Mott transition and suppression of orbital fluctuations in orthorhombic 3d\textsuperscript{1} perovskites

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Transition-metal perovskites have attracted much interest because of their unusual electronic and magnetic properties arising from narrow 3d bands and strong Coulomb correlations \cite{1}. The 3d\textsuperscript{1} perovskites are particularly interesting, since seemingly similar materials have very different electronic properties: SrVO\textsubscript{3} and CaVO\textsubscript{3} are correlated metals with mass-enhancements of respectively 2.7 and 3.6 \cite{2} while LaTiO\textsubscript{3} and YTiO\textsubscript{3} are Mott insulators with gaps of respectively 0.2 and 1 eV \cite{3}.

In the Mott-Hubbard picture the metal-insulator transition occurs when the ratio of the on-site Coulomb repulsion and the one-electron bandwidth exceeds a critical value $U_c/W$, which increases with orbital degeneracy \cite{4, 5}. In the ABO\textsubscript{3} perovskites the transition-metal ions (B) are on a nearly cubic (orthorhombic) lattice and at the centers of corner-sharing O\textsubscript{6} octahedra. The 3d band splits into $p\sigma$-coupled $t_{2g}$ bands and $p\pi$-coupled $e_g$ bands, of which the former lie lower, have less O character, and couple less to the octahedra than the latter. Simplest theories for the d\textsuperscript{1} perovskites \cite{1} are therefore based on a Hubbard model with 3 degenerate, $\frac{1}{6}$-filled $t_{2g}$ bands per B-ion, and the variation of the electronic properties along the series is ascribed to a progressive reduction of $W$ due to the increased bending of the $p\pi$ hopping paths (BOB bonds).

This may not be the full explanation of the Mott transition however, because a splitting of the $t_{2g}$ levels can effectivly lower the degeneracy. In the correlated metal, the relevant energy scale is the reduced bandwidth associated with quasiparticle excitations. Close to the transition, this scale is of order $Z W$, with $Z \sim 1 - U/U_c$, and hence much smaller than the original bandwidth $W$. A level splitting by merely $Z W$ is sufficient to lower the effective degeneracy all the way from three-fold to a non-degenerate single band\cite{6}. This makes the insulating state more favorable by reducing $U_c/W$ \cite{5, 6}. Unlike in $e_g$-band perovskites, such as LaMnO\textsubscript{3}, where large (10\%) cooperative Jahn-Teller (JT) distortions of the octahedra indicate that the orbitals are spatially ordered, in the $t_{2g}$-band perovskites the octahedra are almost perfect. The $t_{2g}$ orbitals have therefore often been assumed to be degenerate. If that is true, it is conceivable that quantum fluctuations lead to an orbital liquid \cite{7} rather than orbital ordering. An important experimental constraint on the nature of the orbital physics is the observation of an isotropic, small-gap spin-wave spectrum in both insulators \cite{8}. This is remarkable because LaTiO\textsubscript{3} is a G-type antiferromagnet with $T_N=140$ K, $m=0.45 \mu_B$, and a 3% JT stretching along a \cite{9}, while YTiO\textsubscript{3} is a ferromagnet with $T_C=30$ K, $m\sim 0.8 \mu_B$, and a 3% stretching along y on sites 1 and 3, and x on 2 and 4 \cite{10} (see Fig. 1).

We shall find that the $t_{2g}$ degeneracy is lifted at the classical level. This is not due to the small JT distortions via OB $p\pi$-coupling, but to the GdFeO\textsubscript{3}-type distortion which tilts the corner-sharing octahedra around the b-axis (by 0, 9, 12, and 20°) and rotates them around the c-axis (by 0, 7, 9, and 13°), as we progress from cubic SrVO\textsubscript{3} via CaVO\textsubscript{3} and LaTiO\textsubscript{3} to YTiO\textsubscript{3} \cite{9, 10, 11, 12}. This distortion is driven by the increasing oxygen-cation (OA) $p\sigma$-covalency, and it primarily pull closer 4 of the 12 oxygens neighboring a given cation\cite{13}. Moreover, 2 to 4 of the 8 cations neighboring a given B ion are pulled closer \cite{14}. The $t_{2g}$ orbitals couple to the OA distortion via oxygen (BOA $d_{px}-p\sigma$), and they couple directly (AB $dd\sigma$) to the AB distortion. As seen in Fig. 1, the orthorhombic GdFeO\textsubscript{3}-type distortion also leads to quadrupling of the cell. These findings are consistent with conclusions drawn in the most recent model Hartree-Fock study\cite{15}. The correct magnetic orders in LaTiO\textsubscript{3} and YTiO\textsubscript{3} were also obtained with the LDA+ U method \cite{16}. The predicted moment and orbital order in YTiO\textsubscript{3} were confirmed by NMR \cite{17} and neutron scattering \cite{18}, but not in LaTiO\textsubscript{3}. These static mean-field methods are not appropriate for the metallic systems, however.

In this letter, we shall (i) present a new implementation of a many-body method \cite{19, 20}, which allows for a quantitative, material-specific description of both the Mott transition and the orbital physics, and (ii) use it to explain why some of the d\textsuperscript{1} perovskites are metallic and others are insulators, why the metals have different mass enhancements and the insulators different gaps. Such properties can be described by a low-energy, multi-band
Hubbard Hamiltonian,

\[ H = H_{LDA}^{LDA} + \frac{1}{2} \sum_{m,m'\sigma} U_{mm'\sigma} n_{m\sigma} n_{m'\sigma} + \frac{1}{2} \sum_{m,\langle m' \rangle} (U_{mm'} - J_{mm'}) n_{m\sigma} n_{m'\sigma}, \]  

where \( n_{m\sigma} = a_{m\sigma}^+ a_{m\sigma} \), and \( a_{m\sigma}^+ \) creates an electron with spin \( \sigma \) in a localized orbital \( m \) at site \( i \). This Hamiltonian depends on how the \( im\sigma \)-orbitals are chosen. \( H_{LDA}^{LDA} \) is the one-electron part given by density-functional theory (LDA), which should provide the proper material dependence. Recently it has become feasible to solve (1) using the dynamical mean-field approximation (DMFT) \([19]\) and to obtain realistic physical properties \([20]\). In the original LDA+DMFT implementations it was assumed that the on-site block(s) of the single-particle Green function is diagonal in the space of the correlated orbitals, and these were taken as orthonormal LMTOs approximated by truncated and renormalized partial waves. Although these approximations are good for cubic \( t_{2g} \) systems such as SrVO\(_3\) \([21]\), they deteriorate with the degree of distortion. Our new implementation of LDA+DMFT uses a set of localized Wannier functions in order to construct a realistic Hamiltonian (1), which is then solved by DMFT, including the non-diagonal part of the on-site self-energy.

For an isolated set of bands, a set of Wannier functions constitutes a complete, orthonormal set of orbitals with one orbital per band. For the \( d^1 \) perovskites we take the correlated orbitals to be three localized \( t_{2g} \) Wannier-orbitals, and in \( H_{LDA}^{LDA} \) we neglect the degrees of freedom from all other bands. In order to be complete, such a Wannier orbital must have a tail with e.g. \( O \) or \( A_d \) characters. Our Wannier orbitals are symmetrically orthonormalized \( N \)th-order muffin-tin orbitals (NMTOs) \([22]\), which have all partial waves other than \( B_{xy}, yz, \) and \( xz \) downfolded. Such a \( t_{2g} \) NMTO can have on-site \( e_g \) character, and that allows the orbital to orient itself after the surroundings, although \( xz, yz, \) and \( xz \) refers to the global cubic axes defined in Fig. 1. Fourier transformation of the orthonormalized \( 12 \times 12 \) NMTO Hamiltonian, \( H_{LDA}^{LDA} (k) \), yields on-site blocks and hopping integrals. For the on-site Coulomb interactions in Eq. (1), we use the common assumption that, as in the isotropic case, they can be expressed in terms of two parameters: \( U_{mm} = U, \) \( U_{mm'} = U - 2J \), and \( J_{mm'} (d\neq m) = J \) \([23]\). From Ref. 24, \( J = 0.68 \text{ eV} \) for the vanadates and 0.64 eV for the titanates. Since our Hamiltonian involves only correlated orbitals, so that the number of correlated electrons is fixed, the double-counting correction amounts to an irrelevant shift of the chemical potential. \( H \) is now solved within DMFT, i.e. under the assumption that the components of the self-energy between different sites can be neglected. As a result, the self-energy can be obtained from the solution of an effective local impurity model which involves only 3 correlated orbitals. In contrast to all previous studies, we take all components of the self-energy matrix \( \Sigma_{mm'} \) between different Wannier functions on a given \( B \)-site into account \([25]\). From this \( 3 \times 3 \) matrix, by use of the \( Pbnm \) symmetry (Fig. 1), we con-
(struct a 12x12 block-diagonal self-energy matrix. The latter is then used together with \( H_{\text{LDA}}^L (k) \) to obtain the Green function at a given k-point. Fourier transformation over the entire Brillouin zone yields the local Green function associated with a primitive cell and its 3x3 onsite block is used in the DMFT self-consistency condition in the usual manner. The 3-orbital impurity problem is solved by a numerically exact quantum Monte Carlo scheme [26]. To access temperatures down to 770 K, we use up to 100 slices in imaginary time. 10^6 QMC sweeps and 15-20 DMFT iterations suffice to reach convergence. Finally, the spectral function is obtained using the maximum entropy method [27].

We now present the LDA results for the four perovskites. Fig. 2 displays the on-site DOS matrix \( N_{mm'}(\varepsilon) \) in the representation of the \( xy, yz, \) and \( zx \) Wannier functions. SrVO_3 is cubic and its \( t_{2g} \) band with a width \( W = 2.8 \text{ eV} \) consists of 3 non-interacting subbands, each of which is nearly 2D and gives rise to a nearly logarithmic DOS peak. In CaVO_3, \( W \) is reduced to 2.4 eV because the Wannier orbitals are misaligned by the GdFeO_3-type distortion and because some of their \( O2p \) character is stolen by the increased OA covalency, which drives this distortion. The energy of the \( xy \) Wannier orbital (the center of gravity of \( N_{xy,xy} \)) is 80 meV lower than that of the degenerate \( xx \) and \( yz \) orbitals, and small off-diagonal DOS elements appear. Going from the vanadates to the titanates, the effects of OA and \((A d)(B t_{2g})\) covalency increase dramatically, because now A and B are 1st rather than 3rd-nearest neighbors in the periodic table. As consequences, the increased misalignment and loss of oxygen character reduces the bandwidths to 2.1 and 2.0 eV in LaTiO_3 and YTiO_3, and weak hybridization with the \( A d \) bands deforms the \( t_{2g} \) band. A pseudogap which starts out as a splitting of the van Hove peak in CaVO_3, deepens and moves to lower occupancy as we progress to LaTiO_3 and YTiO_3. The deep pseudogap in YTiO_3 is mainly caused by the hybridization with the \( Y xy \) orbital. The \( xy, yz, \) and \( zx \) Wannier orbitals are now strongly mixed and diagonalization of the on-site blocks of \( H_{\text{LDA}} \) yields three singly-degenerate levels with the middle (highest) being 140 (200) meV above the lowest in LaTiO_3 and 200 (330) meV in YTiO_3. This splitting is not only an order of magnitude smaller than the \( t_{2g} \) bandwidth, but also smaller than the subbandwidths, in particular for LaTiO_3. As a consequence, the eigenfunction for the lowest level is occupied by merely 0.15 electron in LaTiO_3 and 0.50 in YTiO_3, while the remaining 0.55 (0.50) electron occupies the two other eigenfunctions. The eigenfunction on site 1 with the lowest energy is \( 0.604|xy| + 0.353|zx| + 0.714|yz| \) in LaTiO_3 and \( 0.619|xy| - 0.073|zx| + 0.782|yz| \) in YTiO_3. The splittings are large compared with the spin-orbit splitting (20 meV) and \( kT \), and they are not caused by the JT distortions, as we have verified by turning them off in the calculations.

Next, we turn to the LDA+DMFT results. Calculations were performed for several values of \( U \) between 3 and 6 eV. We found that the critical ratio \( U_c/W \) decreases when going along the series: SrVO_3, CaVO_3, LaTiO_3, and YTiO_3. This is consistent with the increasing splitting of the \( t_{2g} \) levels and indicates that the Mott transition in the \( d^1 \) series is driven as much by the decrease of effective degeneracy as by the reduction of bandwidth. The main features of the photoemission spectra for all four materials, as well as the correct values of the Mott-Hubbard gap for the insulators [3], are reproduced by taking \( U \) constant \( \sim 5eV \). This is satisfying, because \( U \) is expected to be similar for vanadates and titanates, although slightly smaller for the latter [24]. In Fig. 3 we show the DMFT spectral functions together with the LDA total DOS. For cubic SrVO_3 we reproduce the results of previous calculations [21, 28]: the lower Hubbard band (LHB) is around \(-1.8\text{ eV} \) and the upper Hubbard band (UHB) around 3 eV. Going to CaVO_3, the quasi-particle peak loses weight to the LHB, which remains at \(-1.8\text{ eV} \), while the UHB moves down to 2.5 eV. These results are in good agreement with photoemission data [29] and show that SrVO_3 and CaVO_3 are rather similar, with the latter slightly more correlated. Similar conclusions were drawn in Ref. 21. From the linear regime of the self-energy at small Matsubara frequencies we estimate the quasi-particle weight to be \( \beta = 0.45 \) for SrVO_3 and 0.29 for CaVO_3. For a \( k \)-independent self-energy, as assumed in DMFT, this yields \( m^*/m = 1/\beta = 2.2 \) for SrVO_3 and 3.5 for CaVO_3, in reasonable agreement with the optical-conductivity values 2.7 and 3.6 [2].

For LaTiO_3 and YTiO_3 the LHB is around \(-1.5\text{ eV} \), in accord with photoemission [30]. Despite very similar bandwidths, the gaps are very different, 0.3 and 1 eV, and this also agrees with experiments [3]. This is consistent with our findings that the \( t_{2g} \)-level splittings are smaller and \( (U - 2J_c)/W \) is larger in LaTiO_3 than in YTiO_3, where the orbital degeneracy is effec-
tively. 1. Diagonalization of the matrix of occupation numbers reveals that for the titanates one orbital per site is nearly full, in contrast to LDA. It contains 0.88 electron in LaTiO$_3$ and 0.96 in YTiO$_3$. The orbital polarization increases around the metal-insulator transition and becomes complete thereafter. Thus, for the vanadates, each orbital is approximately 1/3 occupied for all U in the range 0 to 6 eV. The nearly complete orbital polarization found by LDA+DMFT for the two insulators indicates that correlation effects in the paramagnetic Mott insulating state considerably decrease orbital fluctuations, and makes it unlikely that YTiO$_3$ is a realization of an orbital liquid [7]. In LaTiO$_3$ some orbital fluctuations are still active, although quite weak. The occupied orbital in LDA+DMFT is 0.586$|xy\rangle + 0.762|yz\rangle$ for LaTiO$_3$ and 0.622$|xy\rangle − 0.029|xz\rangle + 0.782|yz\rangle$ for YTiO$_3$. Hence, it is nearly identical with the ones we obtained from the LDA as having the lowest energy. For YTiO$_3$ our orbital is similar to the one obtained in Ref. [16] and for LaTiO$_3$ it is similar to the one obtained in Refs. [9, 15]. Our accurate Wannier functions show why these orbitals (Fig. 1, left) have the lowest energy: The positive (blue) lobes have bonding $3z^2_r−1 = [(|xy\rangle + |xz\rangle + |yz\rangle)/\sqrt{3}$ character on the nearest cations—the ones along [111]—and the negative (red) lobes have bonding $xy$ character on the next-nearest cations—the ones along [111]—whose oxygen surrounding is favorable for this type of bond, i.e. where $(O_p)(Y_{xy})$ p-c$\cdot$r-hybridization is strong. The former type of AB covalency dominates in LaTiO$_3$, while the latter dominates in YTiO$_3$, where the shortest YO bond is merely 10% longer than the TiO bond. The difference seen (Fig. 1, right side) between the orbital orders in the two compounds is therefore quantitative rather than qualitative; it merely reflects the extent to which the orbital has the bc-plane as mirror. The two different JT distortions of the oxygen square is a reaction to, rather than the cause of the difference in the orbital orders. This difference is reflected in the hopping integrals between nearest neighbors: $t_{xy}=t_{yz}=99$ (38) meV and $t_{xz}=105$ (48) meV for LaTiO$_3$ (YTiO$_3$). These hoppings are fairly isotropic and twice larger in LaTiO$_3$ than in YTiO$_3$. Moreover, the hoppings to the two excited orbitals are stronger in YTiO$_3$ than in LaTiO$_3$. All of this is consistent with LaTiO$_3$ being G-type anti- and YTiO$_3$ ferromagnetic at low temperature, and it warrants detailed future calculations of the spin-wave spectra.

In conclusion, we have extended the LDA+DMFT approach to the non-cubic case using ab-initio downfolding in order to obtain a low-energy Wannier Hamiltonian. Applying this method to the Mott transition in 3d$^1$ perovskites, we have explained the photoemission spectra and the values of the Mott gap without adjustable parameters, except a single value of U. The Mott transition is driven by correlation effects and GdFeO$_3$-type distortion through reduction, not only of bandwidth, but also of effective orbital degeneracy. Correlation effects and cation covalency suppress orbital fluctuations in the high-temperature paramagnetic insulating phase of LaTiO$_3$ and YTiO$_3$.

We thank J. Nuss, G. Khaliullin, E. Koch, J. Merino, M. Rozenberg, A. Bringer, M. Imada for useful discussions and the KITP Santa Barbara for hospitality and support (NSF Grant PHY99-07949). Calculations were performed at MPI-KFK Stuttgart and IDRIS Orsay (project No. 021393). S.B. acknowledges support from the CNRS and the EU (Contract No. HPMF-CT-2000-00658).

[13] By 0, 3, 4, and 10% of the average AB distance.
[14] By 0, 10, 13, and 21% of the average OA distance.
[15] By 0, 3, 4, and 10% of the average AB distance.
[25] $\Sigma_{mm'}(\pm m)$ points to a large $N_{mm'}(\pm m)$ to a large $N_{mm'}(\pm m)$.