Orbital fluctuations in the different phases of LaVO$_3$ and YVO$_3$

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We investigate the importance of quantum orbital fluctuations in the orthorhombic and monoclinic phases of the Mott insulators LaVO$_3$ and YVO$_3$. First, we construct ab-initio material-specific $t_{2g}$ Hubbard models. Then, by using dynamical mean-field theory, we calculate the spectral matrix as a function of temperature. Our Hubbard bands and Mott gaps are in very good agreement with spectroscopy. We show that in orthorhombic LaVO$_3$, quantum orbital fluctuations are strong and that they are suppressed only in the monoclinic 140 K phase. In YVO$_3$ the suppression happens already at 300 K. We show that Jahn-Teller and GdFeO$_3$-type distortions are both crucial in determining the type of orbital and magnetic order in the low temperature phases.

PACS numbers: 71.27.+a, 71.30.+h, 71.15.Ap

The Mott insulating $t_{2g}^3$ perovskites LaVO$_3$ and YVO$_3$ exhibit an unusual series of structural and magnetic phase transitions (Fig. 1) with temperature-induced magnetization reversal phenomena [1] and other exotic properties [2,3]. While it is now recognized that the V-$t_{2g}$ orbital degrees of freedom and the strong Coulomb repulsion are the key ingredients, it is still controversial whether classical (orbital order) [1,4,5,6,7,8] or quantum (orbital fluctuations) [2,9] effects are responsible for the rich physics of these vanadates.

At 300 K, LaVO$_3$ and YVO$_3$ are orthorhombic paramagnetic Mott insulators. Their structure (Fig. 2) can be derived from the cubic perovskite ABO$_3$, with A=La,Y and B=V, by tilting the VO$_6$ octahedra in alternating directions around the b-axis and rotating them around the c-axis. This GdFeO$_3$-type distortion is driven by AO covalency which pulls a given O atom closer to one of its four nearest A-neighbors [10,11]. Since the Y 4$d$ level is closer to the O 2$p$ level than the La 5$d$ level, the AO covalency increases when going from LaVO$_3$ to YVO$_3$ and, hence, the shortest AO distance decreases from being 14 to being 20 % shorter than the average, while the angle of tilt increases from 12 to 18$^\circ$, and that of rotation from 7 to 13$^\circ$ [12,13]. Finally, the A-cube is deformed such that one or two of the ABA body-diagonals is smaller than the average by, respectively, 4 and 10 % in LaVO$_3$ and YVO$_3$. These 300 K structures are determined mainly by the strong covalent interactions between O 2$p$ and the empty B e$_g$ and A d orbitals, hardly by the weak interactions involving B t$_{2g}$ orbitals, and are thus very similar to the structures of the $t_{2g}^4$ La and Y titanates [10,11].

The $t_{2g}^3$ vanadates, however, have a much richer phase diagram than the $t_{2g}^4$ titanates. At, respectively, 140 K and 200 K, LaVO$_3$ and YVO$_3$ transform to a monoclinic structure in which c is turned slightly around a whereby the two subcells along c, related by a horizontal mirror plane in the orthorhombic structure, become independent (Fig. 2). Most important: a sizable (3-4%) Jahn-Teller (JT) elongation of a VO bond, that along y in cells 1 and 4, and along x in cells 3 and 2, deforms the VO$_6$ octahedra. At about 140 in LaVO$_3$ and 116 K in YVO$_3$, antiferromagnetic C-type order develops (FM stacking of AFM ab-layers). At 77 K, YVO$_3$ recovers the orthorhombic structure and the magnetic order changes from C- to G-type (3D-AFM), while the long VO bond becomes that along x in cells 1 and 3, and along y in 2 and 4.

It has been suggested [1] that these phase transitions are driven by the changes in a static orbital order (OO) following the observed pattern of JT-distortions [2,14]. According to this JT-OO model, which assumes that the
crystal-field (CF) is due to the oxygen octahedra, the $t_{2g}$ orbital which is most antibonding with the O 2p orbitals, i.e. $|sz\rangle$ where $s$ is the direction of the short in-plane VO bond, is empty; the other two $t_{2g}$ orbitals, due to Hund’s rule coupling, are singly occupied. This OO is C-type in the orthorhombic structure and G-type in the monoclinic structure. Later, this JT-OO model was challenged by a theory which assumes that the two highest orbitals, $|xz\rangle$ and $|yz\rangle$, are basically degenerate so that orbital fluctuations play a key role. Recently, ab initio LDA+U calculations gave support to the JT-OO model.

In this Letter we show that in LaVO$_3$ quantum effects are strong down to 300 K, however they become negligible in the AF-C monoclinic phase. For VVO$_3$ orbital fluctuations are suppressed already at 300 K, and the 77 K magnetic transition is associated with a change of OO. We show that the CF splittings result not only from the JT-, but also from the GdFeO$_3$-type distortions, and thus OO is intermediate between C- and G-type. The influence of the JT- and the GdFeO$_3$-type distortion is, respectively, stronger and weaker than in the $t_{2g}$ titanates.

The electronic structure is calculated with the LDA+DMFT method, fully accounting for the orbital degrees of freedom. First, we compute the LDA bands with the $N^\text{th}$-order muffin-tin-orbital (NTO) method; we obtain (for all structures) $\frac{1}{2}$-filled $t_{2g}$ bands separated by a $\sim$0.5 eV gap from the empty $e_g$ bands and by a $\sim$2 eV gap from the filled O 2p bands. Next, we Löwdin downfold to V $t_{2g}$ and remove the energy dependence of the downfolded orbitals by “N-ization.” These orbitals are strongly localized, having $V_{t_{2g}}$ character only in their heads. Symmetric orbital-diagonalization finally yields localized spin $t_{2g}$ Wannier functions and their corresponding Hamiltonian, $H^{\text{LDA}}$.

The many-body Hamiltonian is then a material-specific $t_{2g}$ Hubbard model, $H = H^{\text{LDA}} + U$, where for the on-site Coulomb repulsion, $U$, we use the conventional expression:

$$U = \frac{1}{2} \sum_{n,m'} \epsilon_m' n_{m'a} n_{ma} n_{ma}.$$ 

Let us start by describing the LDA $t_{2g}$ bands in the orthorhombic 300 K phase. Remarkably, the CF orbitals $|j\rangle$ (Table | $j = 1,2,3)$, obtained by diagonalizing the on-site $i$ block of $H^{\text{LDA}}$, the hopping integrals $t_{i,j}$ (Table | $j = 1,2,3)$, the $t_{2g}$ band-shapes and band-width W (Fig. | are rather similar to those of the $t_{1g}$ titanates. These similarities are due to the similarity of the crystal
structures. Like in the titanates, the CFs are essentially determined by the GdFeO$_3$-type distortion, mainly via the A-ligand field, specifically the AB and AOB covalency. However, in the vanadates the CF splittings are about half those of the respective titanates and the CF orbitals and the Hubbard bands are centered around -1.5 eV and 2.5 eV, in very good agreement with photoemission [28]. And the enhancement is stronger the closer the system is to half-filling [29]. So the gap should be smaller for a transition, orbital degeneracy increases the critical ratio for the Mott transition, strongly by cation covalency [24]. This is due to the Ti → V substitution [26]: since V is on the right of Ti in the periodic table, the V 3d level is closer to the O 2p and further from the A d level that the Ti 3d. Thus the sensitivity of the B t$_{2g}$ Wannier functions to GdFeO$_3$-type distortions decreases, while the sensitivity to JT increases.

Now, turning on the Coulomb repulsion transforms the metallic LDA density of states (DOS) into the spectral matrix of a Mott insulator (Fig. 3). For LaVO$_3$, the Mott gap is $\sim 1$ eV, in accord with optical conductivity data [27], and the Hubbard bands are centered around -1.5 eV and 2.5 eV, in very good agreement with photoemission and inverse photoemission [28]. For YVO$_3$, the gap is slightly larger, $\sim 1.2$ eV, in accord with optical data [27], and the Hubbard bands are centered around -1.5 eV and 3 eV, in agreement with photoemission [28].

The Mott gaps in the vanadates are somewhat larger than in the titanates, for which the measured gaps are $\sim 0.2$ eV in LaTiO$_3$ and $\sim 1$ eV in YTiO$_3$ [27], in line with LDA+DMFT results [11]. This could appear surprising: orbital degeneracy increases the critical ratio for the Mott transition, $U_c/W$, by enhancing the effective band-width, and the enhancement is stronger the closer the system is to half-filling [29]. So the gap should be smaller for a t$_{2g}$ system, everything else remaining the same. However, the Hund's rule exchange energy, $J$, strongly suppresses this enhancement, as shown for half-filling in Ref. [20]. For $n=\frac{1}{3}$ and $n=\frac{2}{3}$, and using a 3-fold degenerate Hubbard model with a rectangular DOS, $\gamma=770$ K, and $J/W=\gamma$ (like in the vanadates where $J/W=0.68/1.9$), we find that the metal to insulator transition occurs for $U'/W=1.5$ when $n=\frac{1}{3}$, and for $U'/W=1.3$ when $n=\frac{2}{3}$. So the Hund's rule coupling dominates, and thus the vanadates can have larger gaps than the titanates.

Like for the titanates [11], diagonalization of the DMFT occupation matrix yields three eigenvectors nearly identical to the LDA CF orbitals. For LaVO$_3$ at 770 K, the Coulomb repulsion only slightly increases the orbital polarization by changing the occupations as follows: 0.78$\rightarrow$0.87, 0.63$\rightarrow$0.65, and 0.59$\rightarrow$0.48. Thus, surprisingly, orbital fluctuations are sizable and remain so down to room temperature: $n_3=0.26$ at 290 K. Due to the stronger cation covalency in YVO$_3$, the Coulomb repulsion causes substantial orbital polarization already at 770 K (see Fig. 1). At 300 K, we find that only $c_{3,4} c_{i,4}^T |0\rangle$, paramagnetic with $S=1$, is occupied. Thus, YVO$_3$ is only a singly occupied state not far from ours [31], but, without analyzing the results, the OO was ascribed to the JT distortions. In contrast, we find that the CF orbitals depend crucially also on the GdFeO$_3$-type distortions and that the OO is not of G-type, but is intermediate between C- and G-type.

For LaVO$_3$, the CF splittings are similar to those of the 300 K phase, but quantum effects are negligible (Fig. 1). On all sites in the monoclinic structure the empty orbital is almost the same as in the orthorhombic 300 K phase so OO does not follow the JT distortions $(3)_1 \approx - (3)_3 \approx |xz\rangle, (3)_2 \approx - (3)_4 \approx |yz\rangle$, but is almost C-type. In the orthorhombic 77 K phase, the empty orbital at site 1, $(3)_1$, only roughly equals $|xz\rangle$. Our results are consistent with resonant x-ray scattering [3] and magnetization [1] data. LDA+$U$ [6] yields results close to ours [31].

Finally, we find that the monoclinic structure favors C-type magnetic order over G-type by increasing some hopping integrals $t_{j,j'}^{i,i'}$ (Table I) to the empty orbital $|3\rangle$ along the c-direction. Assuming complete OO, conventional theory yields, for the superexchange couplings,

$$J_{SE}^{i,i'} \sim \frac{1 + J/U}{U + 2J} \sum_{j,j'<2} |t_{j,j'}^{i,i'}|^2 - \frac{J/U}{U - 3J} \sum_{j,j'<2} \left( |t_{j,j'}^{i,i'}|^2 + |t_{j,j'}^{i',i}|^2 \right)$$

with $j,j'$ CF orbitals and $i,i'$ neighboring sites. We find that C-type order ($J_{SE}^{i,i+2} < 0$, $J_{SE}^{i,i+\infty} = J_{SE}^{i,i+2} > 0$) is fa-

![FIG. 3: (color on-line) LDA+DMFT spectral matrix $A_{\alpha,\beta'}$ in the crystal-field basis. The off-diagonal terms are $\sim 5$ times smaller than in LDA. In black, the LDA DOS.](image)
vored over G-type, for which all couplings are positive, if \( J/U \approx 0.16 \). While the actual values of \( J_{\text{SE}}^{i,i'} \) are sensitive to details \([4,7,10]\), this provides a microscopic explanation of C-type order in monoclinic LaVO\(_3\) and YVO\(_3\), the change from C- to G-type across the structural phase transition in YVO\(_3\), and thus could also explain the magnetization-reversal phenomena \([1]\).

In conclusion, we find that the orthorhombic LaVO\(_3\) is one of the few Mott insulators which exhibits large quantum effects at room temperature. This is not the case for YVO\(_3\) (and \( t_{2g}^3 \) titanates \([11]\)). In the low temperature phases, orbital fluctuations are negligible for both vanadates. This supports the view \([1,11,14]\) that the magnetic structures of the vanadates can be explained by orbital-order. Recent LDA+U \([3]\) and LDA+PIRG \([8]\) calculations agree with this, but previous literature ascribed OO mainly to JT-distortions. In contrast, we proved that both the JT and the GdFeO\(_3\)-type distortions are crucial for the CF orbitals and their hopping integrals, and thus for the type of orbital and magnetic order. The effects of the GdFeO\(_3\)-type distortions are weaker and those of JT stronger than in \( t_{2g}^3 \) titanates; their interplay is responsible for the rich phase diagram of the vanadates.

We thank E. Koch, A.I. Lichtenstein, S. Biermann, and A. Georges for discussions and J. Nuss for graphics support. Computations were done on the Jülich BlueGene. M. D. thanks the MPG Partnergroup program.

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**TABLE II:** Hopping integrals \( t_{i,i'}^{j,j'} / \text{meV} \) from site \( i \) to a site \( i' = i + bx + my + nz \), in the basis \((j,j')\) of crystal-field orbitals. Here \( i = 1 \) and (P2\(_1\)/a only) \( i = 3 \). Notice that \( t_{i,i'}^{j,j'} = t_{i',j}^{j,i} \) and \( t_{j,j'}^{i,i'} = t_{j',j}^{i,i} \). For Pbnm structures only: \( t_{i,i'}^{j,j'} = t_{i',j}^{j,i} \).

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\( n_{xy} < 2 \), so a full comparison is not possible.