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 local density approximation + Hubbard U calculations using experimental structures, in terms of the JT orbital. The observed splitting of the spin-wave dispersions for YVO_3 in a *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 [1–3]. For cubic perovskites, quantum orbital fluctuation (QOF) would be expected due to the degeneracy in the orbital sector, and a particular spin and orbital ordered phase can be selected by maximizing the energy gain from the QOF [4–7]. On the other hand, Jahn-Teller (JT) distortions will lift the orbital degeneracy and suppress the QOF [8–11]. 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 a much reduced ordered moment from that expected by mean field theory, and isotropic spin dynamics [4]. On one hand, the relevance of QOF was emphasized [5] 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 a polarized orbital caused by the lattice distortions [10–14] and that the predicted orbital entropy from QOF was not observed [15].

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 [16–18]. First, $LaVO_3$ has *G*-type [19] JT distortion and a *C*-type antiferromagnetic (AF) state below 140 K [16]. YVO_3 has the same between $77\text{ K} < T < 116\text{ K}$, but shows *C*-type JT distortion and a *G*-type AF state below 77 K [17]. Very recently, an unusual magnetic structure and dynamic in YVO_3 was reported [7], especially a splitting of the *c*-axis spin-wave dispersions observed for the intermediate temperature ($77\text{ K} < T < 116\text{ K}$) phase of YVO_3, where the *c*-axis lattice dimerization is vanishingly weak [17,20]. 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, the spin-orbital superexchange (SE) model was analyzed, and an "orbital-Peierls state" due to the formation of orbital singlet was proposed [7]. However, the spin system cannot be regarded as 1D while the orbital system is due to the destructive interference of the interchain exchange processes [6]. Furthermore, from this QOF picture it is hard to understand the observed large JT distortion and its clear temperature dependence [17]. It is therefore an interesting and challenging problem to judge the underlying physics here, especially by first-principles calculations.

In this Letter, we present firm evidence 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 local density approximation + Hubbard U (LDA + U) calculations in terms of the JT orbital. The "unexpected features" of a spin wave in YVO_3 [7], namely, (i) the splitting of the *c*-axis spin wave and (ii) $|J_c| > |J_{ab}|$ (J_c and J_{ab} are the *c* axis and *ab*-plane exchange couplings, respectively), can be naturally explained from a structural point of view. A similar picture is also predicted for $LaVO_3$. We further point out that the theoretical simplification to treat the system as quasi-1D lacks a firm base.

The calculations are done based on the LDA + U scheme [21] in the plane-wave pseudopotential method [22]. For such well-defined insulating systems with long range ordering, the LDA + U method typically can give reasonable results. The parameter [23] $U_{\text{eff}} = 3.0$ eV is used to reproduce the experimental band gaps properly [24]. In all of the discussions, we use the unit cell with $a \approx b \approx c/\sqrt{2}$, which includes 4 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, and z as the $[110]$, $[\bar{1}10]$, and $[001]$ directions of the unit cell. We performed ground state calculations for three structures, YVO_3 at 65 and 100 K and $LaVO_3$ at 10 K [16,17]. Four magnetic structures [i.e., ferromagnetic (FM) and *A*-, *C*-, and *G*-type AF states [19]] were calculated for each fixed experimental structure.

Let us start from the low temperature phase of YVO_3, which has *C*-type JT distortion [17]. As shown in Table I, among the four magnetic structures, the *G*-AF state is the most stable state, consistent with experimental observations and earlier calculations [9]. The obtained magnetic moment ($1.68\mu_B$) and band gap (1.2e V) are also in excellent agreement with experimental ones ($1.72\mu_B$ [7] and 1.2 eV [24]), demonstrating the validity of our approach. The stabilization of the *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 stabilizes the *C*-type orbital ordering (OO), where *yz*, *zx*, *yz*, *zx* orbital is occupied for 4 V sites (1, 2, 3, 4), respectively, and the *xy* orbital is occupied for all V sites. In this OO pattern, the 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 the *ab* plane: the FM one due to the nearly orthogonal *yz*, *zx* orbital arrangement and the AF one coming from the *xy* orbital. The net coupling will depend on the relative polarization of those orbitals. The calculated orbital occupation numbers (n_{xy}, n_{yz}, and n_{zx}) 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 the *xy* state. As a result, we would expect the AF exchange coupling both along the *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 YVO_3 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 $LaVO_3$. 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 E_g (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

$$\begin{aligned} J_c &= (1/4S^2)[E(F) - E(G) - E(A) + E(C)], \\ J_{ab} &= (1/8S^2)[E(F) - E(G) + E(A) - E(C)], \end{aligned} \tag{1}$$

where $S = 1$ is the moment. For YVO_3 at 65 K, we get $J_c = 7.8$ meV and $J_{ab} = 7.5$ meV, which is quite isotropic, as suggested by experiments [7], and can be reasonably compared with the experimental values, as shown in Table II. Up to this point, we show that the low temperature phase of YVO_3 can be well explained by the JT orbital physics.

For YVO_3 at 100 K, the experimental *G*-type JT distortion will stabilize the *G*-type OO, in which the *yz* and the *zx* orbitals are occupied alternatively (antiferro-orbital) along the *c* axis, instead of the ferro-orbital chain below 77 K. For the four magnetic states, we all obtained the *G*-type OO pattern. In such *G*-type OO states, the antiferro-orbital chain along *c* axis will favor FM coupling along the chain, while the exchange coupling in *ab* plane are basically the same as that of YVO_3 at 65 K, resulting in the experimental *C*-AF state (see Table I) [26]. Now the question is how to understand the unexpected features of the spin wave, which were argued to be the result of orbital dimer formation [7]. (i) The *c*-axis spin-

TABLE I. The calculated total energies E(meV/f.u.), magnetic moment $M(\mu_B/\text{site})$, and band gap E_g(eV) for various compounds in different magnetic states. For YVO_3 (100 K) and $LaVO_3$ (11 K), 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	45.9	27.2	12.8	**0.0**
YVO_3 (65 K)	M	1.75	1.72	1.70	**1.68**
	E_g	0.8	1.0	0.8	**1.2**
	E	16.7	27.6	**0.0**	19.1
YVO_3 (100 K)	M	1.75(1.77)	1.72(1.75)	**1.70(1.72)**	1.68(1.70)
	E_g	0.8	1.1	**1.2**	1.0
	E	38.3	42.0	**0.0**	23.5
$LaVO_3$ (10 K)	M	1.74(1.75)	1.72(1.72)	**1.70(1.71)**	1.69(1.70)
	E_g	0.7	1.0	**1.2**	0.9

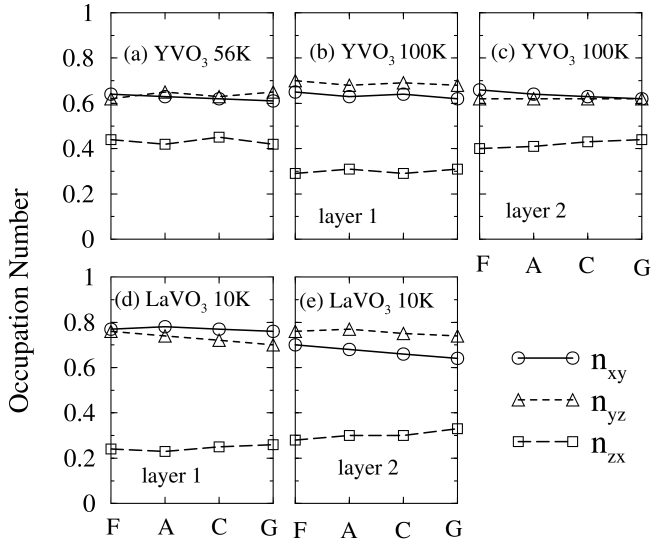

FIG. 1. The calculated t_{2g} orbital occupation numbers for different compounds as a function of different magnetic orderings. Since the OO patterns are fixed by the structures, only the occupations for one of the transition-metal sites are shown.

wave splits into two branches and open a gap; (ii) $|J_c| > |J_{ab}|$, while, according to GKR, FM SE (J_c in this case) is generally weaker than AF SE (J_{ab}). X-ray diffraction results [17] suggest 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 [20] suggest the possible lowering of the symmetry group to $Pb11$ or $P_{\bar{1}}$. However, this lowering will not violate our following discussions due to (i) the emergence of new phonons is one order or two orders weaker in intensity [20] compared with the main modes and (ii) the following arguments are common for all those possible symmetries. A characteristic point of the lattice structure of YVO$_3$ in the 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 the c direction, resulting in two inequivalent VO$_2$ layers, which have different amounts of JT distortion. As a result, we obtain two J_{ab} (0.8 and 5.3 meV) for two different layers [27], which stack along the c axis alternatively. This is in qualitative difference with the experimental analysis, in which they assumed alternative J_c but the 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 5 meV). 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 the ab plane will dramatically affect the spin-wave behavior along the 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.

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 ‡ point to Refs. [7,25], respectively.

		YVO$_3$ (65 K)	YVO$_3$ (100 K)	LaVO$_3$ (10 K)
Calculated	J_c	7.8	−7.2	−6.5
	J_{ab}	7.5	0.8(5.3)	5.8(7.7)
Experimental	J_c	5.7†	−2.0(−4.2)†	−4.0‡
	J_{ab}	5.7†	2.6†	6.5‡

The dramatic difference between two J_{ab} comes from different distortions of two layers. For YVO$_3$ at 100 K, the JT distortion is about 4% for one layer (say, layer 1), while it is about 2% for another layer (say, layer 2). Such a difference will modify the orbital polarization as shown in Figs. 1(b) and 1(c). The polarization between the yz and the zx orbitals for layer 1 is larger than that of layer 2, while the n_{xy} is almost same for the two layers. The larger polarization tends to enhance the FM coupling coming from the orthogonal yz and zx occupation in the ab plane, which will compensate the AF coupling from the xy orbital. Therefore, the net AF coupling is significant suppressed, from 5.3 meV for layer 2 to 0.8 meV for layer 1.

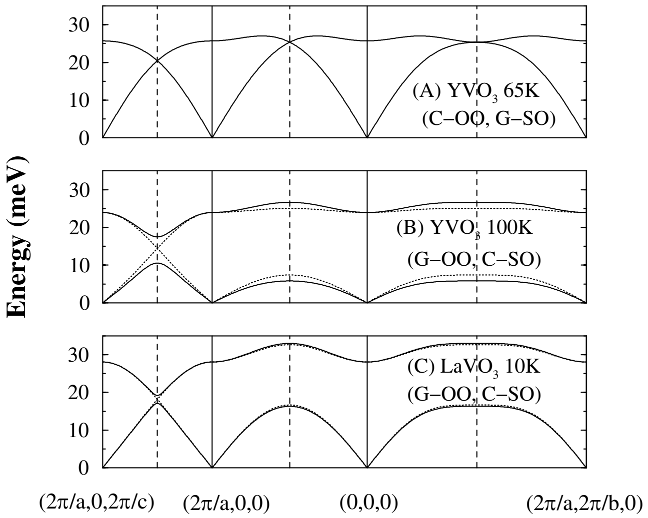

FIG. 2. The calculated spin-wave dispersions for various compounds in the Heisenberg model. Solid lines are results using calculated exchange coupling constants, while dotted lines are that using the single average of two J_{ab}.

This fact will also explain why $|J_c| > |J_{ab}|$ in this case and again suggests the crucial role of lattice distortions.

Because of the same symmetry, we obtain similar results for $LaVO_3$ at 10 K; 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 $1.3\mu_B$ [25]). 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 Tables I and II and Figs. 1 and 2). This prediction should be verified by future experiments.

Finally, we have two comments about the C-AF phase of YVO_3. First, the experimental moment (about $1.05\mu_B$) is much smaller than our calculated one ($1.70\mu_B$ 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 77 K is far from saturated. By extrapolating that intensity versus temperature data down to 0 K, we can easily get an 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° is argued from the experimental side [7], 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 the 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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[26] In the early calculations by Sawada *et al.* [9], the stable C-AF state of YVO_3 at intermediate temperature could not be predicted, in contradiction to our present results. This is due to the absence of the structural information presented in Ref. [17] for Sawada's calculations.

[27] To separate the contributions from different layers for the spin exchange interactions, two additional spin configurations, in which only one of the four spins is flipped, have been calculated.