**Quantum Versus Jahn-Teller Orbital Physics in YVO$_3$ and LaVO$_3$**

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We argue that the large Jahn-Teller (JT) distortions in YVO$_3$ and LaVO$_3$ should suppress the quantum orbital fluctuation. The unusual magnetic properties can be well explained based on LDA+U calculations using experimental structures, in terms of the JT orbital. The observed splitting of the spin-wave dispersions for YVO$_3$ in C-type antiferromagnetic state is attributed to the inequivalent VO$_2$ layers in the crystal structure, instead of the “orbital Peierls state”. Alternative stacking of $ab$-plane exchange couplings produces the $c$-axis spin-wave splitting, thus the spin system is highly three dimensional rather than quasi-one-dimensional. Similar splitting is also predicted for LaVO$_3$, although it is weak.

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An essential subject, which is responsible for the rich physics in transition-metal oxides, is the orbital degree of freedom (ODF) and its interplay with the spin, charge and lattice degrees of freedom. For cubic perovskites, quantum orbital fluctuation (QOF) would be expected due to the degeneracy in orbital sector, and a particular spin and orbital ordered phase can be selected by maximizing the energy gain from the QOF. On the other hand, Jahn-Teller (JT) distortions will lift the orbital degeneracy, and suppress the QOF. The competing QOF versus JT physics has thus been the central issue for the recent discussions on $t_{2g}$ perovskites. A typical example is LaTiO$_3$, which shows much reduced ordered moment from that expected by mean field theory, and isotropic spin dynamics. At one side, the relevance of QOF was emphasized by neglecting the crystal field effects and treating the systems essentially as cubic. On the other hand, this scenario is questioned by the recent examinations, which demonstrated that those unusual magnetic properties can be understood from polarized orbital caused by the lattice distortions, and that the predicted orbital entropy from QOF was not observed.

YVO$_3$ and LaVO$_3$ are $t_{2g}$ perovskites with two localized 3d electrons per V. Early experimental results showed complicated phases for those compounds. First, LaVO$_3$ has G-type JT distortion and the C-type antiferromagnetic (AF) state below 140K. YVO$_3$ does the same between 77K < $T$ < 116K, but shows the C-type JT distortion, and the G-type AF state below 77K. Very recently, an unusual magnetic structure and dynamic in YVO$_3$ was reported, especially a splitting of the $c$-axis spin-wave dispersions was observed for the intermediate temperature (77K < $T$ < 116K) phase of YVO$_3$, where the $c$-axis lattice dimerization is vanishingly weak. The QOF was thus argued for those compounds by neglecting the strong JT distortions present (about 2~4%). Theoretically, by treating the system as quasi one-dimensional (1D), the spin-orbital superexchange model was analyzed, and an “orbital-Peierls state” due to the formation of orbital singlet was proposed. However, the spin system can not be regarded as 1D, while the orbital system is due to the destructive interference of the interchain exchange processes. Furthermore, from this QOF picture it is hard to understand the observed large JT distortion and its clear temperature dependence. It is therefore an interesting and challenging problem to judge the underlying physics here, especially by first-principles calculations.

In this letter, we will present firm evidences for the crucial role of lattice distortion for YVO$_3$ and LaVO$_3$. The experimentally observed spin orderings (SO) can be systematically explained by our LDA+U calculations, in terms of the JT orbital. The “unexpected features” of spin wave in YVO$_3$ namely, 1) splitting of $c$-axis spin wave; 2) $|J_c| > |J_{ab}|$ ($J_c$ and $J_{ab}$ are $c$-axis and $ab$-plane exchange couplings, respectively), can be naturally explained from the structural point of view. Similar picture is also predicted for LaVO$_3$. We further point out that the theoretical simplification to treat the system as quasi 1D is lack of firm bases.

The calculations are done based on the LDA+U scheme in plane-wave pseudopotential method. For such well defined insulating systems with long range ordering, LDA+U method typically can give reasonable results. The parameter $U_{\text{eff}}=3.0$eV is used to reproduce the experimental band gaps properly. For all the discussions, we use the unit cell with $a \approx b \approx c/\sqrt{2}$, which includes four V sites (sites 1 and 2 in one layer, with sites 3 and 4 on top of 1 and 2, respectively), and define the local axes $x, y, z$ as the [110], [110], [001] directions of the unit cell. We performed ground state calculations for three structures, YVO$_3$ at 65 K, at 100K, and LaVO$_3$ at 10K. Four magnetic structures (i.e.,
FM and A-, C-, G-type AF states were calculated for each fixed experimental structures. Let us start from the low temperature phase of YVO₃, which has C-type JT distortion. As shown in Table I, among the four magnetic structures, the G-AF state is the most stable state, consistent with experimental observation and earlier calculations. The obtained magnetic moment (1.68μB) and band gap (1.2eV) are also in excellent agreement with experimental ones (1.72μB [2] and 1.2eV [23]), demonstrating the validity of our approaches. The stabilization of G-AF state can be naturally explained in terms of the JT orbital as follows. By calculating the occupation numbers, it is easy to find that the C-type JT distortion stabilize the C-type orbital ordering (OO), where yz, zx, yz, zx orbital is occupied for four V sites (1,2,3,4) respectively, and xy orbital is occupied for all V sites. In this OO pattern, the super-exchange (SE) along the c-axis is expected to be AF due to the ferro-orbital chain arrangement of yz and zx, according to the Goodenough-Kanamori rules (GKR). There are two contributions, however, for the SE in ab-plane, the FM one due to the nearly orthogonal yz, zx orbital arrangement, and the AF one coming from xy orbital. The net coupling will depend on the relative polarization of those orbital. The calculated orbital occupation numbers (nₓᵧ, nᵧz, and nₓz) for one of the V sites (shown in Fig.1(a)) clearly show that the polarization between the yz and the zx states is not so strong, and the net magnetic interaction is dominated by the AF SE from xy state. As the results, we would expect the AF exchange coupling both along c-axis and in the ab-plane. This will explain the ground state G-type SO.

Importantly, the calculated OO patterns and magnetic moments are not sensitive to the SO. For the fixed structure of YVO₃ at 65 K, we always get the C-type OO for the four magnetic states. Furthermore, even the occupation numbers of each orbital do not change so much for different magnetic states, as shown in Fig.1. The situation is quite general for all the examples considered here, and is also true for LaVO₃. This clearly suggests the crucial role of lattice distortions for those compounds. The experimentally observed JT distortions are essentially important to reproduce the correct magnetic orderings. Giving the facts that all those calculated magnetic states have basically the same OO pattern, and that the charge gap (see Table I) is much larger than the spin excitation energies (typically the order of meV), we can approximately decouple the spin degree of freedom, and treat it in terms of the Heisenberg model. Then the exchange interactions can be estimated by mapping the calculated total energies for each magnetic state, E(F), E(A), E(C) and E(G), to the Heisenberg model. The nearest neighboring exchange coupling constants are then given by:

\[ J_c = (1/4S^2)[E(F) - E(G) - E(A) + E(C)] \]
\[ J_{ab} = (1/8S^3)[E(F) - E(G) + E(A) - E(C)] \]  

where S=1 is the moment. For YVO₃ at 65K, we got Jₓᵧ=7.8meV and Jₓz=7.5meV, which is quite isotropic as suggested by experiments [2], and can be reasonably compared with the experimental values as shown in Table II. Up to this stage, we show that the low temperature phase of YVO₃ can be well explained by the JT orbital physics.

For YVO₃ at 100K, the experimental G-type JT distortion will stabilize the G-type OO, in which the yz and zx orbital are occupied alternatively (antiferro-orbital) along the c-axis, instead of the ferro-orbital chain below 77K. For the four magnetic states, we all obtained the G-type OO pattern. In such G-type OO state, the antiferro-orbital chain along c-axis will favor FM coupling along the chain, while the exchange coupling in

### Table I: The calculated total energies E(meV/f.u.), magnetic moment M(μB/site), and band gap Eg(eV), for various compounds in different magnetic states. For YVO₃ (100K) and LaVO₃ (11K), two magnetic moments are given for two inequivalent layers. Bold numbers correspond to most stable magnetic state.

|       | FM     | A-AF   | C-AF   | G-AF   |
|-------|--------|--------|--------|--------|
|       | E      | M      | E      | M      |
| YVO₃  |       |        |        |        |
| (65 K)| 45.9   | 1.75   | 1.70   | 1.68   |
|       | 27.2   | 1.72   | 1.70   | 1.68   |
|       | 12.8   | 1.70   | 1.70   | 1.68   |
|       | 0.0    | 1.70   | 1.70   | 1.68   |
|       | 1.2    | 1.70   | 1.70   | 1.68   |
|       |        |        |        |        |
| YVO₃  |       |        |        |        |
| (100 K)| 16.7  | 1.75(1.77)| 1.70(1.72)| 1.70(1.72)|
|       | 27.6   | 1.72   | 1.72   | 1.72   |
|       | 0.8    | 1.72   | 1.72   | 1.72   |
|       | 1.0    | 1.72   | 1.72   | 1.72   |
|       | 0.0    | 1.72   | 1.72   | 1.72   |
|       | 19.1   | 1.72   | 1.72   | 1.72   |
|       | 1.0    | 1.72   | 1.72   | 1.72   |
|       |        |        |        |        |
| LaVO₃ |       |        |        |        |
| (10 K)| 38.3   | 1.74(1.75)| 1.70(1.71)| 1.70(1.71)|
|       | 42.0   | 1.72   | 1.72   | 1.72   |
|       | 0.0    | 1.72   | 1.72   | 1.72   |
|       | 23.5   | 1.72   | 1.72   | 1.72   |
|       | 1.0    | 1.72   | 1.72   | 1.72   |
|       | 1.2    | 1.72   | 1.72   | 1.72   |
|       | 0.9    | 1.72   | 1.72   | 1.72   |

FIG. 1: The calculated tₓᵧ orbital occupation numbers for different compounds as function of different magnetic orderings. Since the OO patterns are fixed by the structures, only the occupations for one of the transition-metal site are shown.
TABLE II: The comparison of calculated and experimental spin coupling constants $J_c$ and $J_{ab}$ (meV) for various compounds. The numbers with parentheses are two inequivalent values as discussed in the text. The symbols $\|$ and $\perp$ point to Ref. 22 and 23 respectively.

|          | YVO$_3$ (65 K) | YVO$_3$ (100 K) | LaVO$_3$ (10 K) |
|----------|----------------|-----------------|-----------------|
| Cal. $J_c$ | 7.8            | -7.2            | -6.5            |
| $J_{ab}$  | 7.5            | 0.8 (5.3)       | 5.8 (7.7)       |
| Exp. $J_c$ | 5.7$^\perp$    | -2.0 (4.2)$^\perp$ | -4.0$^\perp$    |
| $J_{ab}$  | 5.7$^\perp$    | 2.6$^\perp$     | 6.5$^\perp$     |

ab-plane are basically the same as that of YVO$_3$ at 65 K, resulting in the experimental C-AF state (see Table I) 24. Now the question is how to understand the “unexpected features” of spin wave, which were argued to be the result of orbital dimer formation 25. 1) The c-axis spin wave splits into two branches and open a gap; 2) $|J_c| > |J_{ab}|$, while according to GKR, FM SE ($J_c$ in this case) is generally weaker than AF SE ($J_{ab}$). X-ray diffraction results 20 suggested that YVO$_3$ in the C-AF phase has $P2_1/a$ symmetry, which has no c-axis dimerization. The recent far-infrared spectroscopy data 19 suggested the possible lowering of the symmetry group to $P6\text{il}$ or $P1$. However, this lowering will not violate our following discussions due to: 1) the emergence of new phonons is one or two order weaker in intensity 19 compared with the main modes; 2) the following arguments are common for all those possible symmetries. A characteristic point of the lattice structure of YVO$_3$ in C-AF state, in sharp contrast with the low temperature phase ($Pbnm$ space group), is the absence of any symmetry operation to transfer one VO$_2$ layer to the neighboring layer along c-direction, resulting in two inequivalent VO$_2$ layers, which have different amounts of JT distortion. As the results, we obtain two $J_{ab}$ ($=0.8$ and $5.3$meV) for two different layers 25, which stacking along the c-axis alternatively. This is in qualitative difference with the experimental analysis, in which they assumed alternative $J_c$ but same $J_{ab}$ to fit the experimental spin-wave. By using the calculated exchange parameters (alternative $J_{ab}$), our obtained spin-wave dispersions (shown in Fig.2(B)) definitely shows a c-axis spin-wave splitting, which is comparable in size with the experimental one (about 5meV). The overall shape of our obtained spin-wave is also in good agreement with the experimental one. We conclude that the observed spin-wave splitting is due to the inequivalent VO$_2$ layers in this compounds. For such strongly coupled systems both spin and orbital behaviors are essentially three dimensional. Especially for the spin degree of freedom, the exchange coupling in $ab$-plane will dramatically affect the spin wave behavior along c-axis. It is generally not suitable to treat the system as quasi 1D as assumed in previous studies 7. The

“orbital Peierls states” will be easily suppressed by the increased JT distortions.

The dramatic difference of two $J_{ab}$ comes from different distortions of two layers. For YVO$_3$ at 100K, the JT distortion is about 4% for one layer (say layer 1), while about 2% for another layer (say layer 2). Such a difference will modify the orbital polarization as shown in Fig.1(b) and (c). The polarization between the $yz$ and $zx$ orbital for layer 1 is larger than that of layer 2, while the $n_{xy}$ is almost same for two layers. The larger polarization tend to enhance the FM coupling coming from the orthogonal $yz$ and $zx$ occupation in the $ab$-plane, which will compensate the AF coupling from $xy$ orbital. Therefore, the net AF coupling are significant suppressed, from 5.3meV for layer 2 to 0.8meV for layer 1. This fact will also explain why $|J_c| > |J_{ab}|$ in this case, and again suggest the crucial role of lattice distortions.

Due to the same symmetry, we obtain the similar results for LaVO$_3$ at 10K, i.e., the observed G-type JT distortion will stabilize the G-type OO robustly, and as the result, the C-AF ground state is obtained. Our calculated magnetic moment (1.7$\mu_B$) is somehow larger than the early experimental value (about 1.3$\mu_B$ 26). The c-axis spin-wave gap is also predicted in this case, although it is weak due to the smaller structural difference between the two VO$_2$ layers (see Table I, II and Fig.1, 2). This prediction should be verified by future experiments.

Finally, we have two comments for the C-AF phase of YVO$_3$. First, the experimental moment (about 1.05$\mu_B$) is much smaller than our calculated one (1.70 and 1.72 $\mu_B$ for two inequivalent V sites). This fact has been used as an argument for the QOF nature. However, from the neutron data 7, we find that the C-type spin diffraction intensity above 77K is far from saturated. By extrapolat-
ing that intensity versus temperature data down to 0K, we can easily get a increased moment by a factor of 1.7. Therefore, the reduced magnetic moment could be due to the elevated temperature. Second, the spin canting of 16 degrees is argued from experimental side, while it is not included in our calculations. Nevertheless, we should say such a canting may quantitatively affect our results discussed above (such as the calculated moments for YVO\(_3\) and LaVO\(_3\) in C-AF state), but not qualitatively, especially for the main conclusion about the structural origin of spin wave gap.

In summary, we show that the reported unusual magnetic properties for YVO\(_3\) and LaVO\(_3\) can be reasonably explained by a systematic JT picture from LDA+U calculations. For fixed structures, the obtained OO patterns are not sensitive to SO, suggesting that any meaningful orbital fluctuation must be via the phonon degrees of freedom. It will be an interesting future subject to study the phonon-mediated orbital fluctuations for those compounds.

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