Mott transition and suppression of orbital fluctuations in orthorhombic 3d$^1$ perovskites

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Using $t_{2g}$ Wannier-functions, a low-energy Hamiltonian is derived for orthorhombic 3d$^1$ transition-metal oxides. Electronic correlations are treated with a new implementation of dynamical mean-field theory for non-cubic systems. Good agreement with photoemission data is obtained. The interplay of correlation effects and cation covalency (GdFeO$_3$-type distortions) is found to suppress orbital fluctuations in LaTiO$_3$, and even more in YTiO$_3$, and to favor the transition to the insulating state.

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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 [1]. The 3d$^1$ perovskites are particularly interesting, since seemingly similar materials have very different electronic properties: SrVO$_3$ and CaVO$_3$ are correlated metals with mass-enhancements of respectively 2.7 and 3.6 [2] while LaTiO$_3$ and YTiO$_3$ are Mott insulators with gaps of respectively 0.2 and 1 eV [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 [4, 5]. In the ABO$_3$ perovskites the transition-metal ions (B) are on a nearly cubic (orthorhombic) lattice and at the centers of corner-sharing O$_6$ octahedra. The 3d band splits into $pd\pi$-coupled $t_{2g}$ bands and $pd\sigma$-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 $d^1$ perovskites [4] 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 $pd\pi$ 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 bandwith associated with quasiparticle excitations. Close to the transition, this scale is of order $\sim ZW$, with $Z \sim 1 − U/U_c$, and hence much smaller than the original bandwidth $W$. A level splitting by merely $ZW$ is sufficient to lower the effective degeneracy all the way from three-fold to a non-degenerate single band [4, 5]. Unlike in $e_g$-band perovskites, such as LaMnO$_3$, 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 [6] 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 [7]. This is remarkable because LaTiO$_3$ is a G-type antiferromagnet with $T_N=140$K, $m=0.45\mu_B$, and a 3% JT stretching along $a$ [8], while YTiO$_3$ 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 [9] (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 $pd\pi$-coupling, but to the GdFeO$_3$-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$_3$ via CaVO$_3$ and LaTiO$_3$ to YTiO$_3$ [8, 10, 11, 12]. This distortion is driven by the increasing oxygen-cation (OA) $pd\sigma$-covalency, and it primarily pulls closer 4 of the 12 oxygens neighboring a given cation [13]. Moreover, 2 to 4 of the 8 cations neighboring a given B ion are pulled closer [14]. The $t_{2g}$ orbitals couple to the OA distortion via oxygen (BOA $d\pi$-$pd\pi$), and they couple directly (AB $dd\sigma$) to the AB distortion. As seen in Fig. 1, the orthorhombic GdFeO$_3$-type distortion also leads to quadrupling of the cell. These findings are consistent with conclusions drawn in the most recent model Hartree-Fock study [15]. The correct magnetic orders in LaTiO$_3$ and YTiO$_3$ were also obtained with the LDA+$U$ method [16].

The predicted moment and orbital order in YTiO$_3$ were confirmed by NMR [17] and neutron scattering [18], but not in LaTiO$_3$. 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 [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 $d^1$ 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,

\[
H = H^{LDA} + \frac{1}{2} \sum_{m\neq n,\sigma} U_{mm} n_{im\sigma} n_{im\sigma}^\dagger + \frac{1}{2} \sum_{m\neq n,\sigma} (U_{mm'} - J_{mm'}) n_{im\sigma} n_{im'\sigma},
\]

where \( n_{im\sigma} = a_{im\sigma}^+ a_{im\sigma} \), and \( a_{im\sigma}^+ \) creates an electron with spin \( \sigma \) in a localized orbital \( m \) at site \( i \). This Hamiltonian depends on how the \( im\)-orbitals are chosen. \( H^{LDA} \) 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 \( H^{LDA} \) using the dynamical mean-field approximation (DMFT) \[14\] 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 \( H^{LDA} \) 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. \( O p\pi \) and \( A d \) characters. Our Wannier orbitals are symmetrically orthonormalized Nth-order muffin-tin orbitals (NMTOs) \[22\], which have all partial waves other than \( B xy, yz, \) and \( z x \) 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 \( xy, yz, \) and \( zx \) refers to the global cubic axes defined in Fig. 1. Fourier transformation of the orthonormalized 12×12 NMTO Hamiltonian, \( H^{LDA}(\mathbf{k}) \), 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: \( U_{mm}=U, \ U_{nm'}=U-2J, \) and \( J_{mm'\neq m}=J \) \[22\]. From Ref \[24\] \( J=0.68 \) 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 3×3 matrix, by use of the \( Pbnm \) symmetry (Fig. 1), we con-

**FIG. 1:** \( Pbnm \) primitive cell (right), subcell 1 (left), and the occupied \( t_{2g} \) orbitals for LaTiO\(_3\) (top) and YTiO\(_3\) (bottom) according to the LDA+DMFT calculation. The oxygens are violet, the octahedra yellow and the cations orange. In the global, cubic \( xyz \)-system directed approximately along the Ti-O bonds, the orthorhombic translations are \( a=(1,-1,0) \), \( b=(1,1,0) \), \( c=(0,0,2) \), with \( \alpha, \beta, \gamma \) small. The Ti sites 1 to 4 are: \( \frac{a}{2}, \frac{b}{2}, (a+c)/2, \) and \( (b+c)/2 \). The La(Y) \( ab \)-plane is a mirror \( (x \leftrightarrow -z) \), and so is the Ti \( bc \)-plane \( (x \leftrightarrow y) \) when combined with the translation \( (b-a)/2 \). See: [http://www mpi-stuttgart.mpg.de/andersen/cm/0309102.html](http://www mpi-stuttgart.mpg.de/andersen/cm/0309102.html).
struct a 12×12 block-diagonal self-energy matrix. The latter is then used together with $H^{LDA}(k)$ 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 3×3 on-site 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. 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.

We now present the LDA results for the four perovskites. Fig. 2 displays the on-site DOS matrix $N_{m
u}(\varepsilon)$ in the representation of the $xy$, $yz$, and $zx$ Wannier functions. SrVO$_3$ is cubic and its $t_{2g}$ band with a width $W=2.8$ 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 $xz$ 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 $H^{LDA}$ 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 0.45 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($xz$) + 0.714($yz$) in LaTiO$_3$ and 0.619($xy$)−0.073($xz$) + 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 $d^3$ 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, are reproduced by taking $U$ constant ≈5 eV. This is satisfying, because $U$ is expected to be similar for vanadates and titanates, although slightly smaller for the latter. 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: the lower Hubbard band (LHB) is around −1.8 eV and the upper Hubbard band (UHB) around 3 eV. Going to CaVO$_3$, the quasiparticle peak looses weight to the LHB, which remains at −1.8 eV, while the UHB moves down to 2.5 eV. These results are in good agreement with photoemission data 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 quasiparticle weight to be $Z=0.45$ for SrVO$_3$ and 0.29 for CaVO$_3$. For a k-independent self-energy, as assumed in DMFT, this yields $m^*/m=1/Z=2.2$ for SrVO$_3$ and 3.5 for CaVO$_3$, in reasonable agreement with the optical-conductivity values 2.7 and 3.6.

For LaTiO$_3$ and YTiO$_3$ the LHB is around −1.5 eV, in accord with photoemission. Despite very similar bandwidths, the gaps are very different, 0.3 and 1 eV, and this also agrees with experiments. This is consistent with our findings that the $t_{2g}$-level splittings are smaller and $(U − 2J)/W$ is larger in LaTiO$_3$ than in YTiO$_3$, where the orbital degeneracy is effec-

![FIG. 3: DMFT spectral function at $T = 770K$ (thick line) and LDA DOS (thin line). $\mu = 0$.](image-url)
tion through reduction, not only of bandwidth, but also
is driven by correlation effects and GdFeO$_3$.

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[1] M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys.
70, 1039 (1998).
[2] H. Makino et al., Phys. Rev. B 58, 4384 (1998).
[3] Y. Okimoto et al., Phys. Rev. B 51, 9581 (1995).
[4] M.J. Rozenberg, Phys. Rev. B 55, R4855 (1997).
[5] E. Koch, O. Gunnarsson, R.M. Martin, Phys. Rev. B 60,
15714 (1999); S. Flores et al., ibid. 66, 205102 (2002).
[6] N. Manini, G.E. Santoro, A. Dal Corso, and E. Tosatti,
Phys. Rev. B 66, 115107 (2002).
[7] G. Khaliullin, S. Maekawa, Phys. Rev. Lett. 85, 3950 (2000).
[8] B. Keimer et al., Phys. Rev. Lett. 85, 3946 (2000); C.
Ulrich et al., Phys. Rev. Lett. 89, 167202 (2002).
[9] M. Cwik et al., cond-mat/0302087.
[10] M. Eitel et al., J. Less-Common Met. 115, 96 (1986).
[11] M.J. Rey et al., J. Solid State Chem. 86, 101 (1990).
[12] M.H. Jung, and H. Nakotte, unpublished.
[13] By 0, 10, 13, and 21% of the average OA distance.
[14] By 0, 3, 4, and 10% of the average AB distance.
[15] M. Mochizuki, and M. Imada, Phys. Rev. Lett. 91, 167203
(2003); T. Mizokawa, D.I. Khomskii, and G.A. Sawatzky,
Phys. Rev. B 60, 7309 (1999).
[16] I. Solovyev, N. Hamada, and K. Terakura, Phys. Rev B
53, 7158 (1996); H. Sawada, and K. Terakura, ibid. 58,
6831 (1998).
[17] M. Ito et al. J. Phys. Soc. Jap. 68, 2783 (1999).
[18] J. Akimitsu et al. J. Phys. Soc. Japan 70, 3475 (2001).
[19] A. Georges, G. Kotliar, W. Kraut, M.J. Rozenberg, Rev.
Mod. Phys. 68, 13 (1996).
[20] V. Anisimov et al. J. J.Phys: Cond. Matt. 9, 7359 (1997);
A. I. Lichtenstein and M. I. Katsnelson, Phys. Rev. B 57,
6884 (1998).
[21] I.A. Nekrasov et al., cond-mat/0211508.
[22] O.K. Andersen and T. Sahia-Dasgupta, Phys. Rev B 62,
16219 (2000); Bull. Mater. Sci. 26, 19 (2003).
[23] R. Fressard and G. Kotliar, Phys. Rev. B 56, 12900 (1997).
[24] T. Mizokawa and A. Fujimori, Phys. Rev. B 54, 5369 (1996).
[25] $\Sigma_{nm}(|\phi\rangle \langle \phi|)$ in non-cubic systems, also in the eigen-
representation of the density matrix. In Fig. 2, a large
$N_{nm}(|\phi\rangle \langle \phi|)$ points to a large $\Sigma_{nm}(|\phi\rangle \langle \phi|)$.
[26] J.E. Hirsch and R.M. Fye, Phys. Rev. Lett. 56, 2521 (1986).
[27] J.E. Gubernatis, M. Jarrell, R. N. Silver and D. S. Sivia,
Phys. Rev. B 44, 6011 (1991).
[28] A. Liebsch, Phys. Rev. Lett. 90, 096401 (2003).
[29] K. Maiti et al., Europhys. Lett. 55, 246 (2001); A.
Sekiyama et al., cond-mat/0206471.
[30] A. Fujimori et al., Phys. Rev. B 46, 9841 (1992); K.
Morikawa et al., ibid. 54, 8446 (1996).