Transition metal perovskites have been studied for decades because of their unusual electronic and magnetic properties arising from narrow 3d bands and strong Coulomb correlations. The 3d\textsuperscript{1} perovskites are particularly interesting since despite the lack of multiplet effects similar materials have very different electronic properties: strontium and calcium vanadate are correlated metals with mass-enhancements of respectively 2.7 and 3.6, while lanthanum and yttrium titanate are Mott insulators with gaps of respectively 0.2 and 1 eV.

Associated with the increasing electron localization along this series is a structural GdFeO\textsubscript{3}-type distortion (Fig. 1 top): Whereas SrVO\textsubscript{3} is cubic, the corner-sharing BO\textsubscript{3} octahedra of the other perovskites are tilted and rotated in such a way that there are 4 equivalent octahedra per primitive cell. The reason often given for the progression of this distortion is that the size of the A cation relatively to that of the BO\textsubscript{3} octahedron shrinks along the series, i.e., that $r$(Sr\textsuperscript{2+})$>$$r$(Ca\textsuperscript{2+})$>$$r$(La\textsuperscript{3+})$>$$r$(Y\textsuperscript{3+}), while $r$(V\textsuperscript{5+})$<$$r$(Ti\textsuperscript{3+}).
In addition, local density approximation (LDA) band structures (Fig. 1 bottom) point to the role of covalency between the cation $d$ states (green) and the oxygen $2p$ states (blue): In cubic SrVO$_3$ each Sr ion has 12 nearest oxygens at the face centers. The 3$d$ band of Ca lies lower, and thereby closer to the oxygen 2$p$ band than the 4$d$ band of Sr, and it is therefore conceivable that a GdFeO$_3$-type distortion, which pulls some of the oxygen neighbors closer to the A ion and thereby increases the covalency with those, is energetically more favorable in CaVO$_3$ than in SrVO$_3$. The figure shows the associated increase of the Ca 4$d$–O 2$p$ gap. Going now from the vanadates to the titanates, the A and B cations become first- rather than third-nearest neighbors in the periodic table, and the A 4$d$ band therefore becomes nearly degenerate with the Ti 3$d$ band, and more so for Y 4$d$ than for La 5$d$. Here it is only the GdFeO$_3$ distortion which, through increase of the A 4$d$–O 2$p$ covalency, pushes the A 4$d$ band above the Fermi level. This, as well as the concomitant lowering of the O 2$p$ band, is seen in the figure.

The B 3$d$ band is split by covalency with the 2$p$ orbitals on the O$_6$ octahedron into three $p$-$d\pi$-coupled, low-lying $t_{2g}$ bands and two $p$-$d\sigma$-coupled, higher-lying $e_g$ bands. Simplest theories for the electronic properties of the $d^1$ perovskites are therefore based on a Hubbard model with 3 degenerate, $\frac{1}{6}$-filled $t_{2g}$ bands per B ion. For such a model, the metal-insulator transition occurs when the ratio of the on-site Coulomb repulsion to the one-electron bandwidth exceeds a critical value $U_c/W = 2$. The progressive localization of the electron along the series is therefore ascribed to a progressive reduction of the $t_{2g}$ bandwidth due to the increased bending of the $p$-$d\pi$ hopping paths (BOB bonds) and, as may be seen from Fig. 1, also to the increased theft of oxygen character by A orbitals. This may not be the full explanation of the Mott transition, however, because if the orbital degeneracy can be reduced, $U_c/W$ will be reduced because there are more hopping processes in many-particle than in single-particle theory. Now, reduction of the orbital degeneracy requires a $t_{2g}$ level-splitting, $\Delta$, merely of size $ZW$, the bandwidth associated with quasiparticle excitations. Close to the Mott transition, $Z \sim 1 - U_c/W$. Unlike in $e_g$-band perovskites such as the $d^{3+x}$ manganites where large (10%) cooperative Jahn-Teller (JT) distortions of the octahedra indicate that the $e_g$ degeneracy is reduced and 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, Khaikullin et al. predicted that quantum fluctuations will lead to an orbital liquid [Ulrich et al. in the Progress Report 2002, pp 47–51]. Moreover, 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. This is remarkable because LaTiO$_3$ is a 3-dimensional antiferromagnet with $T_N = 140$ K, a small moment $(0.45 \mu_B)$, and a recently discovered small JT distortion (3% stretching along $a$), while YTiO$_3$ is a ferromagnet with a low Curie temperature ($T_C = 30$ K), a good-sized moment $(0.8 \mu_B)$, and a JT distortion of different type (3% stretching along alternatively $x$ and $y$).

We have calculated the electronic properties in the high-temperature ($T > T_N$) paramagnetic phases using a low-energy multiband Hubbard Hamiltonian,

$$H = H^{\text{LDA}} + \frac{1}{2} \sum_{\sigma \sigma'} U_{\text{im}}^{\sigma} \hat{n}_{\text{im}}^{\sigma} \hat{n}_{\text{im}}^{\sigma'} - \text{d.c.,}$$

whose one-electron part is given by the local approximation to density-functional theory (LDA) and whose on-site ($i$) Coulomb interactions are included for a subspace of localized orbitals ($im$). The LDA provides a parameter-free account of the materials dependence, i.e., the chemistry. Recently it has become possible to solve this Hamiltonian in the dynamical mean-field approximation (DMFT), as is described in the contribution by Held et al. (see pp 50). In previous LDA+DMFT implementations it was assumed that the on-site block of the single-particle Green function is diagonal in the space of the correlated orbitals which were taken as orthonormal LMTOs, approximated by truncated and renormalized partial waves. These approximations are good for cubic $t_{2g}$ systems such as SrVO$_3$, but they deteriorate with the degree of distortion. We have therefore used localized Wannier functions and included the non-diagonal part of the on-site self-energy in the DMFT.
For an isolated set of bands, a set of Wannier functions constitutes a complete, orthonormal set of orbitals with one orbital per band (Fig. 2). For the $d^9$ perovskites we take the correlated orbitals to be three localized B $t_{2g}$ Wannier orbitals, and in $H^{\text{LDA}}$ 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 $p$ and A $d$ characters. Our Wannier orbitals are symmetrically orthonormalized $N^{\text{th}}$-order muffin-tin orbitals (NMTOs), which have all partial waves other than $B_{xy}, yz,$ and $zx$ downfolded. For the on-site Coulomb interactions we use the common assumption that, as in the isotropic case, they can be expressed in terms of two parameters, $U$ and $J$. The former we take to be 5 eV for all four perovskites, and the latter has been calculated to be 0.68 eV for the vanadates and 0.64 eV for the titanates. The self-energy can now be obtained from the solution of an effective Anderson impurity model which involves only 3 correlated orbitals. All components of the self-energy matrix $\Sigma_{mm'}(\omega)$ between different Wannier functions on a given B-site are taken into account. From this $3 \times 3$ matrix, by use of the symmetry (Fig. 1), we construct a $12 \times 12$ block-diagonal self-energy matrix. This is then used together with $H^{\text{LDA}}(\mathbf{k})$ to obtain the Green function at a given $\mathbf{k}$-point. Fourier transformation over the entire Brillouin zone yields the local Green function associated with a primitive cell and its $3 \times 3$ on-site block is used in the DMFT self-consistency condition in the usual manner. The 3-orbital impurity problem is solved by a quantum Monte Carlo scheme which is accurate at high temperature.

Figure 3 displays the LDA on-site DOS matrix, $N_{mm'}(\epsilon)$, in that representation of the $t_{2g}$ Wannier orbitals which diagonalizes the on-site term of $H^{\text{LDA}}$, i.e., the ligand and crystal-field term. The $t_{2g}$ band of cubic SrVO$_3$ consists of three degenerate subbands, and since the $xy, yz,$ and $zx$ orbitals hardly interact, each subband is nearly...
2-dimensional and gives rise to a nearly logarithmic DOS peak. Going to CaVO$_3$, the bandwidth is reduced from 2.8 to 2.4 eV for the reasons mentioned before, and the energy of the $xy$ orbital (the center of gravity of $N_{xy,xy}$) is lowered by 0.08 eV compared to that of the degenerate $xz$ and $yz$ orbitals. Going from the vanadates to the titanates, the increased misalignment and loss of oxygen character further reduce the bandwidths to 2.1 and 2.0 eV. Moreover, the $xy$, $yz$, and $zx$ Wannier orbitals mix and the levels split with the middle (highest) being 0.14 (0.20) eV above the lowest in LaTiO$_3$, and 0.20 (0.33) eV in YTiO$_3$. Finally, there are strong off-diagonal elements of the DOS matrix even in the eigenrepresentation of $H_{\text{LDA}}$ in YTiO$_3$, the diagonal DOS element for the orbital with the lowest energy exhibits a pseudogap. Despite the strong increase of the level splittings, $\Delta$, they remain an order of magnitude smaller than the $t_{2g}$ bandwidths, and also smaller than the subband-widths.

As a consequence, the eigenfunction for the lowest level is occupied by merely 0.45 electron in LaTiO$_3$ and 0.50 in YTiO$_3$. Nevertheless, 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.

By performing LDA+DMFT calculations for several values of $U$ between 3 and 6 eV, we found that the critical ratio ($U - 2Jc$) / $W$ decreases from 2 to 1.4 when going along the series. This is consistent with an increasing $\Delta$, and it indicates that the Mott transition is driven as much by the decrease of effective degeneracy (from 3 to almost 1) as by the reduction of bandwidth. As shown in Fig. 4, the main features of the experimental photoemission spectra for all four materials, as well as the correct values of the mass enhancements for the metals and the Mott-Hubbard gap for the insulators, are reproduced by taking $U$ constant $\approx 5$ eV. This is satisfying, because $U$ is expected to be similar for vanadates and titanates. Despite very similar bandwidths for LaTiO$_3$ and YTiO$_3$, the gaps are very different, 0.2 and 1 eV. This is consistent with our findings that the $t_{2g}$ level splittings are larger and $(U - 2Jc) / W$ smaller in YTiO$_3$ than in LaTiO$_3$. Diagonalization of the matrix of occupation numbers reveals that for the titanates one orbital per site is nearly full and that this orbital is nearly identical with the one we obtained from the LDA as having the lowest energy. The Coulomb correlations increase its occupation from 0.45 to 0.88 in LaTiO$_3$ and from 0.50 to 0.96 in YTiO$_3$. This orbital polarization increases around the metal-insulator transition and becomes complete thereafter. In the vanadates, each orbital is approximately 1/3 occupied for all $U$ in the range from 0 to 6 eV. The nearly complete orbital polarization in the titanates 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. In LaTiO$_3$ some orbital fluctuations are still active, although quite weak. Whereas the localization is caused by Coulomb correlations, the chemistry (LDA) selects the orbital (Fig. 5). For illustration of the orbital order, we have placed this orbital on each of the 4 Ti-sites. Although LaTiO$_3$ and YTiO$_3$ have the same space group, their orbital orders look different.

![Fig. 4. LDA DOS (thin) and LDA+DMFT spectral function calculated with $U = 5$ eV and $T = 770$ K (thick). Results from optical conductivity and photoemission measurements are indicated in blue.](image-url)
This difference reflects the extent to which the orbital has the bc-plane through Ti as a mirror, and is only quantitative. What causes this particular Ti $t_{2g}$ orbital to have the lowest energy is cation covalency and crystal-field effects; the positive (blue) lobes have bonding $3z^2 - 1 = (xy + xz + yz)/\sqrt{3}$ character on the nearest A cations and the negative (red) lobes have bonding $xy$ character on the next-nearest A cations which continues in bonding $(x - y)/\sqrt{2}$ character on the oxygen closest to that cation. The former type of AB covalency dominates in LaTiO$_3$, while the latter type of ABO covalency dominates in YTiO$_3$, where the shortest YO bond is merely 10% longer than the TiO bond. The LDA pseudogaps as well as the level splittings are thus caused by the A $d$ character not used to drive the GdFeO$_3$ distortion, but left behind in the Ti $t_{2g}$ band (Fig. 1).

The different JT distortions of the oxygen square in LaTiO$_3$ and YTiO$_3$ are a reaction to, rather than the cause of the difference in the orbital orders. The difference in the orbital orders is reflected in the hopping integrals between nearest neighbors: $t_x = t_y = 99$ (38) meV and $t_z = 105$ (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 3-dimensional anti- and YTiO$_3$ ferromagnetic at low temperature, and it warrants detailed future calculations of the spin-wave spectra.

We have thus seen that the B $t_{2g}$ 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. This distortion is driven by the increasing OA $pd\sigma$-covalency, and it primarily pulls 4 of the 12 oxygens neighboring a given A cation closer to it. Moreover, 2 to 4 of the 8 A cations neighboring a given transition metal ion (B) are pulled closer. The B $t_{2g}$ orbitals couple to the OA distortion via oxygen (BOA $dp\pi - pd\pi$), and they couple directly (AB $dd\sigma$) to the AB distortion.

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 3$d^1$ 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$_3$. 

FIG. 5. The almost fully occupied localized orbital in LaTiO$_3$ (left) and YTiO$_3$ (right), placed on each of the 4 Ti-sites to exhibit the orbital order. On site 1, this orbital is the linear combination $0.586|xy⟩ + 0.275|xz⟩ + 0.762|yz⟩$ of the Ti $t_{2g}$ Wannier functions in LaTiO$_3$ and $0.622|xy⟩ - 0.029|xz⟩ + 0.782|yz⟩$ in YTiO$_3$. Blue and red indicate respectively positive and negative values. A relatively low numerical value of the contour has been used in order to bring out covalency effects.