1030-nm center wavelength) Yb fiber laser providing pulse width of 250 fs that is focused to approximately 200 μm diameter onto the sample using a series of focusing lenses and a Keplerian-type beam expander [see Supplemental Material [32], Fig. S12(c)]. The laser beam profile is displayed in Supplemental Material Fig. S12(d) [32], confirming the high-quality Gaussian shape of our beam. The optics is placed out of vacuum for simplicity, and a continuous-wave (cw) alignment laser (633 nm) is integrated into the same optical path of the ultrafast laser beam by means of a beam splitter [see Supplemental Material [32], Fig. S12(c)]. In this case, the ultrafast laser spot will retrace the beam path of the cw laser and shine at roughly the same position on the sample. A camera sensitive to infrared light is used for fine-tuning the location of the laser beam on the sample and align it to the x-ray beam [see Supplemental Material [32], Fig. S12(b)]. The x-ray beam size is around $2 \times 20 \mu\text{m}$, which is 10 times smaller compared to the laser spot. In this case, we confirm our measured area is fully irradiated by the laser and any photoinduced effect is real. The laser average power is measured by a power meter with an attached thermal power sensor. The laser power can be controlled by varying the transmission percentage of the oscillator of the laser. The maximum average power at 1 kHz is about 7000 μW [see Supplemental Material [32], Fig. S12(e)] and the beam size is approximately 200 μm , which gives a maximum laser fluence of 34.9 mJ/cm^2 at an incident angle of 40° [see Supplemental Material [32], Fig. S12(f)]. The fluence values quoted here include the projection factor associated with the incident angle. The fluence is varied under different laser power. We also measured the average laser power at different repetition rate from 1 Hz to 500 kHz, confirming the laser pulse energy does not vary much when changing the repetition rate.

D. RIXS and XAS measurements

RIXS and XAS at the O- K and Mn L_3 edges were performed at the 2ID-SIX beam line at NSLS-II, Brookhaven National Laboratory (USA). The sample is mounted in a manipulator with four degrees of freedom (x , y , z , and θ) [see Supplemental Material [32], Fig. S12(c)]. To overlap the ultrafast laser with the x-ray beam spot, we use the grazing-out geometry [Fig. 1 and see Supplemental Material [32], Fig. S12(c)], in which the grazing angle θ is fixed at 140° to maximize the laser fluence. The scattering

angle (2Θ) is fixed at 150° to maximize the momentum transfer [see Supplemental Material [32], Fig. S12(c)]. The corresponding wave vector of the polaron is $Q \approx [0.095, 0.095, 0.289]$. For the momentum dependence measurements on the polaron [see Supplemental Material [32], Fig. S4(a)], we use the grazing-in geometry with σ polarization of the incident x-ray. Since the film is three-dimensional, we measure the polaron dispersion under the specular condition by varying θ and 2Θ correspondingly ($\theta = [(2\Theta)/2]$) to allow the momentum transfer along the $[h, h, h]$ direction (pseudocubic notation). The XAS spectra were collected in total fluorescence yield, using both vertical σ . The σ and π polarizations are defined in Fig. 1. All the XAS and RIXS spectra displayed in this paper are collected using the σ polarization. The RIXS energy resolution is about 27 meV at the O-K edge, as determined by elastic measurements of a multilayer reference sample. An aluminum filter is used to remove any infrared photons on the RIXS detector. The fitting of RIXS spectra is detailed in Supplemental Material [32]. For better visualization in Fig. 4 and Supplemental Material Figs. S2, S7, and S8 [32], spectra were binned by a two-point adjacent average (effective width ≈ 23 meV < instrumental resolution ≈ 27 meV). All fits were cross-checked on raw and binned data and yielded consistent parameters within the experimental uncertainty (see Supplemental Material [32], Fig. S10).

E. First-principles calculations

First-principles DFT calculations were performed using the Vienna *Ab Initio* Simulation Package (VASP) [68] within the projector-augmented wave framework [69]. The revised generalized-gradient approximation as parametrized by Perdew, Burke, and Ernzerhof (PBEsol) was employed for exchange-correlation functional [70]. Ten ($3s^2 3p^6 4s^2$), 11 ($5s^2 5p^6 5d^1 6s^2$), 13 ($3p^6 3d^5 4s^2$), and six ($2s^2 2p^4$) valence electrons were considered in the projector-augmented wave pseudopotentials of Ca, La, Mn, and O, respectively. Strong correlation effects for Mn $3d$ electrons were treated at the mean-field level using the rotationally invariant DFT + U method introduced by Liechtenstein, Anisimov, and Zaanen [71]. We set $U(\text{Mn-}3d) = 4$ eV, $J(\text{Mn-}3d) = 1$ eV, $U(\text{La-}4f) = 6$ eV, and $J(\text{La-}4f) = 0$ eV following Ref. [22]. We find that this set of values appropriately describes the lattice parameters, magnetic structure, and vibrational properties of $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$. La/Ca concentration ratio of 0.67/0.33 was simulated using the virtual-crystal approximation [72], which has been reported to produce reliable results for similar systems [73]. The total energy convergence and residual force convergence criteria were set to 10^{-7} eV and 10^{-3} eV/Å, respectively. The cutoff energy for the plane-wave basis set was set at 600 eV. We used a Monkhorst-pack k mesh [74] of size $12 \times 12 \times 9$ to sample

the reciprocal space. Electronic structure was analyzed using the PYPROCAR package [75].

ACKNOWLEDGMENTS

We thank Dr. John Freeland, Professor Andrew Millis, Dr. Mark Dean, and Professor Jingdi Zhang for useful discussions. Work at Brookhaven National Laboratory was supported by the U.S. Department of Energy (DOE) Office of Science under Contract No. DE-SC0012704. This work was supported by the Laboratory Directed Research and Development project of Brookhaven National Laboratory No. 21-037. U.K. was supported by the U.S. Department of Energy, Office of Basic Energy. This work was supported by the DOE Office of Science, Early Career Research Program. This research used beam line 2-ID of the National Synchrotron Light Source II, a DOE Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under Contract No. DE-SC0012704. This research used the wire bonding machine of the Center for Functional Nanomaterials (CFN), which is a U.S. Department of Energy Office of Science User Facility, at Brookhaven National Laboratory, under Contract No. DE-SC0012704. The authors at the University of Science and Technology of China acknowledge the financial support from Quantum Science and Technology Major Project, with Grant No. 2024ZD0301300. The authors also acknowledge the Anhui Provincial Natural Science Foundation with Grant No. 2308085 MA15. S.S. was supported by the U.S. Department of Energy, Office of Science, Office of Fusion Energy Sciences, Quantum Information Science program under Award No. DE-SC-0020340. S.S. also acknowledges support from the Furth Research Fund at the University of Rochester. O. S. B. and A. S. M. acknowledge financial support from the Croatian Science Foundation, Grants No. HRZZ-IP-2022-10-3382 and No. HRZZ-IP-2024-05-2406, respectively.

The authors declare no competing interests.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon request.

-
- [1] A. S. McLeod, J. Zhang, M. Q. Gu, F. Jin, G. Zhang, K. W. Post, X. G. Zhao, A. J. Millis, W. B. Wu, J. M. Rondinelli, R. D. Averitt, and D. N. Basov, *Multi-messenger nanoprobes of hidden magnetism in a strained manganite*, Nat. Mater. **19**, 397 (2019).
 - [2] X. Li, T. Qiu, J. Zhang, E. Baldini, J. Lu, A. M. Rappe, and K. A. Nelson, *Terahertz field-induced ferroelectricity in quantum paraelectric SrTiO₃*, Science **364**, 1079 (2019).

- [3] T. F. Nova, A. S. Disa, M. Fechner, and A. Cavalleri, *Metastable ferroelectricity in optically strained SrTiO₃*, *Science* **364**, 1075 (2019).
- [4] J. Zhang, X. Tan, M. Liu, S. W. Teitelbaum, K. W. Post, F. Jin, K. A. Nelson, D. N. Basov, W. Wu, and R. D. Averitt, *Cooperative photoinduced metastable phase control in strained manganite films*, *Nat. Mater.* **15**, 956 (2016).
- [5] S. W. Teitelbaum, B. K. Ofori-Okai, Y. H. Cheng, J. Zhang, F. Jin, W. Wu, R. D. Averitt, and K. A. Nelson, *Dynamics of a persistent insulator-to-metal transition in strained manganite films*, *Phys. Rev. Lett.* **123**, 267201 (2019).
- [6] F. Y. Gao, Z. Zhang, Z. Sun, L. Ye, Y. H. Cheng, Z. J. Liu, J. G. Checkelsky, E. Baldini, and K. A. Nelson, *Snapshots of a light-induced metastable hidden phase driven by the collapse of charge order*, *Sci. Adv.* **8**, eabp9076 (2022).
- [7] M. P. M. Dean *et al.*, *Ultrafast energy- and momentum-resolved dynamics of magnetic correlations in the photo-doped Mott insulator Sr₂IrO₄*, *Nat. Mater.* **15**, 601 (2016).
- [8] D. Fausti, R. I. Tobey, N. Dean, S. Kaiser, A. Dienst, M. C. Hoffmann, S. Pyon, T. Takayama, H. Takagi, and A. Cavalleri, *Light-induced superconductivity in a stripe-ordered cuprate*, *Science* **331**, 189 (2011).
- [9] A. Zong, Y. Q. B. A. Kogar, T. Rohwer, C. Lee, E. Baldini, E. Ergeçen, M. B. Yilmaz, B. Freelon, E. J. Sie, H. Zhou, J. Straquadine, P. Walmsley, P. E. Dolgirev, A. V. Rozhkov, I. R. Fisher, P. J.-Herrero, B. V. Fine, and N. Gedik, *Evidence for topological defects in a photoinduced phase transition*, *Nat. Phys.* **15**, 27 (2019).
- [10] R. Mankowsky, A. Subedi, M. Först, S. O. Mariager, M. Chollet, H. T. Lemke, J. S. Robinson, J. M. Glowina, M. P. Minitti, A. Frano, M. Fechner, N. A. Spaldin, T. Loew, B. Keimer, A. Georges, and A. Cavalleri, *Nonlinear lattice dynamics as a basis for enhanced superconductivity in YBa₂Cu₃O_{6.5}*, *Nature (London)* **516**, 71 (2014).
- [11] P. Beaud *et al.*, *A time-dependent order parameter for ultrafast photoinduced phase transitions*, *Nat. Mater.* **13**, 923 (2014).
- [12] V. Esposito, M. Fechner, R. Mankowsky, H. Lemke, M. Chollet, J. M. Glowina, M. Nakamura, M. Kawasaki, Y. Tokura, U. Staub, P. Beaud, and M. Först, *Nonlinear electron-phonon coupling in doped manganites*, *Phys. Rev. Lett.* **118**, 247601 (2017).
- [13] V. A. Stoica, D. Puggioni, J. Zhang, R. Singla, G. L. Dakovski, G. Coslovich, M. H. Seaberg, M. Kareev, S. Middey, P. Kissin, R. D. Averitt, J. Chakhalian, H. Wen, J. M. Rondinelli, and J. W. Freeland, *Magnetic order driven ultrafast phase transition in NdNiO₃*, *Phys. Rev. B* **106**, 165104 (2022).
- [14] Z. Sun and A. J. Millis, *Transient trapping into metastable states in systems with competing orders*, *Phys. Rev. X* **10**, 021028 (2020).
- [15] V. R. Morrison, R. P. Chatelain, K. L. Tiwari, A. Hendaoui, A. Bruhács, M. Chaker, and B. J. Siwick, *A photoinduced metal-like phase of monoclinic VO₂ revealed by ultrafast electron diffraction*, *Science* **346**, 445 (2014).
- [16] M. Mitrano, S. Johnston, Y. J. Kim, and M. P. M. Dean, *Exploring quantum materials with resonant inelastic x-ray scattering*, *Phys. Rev. X* **14**, 040501 (2024).
- [17] M. Ono, M. Hata, M. Tsunekawa, K. Nozaki, H. Sumikura, H. Chiba, and M. Notomi, *Ultrafast and energy-efficient all-optical switching with graphene-loaded deep-subwavelength plasmonic waveguides*, *Nat. Photonics* **14**, 37 (2020).
- [18] T. Li, A. Patz, L. Mouchliadis, J. Yan, T. A. Lograsso, I. E. Perakis, and J. Wang, *Femtosecond switching of magnetism via strongly correlated spincharge quantum excitations*, *Nature (London)* **496**, 69 (2013).
- [19] H. Ichikawa, S. Nozawa, T. Sato, A. Tomita, K. Ichiyonagi, M. Chollet, L. Guerin, N. Dean, A. Cavalleri, S. Adachi, T. Arima, H. Sawa, Y. Ogimoto, M. Nakamura, R. Tamaki, M. K., and S. Koshihara, *Transient photoinduced 'hidden' phase in a manganite*, *Nat. Mater.* **10**, 101 (2011).
- [20] H. Zhang, Y. Zhang, R. Li, J. Yu, W. Dong, C. Chen, K. Wang, X. Tang, and J. Chen, *Room temperature hidden state in a manganite observed by time-resolved X-ray diffraction*, *npj Quantum Mater.* **4**, 31 (2019).
- [21] F. Jin, M. Gu, C. Ma, E. Guo, J. Zhu, L. Qu, Z. Zhang, K. Zhang, L. Xu, B. Chen, F. Chen, G. Gao, J. M. Rondinelli, and W. Wu, *Uniaxial strain-controlled ground states in manganite films*, *Nano Lett.* **20**, 1131 (2020).
- [22] S. S. Hong, M. Gu, M. Verma, V. Harbola, B. Wang, D. Lu, A. Vailionis, Y. Hikita, R. Pentcheva, J. M. Rondinelli, and H. Y. Hwang, *Extreme tensile strain states in La_{0.7}Ca_{0.3}MnO₃ membranes*, *Science* **368**, 71 (2020).
- [23] A. J. Millis, B. I. Shraiman, and R. Mueller, *Dynamic Jahn-Teller effect and colossal magnetoresistance in La_{1-x}Sr_xMnO₃*, *Phys. Rev. Lett.* **77**, 175 (1996).
- [24] K. H. Kim, J. Y. Gu, H. S. Choi, G. W. Park, and T. W. Noh, *Frequency shifts of the internal phonon modes in La_{0.7}Ca_{0.3}MnO₃*, *Phys. Rev. Lett.* **77**, 1877 (1996).
- [25] Y. Yamada, O. Hino, S. Nohdo, R. Kanao, T. Inami, and S. Katano, *Polaron ordering in low-doping La_{1-x}Sr_xMnO₃*, *Phys. Rev. Lett.* **77**, 904 (1996).
- [26] C. Jooss, L. Wu, T. Beetz, R. F. Klie, M. Beleggia, M. A. Schofield, S. Schramm, J. Hoffmann, and Y. Zhu, *Polaron melting and ordering as key mechanisms for colossal resistance effects in manganites*, *Proc. Natl. Acad. Sci. U.S.A.* **104**, 13597 (2007).
- [27] T. Mertelj, D. Kuscer, M. Kosec, and D. Mihailovic, *Photoinduced infrared absorption in La_{1-x}Sr_xMnO₃: Changes of the small polaron binding energy with doping*, *Phys. Rev. B* **61**, 15102 (2000).
- [28] Luuk J. P. Ament, M. V. Veenendaal, T. P. Devereaux, J. P. Hill, and J. vanden Brink, *Resonant inelastic x-ray scattering studies of elementary excitations*, *Rev. Mod. Phys.* **83**, 705 (2011).
- [29] V. K. Bhattiya, R. Hartmann, F. Forte, F. Gabriele, T. Kim, G. Cuono, C. Autieri, S. Fan, K. Kisslinger, F. Camino, M. Lettieri, R. Fittipaldi, C. Mazzoli, D. N. Basov, J. Pellicciari, A. Di Bernardo, A. Vecchione, M. Cuoco, and V. Bisogni, *Evidence of electronic states driving current-induced insulator-to-metal transition*, *arXiv:2504.17871*.
- [30] J. Hales, U. Bajpai, T. Liu, D. R. Baykusheva, M. Li, M. Mitrano, and Y. Wang, *Witnessing light-driven entanglement using time-resolved resonant inelastic x-ray scattering*, *Nat. Commun.* **14**, 3512 (2025).
- [31] E. Paris, C. W. Nicholson, S. Johnston, Y. Tseng, M. Rumo, G. Coslovich, S. Zohar, M. F. Lin, V. N. Strocov, R. Saint-Martin, A. Revcolevschi, A. Kemper, W. Schlotter, G. L. Dakovski, C. Monney, and T. Schmitt, *Probing the interplay*

- between lattice dynamics and short-range magnetic correlations in CuGeO_3 with femtosecond RIXS, *npj Quantum Mater.* **6**, 51 (2021).
- [32] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/24wn-q427> for sample characterization, additional experimental details, and supplemental figures, which includes Refs. [33–38].
- [33] L. Hu, L. Q. Yu, P. Xiong, X. L. Wang, J. H. Zhao, L. F. Wang, Z. Huang, and W. B. Wu, *Static and dynamic signatures of anisotropic electronic phase separation in $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$* , *Phys. Rev. B* **97**, 214428 (2018).
- [34] S. Valencia, A. Gaupp, W. Gudat, L. Abad, L. Balcells, A. Cavallaro, B. Martínez, and F. J. Palomares, *Mn valence instability in $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ thin films*, *Phys. Rev. B* **73**, 104402 (2006).
- [35] S. Grenier, J. P. Hill, V. Kiryukhin, W. Ku, Y. J. Kim, K. J. Thomas, S. W. Cheong, Y. Tokura, Y. Tomioka, D. Casa, and T. Gog, *$d-d$ excitations in manganites probed by resonant inelastic x-ray scattering*, *Phys. Rev. Lett.* **94**, 047203 (2005).
- [36] F. Weber, S. Rosenkranz, J. P. Castellán, R. Osborn, J. F. Mitchell, H. Zheng, D. Casa, J. H. Kim, and T. Gog, *$d-d$ excitations in bilayer manganites probed by resonant inelastic x-ray scattering*, *Phys. Rev. B* **82**, 085105 (2010).
- [37] T. Inami, T. Fukuda, J. Mizuki, S. Ishihara, H. Kondo, H. Nakao, T. Matsumura, K. Hirota, Y. Murakami, S. Maekawa, and Y. Endoh, *Orbital excitations in LaMnO_3 studied by resonant inelastic x-ray scattering*, *Phys. Rev. B* **67**, 045108 (2003).
- [38] H. J. Lee, K. H. Kim, J. H. Jung, T. W. Noh, R. Suryanarayanan, G. Dhalenne, and A. Revcolevschi, *Optical studies of a layered manganite $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$: Polaron correlation effect*, *Phys. Rev. B* **62**, 11320 (2000).
- [39] N. Ramesh, H. Banerjee, J. E. N. Swallow, E. Björklund, A. Dean, P. Didwal, M. Fraser, C. M. E. Phelan, L. An, J. Singh, J. Lewis, W. Song, R. A. House, A. J. Morris, R. S. Weatherup, and R. J. Nicholls, *Atomistic interpretation of the oxygen K-edge x-ray absorption spectra of layered Li-ion battery cathode materials*, *Chem. Mater.* **36**, 11051 (2024).
- [40] F. Jin, S. Fan, M. Gu, Q. Lv, M. Ge, Z. Zhang, J. Zhang, J. Lu, T. Kim, V. Bhartiya, Z. Huang, L. Wang, V. Bisogni, J. Pellicciari, and W. Wu, *Topotactic reduction-driven crystal field excitations in brownmillerite manganite thin films*, *Adv. Funct. Mater.* **250**, 1893 (2025).
- [41] S. Satpathy, Z. S. Popović, and F. R. Vukajlović, *Electronic structure of the perovskite oxides: $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$* , *Phys. Rev. Lett.* **76**, 960 (1996).
- [42] S. Valencia, A. Gaupp, W. Gudat, L. Abad, L. Balcells, B. Martínez, and V. Laukhin, *Soft x-ray absorption spectroscopy of strained epitaxial manganite thin films*, *Appl. Phys. Lett.* **89**, 172512 (2006).
- [43] O. Toulemonde, F. Millange, F. Studer, B. Raveau, J. H. Park, and C. T. Chen, *Changes in the Jahn-Teller distortion at the metal-insulator transition in CMR manganites $(\text{Pr}, \text{Nd})_{0.7}(\text{Sr}, \text{Ca})_{0.3}\text{MnO}_3$* , *J. Phys. Condens. Matter* **11**, 109 (1999).
- [44] S. Y. Zhou, Y. Zhu, M. C. Langner, Y. D. Chuang, P. Yu, W. L. Yang, A. G. Cruz Gonzalez, N. Tahir, M. Rini, Y. H. Chu, R. Ramesh, D. H. Lee, Y. Tomioka, Y. Tokura, Z. Hussain, and R. W. Schoenlein, *Ferromagnetic enhancement of CE-type spin ordering in $(\text{Pr}, \text{Ca})\text{MnO}_3$* , *Phys. Rev. Lett.* **106**, 186404 (2011).
- [45] C. G. Fatuzzo, M. Dantz, S. Fatale, P. Olalde-Velasco, N. E. Shaik, B. Dalla Piazza, S. Toth, J. Pellicciari, R. Fittipaldi, A. Vecchione, N. Kikugawa, J. S. Brooks, H. M. Rønnow, M. Grioni, C. Rüegg, T. Schmitt, and J. Chang, *Spin-orbit-induced orbital excitations in Sr_2RuO_4 and Ca_2RuO_4 : A resonant inelastic x-ray scattering study*, *Phys. Rev. B* **91**, 155104 (2015).
- [46] D. Jost, H. Y. Huang, M. Rossi, A. Singh, D. J. Huang, Y. Lee, H. Zheng, J. F. Mitchell, B. Moritz, Z. X. Shen, T. P. Devereaux, and W. S. Lee, *Low temperature dynamic polaron liquid in a manganite exhibiting colossal magnetoresistance*, *Phys. Rev. Lett.* **132**, 186502 (2024).
- [47] M. Quijada, J. Cerne, J. R. Simpson, H. D. Drew, K. H. Ahn, A. J. Millis, R. Shreekala, R. Ramesh, M. Rajeswari, and T. Venkatesan, *Optical conductivity of manganites: Crossover from Jahn-Teller small polaron to coherent transport in the ferromagnetic state*, *Phys. Rev. B* **58**, 16093 (1998).
- [48] J. H. Jung, K. H. Kim, T. W. Noh, E. J. Choi, and J. Yu, *Midgap states of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$: Doping-dependent optical-conductivity studies*, *Phys. Rev. B* **57**, R11043 (1998).
- [49] S. G. Kaplan, M. Quijada, H. D. Drew, D. B. Tanner, G. C. Xiong, R. Ramesh, C. Kwon, and T. Venkatesan, *Optical evidence for the dynamic Jahn-Teller effect in $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$* , *Phys. Rev. Lett.* **77**, 2081 (1996).
- [50] C. Hartinger, F. Mayr, J. Deisenhofer, A. Loidl, and T. Kopp, *Large and small polaron excitations in $\text{La}_{2/3}(\text{Sr}/\text{Ca})_{1/3}\text{MnO}_3$ films*, *Phys. Rev. B* **69**, 100403(R) (2004).
- [51] C. Franchini, M. Reticcioli, M. Setvin, and U. Diebold, *Polarons in materials*, *Nat. Rev. Mater.* **6**, 560 (2021).
- [52] D. Emin, *Optical properties of large and small polarons and bipolarons*, *Phys. Rev. B* **48**, 13691 (1993).
- [53] L. Braicovich, M. Rossi, R. Fumagalli, Y. Peng, Y. Wang, R. Arpaia, D. Betto, G. M. De Luca, D. Di Castro, K. Kummer, M. Moretti Sala, M. Pagetti, G. Balestrino, N. B. Brookes, M. Salluzzo, S. Johnston, J. van den Brink, and G. Ghiringhelli, *Determining the electron-phonon coupling in superconducting cuprates by resonant inelastic x-ray scattering: Methods and results on $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$* , *Phys. Rev. Res.* **2**, 023231 (2020).
- [54] D. Emin, *Semiclassical small-polaron hopping in a generalized molecularcrystal model*, *Phys. Rev. B* **43**, 11720 (1991).
- [55] A. S. Mishchenko, N. Nagaosa, G. De Filippis, A. de Candia, and V. Cataudella, *Mobility of Holstein polaron at finite temperature: An unbiased approach*, *Phys. Rev. Lett.* **114**, 146401 (2015).
- [56] M. Ziese and C. Srinitiwara Wong, *Polaronic effects on the resistivity of manganite thin films*, *Phys. Rev. B* **58**, 11519 (1998).
- [57] A. S. Mishchenko, L. Pollet, N. V. Prokof'ev, A. Kumar, D. L. Maslov, and N. Nagaosa, *Polaron mobility in the “Beyond Quasiparticles” regime*, *Phys. Rev. Lett.* **123**, 076601 (2019).
- [58] O. Gunnarsson, M. Calandra, and J. E. Han, *Colloquium: Saturation of electrical resistivity*, *Rev. Mod. Phys.* **75**, 1085 (2003).

- [59] S. Y. Zhou, M. C. Langner, Y. Zhu, Y. D. Chuang, M. Rini, T. E. Glover, M. P. Hertlein, A. G. C. Gonzalez, N. Tahir, Y. Tomioka, Y. Tokura, Z. Hussain, and R. W. Schoenlein, *Glass-like recovery of antiferromagnetic spin ordering in a photo-excited manganite* $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, *Sci. Rep.* **4**, 4050 (2014).
- [60] V. Esposito, L. Rettig, E. Abreu, E. M. Bothschafter, G. Ingold, M. Kawasaki, M. Kubli, G. Lantz, M. Nakamura, J. Rittman, M. Savoini, Y. Tokura, U. Staub, S. L. Johnson, and P. Beaud, *Photoinduced transitions in magnetoresistive manganites: A comprehensive view*, *Phys. Rev. B* **97**, 014312 (2018).
- [61] T. Hashimoto, S. Ishibashi, and K. Terakura, *Jahn-Teller distortion and magnetic structure in LaMnO_3 : A first-principles theoretical study with full structure optimizations*, *Phys. Rev. B* **82**, 045124 (2010).
- [62] A. de la Torre, D. M. Kennes, M. Claassen, S. Gerber, J. W. McIver, and M. A. Sentef, *Colloquium: Nonthermal pathways to ultrafast control in quantum materials*, *Rev. Mod. Phys.* **93**, 041002 (2021).
- [63] M. Lucchini, F. Medeghini, Y. Wu, F. Vismarra, R. B. Varillas, A. Crego, F. Frassetto, L. Poletto, S. A. Sato, H. Hübener, U. D. Giovannini, A. Rubio, and M. Nisoli, *Controlling Floquet states on ultrashort time scales*, *Nat. Commun.* **13**, 7103 (2022).
- [64] M. Budden, T. Gebert, M. Buzzi, G. Jotzu, E. Wang, T. Matsuyama, G. Meier, Y. Laplace, D. Pontiroli, M. Riccò, F. Schlawin, D. Jaksch, and A. Cavalleri, *Evidence for metastable photo-induced superconductivity in K_3C_{60}* , *Nat. Phys.* **17**, 611 (2021).
- [65] L. Stojchevska, I. Vaskivskiy, T. Mertelj, P. Kusar, D. Svetin, S. Brazovskii, and D. Mihailovic, *Ultrafast switching to a stable hidden quantum state in an electronic crystal*, *Science* **344**, 177 (2014).
- [66] J. Maklar, J. Sarkar, S. Dong, Y. A. Gerasimenko, T. Pincelli, S. Beaulieu, P. S. Kirchmann, J. A. Sobota, S. Yang, D. Leuenberger, R. G. Moore, Z. X. Shen, M. Wolf, D. Mihailovic, R. Ernstorfer, and L. Rettig, *Coherent light control of a metastable hidden state*, *Sci. Adv.* **9**, eadi4661 (2023).
- [67] Q. M. Liu, D. Wu, Z. A. Li, L. Y. Shi, Z. X. Wang, S. J. Zhang, T. Lin, T. C. Hu, H. F. Tian, J. Q. Li, T. Dong, and N. L. Wang, *Photoinduced multistage phase transitions in Ta_2NiSe_5* , *Nat. Commun.* **12**, 2050 (2021).
- [68] G. Kresse and J. Furthmüller, *Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set*, *Phys. Rev. B* **54**, 11169 (1996).
- [69] P. E. Blöchl, *Projector augmented-wave method*, *Phys. Rev. B* **50**, 17953 (1994).
- [70] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, *Restoring the density-gradient expansion for exchange in solids and surfaces*, *Phys. Rev. Lett.* **100**, 136406 (2008).
- [71] A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen, *Density-functional theory and strong interactions: Orbital ordering in Mott-Hubbard insulators*, *Phys. Rev. B* **52**, R5467 (1995).
- [72] L. Bellaïche and D. Vanderbilt, *Virtual crystal approximation revisited: Application to dielectric and piezoelectric properties of perovskites*, *Phys. Rev. B* **61**, 7877 (2000).
- [73] R. Trappen, A. C. Garcia-Castro, V. T. Tra, C.-Y. Huang, W. Ibarra-Hernandez, J. Fitch, S. Singh, J. Zhou, G. Cabrera, Y.-H. Chu, J. M. LeBeau, A. H. Romero, and M. B. Holcomb, *Electrostatic potential and valence modulation in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin films*, *Sci. Rep.* **8**, 14313 (2018).
- [74] H. J. Monkhorst and J. D. Pack, *Special points for Brillouin-zone integrations*, *Phys. Rev. B* **13**, 5188 (1976).
- [75] U. Herath, P. Tavadze, X. He, E. Bousquet, S. Singh, F. Muñoz, and A. H. Romero, *PyProcar: A Python library for electronic structure pre/postprocessing*, *Comput. Phys. Commun.* **251**, 107080 (2020).

Correction: The omission of a funding statement in the Acknowledgments section has been rectified.