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Authors

Hasan, Zubia

Pan, Grace A

LaBollita, Harrison

et al.

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Unconventional polaronic ground state in superconducting LiTi_2O_4

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Zubia Hasan ^{1,16}, Grace A. Pan ^{1,16}, Harrison LaBollita ², Austin Kaczmarek ³, Suk Hyun Sung⁴, Shekhar Sharma², Purnima P. Balakrishnan ⁵, Edward Mercer^{6,7}, Vivek Bhartiya ⁸, Alpha T. N'Diaye ⁹, Zaher Salman ¹⁰, Thomas Prokscha ¹⁰, Andreas Suter ¹⁰, Alexander J. Grutter ⁵, Mirian Garcia-Fernandez ¹¹, Ke-Jin Zhou ¹¹, Jonathan Pelliciari ⁸, Valentina Bisogni ⁸, Ismail El Baggari⁴, Darrell G. Schlom ^{12,13,14,15}, Matthew R. Barone¹², Charles M. Brooks¹, Katja C. Nowack ³, Antia S. Botana², Brendan D. Faeth¹², Alberto de la Torre ^{6,7} ✉ & Julia A. Mundy ¹ ✉

Geometrically frustrated lattices can display a range of correlated phenomena, ranging from spin frustration and charge order to dispersionless flat bands due to quantum interference. One particularly compelling family of such materials is the half-valence spinel LiB_2O_4 materials. On the *B*-site frustrated pyrochlore sublattice, the interplay of correlated metallic behavior and charge frustration leads to a superconducting state in LiTi_2O_4 and heavy fermion behavior in LiV_2O_4 . To date, however, LiTi_2O_4 has primarily been understood as a conventional BCS superconductor despite a lattice structure that could host more exotic ground states. Here, we present a multimodal investigation of LiTi_2O_4 , combining ARPES, RIXS, proximate magnetic probes, and ab-initio many-body theoretical calculations. Our data reveals a novel mobile polaronic ground state with spectroscopic signatures that underlie co-dominant electron-phonon coupling and electron-electron correlations also found in the lightly doped cuprates. The cooperation between the two interaction scales distinguishes LiTi_2O_4 from other superconducting titanates, suggesting an unconventional origin to superconductivity in LiTi_2O_4 . Our work deepens our understanding of the rare interplay of electron-electron correlations and electron-phonon coupling in unconventional superconducting systems. In particular, our work identifies the geometrically frustrated, mixed-valence spinel family as an under-explored platform for discovering unconventional, correlated ground states.

The interplay between electron–electron correlations and electron–phonon coupling has been of long-standing interest in understanding superconductivity. In traditional Bardeen-Cooper-Schrieffer (BCS) superconductors, Coulomb repulsion between electrons is thought to screen electron-phonon coupling and reduce the superconducting transition temperature T_c ¹. In unconventional superconductors, however, there can be a more complex interplay between

electron–phonon coupling and electron–electron interactions. Strong correlations can further strengthen the electron-phonon coupling and enhance T_c ^{2–4}. In certain cases, as explored for cuprates⁵, the energy scales of strong electron–electron correlations can overwhelm those of electron–phonon interactions, leading to charge and spin fluctuations that compete with or enhance superconductivity⁶. Thus, understanding how electronic correlations and electron–phonon coupling interact in

A full list of affiliations appears at the end of the paper. ✉ e-mail: a.delatorreduran@northeastern.edu; mundy@fas.harvard.edu

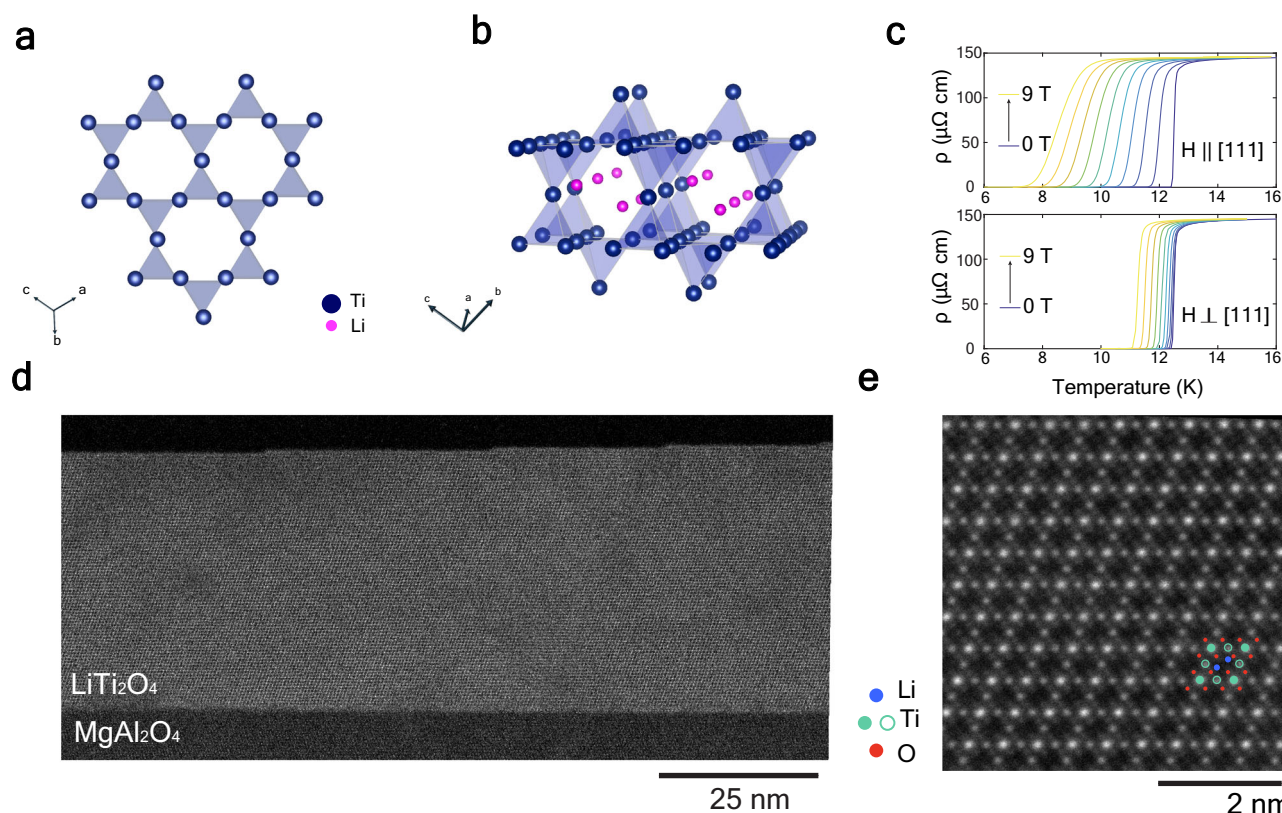


Fig. 1 | Structural and electrical characterization of LiTi_2O_4 . **a** The (111) plane of LiTi_2O_4 showing the titanium kagome sublattice inherent to the spinel structure. **b** Side-view of the (111) plane shown in **a**, highlighting the three-dimensional nature of the geometric frustration in LiTi_2O_4 . **c** Resistivity ρ vs temperature of LiTi_2O_4 with

magnetic field (0 to 9 T) parallel and perpendicular to the sample. **d** Large field-of-view HAADF-STEM image of LiTi_2O_4 showing uniform crystallinity over a large area. **e** Local HAADF-STEM image of LiTi_2O_4 overlaid with the corresponding atoms.

superconductors is important in identifying new families of unconventional superconductors and ascertaining the mechanisms behind high-temperature superconductivity.

Although superconductivity was discovered in LiTi_2O_4 before the cuprates⁷, it remains a unique instance of a spinel superconductor and with the highest T_c for a mixed-valence titanate. In this crystal structure, $d^{0.5}$ titanium atoms form a pyrochlore sublattice, composed of alternating planes of Kagome and triangles (Fig. 1a, b). While this geometric construction has given rise to strong electron correlations in other systems⁸, these interactions have been largely unexplored in LiTi_2O_4 . Indeed, superconductivity in LiTi_2O_4 has primarily been considered as phonon-mediated BCS-like, supported by specific heat, tunneling spectroscopy, and muon spin rotation measurements^{9–11}. In contrast, anomalous magnetotransport behavior and scanning tunneling spectroscopy experiments have suggested the presence of spin fluctuations, orbital ordering, and pseudo-gap-like states in LiTi_2O_4 , all of which are typically associated with unconventional superconductors and strongly correlated materials^{10,12,13}. Interestingly, previous theoretical studies of LiTi_2O_4 have suggested non-BCS-like superconducting mechanisms, such as bipolaronic^{14,15} or resonating valence bond (RVB) superconductivity^{16,17}. While there have been speculations about the role of electron–electron correlations^{9,18}, a more detailed investigation into the strength and nature of various correlations is needed to explore the notion of “unconventional superconductivity” in LiTi_2O_4 .

Here, we reveal the complex interplay between electron–phonon coupling and electron–electron interactions in LiTi_2O_4 . We use molecular-beam epitaxy (MBE) to synthesize epitaxial thin films of superconducting LiTi_2O_4 , enabling a detailed spectroscopic investigation using resonant inelastic x-ray scattering (RIXS) and angle-resolved

photoemission spectroscopy (ARPES). The combination of the element-specific sensitivity to structural and local excitations of RIXS, together with the unique capability of ARPES to reveal energy and momentum dependence of the quasiparticle self-energy, enables us to provide a comprehensive description of the low-energy physics of LiTi_2O_4 . We observe evidence of strong electronic correlations and signatures of strong electron–phonon coupling. The cooperation between these two interaction scales gives rise to a novel polaronic ground state—also found in weakly doped cuprates¹⁹—that dynamically localizes titanium states in LiTi_2O_4 . This interpretation is further supported by our theoretical calculations, which can reproduce some of the spectral features in our ARPES data when considering electron correlations or electron–phonon interactions separately, but are unable to reproduce polaronic phenomena associated with the interplay of both interactions. Our work thus challenges the notion of phonon-dominated BCS superconductivity in LiTi_2O_4 by revealing the complex correlations present in this material, hearkening comparisons to cuprate-like physics.

Results

Synthesis and characterization of superconducting LiTi_2O_4

Thin films of LiTi_2O_4 were grown via reactive oxide MBE on (111)-oriented MgAl_2O_4 substrates (see “Methods”). As shown in Fig. 1c, the films display a superconducting transition with $T_c \sim 12.5$ K and a residual resistivity ratio (RRR) of ~ 5.85 (Fig. S3), consistent with previous reports of the highest quality LiTi_2O_4 ^{7,10}. Figure 1d, e show high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images of LiTi_2O_4 , attesting to the high structural quality of our films (also see Supplementary Fig. S1).

Additionally, we confirm the onset of superconductivity and probe the superconducting order parameter using scanning

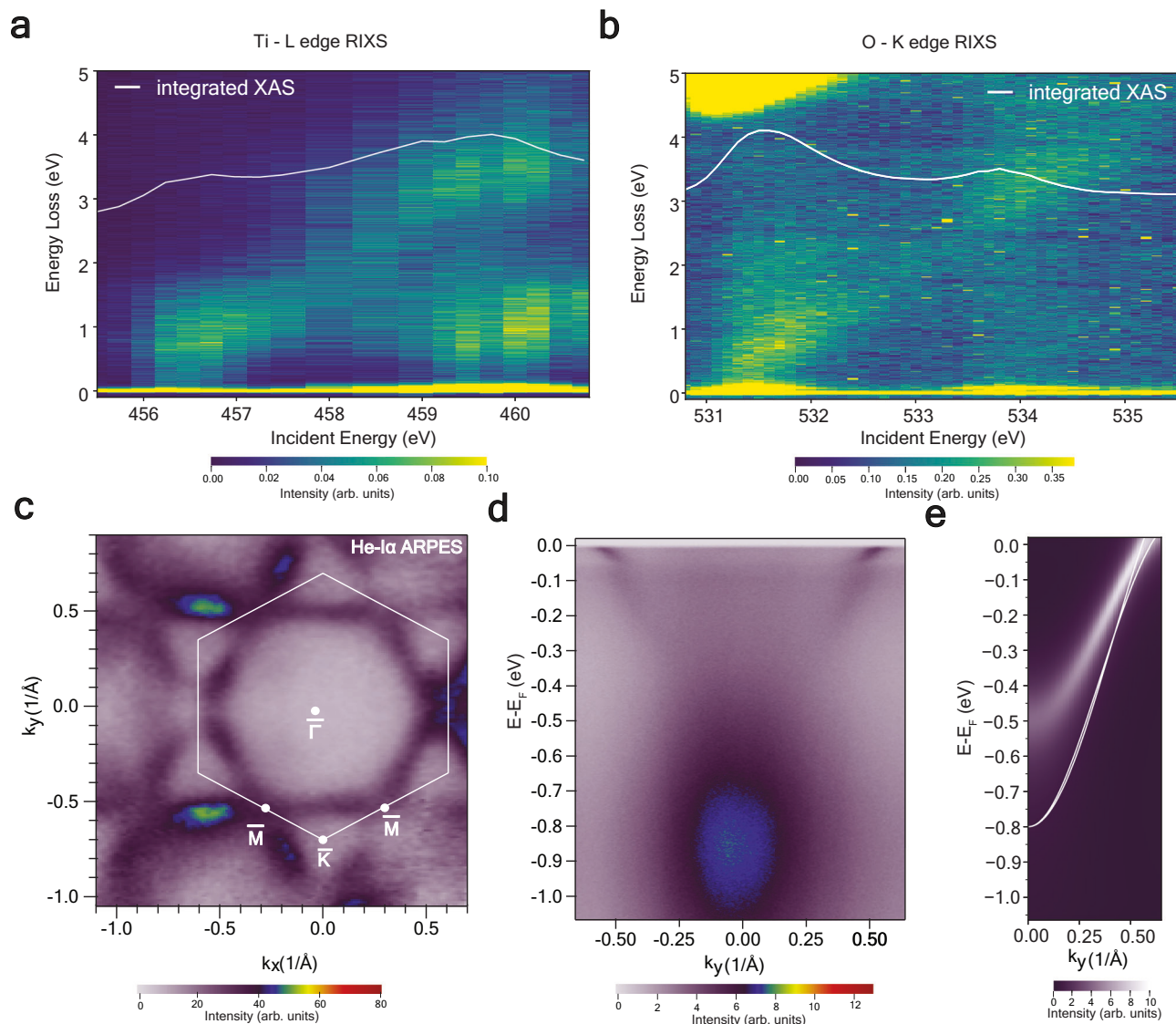


Fig. 2 | Electron-electron correlations in LiTi_2O_4 . **a** RIXS intensity at the Ti- L_3 edge. **b** RIXS intensity at the O K-edge. **c** Iso-energy map at the Fermi level taken with He-I α showing a hexagonal Fermi surface. The white hexagon indicates the first

Brillouin zone. **d** Experimental band structure in the $\bar{K} - \bar{\Gamma} - \bar{K}$ direction. **e** DMFT and DFT (white) comparison along $\bar{\Gamma} - \bar{K}$ indicating the mass renormalization due to electron-electron correlations.

superconducting quantum interference device (SQUID) microscopy, which locally measures magnetic susceptibility (Fig. S4). The measured magnetic susceptibility can be used to extract the temperature dependence of the reduced London penetration depth (Supplementary Material Section S3), which can be well-fit by a fully gapped order parameter, consistent with *s*-wave-like pairing. The observation of the 2-D thin film limit of superconductivity, the high RRR, as well as a homogeneous diamagnetic response from scanning SQUID, demonstrates the high structural quality of our films, ensuring that further measurements probe the intrinsic behavior of LiTi_2O_4 .

Electron-electron correlations in LiTi_2O_4

Poised with high-quality thin films, we first probe the electronic structure using elemental-specific RIXS measurements. Figure 2a shows the RIXS intensity of LiTi_2O_4 near the Ti- L_3 edge. Our x-ray absorption spectroscopy (XAS) data (Fig. S16a) display resonant features associated with the mixed valence Ti^{4+} and Ti^{3+} states (for a detailed discussion on the mixed-valence XAS, see Supplementary Section S9). Given the lack of *dd* excitations expected for a trivial d^0 state, we conclude that the broad Raman-like *dd* features centered at

$E_{\text{loss}} = 1.5$ eV and $E_{\text{loss}} = 4$ eV, reflect a d^1 titanium occupation state, which, given the lack of charge order in LiTi_2O_4 , can only be dynamically populated²⁰. These Raman-like excitations, along with the suppressed fluorescence contribution, are unexpected, given that the itinerant charge carriers in our metallic and superconducting samples are proposed to have a dominant Ti-3d band character near the Fermi level^{21,22}. We note that our RIXS data resemble that of MgTi_2O_4 ²³ despite LiTi_2O_4 lacking large static local trigonal distortions of the TiO_6 octahedra and Ti-Ti dimerization (Supplementary Figs. S1 and S22). The qualitative similarities between the RIXS energy maps in metallic LiTi_2O_4 and Mott-insulating systems like MgTi_2O_4 are suggestive of the presence of localized excitations in LiTi_2O_4 .

In addition to the Raman-like excitations, we observe spectral weight associated with a fluorescence contribution with a linear dispersion in E_i that extends below $E_{\text{loss}} \leq 1.5$ eV. This resembles the superposition of localized and delocalized excitations observed in negative charge transfer insulators²⁴. Moreover, O K-edge RIXS, shown in Fig. 2b, also shows Raman-like and fluorescence contributions below the charge transfer gap, $\Delta \approx 4.5$ eV. This is the same energy as the intra-*dd* excitations at the Ti L_3 -edge, suggesting strong hybridization

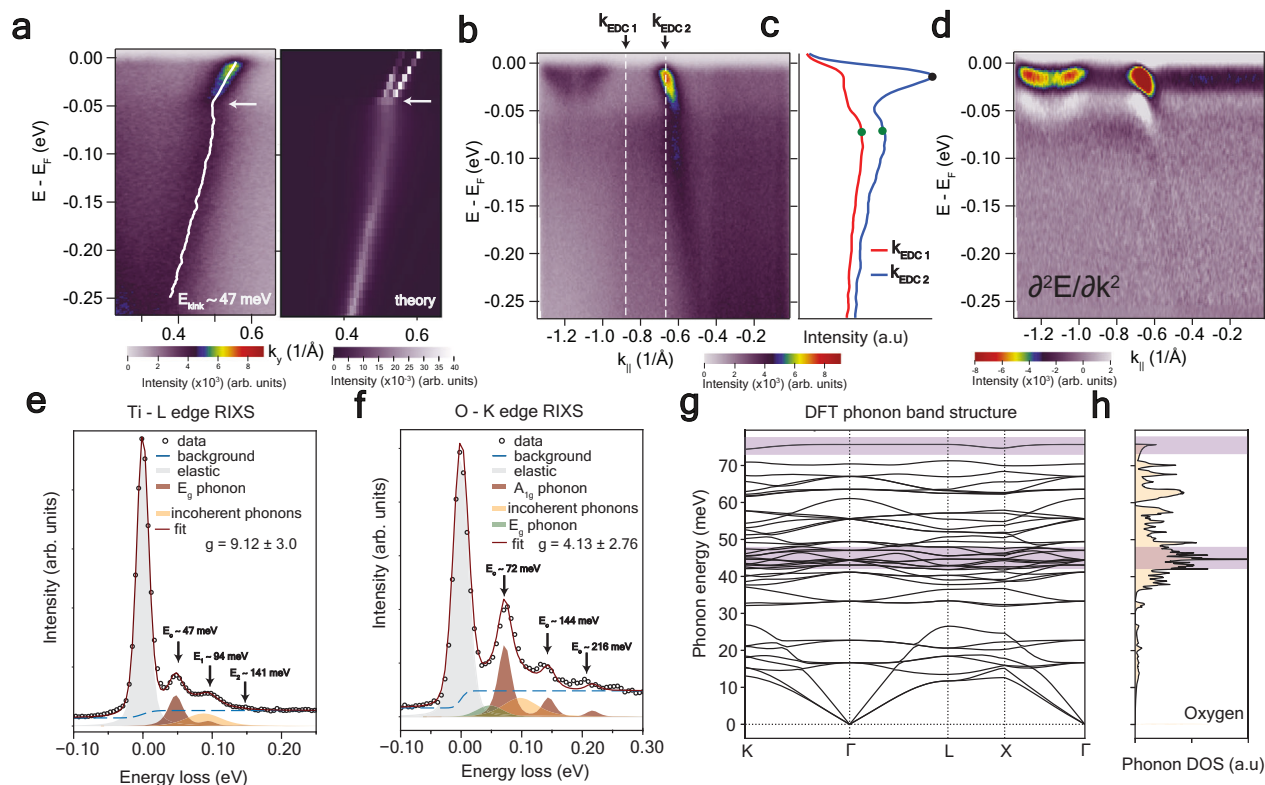


Fig. 3 | Electron-phonon coupling in LiTi_2O_4 . **a** Comparison of the $\bar{\Gamma} - \bar{K}$ ARPES data to density-functional perturbation theory (DFPT) highlighting the kink feature at 47 meV at $\bar{\Gamma} - \bar{K}$ at $T = 7$ K. **b** Energy - momentum ARPES spectra along the $\bar{\Gamma} - \bar{K} - \bar{M}$ direction. **c** EDC cuts at two different $k_{||}$ highlighted in **(b)** with dotted white lines. Black and green dots correspond to the top of the two EDC poles. **d** Second-derivative plot from **(b)** highlighting a dispersionless spectral intensity at the second pole denoted by a black arrow in **(c)** also observable in the raw data in **(b)**. A spectral gap is also prominent at the same energy scale where the

dispersionless feature interrupts the main band. **e** Quasi-elastic RIXS excitations shown at $E_{\text{inc}} = 460$ eV for the Ti-L₃ edge. **f** Quasi-elastic RIXS excitations shown at $E_{\text{inc}} = 531.5$ eV for the O K-edge. The total intensity is a fit (red solid line) to a Voigt peak (gray shading), a background step function (blue dashed lines), one (two) Gaussian(s) and an Ament model fit to the phonon spectra (maroon) in **(e)**, **(f)**, respectively. **g**, **h** Calculated phonon band structure and total oxygen phonon density of states, respectively. The purple box highlights the energy scale of the A_{1g} and E_g modes, respectively, in both plots.

between titanium and oxygen carriers. While the hybridization between Ti-3d and O-2p states has been previously theorized²¹, the RIXS data is the first instance of direct observation of strong titanium-oxygen hybridization. Moreover, the presence of fluorescence contributions at the O-K-edge near the elastic line (zero energy loss) suggests a larger contribution of oxygen carriers to electronic transport in LiTi_2O_4 than that expected from previous density of states calculations²¹. Thus, our RIXS data suggest the presence of charge localization, Ti-3d and O-2p hybridization, and electron-electron correlations in LiTi_2O_4 .

Electron-electron correlations are also observed in in-situ ARPES measurements on LiTi_2O_4 . Figure 2c shows the Fermi surface of LiTi_2O_4 from our ARPES measurements. Here, k_x and k_y are chosen to lie along the [112] and [110] directions, respectively. The Fermi surface is characterized by large electron pockets with hexagonal symmetry centered at Γ , pushing toward the zone boundary in proximity to a Lifshitz transition, which has led to enhanced electronic interactions near the Fermi surface for other superconductors²⁵. A more detailed discussion of the Fermi surface and its k_z dependence is given in Supplementary Figs. S5, S6 and in the Supplementary Material Section S4.

To analyze the electronic interactions, we look at high-symmetry cuts of the band structure of LiTi_2O_4 . In Fig. 2d, e, we compare our experimental band structure along $\bar{\Gamma} - \bar{K}$ to the momentum-resolved spectral function obtained from density-functional theory plus dynamical mean-field theory (DFT+DMFT). The non-interacting band dispersion is shown in white in Fig. 2e for reference. The DFT+DMFT calculation reproduces the experimental dispersion near Γ , capturing

the large effective mass renormalization compared to the bare DFT band—a clear indication of strong electron correlations in LiTi_2O_4 . The calculated cyclotron mass (Supplementary Material Fig. S9) yields $\frac{m_{\text{eff}}}{m_{\text{bare}}} = 2.53 \pm 0.4$. This method of calculating the renormalization agrees with previous reports of the effective mass of LiTi_2O_4 by other optical probes^{26,27}. Additionally, we observe a broad Gaussian-like, intense incoherent spectral weight centered at $E_B \approx 0.9$ eV that resembles the lower Hubbard band of lightly doped cuprates²⁸. Similar to the cuprates, the spectral weight shows k_z dependence with a transition from a “champagne glass-like dispersion” to a “waterfall” feature²⁹ in the data taken by Ne-1 α photon energy (16.85 eV) (Supplementary Fig. S6b). We note this feature cannot be reproduced by DMFT calculations but is consistent with a previous photoemission spectroscopy measurement of LiTi_2O_4 , where it was interpreted as a signature of polaronic behavior¹⁴. Nonetheless, our combined ARPES and RIXS data provide the first observation of significant electronic correlations in LiTi_2O_4 .

Electron-phonon coupling in LiTi_2O_4

While electronic correlations play a key role in unconventional superconductivity, we also observe signatures of electron-phonon coupling in the electronic structure of LiTi_2O_4 . Consistent with previous ARPES reports³⁰, we observe a “kink” at $E_B \approx 46$ meV as shown in Fig. 3a. This feature is ascribed to an E_g oxygen phonon mode by tunneling spectroscopy measurements³¹ and inelastic neutron scattering³², confirmed by calculations of the spectral function including the self-energy from only electron-phonon interactions

(Supplementary Material Section S5). We extract a band renormalization, $\lambda_{\text{tot}} = 1.80(1)$, three times higher than $\lambda_{e-ph} = 0.65$ determined by specific heat measurements⁹ and ab-initio calculations¹⁸. The extracted band renormalization value from our ARPES data is comparable to that from electronic specific heat measurements, where the larger value is attributed to enhancement from electron–electron correlations or spin fluctuations^{22,33,34}. We note that λ_{tot} includes λ_{e-ph} as well as λ_{e-e} . While a precise determination of just λ_{e-ph} is non-trivial due to the interlinked nature of electron–electron correlations and electron–phonon coupling in this compound, we can approximate $\lambda_{e-ph} \approx 1.3 \pm 0.5$ by fitting the dispersion of the band at lower binding energies as the bare band, consistent with λ_{e-ph} extracted from other ARPES measurements on this compound³⁰. For a more detailed discussion on the calculation of λ_{tot} and λ_{e-ph} as well as their temperature and momentum dependence, see Supplementary Material Section S4 and Fig. S7.

Figure 3b shows an energy-momentum cut along the $\bar{\Gamma} - \bar{K} - \bar{M}$ direction (cut overlaid on the Brillouin zone is shown in Fig. S8a). Here we observe a non-dispersive feature at $E_B = 70.4 \pm 6$ meV at all $k_{\parallel}$, highlighting the accumulation of incoherent spectral weight below the main kink at $E = 46$ meV (Fig. 3a). To examine this flat feature, we present two energy dispersive cuts (EDC) in Fig. 3c, k_{EDC1} which cuts across momentum value devoid of bands and k_{EDC2} which cuts across the k_F of the main LiTi_2O_4 band. The momentum position of these two cuts is indicated by two black arrows pointing to dotted white lines in Fig. 3b. We can see the peak position of this sub-band in the EDC of k_{EDC1} as an abrupt and sharp increase in spectral intensity at $\Omega = 70.4 \pm 6$ meV (green dot), also observed in k_{EDC2} at the same energy scale. Sub-bands like these are indicative of a highly interacting picture³⁵, in stark contrast to a non-interacting picture, where, in the absence of any bands, the expected EDC would not have any additional poles, unlike what is seen in k_{EDC1} . The second derivative plot (Fig. 3d) further highlights this feature and additionally shows a “spectral gap” where the non-dispersive feature interrupts the main dispersive electronic band. We note that the flat feature, in addition to the spectral gap, can also be seen clearly in our raw data in Fig. 2d. These types of sub-bands due to strong electron-phonon coupling are spectral signatures that are consistent with the formation of intra-unit cell small polarons³⁶ that have been observed in other correlated materials^{35,37}.

Our RIXS measurements also corroborate the presence of strong electron-phonon coupling and multiphonon processes in LiTi_2O_4 . Figure 3e shows the RIXS spectra at the Ti L_3 - and O K-edges, respectively. As highlighted by black arrows in Fig. 3e, f, both RIXS spectra are characterized by prominent quasi-elastic peaks that are approximately equally spaced and monotonically decay with E_{loss} , thus resembling the harmonic progression of the multiphononic processes. The low-energy excitations shown in the titanium spectra are well fit by the Ament model³⁸, which considers a single non-dispersive phonon mode coupled to the electronic structure with strength g (See Supplementary Material Section S6 for more details on the Ament model fit). At the Ti- L_3 edge, the Ament model in conjunction with a broad Gaussian peak centered at $E_{\text{loss}} = 90$ meV provides a good fit for a mode centered at $\Omega = 47 \pm 2$ meV, in agreement with the oxygen E_g mode observed in ARPES. We interpret this broad Gaussian peak to represent multiple incoherent phononic excitations that cannot be resolved within the energy resolution of the instrument, also observed in MgTi_2O_4 ²³.

The coupling strength, $g_{\text{Ti}} = 9.1 \pm 3.0$, far exceeds those of other titanates^{39,40}, and is on par with some cuprates measured via RIXS⁴¹ further supporting strong electron-phonon coupling in LiTi_2O_4 . Moreover, the observation of a pure oxygen E_g mode at the titanium edge is indicative of strong hybridization between the O- $2p$ and the Ti- $3d$ orbitals. Similar to the Ti L_3 -edge, the three excitations at the O K-edge can also be well fit by the Ament model in conjunction with two broad Gaussian peaks. The fit gives us the first three harmonics of a phonon mode centered at $\Omega = 72 \pm 1$ meV with $g_{\text{O}} = 4.13 \pm 2.76$.

We assign this mode to the oxygen A_{1g} phonon, which is known to be strongly coupled to the E_g mode⁴⁸. While the A_{1g} mode is coherent at the O K-edge, the broad Gaussian centered at $E \approx 46$ meV, which encodes the coupling to the E_g mode also seen at the Ti L-edge, indicates a reduced coherence of this mode at the O K-edge. The absence of higher harmonics of the E_g mode at the O K-edge might be due to the higher density of oxygen modes at that energy, as shown in Fig. 3h (For a detailed discussion on the different phonon modes, see Supplementary Section 6). We note that our DFT calculations of the phonon band structure (Fig. 3g) show the modes around $\Omega \approx 46$ meV and ≈ 75 meV to be relatively nondispersive, supporting our choice of Ament model fitting for the quasi-elastic peaks at the Ti L_3 - and O K-edges.

Discussion

Our combined spectroscopic data indicate that the effects of electron–electron correlations and electron-phonon coupling cannot be disentangled in LiTi_2O_4 . Moreover, ab-initio calculations (Figs. 2e and 3a) treating electron-phonon coupling and electron–electron correlations separately fail to capture the most salient features of our data, namely the existence of localized excitations in LiTi_2O_4 (Fig. 2a) and the presence of a second pole in the photoemission self-energy (Fig. 3c). While the combined theoretical description of these two energy scales remains challenging and a matter of active research⁴², there is growing evidence that the excitation spectrum, band structure and transport properties of quantum materials such as SrVO_3 ⁴³ and superconductors like alkali-fullerides³⁷ and the cuprates⁴⁴ can only be understood through the interplay of both interaction scales. We note that while competing interactions are generally associated with unconventional superconductivity, our scanning SQUID data are consistent with a conventional s-wave order parameter (Supplementary Section S3). This naturally also raises the question as to how the phonon-mediated attractive interaction—essential for s-wave superconductivity—is robust against or potentially enhanced by the repulsive electronic correlations apparent in LiTi_2O_4 . Within this context, LiTi_2O_4 departs from SrTiO_3 ⁴⁵ and other superconducting titanates^{46,47} where electron-phonon coupling is understood to be the dominant interaction.

We finally comment on the possible mechanism that enables the strong interplay of electron–electron and electron-phonon interactions in LiTi_2O_4 . In this context, it is instructive to consider the $d^{0.5}$ occupation state in LiTi_2O_4 in the context of the d^4 member of the AB_2O_4 family, MgTi_2O_4 . In MgTi_2O_4 , a trigonal distortion driven by E_g and A_{1g} oxygen phonons⁴⁸ lifts the orbital degeneracy of the Ti $3d^4$ state in a perfect cubic octahedral environment (Fig. 4a, b). The combination of this local distortion with the formation of Ti-Ti dimers at $T = 260$ K⁴⁸ leads to a tetragonal, dimerized unit cell and the formation of a correlated insulating state (Fig. 4b) in MgTi_2O_4 . In the $d^{0.5}$ mixed-valence state, the energy gain from dimerization is reduced in favor of a charge-ordered ground state, such as in mixed-valence spinel CuIr_2S_4 ⁴⁹. However, no static symmetry breaking due to orbital or lattice ordering has been reported in LiTi_2O_4 ¹⁰, possibly due to the geometric frustration inherent in the spinel structure. This raises the question of how the d^4 state, with its associated local distortion, is accommodated in LiTi_2O_4 . We speculate that in LiTi_2O_4 with an occupation $d^{0.5}$ in the absence of charge order, two titanium ions share an electron dynamically, such that their occupation state fluctuates between d^4 and d^0 . In this scenario, the transiently occupied d^4 site has an associated local symmetry reduction due to dynamic lattice fluctuations of the E_g and A_{1g} oxygen phonons, as seen in MgTi_2O_4 ⁵⁰. As the electron moves to the unoccupied d^0 site, it drags the local distortion with it, leading to the formation of a polaronic state in which charge motion and lattice distortions are coupled (Fig. 4b). Notably, this polaronic mechanism for Ti^{3+} defect induced carriers in a Ti^{4+} system has already been proposed for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ⁵¹, suggesting a similar

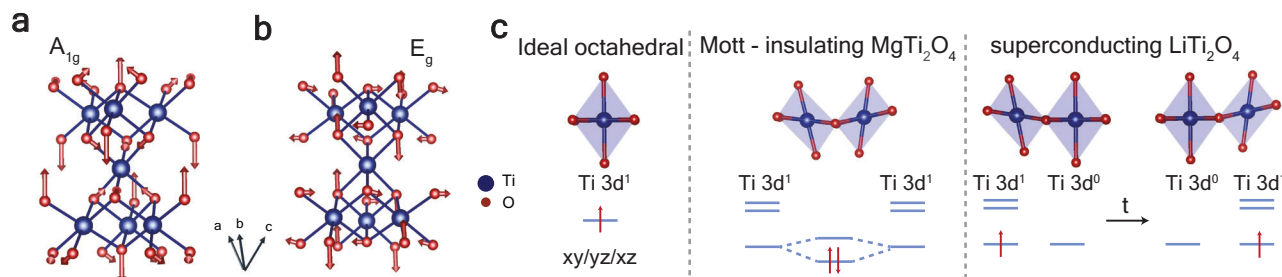


Fig. 4 | Polaron formation in LiTi_2O_4 . **a, b** DFT calculated A_{1g} and E_g oxygen phonon modes in LiTi_2O_4 . **c** An ideal TiO_6 octahedra (left) with a highly degenerate d^1 state in a cubic crystal field. In MgTi_2O_4 , a local trigonal distortion driven by E_g

and A_{1g} phonons is required to achieve a dimerized ground state (middle). Dynamic symmetry-reducing local lattice fluctuations associated with electron hopping leading to polaron formation in LiTi_2O_4 (right).

mechanism for polaronic transport in LiTi_2O_4 where the mixed-valence is native to the material.

Our data reflect the formation of such a small mobile polaronic state in LiTi_2O_4 . First, our ARPES data show a strong coupling ($\lambda > 1$) to a non-dispersive E_g phonon mode. The ratio of the dominant E_g phonon mode energy ($\Omega = 46$ meV), to the bare electron bandwidth ($t \approx 800$ meV), places LiTi_2O_4 in the adiabatic limit ($\Omega/t < 1$) for which the condition $\lambda > 1$ is expected for a small polaron ground state⁵². Second, the observation of the same mode (E_g , oxygen mode) at the Ti-L_3 edge indicates a tightly hybridized state between the localized d^1 titanium electrons and the deformed lattice. Third, we observe large incoherent spectral weight at $E \approx 0.9$ eV, which cannot be accounted for by either of our density-functional perturbation theory (DFPT) or DMFT calculations. We note that polaronic behavior has been previously discussed for LiTi_2O_4 based on the anomalous transport behavior of off-stoichiometric samples⁵³ and previous photoemission and reflectance spectroscopy data^{14,54}. Notably, the metallic behavior of LiTi_2O_4 at all temperatures contrasts with the localized small Holstein polaron behavior of other titanates^{55,56} where a low-temperature insulating state occurs due to reduced lattice mobility. However, in the light regime ($m^* < 10m$), small polarons have been theoretically predicted to be mobile^{57,58}. Polaron delocalization involves a crawling-like motion in which an electron is transiently delocalized over two neighboring sites⁵⁹, similar to the mechanism suggested here for the $d^{0.5}$ state in LiTi_2O_4 (Fig. 4b), in which the dynamical lattice fluctuations are coupled to electron hopping between d^1 and d^0 states. We note that this mobile polaron formation requires an intricate balance between electron–electron correlations and electron–phonon coupling. Dominant electron–electron correlations may choose a charge-ordered ground state⁴⁹ while dominant electron–phonon coupling can lead to bi-polaron formation, as suggested for other titanates, like Ti_4O_7 ⁵⁶. Thus, our data suggests a serendipitous balancing of electron–electron correlations with electron–phonon coupling in this material.

Although LiTi_2O_4 has long been thought of as a well-studied BCS superconductor consistent with phonon-dominated superconductivity as in other titanates^{46,47}, our work forces us to reconsider the notion of conventional superconductivity in LiTi_2O_4 . Here, a re-examination of LiTi_2O_4 using ARPES and RIXS measurements uncovers strong hybridization between titanium and oxygen, considerable electron–electron correlations, and co-existing electron–phonon coupling. In mixed valence LiTi_2O_4 , this balance of energy scales results in a novel mobile polaronic ground state indicative of a unique balance of charge delocalization, electron–electron correlations, and electron–phonon coupling. LiTi_2O_4 becomes a model system to explore predictions of enhancement of superconductivity due to the cooperative effect of electron–electron correlations and electron–phonon coupling in the quarter-filled Hubbard Hamiltonian⁶⁰. Moreover, the proximity of superconductivity to an orbitally ordered phase, the correlated behavior, and the strong hybridization between titanium and oxygen

highlight a rich competition between energy scales found only in special classes of quantum materials. Our work expands our understanding of superconductivity in $d^{0.5}$ systems and demonstrates how mixed-valence spinel-oxide structures can host correlated physics, thus broadening our search for material families that can host such correlated phenomena.

Methods

Synthesis of LiTi_2O_4 thin films via MBE

We used reactive oxide molecular beam epitaxy (Veeco GEN 10) to synthesize thin film LiTi_2O_4 on untreated MgAl_2O_4 (111) substrates (CrysTec GmbH). The lithium and titanium fluxes were matched and set to $\sim 1.5 \times 10^{13}$ atoms/ cm^2s as measured by a quartz crystal microbalance (QCM). We obtained the lithium flux by flowing O_2 during the QCM process and forming Li_2O , as the low atomic mass of elemental lithium yields small frequency changes on the QCM below the detection sensitivity, except for at very high fluxes. For the deposition process, we heated the substrates with a $10.6 \mu\text{m}$ CO_2 laser to 825°C in a pressure of $1.0\text{--}2.0 \times 10^{-7}$ molecular O_2 over a chamber background pressure of $\sim 5.0 \times 10^{-8}$. We co-deposited the lithium and titanium sources for 1 h. After deposition, we shut off the O_2 flow to prevent oxidation of titanium to the 4+ state and cooled at a rate of $100^\circ\text{C}/\text{min}$.

Structural characterization

Annular dark field (ADF) STEM was performed on ThermoFisher Scientific (TFS) Themis (operated at 200 keV, convergence semi-angle 18.9 mrad, ADF collection angle: $36\text{--}200$ mrad). A small ADF inner collection angle was used to increase light element sensitivity. Electron-transparent TEM samples were prepared using TFS Helios DualBeam FIB/SEM.

Transport measurements

We performed all electrical transport measurements in a Hall bar geometry using evaporated Cr/Au (7 nm/100 nm) contacts with the Hall channel defined by a diamond scribe along the $[11\text{--}2]$ crystallographic direction of the MgAl_2O_4 (111) substrate. We loaded the samples in 9 T Dynacool Physical Property Measurement System (PPMS) and used AC lock-in techniques at ~ 15 Hz.

Resonant inelastic X-ray scattering

The XAS and RIXS spectra were collected at the SIX beamline at NSLS-II and the I21 beamline of Diamond Light Source. The Ti L_3 -edge was measured at SIX and I21, while the O K-edge spectra were acquired at I21. The Ti L_3 -edge energy map is collected at $2\theta = 150^\circ$, while the O K-edge energy map is collected at $2\theta = 90^\circ$. All RIXS spectra are collected at $2\theta = 90^\circ$ at grazing incidence of $\theta = 20^\circ$ unless indicated otherwise. The energy resolution was fixed between 20 to 25 meV at both SIX and Diamond, respectively. All data were measured at a base temperature of 22K at both beamlines.

Angle-resolved photoemission spectroscopy

All in situ photoemission measurements were conducted by immediately transferring the samples through a UHV manifold ($P < 2 \times 10^{-9}$ Torr) to a measurement chamber immediately following film growth. ARPES measurements were taken with a Scienta Omicron DA30-L electron analyzer equipped with a Fermion Instruments BL1200s multi-gas discharge lamp using He-I photons at 21.2 eV, Ne-I photons at 16.85 eV, and He-II photons at 40.2 eV. The base pressure in the ARPES system is maintained during measurements at pressures lower than 5×10^{-11} Torr. ARPES measurements were performed at a temperature of 7K and a nominal experimental energy resolution of 10 meV unless otherwise indicated.

Muon spin relaxation measurements

Low-energy muon spin-relaxation (LE- μ SR) measurements were done using the LEM instrument at the Swiss muon source. An applied field of 10 mT was applied transverse to the μ 's spin polarization direction. For more details on the μ SR measurements, refer to Supplementary Material Section S7.

X-ray absorption spectroscopy

XAS of uncapped LiTi_2O_4 thin films was performed at 300 K at Beamline 6.3.1 at the Advanced Light Source at Lawrence Berkeley National Laboratory. XAS of capped LiTi_2O_4 thin films was performed at 300 K at ID-32 at Diamond Light Source. The spectra from Beamline 6.3.1 represent an average of 4 individual scans. All spectra are taken in the total electron yield configuration. The LiTi_2O_4 XAS spectra do not show any polarization dependence. For more details on the XAS, refer to Supplementary Material Section S9.

Data availability

All data used to obtain the conclusions in this paper are presented in the paper and/or the Supplementary Materials. This data may be requested from the authors. Please direct all inquiries to Z.H. (zhasan@g.harvard.edu).

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Author contributions

Z.H., G.A.P., C.M.B., and J.A.M. synthesized the thin films with assistance from M.R.B. and D.G.S. Electrical transport measurements were performed and analyzed by G.A.P. Scanning transmission electron microscopy was performed by S.H.S. and I.E. ARPES measurements were performed by Z.H., G.A.P., and B.D.F. ARPES analysis was done by Z.H. and B.D.F. with support from A.d.I.T. The RIXS measurements were performed by Z.H., E.M., S.H.S., I.B., and A.d.I.T. with support from V.B., J.P., M.G.F., and K.Z. RIXS analysis was done by Z.H., S.H.S., and E.M. under the supervision of A.d.I.T. XAS measurements were supported by A.T.N. μSR measurements were performed by A.J.G. and P.P.B. with support from A.S., Z.S., and T.P. Analysis of μSR data was done by A.J.G. and P.P.B. Scanning SQUID measurements were performed by A.K. and K.C.N. H.L., S.S., and A.S.B. performed the DFT, DMFT, and electron-

phonon calculations. J.A.M. and A.d.I.T. conceived and guided the study. Z.H., G.A.P., J.A.M., and A.d.I.T. wrote the manuscript with contributions and discussion from all authors.

Competing interests

The authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to Alberto de la Torre or Julia A. Mundy.

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¹Department of Physics, Harvard University, Cambridge, MA, USA. ²Department of Physics, Arizona State University, Tempe, AZ, USA. ³Laboratory of Atomic and Solid-State Physics, Cornell University, Ithaca, NY, USA. ⁴The Rowland Institute, Harvard University, Cambridge, MA, USA. ⁵NIST Center for Neutron Research, National Institute for Standards and Technology, Gaithersburg, MD, USA. ⁶Department of Physics, Northeastern University, Boston, MA, USA. ⁷Quantum Materials and Sensing Institute, Northeastern University, Burlington, MA, USA. ⁸National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, NY, USA. ⁹Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA, USA. ¹⁰PSI Center for Neutron and Muon Sciences, Villigen, Switzerland. ¹¹Diamond Light Source, Harwell Campus, Didcot, UK. ¹²Platform for the Accelerated Realization, Analysis, and Discovery of Interface Materials (PARADIM), Cornell University, Ithaca, NY, USA. ¹³Department of Materials Science and Engineering, Cornell University, Ithaca, NY, USA. ¹⁴Kavli Institute at Cornell for Nanoscale Science, Ithaca, NY, USA. ¹⁵Leibniz-Institut für Kristallzüchtung, Berlin, Germany. ¹⁶These authors contributed equally: Zubia Hasan, Grace A. Pan. ✉ e-mail: a.delatorreduran@northeastern.edu; mundy@fas.harvard.edu