

Theory of the orbital-selective Mott transition in ferromagnetic YTiO_3 under high pressure

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We explore the effect of pressure on the electronic properties of the ferromagnetic Mott-Hubbard insulator YTiO_3 . We show that the pressure-induced insulator-metal transition is accompanied by anisotropic structural changes driven by the competition between strongly orbital dependent one-electron hopping and strong, multi-orbital electronic correlations in the real crystal structure of YTiO_3 . Our results are relevant for the general understanding of the intricate and interdependent changes in the orbital and magnetic structure of correlated ferromagnetic insulators showing Mott transitions.

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I. INTRODUCTION

The Mott-Hubbard insulator-metal transition is a clear manifestation of the role of many-body effects in condensed matter physics. Historically, the Mott transition was considered to occur as a function of the expansion of the lattice parameter d . In Mott's picture,¹ a first-order transition from a Mott insulator to a metallic state takes place at a critical value $d=d_0$. [For $d>d_0$, a cubic crystalline array of one-electron atoms should be in a charge insulating state, whereas for $d<d_0$, one should have the metallic state.] The charge gap jumps discontinuously from zero to a finite value at the transition. Mott's original idea was to reduce the ratio U/W between the Coulomb interaction (U) and the kinetic energy of the electrons (W), which defines the phase boundary between the metallic and the gaped (nonmetallic) phase. This can be experimentally achieved by chemical substitution or by applying pressure, which reduces d . The best studied example in this regard is V_2O_3 ,² where its first-order insulator-metal transition from a Mott insulator (MI) into a correlated metal is tuned experimentally by increasing pressure.

The application of external pressure (P) provides a tool to tune the structural and electronic properties of real materials. This tool is more attractive than chemical doping because it only affects the crystal structure without introducing extra chemical disorder. In many cases, it drives the system from a MI to an incoherent and/or Fermi-liquid metal via continuous and/or first-order transition. Pressure-induced electronic transitions were observed in Sm-based compounds,³ in earlier ($3d^1$) transition-metal compounds,^{4,5} perovskite manganites,⁶ cobaltates,⁷ etc. At this point, we shall make a distinction on the lattice evolution across the insulator-metal transition (IMT), which may show sharp (first order) or smooth changes of the lattice constant with pressure. The first class includes V_2O_3 . These materials show discontinuous drop in at least one lattice constant (the c axis in V_2O_3), which is accompanied by a sharp decrease in the resistivity. On the other hand, the underlying common feature in the second class of systems (which includes earlier perovskite titanates^{4,5} and manganites⁶) is the fact that the gap closes continuously as pressure is increased,⁸ tuning the system into a metallic state. In this work, we propose a specific theoret-

ical scenario predicting a first-order Mott transition in ferromagnetic (FM), orbitally ordered YTiO_3 under high pressure.

Orbital correlations are intricately tied to the lattice, charge, and spin degrees of freedom in transition-metal oxides. Theoretically, we are still away from being able to treat these coupled correlations in a fully consistent way. Notable progress has been achieved using the local-density approximation plus dynamical mean-field theory (LDA+DMFT).⁹ However, many questions still remain open; current schemes are not easily extendable to broken-symmetry cases. External perturbations such as pressure, magnetic fields, etc., often drive spectacular effects in real transition-metal oxides:¹⁰ precisely, how this might come about is an open, challenging problem for theory. Here, we study the pressure-induced electronic transitions using an extension of the LDA+DMFT method. This scheme was introduced in Ref. 11 to explain the first-order IMT in V_2O_3 . Within the LDA+DMFT approach, we have also derived a phase transition from a MI to a bad metal in electron-doped TiOCl ,¹² which was indeed later observed experimentally.¹³

The perovskite titanate YTiO_3 is a classical example of a system exhibiting the Mott-Hubbard insulating state.¹⁰ YTiO_3 is a multi-orbital (MO) FM insulator.¹⁴ Thus, it might be a promising candidate for applications in field-effect transistors¹⁵ based on FM heterostructures.¹⁶ In this material, orbital degrees of freedom are known to play an important role, strongly determining its orbital, charge, and magnetic properties.¹⁷ The crystal structure of YTiO_3 at ambient pressure is pseudocubic perovskite with GdFeO_3 -type distortion (see Fig. 1), which is caused by tilt and rotation of the TiO_6 octahedra.¹⁸

Generally, the lattice distortion acts like an *external field* in orbital pseudospin space (see below). In fact, the importance of this quantity, and its pressure dependence, has been identified for V_2O_3 (Refs. 11 and 20) and, most recently, for MnO .²¹ For YTiO_3 , a detailed structural study finds *enhanced* crystal field splitting under pressure and a reduction of the Mott gap (though no metallic phase is seen up to 16 GPa).⁵ The study of Loa *et al.* provides evidence for a pressure-induced orbital *reorientation* characterized by the almost complete occupation of the ground state $|XY\rangle$ orbital. According to Ref. 5, the optical band gap decreases linearly with pressure and, based on linear extrapolation, it is ex-

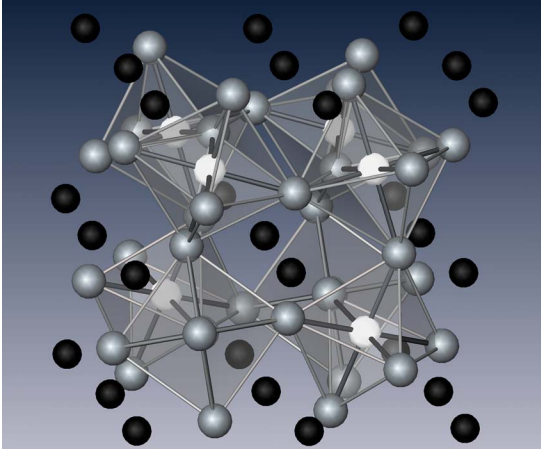


FIG. 1. (Color online) Orthorhombic-distorted crystal structure of YTiO_3 : Y ions (black), Ti ions (white), and O ions (gray) (Ref. 19). In the pseudocubic perovskite structure, the Ti ions are placed in the center of the cornersharing TiO_6 octahedra.

pected to close at pressures around 40 GPa. This behavior contrasts with that observed in V_2O_3 , where a sharp, first-order Mott transition takes place at finite temperatures.² As in V_2O_3 , we show that changes in the crystal field splittings under pressure induce an abrupt (Mott-like) IMT. The intimate link between this Mott transition and the abrupt changes in the structure is also of interest for future investigation of the possibility of inducing spin reorientation transitions under external pressure, and it will be discussed subsequently.

II. METHOD

It is recognized that under external perturbations such as pressure, the hopping elements and the crystal field splittings are renormalized in very nontrivial ways. On the other hand, due to its atomic nature, the one-site Coulomb interaction is expected to be less affected under extreme conditions. In practice, it is very difficult to separate the effects of the hopping from those induced by crystal field splittings, especially if the lattice structure under pressure is not known *a priori*. With this in mind, we study the effect of the orbital splittings on the correlated many-body states of a FM MI. We start with the LDA spectral function [density of states (DOS)] at ambient pressure in our calculation. We do *not* change this LDA DOS to derive the pressure-induced phase transitions but to search for the instability of the low- P phase to a separate phase as P is varied.¹¹ This approximation is justified because we do not expect much correspondence between changes in the one-band quantities with those affected in nontrivial ways by dynamical electronic correlations. With our choice for the magnetic state, we drop the spin degrees of freedom, an approximation which should be valid up to energies $O(2.0 \text{ eV})$, as shown in Ref. 22 by a comparison of the LDA+DMFT spectra with experimental optical conductivity for the paramagnetic phase. From the experiment, it is seen that this also remains valid in the FM phase.¹⁴ This considerably simplifies the many-body problem, allowing for

a concrete investigation of electronic phase transitions in YTiO_3 under external pressure. To access the Mott transition, we monitor the correlated electronic DOS $\rho^\alpha(\omega)$, the renormalized orbital occupation $n^\alpha = \int_{-\infty}^{E_F} \rho^\alpha(\omega) d\omega$, along with changes in the renormalized orbital displacement δ_α .

In a recent work,²³ we have shown that the one- and two-particle charge responses near the Fermi level (E_F) in FM YTiO_3 up to energies $O(2.0 \text{ eV})$ are very well accounted for by including only the majority spin channel. With these caveats, in this work, we will analyze the effect of lattice distortions in this correlated spin channel. The many-body Hamiltonian considered here for FM YTiO_3 under pressure at zero temperature ($T=0$) is

$$H = \sum_{\mathbf{k}\alpha} \varepsilon_{\mathbf{k}}^\alpha c_{\mathbf{k}}^\dagger c_{\mathbf{k}}^\alpha + U' \sum_{i\alpha\beta} n_i^\alpha n_i^\beta + \sum_{i\alpha} \Delta_\alpha n_i^\alpha,$$

where α, β label the three majority t_{2g} ($|XY\rangle$, $|YZ\rangle$, and $|ZX\rangle$) orbitals, $\varepsilon_{\mathbf{k}}^\alpha$ is the one-electron band dispersion, which encodes details of the actual one-electron band structure,²³ U' is the interorbital Coulomb repulsion, and $\Delta_{XY} = -\Delta$, $\Delta_{YZ} = \Delta_{ZX} = \Delta > 0$ are the *trial* one-particle energy splittings which simulate the changes in the octahedral TiO_6 distorted environment. Without external pressure, the Δ_α are read off from the local-spin-density approximation (LSDA): these are inputs for the multiorbital DMFT which generates a Mott insulating state for $U' = 2.75 \text{ eV}$ at $P=0$.²³ To study the effect of pressure ($P > 0$) on this correlated MI, we do not revert back to the LSDA values because strong MO correlations have already modified these by MO Hartree shifts.^{22,23} Instead, we use a strategy developed earlier,^{11,24} where the LSDA+DMFT value of Δ is changed in small trial steps, and the renormalized LDA+DMFT values δ_α are used to monitor the pressure-driven transitions. In our theory, Δ acts like an external field in the orbital sector (orbital fields), sensitively controlling the occupations of the t_{2g} orbitals (orbital polarization) in much the same way as the magnetization of a paramagnet is a function of an external magnetic field.

As in Refs. 22, 23, and 25, here, we work in orbital basis which diagonalizes the one-particle density matrix in LDA, so that $G_{\alpha\beta}^{(0)}(k, \omega) = \delta_{\alpha\beta} G_{\alpha\alpha}^{(0)}(k, \omega)$. We use MO-DMFT for our FM three-orbital model at $T=0$ with the MO iterated perturbation theory (IPT) as impurity solver. The detailed formulation of MO-IPT for orbitally nondegenerate FM systems has already been developed and used,^{24,26} so we do not repeat the equations here. For YTiO_3 , we start with the ambient pressure band-structure computed within LSDA.²³ With $U' = 2.75 \text{ eV}$,²³ we have derived the correlated DOS in the $T=0$ Mott phase at ambient P : the result is reproduced in Figs. 2–4 with full (red) line. The insulating behavior is readily apparent, and the Mott-Hubbard gap is in very good agreement with experimental indications.¹⁴

III. RESULTS AND DISCUSSION

Motivated by the possibility of IMT in YTiO_3 under external pressure,⁵ we adopt the following strategy to study this effect. Within our MO-LDA+DMFT scheme, we look for an instability of the ambient P phase as a function of the trial

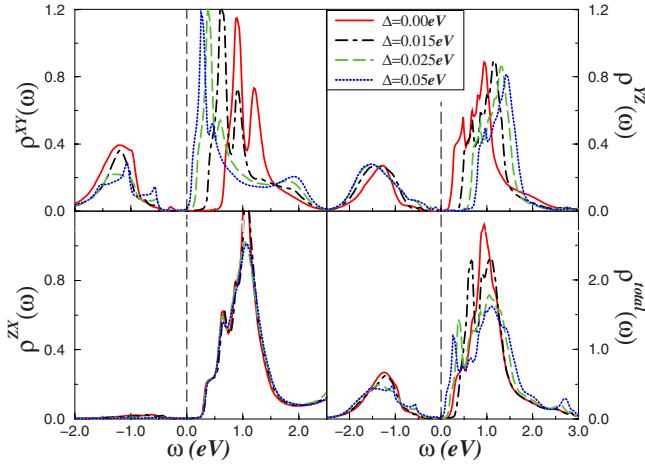


FIG. 2. (Color online) LSDA+DMFT orbital resolved and total DOS for the ferromagnetic insulating phase of YTiO_3 at $T=0$ with $U'=2.75$ eV and different values of the distortion Δ . Notice the crossing points, characteristic of correlated materials, and the evolution of the electronic DOS at different polarizations.

distortion Δ . To be more precise, we vary the (crystal field) splitting of the t_{2g} orbitals in small trial steps, starting from its LSDA+DMFT value in the ambient P phase²³ to derive the correlated electronic structure as a function of P . In a way, similar to that done for V_2O_3 (Ref. 11) and Fe_3O_4 ,²⁴ we begin from the LSDA+DMFT solution with $\Delta=0$ and self-consistently solve the MO-DMFT equations²⁶ for each value of Δ , keeping $U'=2.75$ eV fixed. As seen in Fig. 2, Δ strongly renormalizes the LSDA+DMFT one-particle spectra. Clearly, the $|XY\rangle$ and $|YZ\rangle$ are the most affected orbitals. This response is characteristic of strongly correlated materials, where the orbital occupation is linked to dynamical orbital fluctuations. Crossing (*isosbetic*) points, characteristic of correlated materials,^{10,27} are also seen in the orbital resolved and total DOS. It would be extremely interesting to see whether these would be observable in the experimental optical spectra. The continuous reduction of the Mott-

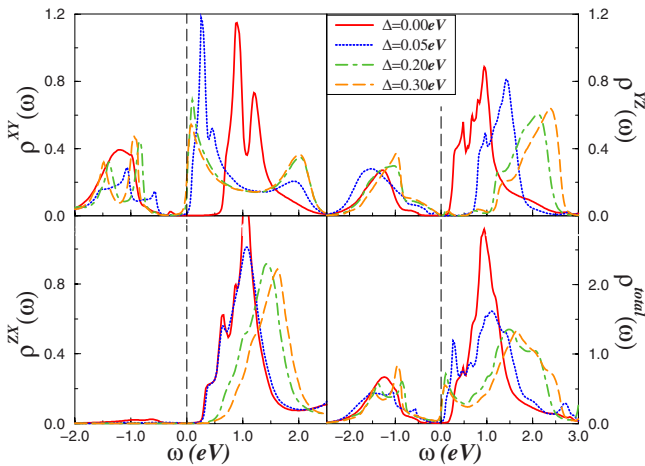


FIG. 3. (Color online) $U'=2.75$ eV LSDA+DMFT results as a function of Δ at $T=0$. Ambient pressure ($\Delta=0$) results (Ref. 23) are plotted for comparison. Crossing points in the spectra as a function of Δ are visible at characteristic energies.

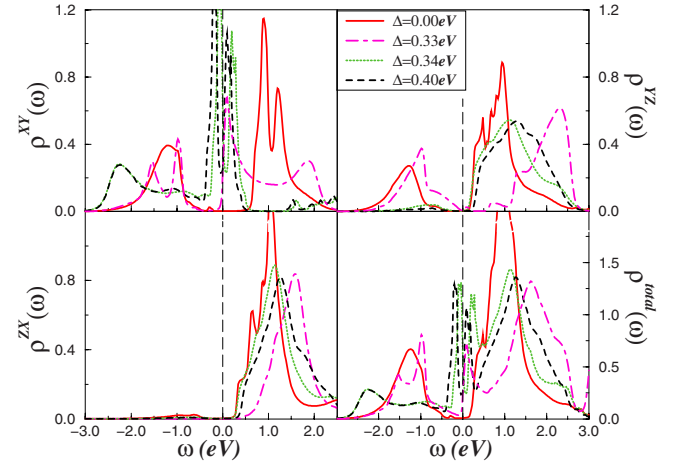


FIG. 4. (Color online) $U'=2.75$ eV LSDA+DMFT results across the $T=0$ first-order insulator-metal transition point. As in Fig. 3, ambient pressure ($\Delta=0$) results are shown for comparison. The internal structure of ρ^{XY} near E_F controls the evolution of $\rho^{\text{tot}}(E_F)$ in the Fermi-liquid metallic phase. Notice the abrupt rearrangement of the electronic states across the first-order transition point.

Hubbard gap shown in Fig. 2 is consistent with observations by Loa *et al.*⁵ Based on this agreement, we argue that our results represent a quantitative description of basic orbital-selective charge dynamics for YTiO_3 under external pressure.

By increasing Δ , at high P , we find a first-order Mott transition to a correlated (Fig. 4) half-metallic state at low energy. Actually, our calculation reveals *two* phase transitions. The one corresponding to Fig. 3 takes place at lower pressures, corresponding to $\Delta_1 \approx 0.133$ eV, where only a small switch in δ_α between the $|XY\rangle$ and $|ZX\rangle$ orbitals is found (see Fig. 5). This is possibly not accompanied by an IMT, but, if indeed found, it should correspond to a reorien-

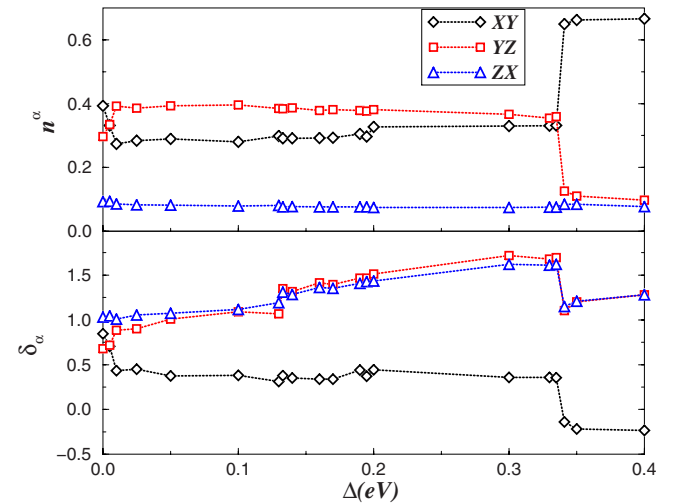


FIG. 5. (Color online) $U'=2.75$ eV orbital resolved LSDA+DMFT results for the orbital occupations n^α (top) and the renormalized orbital splittings δ_α (bottom). Notice that n^α ($\alpha=XY, YZ$) jumps at the first-order transition. This behavior is characteristic of a Mott transition.

tation of orbital and magnetic order under pressure. The second transition at $\Delta_2=0.332$ eV is, on the other hand, of the MO Mott-Hubbard type and it is accompanied by a first-order switch in the orbital occupations.¹¹ The role of Δ is more apparent in this transition. Here, Δ acts exactly like an external orbital field. As expected, orbital polarization is enhanced under the application of an external P , driving large changes in orbital occupations. The large changes in dynamical spectral weight transfer from high to low energies accompanying this (much smaller) structural change at Δ_2 destabilize the Mott insulating state under pressure. Specifically, they stabilize the second, metallic solution at a critical value of $\Delta_2=0.332$ eV (see Fig. 5). This transition is actually characterized by a *reversal* of orbital polarization. As shown in Fig. 5, the *renormalized* orbital field switches at $\Delta_0=0.005$ eV, as well as around Δ_1 , smoothly increasing with a very small slope until one reaches the second (Mott transition) solution at Δ_2 .

We now discuss how the changes in the Mott-Hubbard gap of FM YTiO₃ are understood within our picture. As seen in Fig. 4, the reduction of the charge gap results from large changes in dynamical transfer of spectral weight from high to low energies in the $|XY\rangle$ sector following by small changes in δ_α . According to our theory, the transition toward to a metallic state is controlled by the large peak of the $|XY\rangle$ upper band (see Fig. 3) which is pulled down across the IMT. In Fig. 4, we see a clear reduction of the Mott-Hubbard gap in the $|XY\rangle$ channel while the other two orbitals remain insulating, indicating an orbital-selective IMT in YTiO₃ under pressure. The metallic state may now be understood in an “effective” one-orbital ($|XY\rangle$) picture, except that the other two orbitals act as strong scattering channels, as viewed by the $|XY\rangle$ band electrons. Reference 5 argues that the octahedral compression along the c axis induces predominant occupation of the $|XY\rangle$ orbital. With our choice for the trial orbital fields, we would expect to realize the scenario of Loa *et al.* for the orbital occupations. However, for $\Delta_0 < \Delta < \Delta_2$, the reverse polarization described above introduces a novel scenario for the pressure-induced changes in the electronic structure due to nontrivial dynamical effects in correlated MO systems.

The continuous reduction of the Mott-Hubbard gap at small distortions is fully consistent with observations by Loa *et al.*⁵ At larger pressures, we predict a first-order, orbital-selective Mott transition (OSMT) to a correlated Fermi-liquid (FL)-like half-metal at low T . This is in partial agree-

ment with the OSMT found in the generalized two-orbital Hubbard model²⁸ using quantum Monte Carlo, where an OSMT and a non-FL metallic state (in the paramagnetic phase) were found to be unstable toward a double-exchange driven ferromagnetic metal at low T . In our work, we find a correlated FL metal. Within the effective Falicov-Kimball model (FKM) framework used to understand OSMT, we recall²⁹ that the metallic state of the FKM becomes FL-like depending upon parameter values (U/W , band filling). We speculate that, in the case of YTiO₃ under high pressure, we are self-consistently in the regime where the metallic state is a FL.

Our work calls for high- P studies on YTiO₃ at pressures higher than hitherto used. Based on our results, we predict at least one structural transition where the orbital and magnetic structure would reorient in the insulating phase and, more importantly, a first-order Mott transition to a half-metal at high pressure. Given the orbital-selective character of this transition, we predict anisotropic changes in spectral responses, in particular, in optical studies. Characteristic strong correlation features such as isosbestic points in the one- and two-particle spectra are also predicted to occur as a function of P . These would constitute proof of the strongly correlated nature of ferromagnetic YTiO₃ and of the importance of treating dynamical correlations adequately to understand its basic physical responses.

IV. CONCLUSION

We have studied the P -driven IMT in FM YTiO₃ using the LDA+DMFT scheme. We found a continuous reduction of the Mott-Hubbard gap at small distortions, which is fully consistent with indications from recent midinfrared optical absorption studies⁵ at ambient temperatures. At larger pressures, we predict a first-order, orbital-selective Mott transition to a correlated half-metal at low T . This transition is shown to be of the Mott-Hubbard type and it is accompanied by an abrupt increase in the itinerant carrier density, correlated with an abrupt switch in orbital occupations. In conjunction with LDA+DMFT studies on other transition-metal oxide systems,⁹ our description is expected to have a wider application to other systems where strong multi-orbital correlations in concert with structural details drive electronic transitions under external perturbations.

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