

Frustration-driven correlated parent states in the spinel superconductor LiTi_2O_4

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Geometrically frustrated transition-metal oxides provide fertile ground for the emergence of novel quantum states. In the spinel superconductor LiTi_2O_4 (superconducting critical temperature $T_c \approx 13$ K, formal $3d^{0.5}$ system), we uncover a prominent dispersion kink near the Fermi energy accompanied by negative thermal expansion below a characteristic temperature $T^* \approx 150$ K. We propose that charge frustration in the pyrochlore lattice leads to a degenerate electronic arrangement on $\text{Ti}^{3+}/\text{Ti}^{4+}$ sites, giving rise to strong intersite Coulomb interactions below T^* . Within this framework, negative thermal expansion arises from the Coulomb repulsion of $3d^1$ electrons, while the prominent kink reflects reduced screening due to enhanced correlations. These findings open up promising avenues for exploring exotic correlated states in frustrated pyrochlore lattices, which are situated near the $3d^1$ Mott state.

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Introduction. The transition-metal spinel oxide AB_2O_4 [Fig. 1(a)] is a well-known material platform that hosts a diverse array of frustration-driven quantum states [1–14]. In this material, element B forms a corner-sharing tetrahedral structure within the pyrochlore network [Fig. 1(b)]. This structure enables various spin, charge, and orbital states to be degenerate and frustrated from a real-space perspective [Figs. 1(c)–1(e)]. On the other hand, gaining a deeper understanding of emergent electronic states from a momentum space perspective is also crucial. Due to the pyrochlore lattice's band structure, a flat band, Dirac points, and saddle points exist inherently [15]. When long-range order emerges as a means of relieving electronic or lattice frustration, its fingerprints typically appear prominently in momentum space. Well-established signatures include band splitting, band folding, and the opening of soft or hard gaps in the underlying parent band structure, as commonly observed in correlated materials without geometrical frustration [16–18]. In contrast,

when intrinsic geometrical frustration suppresses the formation of long-range order, short-range ordering nonetheless leaves behind a residual tendency toward localization, and consequently, reduced electronic screening. Modifications of underlying collective modes, such as phonons, may also occur in association with underlying short-range ordering. These effects can manifest as anomalies in the near Fermi energy (E_F) electronic structure of a metallic system—such as kink-like features—while keeping the Fermi momentum essentially unchanged. However, direct experimental identification of such electronic anomalies has remained largely unexplored in spinel oxides.

Particularly rich frustration-driven phenomena have been recognized adjacent to the formal $3d^1$ Mott system, MgTi_2O_4 (MTO) [14] [Fig. 1(f)]. On the electron-doped side, corresponding to formal $3d^{1.5}$ filling, the heaviest heavy-fermion system within oxides emerges in LiV_2O_4 (LVO) [5–8,19]. On the hole-doped side, LiTi_2O_4 (LTO) with formal $3d^{0.5}$ filling hosts superconductivity with a maximum superconducting critical temperature T_c (~ 13 K) among the spinel compounds [10,11,20]. Both cases exhibit half-integer formal valence states, where charge frustration is expected to play a key role [5,6,8,11]. Understanding the potential impact of charge frustration in LTO is especially important, as a deeper understanding is crucial for developing the physics of exotic superconductors. While the anomalous metallic nature above T_c has been highlighted by transport studies in LTO [21,22], its microscopic picture remains elusive.

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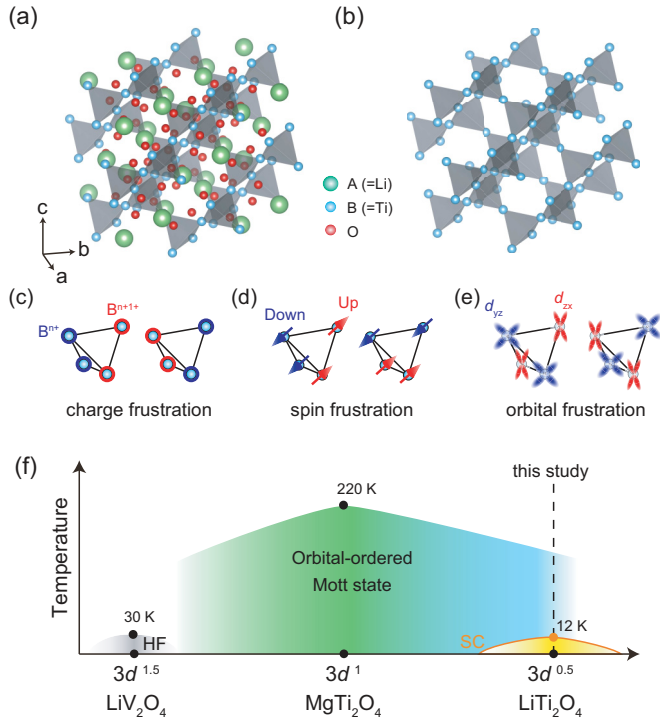


FIG. 1. (a) Crystal structure of LiTi_2O_4 ($Fd-3m$). (b) Pyrochlore lattice of Ti atoms. (c)–(e) Charge, spin, and orbital frustration on the pyrochlore lattice. (f) Phase diagram of spinel oxides near the $3d^1$ electronic configuration. HF and SC denote heavy fermion and superconducting state, respectively. See main text for details.

By combining *in situ* epitaxial thin-film growth with angle-resolved photoemission spectroscopy (ARPES), we directly visualize the band structure of (111)-oriented spinel oxide superconducting LTO films (see Ref. [23] for the method and basic characterizations of the films used in this study). In this study, we propose that the emergence of a frustrated charge state below $T^* \sim 150$ K intriguingly preserves a highly degenerate electronic configuration, forestalling any long-range phase transition until the onset of superconductivity below T_c . Intriguing consequences of prominent kink formation and negative thermal expansion (NTE) are consistently shown.

The Brillouin zone (BZ) and the band structure from a single orbital tight-binding (TB) model for the pyrochlore lattice are shown in Figs. 2(a) and 2(b), respectively. Similar to two-dimensional kagome systems [24–26], the band structure of the pyrochlore lattice hosts flat bands, Dirac points, and saddle points at energy E_{SP} [15]. Because of the formal valence of $\text{Ti}^{3.5+}$, one can roughly expect the appearance of the large Fermi surface (FS) and consequent E_{SP} close to the E_F [see Fig. 2(c)]. Indeed, as shown in Fig. 2(d), a large FS is observed experimentally with the photon energy $h\nu = 21.2$ eV (He-I α) at 12 K. We found that the ARPES data correspond to the k_z plane near Γ , based on the band folding momentum near the BZ boundary [see Fig. 2(a) and Ref. [23] for the detailed discussion on the determination of the k_z values taken with He-I α and He-II α]. In this study, the impact of k_z dispersion is assumed to be negligible for the main scope (see the Supplemental Material [23] for a detailed discussion).

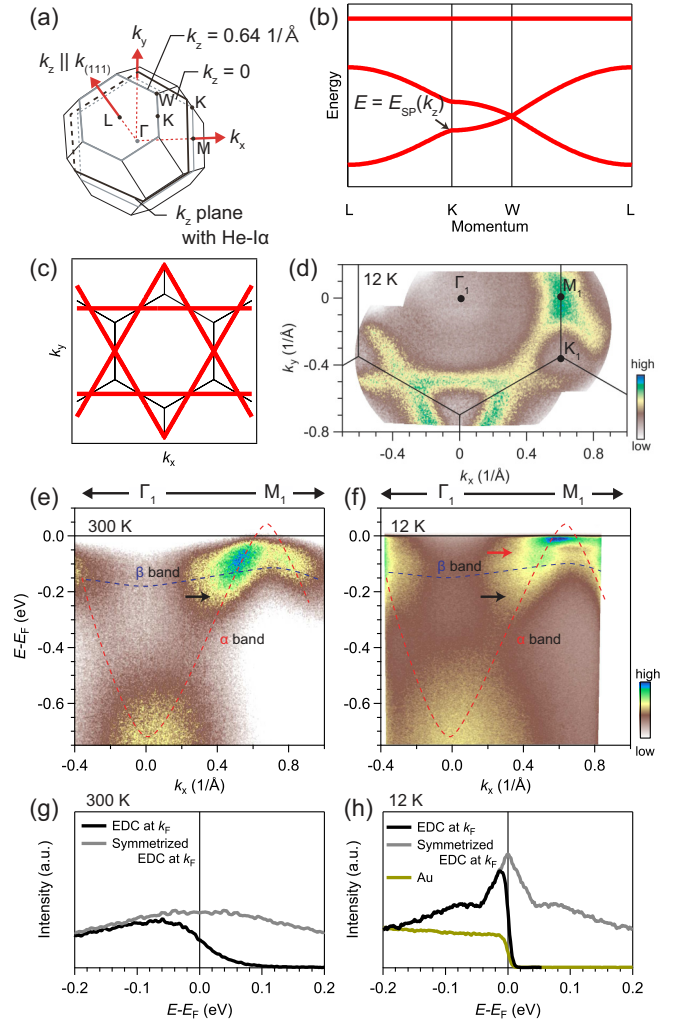


FIG. 2. (a) Rhombohedral BZ with k_z defined along the (111) direction. (b) TB calculation for the pyrochlore lattice; the black arrow mark the saddle point energies E_{SP} , which depend on k_z . (c) TB-derived energy contour at E_{SP} . (d) Fermi surface measured with the He-I light source; black lines are guides to the eye. Γ_1 , M_1 , and K_1 are defined from the observed Fermi surface. (e), (f) ARPES dispersions along Γ_1 – M_1 at 300 and 12 K. Black and red arrows indicate energies with many-body effects; red and blue curves guide the α and β bands, respectively. (g), (h) EDCs and their symmetrized forms at 12 and 300 K. The yellow curve in panel (h) shows the spectrum of the polycrystalline gold reference used to calibrate the E_F position.

In Fig. 2(e), the ARPES dispersion along Γ_1 – M_1 at 300 K is shown. The band dispersion contributing to the FS (denoted as α band) is observed, which can be well reproduced as the nearly degenerate multiple eigenstates derived from the t_{2g} orbitals (see Ref. [23] for the comparison to the density functional theory (DFT) calculations). Note that a relatively flat band observed at $E - E_F \sim -100$ meV at 12 and 300 K [denoted as the β band in Figs. 2(e) and 2(f)] presumably originates from the surface state. While the β band merits future study, its details are not essential to our main conclusion (see Supplemental Note 4 in the Supplemental Material [23] for details). Notably, the many-body effects are observed on the α band, which is also reported in other works [27,28]. While

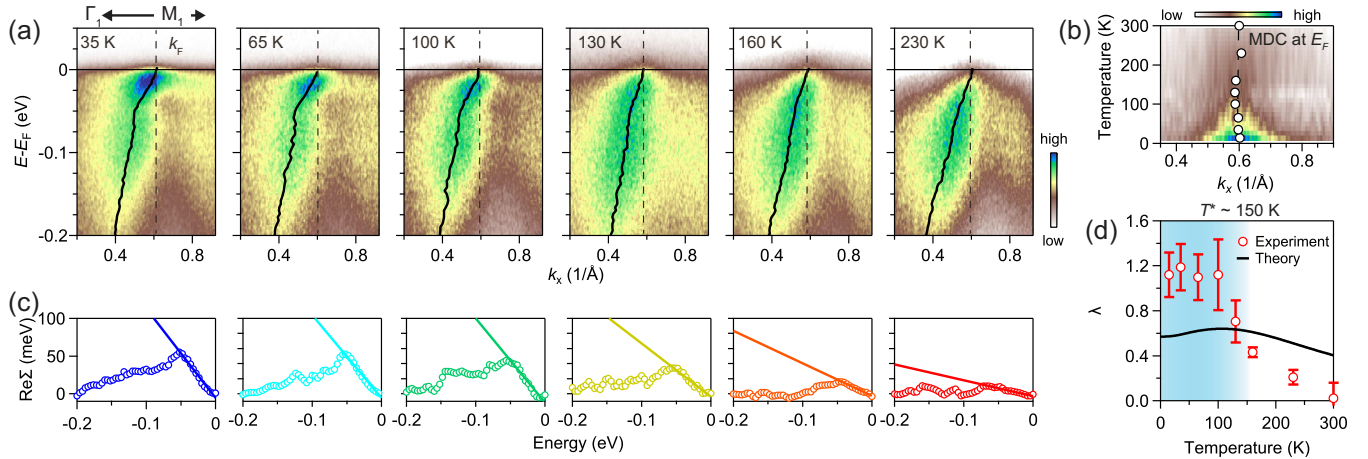


FIG. 3. (a) ARPES spectra along Γ_1-M_1 at various temperatures with dispersion traces (black lines). (b) Temperature-dependent MDC intensity map; data points mark MDC peak positions, showing negligible temperature dependence. (c) Real part of the self-energy used to extract the coupling constant. (d) Temperature dependence of λ , displaying a sudden increase near 150 K. Error bars represent 3σ [σ : standard deviation of the slope in panel (c)], corresponding to 99.7% accuracy. The solid curve shows λ calculated from the Eliashberg function considering only thermal broadening and the phonon density of states. See Supplemental Note 3 in the Supplemental Material [23] for details.

a sudden broadening of the momentum distribution curve (MDC) is observed below $E - E_F = -200$ meV [see black arrows in Figs. 2(e) and 2(f)], this high-energy many-body effect is less temperature dependent. Furthermore, regardless of temperature, the gap opening or band splitting is not observed within our experimental resolution. Absence of a gap or band splitting is consistently observed from the energy-symmetrized energy distribution curves (EDCs) taken at $k_F = 0.6 \text{ \AA}^{-1}$ in Figs. 2(g) and 2(h). While we cannot completely rule out a small, unresolved gap comparable to the superconducting energy scale (a few meV), it is important to emphasize that no gap or band splitting associated with the much larger energy scale of $T^* \sim 150$ K is observed, as discussed later. We note that the E_F position was carefully calibrated using a polycrystalline gold reference sample [yellow curve in Fig. 2(h)].

As the most critical many-body effect, the kink structure is recognized at 12 K with an energy (E_{kink}) of approximately -50 meV [see the red arrow in Fig. 2(f)]. Since the kink energy $E_{\text{kink}} \approx -50$ meV closely matches the peak in the phonon density of states obtained from our DFT calculations, this dispersion kink is likely dominated by electron-phonon coupling. The phonon energy scale may, however, be slightly shifted due to mode softening, as discussed later (see also Ref. [23]). Intriguingly, this near- E_F kink structure is less prominent at 300 K, suggesting the existence of a characteristic temperature, below which the kink structure dominates.

To unveil the characteristic temperature for the kink formation at E_{kink} , we performed temperature-dependent ARPES experiments. Figure 3(a) shows ARPES intensity maps and traces of the dispersion at various temperatures. As the temperature decreases [from right to left in Fig. 3(a)], the kink structure becomes more prominent. The temperature variation of the k_F extracted from the MDC curves is confirmed to be negligible [Fig. 3(b)]. For the quantitative analysis of the kink structure at E_{kink} , which emerged from the electron-phonon coupling, we introduce the coupling constant $\lambda(T)$ extracted

from the real part of the self-energy [Fig. 3(c)] [23,29,30]. We obtained similar values for the other Fermi momenta (see Ref. [23] for detailed information). Importantly, a characteristic temperature of $T^* \sim 150$ K is found in the experimental $\lambda(T)$, below which a relatively abrupt increase is observed [Fig. 3(d)]. To determine whether this enhancement is anomalous or not, we compare the experimental $\lambda(T)$ with a simple calculation based on the Eliashberg function α^2F , taking into account conventional thermal broadening effects [31] [solid curve in Fig. 3(d) and see also Ref. [23] for the detailed method for the calculation]. The much more abrupt temperature evolution seen in experimental $\lambda(T)$ suggests novel physics behind the origin of T^* , indicating rich phenomenology beyond the simple picture within DFT framework.

To search for a possible anomalous temperature dependence of the crystal structure, we carefully investigated the X-ray diffraction (XRD) pattern. Note that our film is basically relaxed from epitaxial strain from the Nb-doped SrTiO₃ (STO) substrate (see Ref. [23] for the reciprocal-space mapping). Figure 4(a) shows the XRD pattern at room temperature, where the well-separated LTO (444) and STO (222) peaks are observed. To highlight the distinct temperature evolution between them, the normalized lattice spacing defined as $\Delta d_{hkl} = \{d_{hkl} - d_{hkl}(300 \text{ K})\}/d_{hkl}(300 \text{ K})$ is shown in Fig. 4(b). From the LTO (444) peak, it is evident that no peak splitting is seen within our experimental resolution (see Ref. [23] for the other indices). This suggests the absence of an apparent structural change, such as the cubic-to-tetragonal transition [9,13,14]. Nevertheless, we found intriguing behavior in the temperature dependence of Δd_{hkl} for LTO (444) as shown in Fig. 4(c) (see Supplemental Material [23] for the details of fitting). While the STO shows a monotonic decrease with temperature, the LTO peak shows a minimum at around 150 K, followed by a slight increase with cooling the sample below 150 K. This observation points to the surprising emergence of so-called NTE below ~ 150 K. Further notable discovery is the excellent agreement between the onset tem-

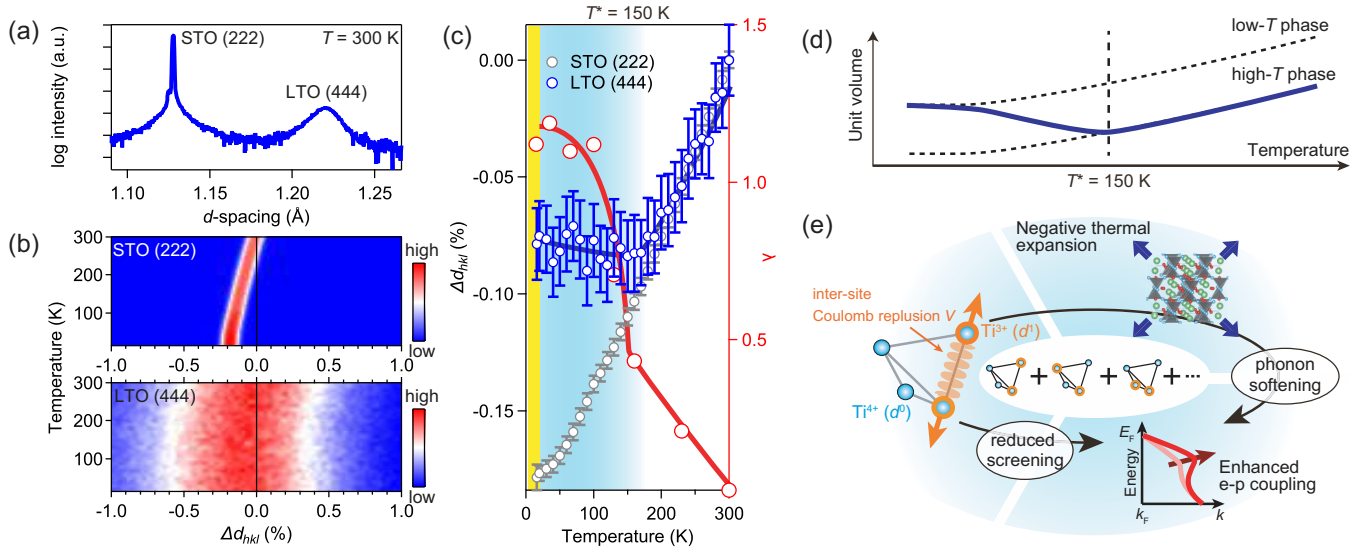


FIG. 4. (a) XRD profile of the LTO(111) film on an STO substrate at room temperature. (b) Temperature dependence of d_{hkl} normalized to the room-temperature value [$\Delta d_{hkl} = \{d_{hkl}(300 \text{ K}) - d_{hkl}(300 \text{ K})\}/d_{hkl}(300 \text{ K})$] for STO (222) (top) and LTO (444) (bottom) peaks. (c) Temperature dependence of Δd_{hkl} (blue curve: guide to the eye). Error bars represent 3σ [σ : standard deviation of the peak position in panel (b)], corresponding to 99.7% accuracy. The coupling constant λ derived from ARPES is shown on the right axis for comparison. Background colors indicate distinct phases revealed in this study: normal (white), correlated (cyan), and superconducting (yellow). For comparison with ARPES on the (111) film, NTE results for (111) films are displayed in panels (b) and (c), though NTE is a bulk property also observed in (100) and (110) films (see Supplemental Note 5 in the Supplemental Material [23]). (d) Schematic summary of NTE and kink formation below $T^* = 150 \text{ K}$. (e) Schematic interpretation of kink formation and NTE based on charge frustration.

perature T^* of the dispersion kink and the NTE, suggesting their intriguing connection [compare left and right axes in Fig. 4(c)].

Conventionally, bond lengths and lattice volume contract upon cooling as phonon excitations are suppressed, resulting in positive thermal expansion [dotted lines in Fig. 4(d)]. NTE can instead arise when distinct or competing electronic or lattice states emerge between high and low temperatures [solid lines in Fig. 4(d)]. In general, NTE at low temperature has been linked either to the development of long-range order [32,33,34] or to short-range spin, charge, or orbital fluctuations coupled to the lattice [35–39]. By analogy, a natural hypothesis for LTO is the emergence of an electronically distinct state below T^* . The presence of a saddle point near E_F could favor long-range order, yet ARPES shows no gap opening, band folding, or band splitting, and XRD reveals no clear structural transition. This absence of ordering highlights the role of geometrical frustration in realizing an exotic state below T^* .

Microscopically, the coexistence of NTE and the dispersion kink can be consistently understood in terms of charge frustration arising from $\text{Ti}^{3+}/\text{Ti}^{4+}$ disproportionation in LTO. The formal $3d^{0.5}$ configuration leads to a degenerate charge arrangement of disproportionated $\text{Ti}^{3+}/\text{Ti}^{4+}$ on the pyrochlore lattice, producing strong inter-site Coulomb repulsion V [Fig. 4(e), left]. This V term can drive NTE by energetically favoring lattice expansion, a mechanism phenomenologically analogous to the role of exchange interactions in frustrated spin-lattice systems exhibiting NTE [35,36,38,39]. At the same time, the V -driven tendency toward stronger localization weakens the screening of ionic

displacements, thereby enhancing the electron-phonon coupling [40] [Fig. 4(e), right bottom]. As a result, both NTE and the dispersion kink can be viewed as manifestations of charge fluctuations and consequent V . The anomalous metallic state below T^* may thus be regarded as a charge-liquid-like regime, where a possible entangled charge configurations persist without forming long-range order [Fig. 4(e), center]. We further note that phonon softening—often invoked as an origin of NTE—can cooperate with this mechanism by modifying the phonon density of states and enhancing electron-phonon coupling [41,42].

Finally, our findings place LTO within the broader landscape of anomalous metallic states emerging near the $3d^1$ Mott regime on a frustrated lattice [Fig. 1(f)]. MTO hosts a cooperative $3d^1$ Mott phase involving multiple degrees of freedom and long-range chiral structural motifs [14], while the half-integer system LVO ($3d^{1.5}$) forms a heavy-electron state shaped by Kondo/Hund coupling, orbital-selective Mottness, and $3d^1$ – $3d^2$ charge disproportionation and frustration [8,19,43–45]. Within this framework, LTO ($3d^{0.5}$) represents the hole-doped half-integer analog of the $3d^1$ state. Here, pronounced $3d^0$ – $3d^1$ disproportionation and frustration allow V -derived states to produce anomalous metallic behavior—a consequence of proximity to the $3d^1$ configuration. Consistent with this, the -0.2 eV high-energy anomaly [Figs. 2(e) and 2(f)] appears as a spectroscopic fingerprint of strong correlations, akin to features reported in other correlated oxides [46–48]. Furthermore, the characteristic temperature T^* evolves smoothly toward the $\sim 220 \text{ K}$ orbital-ordering scale near $3d^1$. Nevertheless, the optimally doped $3d^{0.5}$ regime remains dominated by fluctuated short-range ordering

rather than long-range order—distinct from many unconventional superconductors where symmetry breaking precedes T_c . Taken together, LTO, MTO, and LVO suggest a unified picture in which anomalous metallicity across the $3d^{0.5}-3d^{1.5}$ range arises from a common remnant $3d^1$ nature associated with charge disproportionation and frustration. This systematic perspective offers a well-defined route to examine how charge, spin, and orbital/lattice degrees of freedom cooperatively yield short-range hidden order or long-range ordered phases, involving nontrivial symmetries such as chirality. The recently discovered unconventional superconductivity in LTO further highlights the opportunity to directly connect anomalous metallicity with the emergence of unconventional superconducting states [20,49,50].

In summary, we uncover a hidden correlation effect, driven by charge disproportionation and its frustration, that ties NTE to the emergence of a dispersion kink below $T^* \sim 150$ K. By combining *in situ* ARPES with an advanced thin-film growth

technique, we establish a powerful approach to probe the electronic structure of three-dimensional spinel oxides. This work offers opportunities to explore exotic states of matter proximate to the 3d Mott regime in frustrated pyrochlore lattices, both in bulk and at interfaces.

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

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