Strain-induced insulator-to-metal transition in LaTiO$_3$ within DFT+DMFT

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We present results of combined density functional theory plus dynamical mean-field theory (DFT+DMFT) calculations, which show that the Mott insulator LaTiO$_3$ undergoes an insulator-to-metal transition under compressive epitaxial strain of about $-2\%$. This transition is driven by strain-induced changes in the crystal-field splitting between the Ti $t_{2g}$ orbitals, which in turn are intimately related to the collective tilts and rotations of the oxygen octahedra in the orthorhombically distorted Pbnm perovskite structure. An accurate treatment of the underlying crystal structure is therefore crucial for a correct description of the observed metal-insulator transition. Our theoretical results are consistent with recent experimental observations, and demonstrate that metallic behavior in heterostructures of otherwise insulating materials can emerge also from mechanisms other than genuine interface effects.

Emergent phenomena at oxide interfaces are currently attracting a lot of attention both from basic science as well as due to their prospects for future technological devices.\textsuperscript{1–3} Oxide heterostructures often exhibit properties that are not present in the individual materials. For example, metallic conductivity has been observed in heterostructures consisting of ultrathin layers of LaTiO$_3$ (1–4 unit cells thick) embedded in SrTiO$_3$,\textsuperscript{4} even though the corresponding bulk materials are both insulators. This has been explained by charge transfer between the Ti$^{3+}$ and Ti$^{4+}$ cations at the interfaces between the two components.\textsuperscript{5,6} However, more recently, metallicity has also been found in thin films of LaTiO$_3$ (15–45 nm thick) grown epitaxially on SrTiO$_3$.\textsuperscript{7,8} It has been shown that the sheet carrier density in these films scales linearly with film thickness, which suggests that the metallicity is not just restricted to the interface region. Furthermore, a comparison of LaTiO$_3$ films grown on different substrates, suggests that the metallic properties are controlled by substrate-induced epitaxial strain.\textsuperscript{7}

To better understand the physical mechanisms behind emerging properties in oxide heterostructures, it is important to clearly distinguish the effects of different factors, such as e.g. strain, defects, structural and electronic reconstruction at the interface, etc. Here, we present results of first principles calculations using a combination of density functional theory and dynamical mean-field theory (DFT+DMFT),\textsuperscript{9–12} assessing specifically the effect of epitaxial strain on LaTiO$_3$, independent from interface effects or variations in defect concentration. We find that compressive epitaxial strain can indeed induce a metal-insulator transition, consistent with the experimental observations, whereas tensile strain strongly enforces the insulating character. Furthermore, we show that this behavior is controlled mainly by strain-induced changes in the crystal-field splitting within the Ti $t_{2g}$ bands.

Bulk LaTiO$_3$ at room temperature is a paramagnetic Mott insulator.\textsuperscript{13,14} The theoretical description of such systems is challenging, since the standard local density or generalized gradient approximations are not suitable for describing the Mott-insulating state without any symmetry-breaking long-range order.\textsuperscript{9} However, a good description of LaTiO$_3$ and other perovskite systems with $d^2$ electron configuration of the transition metal cation can be achieved within the DFT+DMFT approach.\textsuperscript{15–17} Using this method, it has been shown that the Mott-insulating character of LaTiO$_3$,\textsuperscript{18} perovskites with Pbnm symmetry, such as LaTiO$_3$,\textsuperscript{19} is controlled by the amplitude of the characteristic structural distortion, i.e. tilts of the oxygen octahedra, the so-called GdFeO$_3$-type distortion (see Fig. 1b and c).\textsuperscript{15}

On the other hand, first principles calculations for a number of Pbnm perovskites have shown that epitaxial strain generally affects both character and amplitude of the octahedral tilts (see Ref. 20 for a review). Since, as stated above, the insulating character of LaTiO$_3$ is controlled by the octahedral tilts, it can be expected that epitaxial strain will have a pronounced effect on the electronic properties of LaTiO$_3$ and eventually even drive the system towards a metallic state. Conversely, in order to understand the effect of epitaxial strain on LaTiO$_3$ it is thus very important to correctly account for the resulting changes in the octahedral tilt distortion.

We therefore start by performing accurate structural relaxations for LaTiO$_3$ under different epitaxial constraints in the following way. We fix the two “in-plane” lattice constants to $a = b = (\epsilon + 1) \cdot a_0$, where the value $a_0 = 5.60$ Å corresponds to the “coherent structure”\textsuperscript{20} i.e. minimal energy under the constraint $a = b$. For each strain $\epsilon$ we then relax the “out-of-plane” lattice constant $c$ and all internal structural parameters (for simplicity we assume that the films grow with the orthorhombic $c$ direction (long axis) perpendicular to the substrate plane). All structural relaxations are performed within the generalized gradient approximation (GGA)\textsuperscript{21} to density functional theory (DFT) using the Quantum ESPRESSO code\textsuperscript{22} with a plane-wave basis and ultrasoft pseudopotentials.\textsuperscript{23} Since our work focuses on the room-temperature paramagnetic phase of LaTiO$_3$, all calculations are performed for the non-spin-polarized case. Further technical details can be found in the supplemental material.

We note that the octahedral tilt distortion in per-
FIG. 1. a) Calculated \(c/a\) ratio (upper panel), octahedral tilt angles (middle panel), and Ti-O bond distances (lower panel) in LaTiO\(_3\) as function of in-plane strain. The \(c/a\) ratio is calculated from the orthorhombic lattice parameters \((c/a \approx \sqrt{2} \text{ for zero strain})\), and is compared to experimental data from Ref. 7 (filled diamonds). b) and c) show projections of the orthorhombically distorted \(Pbnm\) perovskite structure. The three different Ti-O bond distances are denoted as L1-L3. The angles \(\theta\) and \(\phi\) measure in-plane “rotations” and out-of-plane “tilts”, respectively, and are related to specific bond angles which are indicated in b) and c) by capital letters \(\Theta\) and \(\Phi\).

Perovskites is assumed to be driven by the size ratio between the two different cations\(^{24}\) as well as by hybridization between the oxygen anions and the large \(A\)-site cation.\(^{15}\) These effects are generally well described within GGA. Thus, an accurate treatment of electronic correlations is not necessary to describe the structural properties of LaTiO\(_3\). Nevertheless, in order to benchmark the accuracy of our calculated structural parameters, we first perform a full unconstrained structural relaxation of the orthorhombic \(Pbnm\) bulk structure. All calculated lattice parameters agree well with available experimental data. In particular, the octahedral tilt angles deviate by less than 1° from the experimental values (see supplemental information for more details).

We now discuss the results of our structural relaxations under epitaxial strain. Fig. 1a shows the calculated \(c/a\) ratio, the octahedral tilt angles, and the Ti-O bond distances as a function of applied strain. As expected, compressive (tensile) strain results in an elongation (reduction) of \(c\). The calculated \(c/a\) shows good agreement with experimental data from Ref. 7. Furthermore, it can be seen that epitaxial strain has a pronounced effect on the octahedral tilt angles as well as on the Ti-O bond distances. The octahedral tilt angles show the expected behavior, similar to what has been observed in other \(Pbnm\) perovskites.\(^{20}\) The in-plane “rotations”, characterized by the angle \(\theta\), increase under compressive strain, in order to decrease the unit cell area within the \(a-b\) plane. On the other hand, the out-of-plane “tilts”, characterized by \(\phi\), decrease due to the elongation along \(c\), which straightens out the Ti-O-Ti bonds along this direction. Tensile strain leads to the opposite trends. When looking at the Ti-O bond distances, it can be seen that all three bond distances are nearly equal for the unstrained structure, i.e. there is no significant Jahn-Teller distortion of the oxygen octahedra. Under strain the lengths of the two “in-plane” bonds (L2/L3) remain approximately equal and are reduced (elongated) for compressive (tensile) strain. The bond distance along \(c\) (L1) exhibits the opposite trend.

Thus, while the octahedral tilt angles follow the trends expected for a network of rigid octahedra under strain, the octahedra are in fact not completely rigid and also deform as a result of the applied strain. Part of the strain is therefore compensated by changes in the octahedral tilt angles and part of it is compensated by the deformation of the octahedra. The deviation from the behavior of rigid octahedra is especially pronounced for large tensile strain (~ 4-6%) where the angle \(\theta\) becomes nearly constant and even shows a slight increase with increasing strain (see Fig. 1a).

After analyzing the structural changes under strain, we now turn to the electronic properties. Following previous work,\(^{15-17}\) we employ a DMFT treatment to account for the electron-electron interaction within the partially filled bands around the Fermi energy with predominant Ti \(t_{2g}\) character. We express the Kohn-Sham Hamiltonian in a basis of maximally localized Wannier functions\(^{25,26}\) describing the effective Ti \(t_{2g}\) bands, and use this as the noninteracting part \(H_0\) of a multiband Hubbard Hamiltonian \(H = H_0 + H_{\text{int}}\). The local electron-electron interaction \(H_{\text{int}}\) is expressed in the Slater-Kanamori form, including both spin-flip and pair hopping terms, with the parameters \(U\) and \(J\) describing the inter-orbital Coulomb interaction and Hund’s rule coupling, respectively (see e.g. Ref. 27). The local Green’s function is then calculated within DMFT\(^{9}\) at temperature \(T = 1/(k_B \beta)\) using a continuous time hybridization expansion quantum Monte-Carlo solver\(^{28}\) implemented in the TRIQS 0.9 code.\(^{29}\) Off-diagonal elements between different orbitals on the same site are taken into account both for the local Green’s functions and the self-energy. Such off-diagonal elements appear due to the symmetry-lowering associated with the octahedral tilts. No sign problem related to these off-diagonal elements was encountered in the Monte-Carlo calculations. All calculations are performed for \(\beta = 40\ \text{eV}^{-1}\) \((T = 290\ \text{K})\) and \(J = 0.64\ \text{eV}\), while \(U\) is varied between 4 eV and 5.9 eV. More details can be found in the supplemental material.

Fig. 2 shows the trace of the local Green’s function
at imaginary $\tau = \beta/2$ as a function of $U$;\textsuperscript{30} calculated for different strain values. Based on the relation $A(\omega = 0) = -\frac{1}{\pi} \lim_{\beta \to \infty} \beta G(\beta/2)$, this can be taken as a measure of the total spectral function at the Fermi level (see e.g. Ref. 27). It can be seen, that there is a change from $\text{Tr} G(\beta/2) \neq 0$ to $\text{Tr} G(\beta/2) \approx 0$ in the interval $4 \text{ eV} < U < 5.5 \text{ eV}$ for all negative strain values, i.e. the system undergoes a metal-insulator transition with increasing $U$. It can further be seen, that epitaxial strain has a pronounced effect on the critical $U$ for this transition. While tensile strain strongly decreases the critical $U$ (to values smaller than 4 eV for $\epsilon > 2.26 \%$), compressive strain has the opposite effect, and increases the critical $U$ to slightly above 5 eV at $-3.76 \%$ strain. Thus, compressive (tensile) strain favors the metallic (insulating) state.

Thus, irrespective of any uncertainty regarding the appropriate value of $U$ and possible small inaccuracies in the calculated GGA lattice parameters, our calculations clearly show that compressive strain promotes metallicity in LaTiO$_3$, consistent with the experimental observation of metallic conductivity in thin films of compressively strained LaTiO$_3$.\textsuperscript{7} Assuming a realistic $U$ for the Ti $t_{2g}$ Wannier orbitals in the range of 4.5-5 eV, our results show that a strain-induced insulator-to-metal transition occurs for compressive strains around $-2 \%$, which compares well with the lattice mismatch of $-1.6 \%$ for LaTiO$_3$ films grown on SrTiO$_3$. Of course our calculations do not exclude the possibility that other aspects such as oxygen vacancies or interface polarity can also strongly influence the conductivity of the LaTiO$_3$ films.

We now analyze the strain-induced transition in more detail by looking at the occupations and energy levels of the three individual $t_{2g}$ orbitals. Fig. 3 shows the eigenvalues of the occupation matrix $n_{mm'} = -\sum_{\sigma} G^\sigma_{mm'}(\beta)$ together with the “crystal-field levels” of the effective Ti $t_{2g}$ Wannier functions. The latter are obtained by diagonalizing the local on-site Hamiltonian $H_0$. We have verified that the resulting “crystal field basis” is very similar to the basis diagonalizing the local occupation matrix (the scalar product between the eigenvector corresponding to the lowest crystal-field orbital and the eigenvector corresponding to the “nearly-filled” orbital is larger than 0.96 for all strain values).

It can be seen from Fig. 3a that in the unstrained state one orbital is lower in energy by 108 meV compared to the other two $t_{2g}$ states, whereas the splitting between the two energetically higher orbitals is rather small (26 meV). This is consistent with the orbital splittings calculated in Ref. 17 for bulk LaTiO$_3$. We point out that this crystal-field splitting is a result of the octahedral rotations, which lower the symmetry of the Ti sites to triclinic, whereas the Ti-O bond distances are essentially equal along all three directions (see Fig. 1a). Tensile strain conserves the energetic order between the $t_{2g}$ orbitals, i.e. one orbital at lower energy and two nearly degenerate levels at higher energies, and strongly increases the corresponding splitting. In contrast, compressive strain removes the near degeneracy between the two orbitals with higher en-
ergy, while reducing the splitting between the lowest and the intermediate energy level to 65 meV at a compressive strain of $-3.76\%$. Thus, applying strain does not simply increase the overall crystal-field splitting, but leads to qualitative changes in the relative energy differences between the three Ti $t_{2g}$ Wannier orbitals.

The changes in the crystal-field levels are mirrored in the orbital occupations calculated within DMFT (see Fig. 3b). For large tensile strain the energetically lowest orbital is essentially completely filled, whereas the other two orbitals remain empty. With increasing compressive strain one of the two empty orbitals gains some occupation at the expense of the filled orbital. This trend can clearly be seen from the occupations for large $U$, i.e. where the system is insulating. The transition to the metallic phase is then accompanied by a strong charge transfer from the “nearly filled” into the “nearly empty” orbital, while the third orbital remains mostly unaffected.

It thus appears that the decrease of the splitting between the two lowest crystal-field levels under compressive strain is crucial to facilitate the metallic state in LaTiO$_3$. In contrast, tensile strain strongly increases this crystal-field splitting and thus enforces the insulating state, i.e. the critical $U$ for the transition is strongly reduced (see Fig. 2). This is further evidenced by the orbitally-resolved real part of the self energy at zero frequency, which can be viewed as additional “effective” chemical potential shift (see e.g. Ref. 31). As can be seen from Fig. 3c, where $\Sigma(0)$ has been approximated by its value at the lowest Matsubara frequency, the electron-electron interaction strongly enhances the splitting between the energetically lowest and the two higher lying orbitals in the insulating regime and effectively shifts the chemical potential beyond the boundaries of the non-interacting bands. It can also be seen from Fig. 3c that on the other hand the $t_{2g}$ bandwidth is only weakly affected by epitaxial strain. This is a consequence of two competing effects on the dominant nearest neighbor hopping amplitudes: the shorter Ti-O bond distances within the $a$-$b$ plane under compressive strain would in principle lead to an increase in hopping, on the other hand the greater distortion of the corresponding Ti-O-Ti bond angle has exactly the opposite effect (see supplemental information for more details). This suggests that the tendency towards the metallic phase under compressive strain is mainly controlled by strain-induced changes in the crystal-field energies, which are strongly enhanced due to the electron-electron interaction.

Finally, in Fig. 4 we present orbitally-resolved spectral functions for different strain values and $U = 4.78$ eV. The spectral functions are obtained from the imaginary time Green’s functions by analytic continuation using the maximum entropy method $^{32}$ (see also supplemental material). The spectral functions obtained in the insulating state for zero strain agree well with those reported in Ref. 17 for bulk LaTiO$_3$. All spectral weight below zero energy corresponds to the occupied orbital with lowest energy. With increasing compressive strain the systems becomes metallic and strong quasiparticle features appear around zero energy for all three orbitals, consistent with $\text{Tr} \, G(\beta/2) \neq 0$ shown in Fig. 2. Nevertheless, orbital 3 has negligible spectral weight at negative energies for all strain values.

In summary, our calculations demonstrate an insulator-to-metal transition under compressive epitaxial strain in LaTiO$_3$, consistent with recent reports of metallic conductivity in LaTiO$_3$ films grown on SrTiO$_3$. The origin of this transition is the reduced crystal-field splitting under compressive strain, which facilitates electron transfer between the two lowest Ti $t_{2g}$ levels. In contrast, the increase of this splitting under tensile strain leads to a strong reduction of the critical $U$ for the insulating state, which suggests that the insulating character of LaTiO$_3$ could be enhanced by growing it on substrates with slightly larger lattice constants. We note that, while additional interface effects or the presence of defects might further influence the properties of the real system, our results indicate that such effects are not essential for explaining the observed metallic behavior.

The fact that strain can alter the delicate balance between electron hopping and Coulomb interaction, and destroy the Mott insulating state in LaTiO$_3$, has been previously suggested. However, the corresponding calculations were performed for a simplified tetragonal crystal structure without octahedral tilts. Our results demonstrate the close interplay between structure and electronic properties in LaTiO$_3$ and also show that it is crucial to consider realistic crystal structures within DMFT.
calculations.

It is clear that epitaxial strain is an important factor for the emerging properties observed in oxide heterostructures. Therefore, in order to understand the effect of the interface in these heterostructures, the properties of the corresponding strained material should be taken as reference, not the properties of the bulk material. Interface effects can then successively be introduced using slab supercells. For example a fully self-consistent DFT+DMFT study of short period LaTiO$_3$-SrTiO$_3$ multilayer-structures, including full structural relaxation of the unit cell, has been presented recently.\textsuperscript{34} While no detailed analysis of the origin of the metallicity (e.g. strain versus interface effects) or of the degree of octahedral tilts has been presented, Ref. 34 demonstrates the feasibility of such calculations even for complex multilayer structures with large unit cells.

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1 J. Mannhart and D. G. Schlom, Science 327, 1607 (2010).
2 J. Chakhalian, A. J. Millis, and J. Rondinelli, Nature Materials 11, 92 (2012).
3 H. Y. Hwang, Y. Iwasa, M. Kawasaki, B. Keimer, N. Nagaoza, and Y. Tokura, Nature Materials 11, 103 (2012).
4 A. Ohtomo, D. A. Muller, J. L. Grazul, and H. Y. Hwang, Nature 419, 378 (2002).
5 S. Okamoto and A. J. Millis, Nature 428, 630 (2004).
6 S. Okamoto, A. J. Millis, and N. A. Spaldin, Phys. Rev. Lett. 97, 056802 (2006).
7 F. J. Wong, S.-H. Baek, R. V. Chadapkar, V. V. Mehta, H.-W. Jang, C.-B. Eom, and Y. Suzuki, Physical Review B 81, 161101 (2010).
8 C. He, T. D. Sanders, M. T. Gray, F. J. Wong, V. V. Mehta, and Y. Suzuki, Physical Review B 86, 081401 (2012).
9 A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, Rev. Mod. Phys. 68, 13 (1996).
10 V. I. Anisimov, A. I. Poteryaev, M. A. Korotin, A. O. Anokhin, and G. Kotliar, J. Phys.: Condens. Matter 9, 7359 (1997).
11 G. Kotliar and D. Vollhardt, Physics Today , 53 (2004).
12 K. Held, Adv. Phys. 56, 829 (2007).
13 A. Fujimori, I. Hase, H. Namatame, Y. Fujishima, Y. Tokura, H. Eisaki, S. Uchida, K. Takegahara, and F. M. de Groot, Phys. Rev. Lett. 69, 1796 (1992).
14 T. Arima, Y. Tokura, and J. B. Torrance, Physical Review B 48, 17006 (1993).
15 E. Pavarini, S. Biermann, A. Poteryaev, A. I. Lichtenstein, A. Georges, and O. K. Andersen, Phys. Rev. Lett. 92, 176403 (2004).
16 L. Craco, M. S. Laad, S. Leoni, and E. Müller-Hartmann, Physical Review B 70, 195116 (2004).
17 E. Pavarini, A. Yamazaki, J. Nuss, and O. K. Andersen, New J. Phys. 7, 188 (2005).
18 D. A. MacLean, H.-N. Ng, and J. Greedan, Journal of Solid State Chemistry 30, 35 (1979).
19 M. Cwik, T. Lorenz, J. Baier, R. Müller, G. André, F. Bourseé, F. Lichtenberg, A. Freimuth, R. Schmitz, E. Müller-Hartmann, and M. Braden, Phys. Rev. B 68, 060401 (2003).
20 J. M. Rondinelli and N. A. Spaldin, Adv. Mater. 23, 3363 (2011).
21 J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
22 P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. D. Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kolalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Scuseria, A. P. Seitsonen, A. Smogunov, P. Umari, and R. Wentzcovitch, J. Phys.: Condens. Matter 21, 395502 (2009).
23 D. Vanderbilt, Phys. Rev. B 41, 7892 (1990).
24 V. M. Goldschmidt, Naturwissenschaften 14, 477 (1926).
25 N. Marzari, A. A. Mostofi, J. R. Yates, I. Souza, and D. Vanderbilt, Reviews of Modern Physics 84, 1419 (2012).
26 A. A. Mostofi, J. R. Yates, Y.-S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, Comp. Phys. Comm. 178, 685 (2008).
27 R. Kovičič, P. Werner, K. Dymkowski, and C. Ederer, Physical Review B 80, 075130 (2012).
28 E. Gull, A. J. Millis, A. I. Lichtenstein, A. N. Rubtsov, M. Troyer, and P. Werner, Rev. Mod. Phys. 83, 349 (2011).
29 M. Ferrero and O. Parcollet, “TRIQS: A toolbox for research in interacting quantum systems,” http://ipht.cea.fr/triqs.
30 Note that we follow the usual convention of presenting all results as function of the intra-orbital Hubbard interaction $U$, even though the physically relevant quantity determining the metal-insulator transition in a three-orbital model with one or two electrons is $U^\prime = J = U - 3J$, as shown e.g. in Ref. 35.
31 G. Keller, K. Held, V. Eyert, D. Vollhardt, and V. I. Anisimov, Phys. Rev. B 70, 205116 (2004).
32 M. Jarrell and J. E. Gubernatis, Physics Reports 259, 133 (1996).
33 H. Ishida and A. Liebsch, Phys. Rev. B 77, 115350 (2008).
34 F. Lechermann, L. Boehnke, and D. Grieger, Physical Review B 87, 241101 (2013).
35 P. Werner, E. Gull, and A. J. Millis, Phys. Rev. B 79, 115119 (2009).
Supplemental Material — Strain-induced insulator-to-metal transition in LaTiO$_3$ within DFT+DMFT

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Here, we provide supplemental material for our paper “Strain-induced insulator-to-metal transition in LaTiO$_3$ within DFT+DMFT. We present results of our structural relaxation for bulk (unconstrained) $Pbnm$ LaTiO$_3$ as well as the calculated Kohn-Sham bandstructures for LaTiO$_3$ under different strain conditions. We highlight in particular the projection of these bands on atomic Ti $t_{2g}$ orbitals. We also provide further details on the construction of our maximally localized Wannier functions with predominant Ti $t_{2g}$ character, we present real-space pictures of the resulting Wannier functions, and we give a brief discussion of the strain dependence of the nearest neighbor hopping amplitudes. Finally, we provide a more detailed description of the DMFT approach employed in our work.

Technical details of DFT calculations. As already stated in our article, all structural relaxations are performed within the generalized gradient approximation (GGA)$^1$ to density functional theory (DFT) using the Quantum ESPRESSO code$^2$ with a plane-wave basis and ultrasoft pseudopotentials.$^3$ The La(5$s$,5$p$) and Ti(3$s$,3$p$) semicore states are included in the valence. We use a $6 \times 6 \times 4$ k-point mesh and a plane wave kinetic energy cutoff of 40 Ry for the wave-functions and 480 Ry for the charge density. Internal structural degrees of freedom are relaxed until all forces are smaller than $10^{-4}$ Ry/Bohr and the total energy is converged within $10^{-5}$ Ry. The out-of-plane lattice constant for the strained structures is determined by performing a series of calculations where all internal coordinates are relaxed using fixed lattice vectors, and then varying the value of $c$ to find the minimal energy for fixed in-plane constraint $a = b$.

Structural relaxation of bulk LaTiO$_3$. Table I lists the structural parameters we obtain by performing a fully unconstrained structural relaxation for the $Pbnm$ bulk structure. All three lattice constants agree well with the experimental data. Since we are performing nonmagnetic calculations, it is most instructive to compare the calculated values to the structural parameters measured at room temperature, where the system is not magnetically ordered. The only noticeable difference between calculated and measured values occurs for the lattice parameter $a$, where the calculated value is about 1.8 % smaller than the measured values. This could indicate a subtle effect of electronic correlations on this lattice parameter, which shows a slightly unconventional behavior, i.e. $a > b$ in the experimental structure, whereas a tilting of rigid octahedra would lead to $a < b$ for the $a$−$a$−$c$ tilt pattern realized in $Pbnm$ distorted perovskites.$^4,5$ This anomaly is probably also related to the octahedral distortion (different edge lengths) discussed in Ref. 6 for LaTiO$_3$. Nevertheless, the difference between calculated and measured $a$ is still within the typical limits of DFT-based calculations and provides sufficient accuracy for the present study.

The octahedral tilt and rotation angles show excellent agreement with the experimental data. We note that there is also some disagreement between the two different room temperature measurements.

Electronic structure of strained LaTiO$_3$. Fig. 1 shows the total and projected densities of states (DOS) per formula unit for nominally unstrained LaTiO$_3$ ($a = b = a_0$). Energies are expressed relative to the Fermi level $\epsilon_F$.

![DOS](image.png)

**FIG. 1.** Total and projected densities of states (DOS) per formula unit for nominally unstrained LaTiO$_3$ ($a = b = a_0$). Energies are expressed relative to the Fermi level $\epsilon_F$.**

**TABLE I. Orthorhombic lattice constants $a$, $b$, and $c$ of the $Pbnm$ structure of LaTiO$_3$ and octahedral tilt angles $\theta$ and $\phi$ (defined in Fig. 1b and c of the main article). Our calculated values are compared with data from different experiments performed at different temperatures.**

|         | this work | Ref. 6 | Ref. 6 | Ref. 7 |
|---------|-----------|---------|---------|---------|
|         | $T = 8$ K | $T = 293$ K | $T = 298$ K |
| $a$ [Å] | 5.53      | 5.64    | 5.63    | 5.62    |
| $b$ [Å] | 5.62      | 5.59    | 5.62    | 5.61    |
| $c$ [Å] | 7.87      | 7.90    | 7.91    | 7.92    |
| $\theta$ [°] | 8.2      | 9.4    | 9.3     | 8.1     |
| $\phi$ [°] | 12.2    | 13.1   | 12.9    | 11.3    |
t_{2g} character and are separated from bands at lower energy with predominant O p character, while they overlap slightly with La d and Ti e_g bands at higher energies.

The Ti t_{2g} character in the band-structure can also clearly be identified from the “fatbands” shown in Fig. 2. Here, the Ti t_{2g} character of the various bands is visualized by the green dots, the size of which is proportional to the Ti t_{2g} character of the corresponding band. In spite of the small overlap with energetically higher bands of predominant La d character, the Ti t_{2g} bands are well-defined, and in particular there is a rather sharp upper energy boundary, above which the Ti t_{2g} character is negligible.

The comparison of the Ti t_{2g} bands for compressive (Fig. 2a) and tensile (Fig. 2c) strain shows that there are some noticeable changes in the band dispersion, but in all cases the Ti t_{2g} bands remain well-defined within an energy window between −1.0 eV and ∼1.5 eV around the Fermi level. The overall Ti t_{2g} bandwidth is slightly reduced (enlarged) for tensile (compressive) strain compared to the unstrained case.

Construction of maximally localized Wannier functions. Similar to previous DMFT studies of LaTiO$_3$ we focus on the bands with predominant Ti t_{2g} character around the Fermi energy. In order to construct a set of maximally localized Wannier functions for these bands, we define an energy window for each strained structure based on the corresponding Ti t_{2g} “fatbands”. The upper boundary of this energy window is defined as the energy above which the Ti t_{2g} character becomes negligible (see dashed blue lines in Fig. 2). We have verified that small changes (of the order of ∼0.1-0.2 eV) of this upper boundary have no significant effects on our results.

We then use the wannier90 code to obtain three maximally localized Wannier functions per Ti site, starting from initial projections on atomic Ti t_{2g} orbitals. The resulting Wannier functions for the nominally unstrained case are depicted in Fig. 3. It can be seen that the resulting Wannier functions resemble atomic d states with t_{2g} character centered on the Ti sites, but also exhibit strong p-like tails situated at the surrounding oxygen sites. Overall, the orbital character is less obvious compared to similar t_{2g} Wannier functions for SrVO$_3$ (see e.g. Ref. 13). This is due to the tilts and rotations of the oxygen octahedra surrounding the Ti sites. However, there are strong similarities between our Wannier functions and the N'th order muffin-tin orbitals calculated for LaTiO$_3$ in Ref. 10.

Nearest neighbor hopping amplitudes. Fig. 4 shows the hopping amplitudes between neighboring Ti sites as a function of strain. For the out-of-plane hopping the $d_{xz-d_{yz}}$ and $d_{yz-d_{xz}}$ hopping amplitudes are noticeably larger than all other hopping amplitudes. This, to some extent, resembles the case of the perfect cubic perovskite structure, where these two hoppings are the only ones that are allowed by symmetry. However, no clear trend can be observed as function of strain. The $d_{xz}$ hopping increases with increasing (tensile) strain, consistent with the smaller lattice constant along c, but simultaneously the $d_{yz}$ hopping decreases. For the in-plane hoppings, a strong decrease is visible for the $d_{xz-d_{xz}}$ hoppings with increasing tensile strain, but all other hopping amplitudes show only a weak strain dependence. These conflicting trends can partially be explained by the complicated changes in the orbital character as function of the octahedral tilts and strain, but also reflect the fact that the trends expected from the changes in bond distances are opposite to the trends expected from the bond angles. For compressive strain, the shorter in-plane bond distances would in principle enhance the corresponding hopping amplitudes. On the other hand, the simultaneous increase of the angle θ leads to a stronger distortion.

FIG. 2. Bandstructure around the Fermi level for −3.76% strain (a), for the unstrained case (b), and for +6.0% strain (c). The size of the green dots represents the Ti t_{2g} character in the corresponding Bloch function. The dashed blue lines in a) and b) mark the upper boundaries of the energy window used to obtain the maximally localized Wannier functions (in c) there is a small gap between the bands with predominant Ti t_{2g} character and other bands at higher energies). Energies are expressed relative to the Fermi level $E_F$. 
of the in-plane Ti-O-Ti bond angle, which is detrimental to the hopping. Thus, the trends expected from the changes in bond distances and bond angles are opposite to each other and it is unclear how the hopping between the $t_{2g}$ states at neighboring Ti sites will be affected by the structural changes described in the main article.

**Further details of our DMFT approach.** To account for effects of the electron-electron interaction within the partially filled $t_{2g}$ bands, we use dynamical mean-field theory (DMFT), where the local Green’s function corresponding to the effective Ti $t_{2g}$ states is calculated using a momentum-independent self-energy:

$$G_{\text{loc}}(i\omega_n) = \frac{1}{N_k} \sum_{\mathbf{k}} \left[ i\omega_n + H_0(\mathbf{k}) - \Sigma(i\omega_n) \right]^{-1}. \quad (1)$$

The self-energy $\Sigma(i\omega_n)$ is determined through a mapping to a fictitious impurity problem with $G_{\text{imp}} = G_{\text{loc}}$ and the same local interaction as the original lattice problem. The noninteracting Hamiltonian $H_0(\mathbf{k})$ in Eq. (1) corresponds to the Kohn-Sham Hamiltonian expressed in terms of our maximally localized Wannier functions with Ti $t_{2g}$ character. The corresponding full Hamiltonian is then given by $H = H_0 + H_{\text{int}}$, where we use the so-called Slater-Kanamori form for the local electron-electron interaction, including both spin-flip and pair-
hopping terms:

\[
H_{\text{int}} = \sum_a U n_{a,\uparrow} n_{a,\downarrow} + \sum_{a \neq b, \sigma} U' n_{a,\sigma} n_{b,-\sigma}
\]

\[
+ \sum_{a \neq b, \sigma} (U' - J) n_{a,\sigma} n_{b,\sigma}
\]

\[
- \sum_{a \neq b} J (d_{a,\uparrow} d_{b,\downarrow} d_{a,\uparrow} + d_{b,\downarrow} d_{a,\uparrow} d_{a,\downarrow} + \text{h.c.})
\],

where \(d_{a,\sigma}^\dagger\) is the creation operator for an electron in Wannier orbital \(a\) with spin \(\sigma\), \(n_{a,\sigma} = d_{a,\sigma}^\dagger d_{a,\sigma}\), and \(U' = U - 2J\).

The full interacting Green's function of the fictitious impurity problem is then calculated using a continuous time hybridization expansion quantum Monte-Carlo solver\(^\text{15}\) implemented in the TRIQS 0.9 code,\(^\text{16}\) which uses a representation of the Green's function in terms of Legendre polynomials.\(^\text{17}\) Legendre coefficients with \(l > 40\) are set to zero. Spectral functions are calculated from the imaginary time Green's function using the maximum entropy method (classical MaxEnt).\(^\text{18}\)

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\(^1\) J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).

\(^2\) P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. D. Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougousis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. Wentzcovitch, J. Phys.: Condens. Matter 21, 395502 (2009).

\(^3\) D. Vanderbilt, Phys. Rev. B 41, 7892 (1990).

\(^4\) P. M. Woodward, Acta Cryst. B 53, 32 (1997).

\(^5\) A. Zayak, X. Huang, J. Neaton, and K. Rabe, Physical Review B 74, 094104 (2006).

\(^6\) M. Cwik, T. Lorenz, J. Baier, R. Müller, G. André, F. Bourée, F. Lichtenberg, A. Freimuth, R. Schmitz, E. Müller-Hartmann, and M. Braden, Phys. Rev. B 68, 060401 (2003).

\(^7\) M. Eitel and J. Greedan, Journal of the Less Common Metals 116, 95 (1986).

\(^8\) E. Pavarini, S. Biermann, A. Poteryaev, A. I. Lichtenstein, A. Georges, and O. K. Andersen, Phys. Rev. Lett. 92, 176403 (2004).

\(^9\) L. Craco, M. Laad, S. Leoni, and E. Müller-Hartmann, Physical Review B 70, 195116 (2004).

\(^10\) E. Pavarini, A. Yamasaki, J. Nuss, and O. K. Andersen, New J. Phys. 7, 188 (2005).

\(^11\) N. Marzari, A. A. Mostofi, J. R. Yates, I. Souza, and D. Vanderbilt, Reviews of Modern Physics 84, 1419 (2012).

\(^12\) A. A. Mostofi, J. R. Yates, Y.-S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, Comp. Phys. Comm. 178, 685 (2008).

\(^13\) F. Lechermann, A. Georges, A. Poteryaev, S. Biermann, M. Posternak, A. Yamasaki, and O. K. Andersen, Phys. Rev. B 74, 125120 (2006).

\(^14\) A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, Rev. Mod. Phys. 68, 13 (1996).

\(^15\) E. Gull, A. J. Millis, A. I. Lichtenstein, A. N. Rubtsov, M. Troyer, and P. Werner, Rev. Mod. Phys. 83, 349 (2011).

\(^16\) M. Ferrero and O. Parcollet, “TRIQS: A toolbox for research in interacting quantum systems,” http://ipt.cea.fr/triqs.

\(^17\) L. Boehnke, H. Hafermann, M. Ferrero, F. Lechermann, and O. Parcollet, Physical Review B 84, 075145 (2011).

\(^18\) M. Jarrell and J. E. Gubernatis, Physics Reports 259, 133 (1996).