One-Dimensional Confinement and Enhanced Jahn-Teller Instability in LaVO$_3$

Yukitoshi Motome$^1$, Hitoshi Sec$^{2,3}$, Zhong Fang$^1$, and Naoto Nagaosa$^{1,2,4}$

$^1$Tokura Spin SuperStructure Project (SSS), ERATO, Japan Science and Technology Corporation (JST), c/o National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 4, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8562, Japan

$^2$Correlated Electron Research Center (CERC), AIST, Tsukuba Central 4, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8562, Japan

$^3$Domestic Research Fellow, JST, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

$^4$Department of Applied Physics, University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

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Ordering and quantum fluctuations of orbital degrees of freedom are studied theoretically for LaVO$_3$ in spin-C-type antiferromagnetic state. The effective Hamiltonian for the orbital pseudospin shows strong one-dimensional anisotropy due to the negative interference among various exchange processes. This significantly enhances the instability toward lattice distortions for the realistic estimate of the Jahn-Teller coupling by first-principle LDA+$U$ calculations, instead of favoring the orbital singlet formation. This explains well the experimental results on the anisotropic optical spectra as well as the proximity of the two transition temperatures for spin and orbital orderings.

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Orbital degrees of freedom are playing key roles in magnetic and charge transport properties of transition metal oxides [1]. Especially it has been recognized that, in these strongly-correlated systems, spatial shapes of orbitals can give rise to an anisotropic electronic state even in the three-dimensional (3D) perovskite structure [2,3]. There the spin ordering (SO) and orbital ordering (OO) are determined self-consistently [4].

Perovskite vanadium oxides, AVO$_3$ (A is rare-earth element), are typical $t_{2g}$ electron systems which show this interplay between orbital and spin degrees of freedom [2,3,4]. Both magnetic and orbital transition temperatures, $T_N$ and $T_o$, respectively, change systematically according to the ionic radius of the A atom [5], which controls the bandwidth through the tilting of VO$_6$ octahedra. For smaller ionic radii (smaller bandwidth) such as A=Y, $T_o$ for OO of G-type (3D staggered) is much higher than $T_N$ for SO of C-type (rod-type) [5,6]. As the ionic radius increases (the bandwidth increases), $T_o$ decreases while $T_N$ increases, and finally they cross between A=Pr and Ce [7]. In LaVO$_3$, the SO occurs at $T_N \simeq 143K$ first, and at a few degrees below $T_N$ the OO takes place [8]. A remarkable aspect here is its proximity of $T_N$ and $T_o$, which is also observed for all the compounds with $T_N > T_o$, i.e., CeVO$_3$ [9] and La$_{1-x}$Sr$_x$VO$_3$ ($x < 0.17$) [10]. Therefore, in LaVO$_3$, the magnetic correlation appears to develop primarily and to induce the orbital transition immediately once the SO sets in.

Another interesting aspect of LaVO$_3$ is the large anisotropy in the electronic state, which has recently been explored by the optical spectra [11]. Figure 1 shows the temperature dependence of the spectral weights, $I_c$ along the c direction and $I_{ab}$ within the ab plane, which is obtained from the data in ref. [12]. Here we define the spectral weight as an integration of the optical conductivity up to the isosbestic (equal-absorption) point at 2.8eV, namely, $I_\mu = \frac{2\mu}{\hbar^2e^2} \int_0^{2.8eV} \sigma_\mu(\omega)d\omega \ (\mu = c \ or \ ab)$, where $m_0$ and $n$ are the free electron mass and the density of V atoms, respectively. The most striking feature is the temperature dependence. $I_c$ grows rapidly below $T_N$ while $I_{ab}$ is almost temperature independent. Therefore the temperature dependence is almost 1D although the ratio $I_c/I_{ab} \sim 2$ is not so large.

![Figure 1. Temperature dependence of the spectral weight in LaVO$_3$. Filled and open circles represent the data along the c axis $I_c$ and within the ab plane $I_{ab}$, respectively. The inset shows the optical conductivity. The solid curves denote the data along the c axis for $T = 10,14,293K$ from top to bottom, respectively. The data within the ab plane are almost temperature independent which are shown by the dashed curves.](image-url)

Compared with $e_g$ systems, the Jahn-Teller (JT) coupling in $t_{2g}$ systems is expected to be weak, and the quantum fluctuation and/or the singlet formation of the orbital degrees of freedom is a keen issue. Recently, Khalifullin et al. claimed that orbital singlet correlation along the c axis is the driving force to realize the ferromagnetic spin exchange in the C-type antiferromagnetic (AF) phase in LaVO$_3$ [13]. On the other hand, the C-type
SO state with the G-type OO has been obtained by the mean-field theory [13] and the first-principle calculation [10] which are justified for rather weakly-correlated cases and do not take account of quantum fluctuations seriously. There, the AF interactions within the \( ab \) plane concomitant with a single occupation of \( xy \) orbitals play a key role to stabilize the SO and OO. Hence, these two pictures are quite different. Since there are competing interactions with the orbital quantum nature, such as JT coupling and 3D orbital exchange couplings, it is highly nontrivial to what extent the quantum fluctuations are important under the realistic situations, nevertheless the quantitative study on this issue has been missing.

In this Letter, we study ordering and fluctuations of orbital degrees of freedom in the C-type AF phase in LaVO\(_3\). An effective orbital model including the JT and the relativistic spin-orbit couplings is derived using the parameters obtained by first-principle LDA+\( U \) calculations and the optical experiments. We show that the model exhibits a strong 1D anisotropy which explains well the experimental results for the optical spectra and the proximity of \( T_c \) to \( T_K \). It is concluded that the enhanced JT instability due to the 1D confinement dominates the orbital singlet formation in LaVO\(_3\).

Now we derive the effective orbital model. We start from the strong-coupling limit of the Hubbard model with three-fold orbital degeneracy for the \( \tau_2g \) orbitals [2]. The system contains two \( d \) electrons at each V atom which form the high-spin \( S = 1 \) state due to the Hund’s rule coupling. To focus on the orbital sector in this spin-orbital coupled Hamiltonian, we assume the C-type SO. This is a reasonable approximation because the spin \( S = 1 \) has less quantum nature compared to \( S = 1/2 \) and the C-type SO is obtained by the mean-field calculation [13] and the first-principle calculation [10] as mentioned above. At the same time, we assume that the \( xy \) orbital is singly occupied at each V atom, which drives the AF coupling in the \( ab \) plane [14,17]. Then the second electron goes to either \( yz \) or \( z\bar{x} \) orbital. We assign a pseudospin state \( \tau^z = \pm 1/2 \) for the occupancy of these two orbitals [14]. Finally, our total Hamiltonian is written as

\[
\mathcal{H} = \mathcal{H}_{\text{orb}} + \mathcal{H}_{\text{orb}} + \mathcal{H}_{\text{JT}} + \mathcal{H}_{LS},
\]

which strongly depends on the direction, for instance, \( t_{ij}^y = t_{ij}^x = t \) and otherwise zero in the \( c \) direction. From the analysis in ref. , the parameters are estimated as \( U \approx 2.25 eV \), \( U' \approx 1.93 eV \) and \( J_H \approx 0.16 eV \). The transfer integral \( t \) is set to be 0.12 eV based on the estimate of the bandwidth \( \approx 1 eV \) in first-principle calculations [16]. Then the orbital exchange interaction along the \( c \) axis is estimated as \( J_c \approx 33 meV \), while \( J_{ab} \approx 2 meV \). We set \( J_c = 1 \) as an energy unit in the following calculations.

Here we point out two important features in eqs. (1) and (3). One is that the exchange in the \( c \) direction is Heisenberg-type while that within the \( ab \) plane is Ising-type. From this, one might expect a strong quantum fluctuation in the \( c \) direction as pointed out in ref. . However, this quantum nature becomes relevant only when the JT coupling is negligibly small, and this is not the case in LaVO\(_3\) as discussed in the following. The other important feature is the large 1D anisotropy in the orbital exchange couplings. Note that the negative interference among different perturbation processes occurs in the in-plane coupling \( J_{ab} \) in eq. (4), which results in the ratio of the exchange couplings \( J_c/J_{ab} \approx 17 \).

The JT coupling in the subspace of \( \tau \) is given by

\[
\mathcal{H}_{\text{JT}} = \sum_i gQ_i \tau^z_i + \frac{1}{2} \sum_i Q^2_i,
\]

where \( Q_i \) is the JT phonon coordinate at site \( i \). We neglect the kinetic energy of phonons, namely, regard \( Q_i \) as a classical variable. It is crucial to estimate the coupling constant \( g \), and we have done the following first-principle calculation [17]. Assuming the tetragonal symmetry, we calculate the total energy as a function of the JT distortion as shown in Fig. 6. This gives the JT stabilization energy \( \approx 27 meV \), which approximately corresponds to \( E_{\text{JT}} \equiv g^2/8 \) in our model. Thus we obtain the estimate \( E_{\text{JT}} \approx 0.8 J_c \) (\( g \approx 2.6 \)), which is appreciable and cannot be neglected as in ref. .

The last term is the relativistic spin-orbit coupling, which may be important in the \( \tau_2g \) systems. We obtain the effective Hamiltonian by projecting the original form \( \mathcal{H}_{LS} = \sum_i \lambda \vec{L}_i \cdot \vec{S}_i \) to the subspace of \( \tau \) by using the experimental fact that the spins lie within the \( ab \) plane [16]. Here \( \vec{L}_i \) is the orbital angular momentum. Since \( L_x \) has matrix elements between \( xy \) and \( (yz, zx) \) in this case, the spin-orbit interaction is represented by \( \mathcal{H}_{LS} = \sum_i \zeta \tau^\zeta_i \), where \( \zeta \equiv \lambda^2/\Delta \) and \( \Delta \) is the energy separation between \( xy \) and \( (yz, zx) \) orbital levels. This indicates that the

\[
J_{ab}^\pm = \frac{2t^2}{3(U' - J_H)} + \frac{4t^2}{3(U' + 2J_H)} \pm \frac{t^2}{U + 2J_H} \pm \frac{t^2}{U},
\]

where \( U, U' \) and \( J_H \) are the intra-orbital, the inter-orbital Coulomb interaction and the Hund’s-rule coupling, respectively. Neglecting the small tilting of VO\(_6\) octahedra in LaVO\(_3\), the transfer integral \( t \) is taken to be diagonal which strongly depends on the direction, for instance, \( t_{ij}^y = t_{ij}^x = t \) and otherwise zero in the \( c \) direction. From the analysis in ref. , the parameters are estimated as \( U \approx 2.25 eV \), \( U' \approx 1.93 eV \) and \( J_H \approx 0.16 eV \). The transfer integral \( t \) is set to be 0.12 eV based on the estimate of the bandwidth \( \approx 1 eV \) in first-principle calculations [16]. Then the orbital exchange interaction along the \( c \) axis is estimated as \( J_c \approx 33 meV \), while \( J_{ab} \approx 2 meV \). We set \( J_c = 1 \) as an energy unit in the following calculations.

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spin-orbit coupling corresponds to the pseudo magnetic field along the z direction. Using $\lambda \sim 20$meV in V atom and the estimate of $\Delta \sim 1$eV in the band calculation [18], we estimate $\zeta \sim 0.4$meV$\sim 0.01J_c$. This is small enough to be neglected in the following calculations.

As shown in Fig. 3 (b), the ratio becomes larger than 20 for the realistic value of $\Delta_{dp}$ between the d and the oxygen p orbitals as the energy denominator. Since the huge anisotropy in temperature dependences is reproduced with the moderate anisotropy in the total weights, we believe that the orbital 1D confinement in our model plays a major role in the anisotropic electronic state in this material.
domain with the enhanced $J_c$. Note that the disorder of the spins should reduce the effective orbital exchange as easily shown in the spin-orbital coupled Hamiltonian. It is also well-known that 1D systems have an enhanced instability to lattice distortions compared with higher dimensions. Therefore, $T_{0}^{1D} = T_{0}$ under this 1D orbital confinement can be higher than $T_{0}^{3D}$ without the SO when the JT coupling governs the OO transitions. In real materials with $T_{0} > T_{N}$, $T_{0}^{3D}$ decreases as the bandwidth increases, which indicates the relevance of the JT coupling. (If the 3D orbital exchange couplings dominate, $T_{0}^{3D}$ should increase as $T_{N}$ does.) Then, when the inequality $T_{0}^{3D} < T_{N} < T_{0}^{1D}$ is satisfied, the OO transition with the JT lattice distortion should take place as soon as the SO grows and induces the 1D confinement in the orbital channel. In this scenario, comparing $T_{0}^{1D} \text{ with } T_{N}$, we can estimate the lower bound for the value of $g$ to realize this proximity of the transition temperatures. Our estimation for this lower bound from Fig. 4 is $g \sim 1$ which is consistent with the estimate in Fig. 3.

![Graph showing the transition temperature of the orbital ordering under the 1D confinement by the C-type AF spin order.](image)

**FIG. 4.** Transition temperature of the orbital ordering under the 1D confinement by the C-type AF spin order. For comparison, the experimental value of $T_{N}$ in LaVO$_3$ is shown by the dashed line. The gray curve shows the expected $T_{0}^{\text{exp}}$. See the text for details.

Let us discuss this proximity of $T_{N}$ and $T_{0}^{\text{exp}}$ by the Ginzburg-Landau type argument. In this spin-orbital coupled system, we have the term in which the SO parameter $M$ and the OO one $O$ are coupled as $(a(T) - bM^2)O^2$. Here $a(T)$ is the coefficient for the second-order term for OO without SO which is given by $a(T) = a'(T - T_{0}^{3D})$. Our results indicate the relation $a(T) - bM_{\text{sat}}^2 = a'(T - T_{0}^{1D})$, where $M_{\text{sat}}$ is the saturated magnetic moment. $T_{0}^{\text{exp}}$ is given by solving the equation $a(T_{0}^{\text{exp}}) - bM_{\text{sat}}^2 = 0$. Assuming $M(T) = M_{\text{sat}}\sqrt{(T_{N} - T)/(T_{N} - T_{0}^{\text{exp}})}$ for simplicity, the difference between $T_{N}$ and $T_{0}^{\text{exp}}$ is given by $\delta T/T_{N} \approx (T_{N} - T_{0}^{\text{exp}})/T_{N} = (T_{N} - T_{0}^{1D})/(T_{N} + \Delta T)$, where $\Delta T = T_{0}^{1D} - T_{0}^{3D}$. Considering the systematic changes of $T_{N}$ and $T_{0}$ for A-site ions $^{11}$, we expect that $T_{0}^{3D}$ is slightly lower than $T_{N}$ in LaVO$_3$ and CeVO$_3$. Assuming $T_{0}^{3D} = 0.87T_{N}$, we plot the expected $T_{0}^{\text{exp}}$ in Fig. 4 as the gray curve. For the realistic value of $g$, we have $T_{0}^{\text{exp}}$ quite close to $T_{N}$ as observed in these compounds.

To summarize, we have investigated the role of orbitals to understand the electronic state in LaVO$_3$. We have derived the effective orbital model with strong one-dimensional anisotropy assuming the C-type spin ordering. We conclude that with the realistic Jahn-Teller coupling, the orbital 1D confinement leads to an enhanced instability toward lattice distortions suppressing the orbital quantum nature. This gives a comprehensive description of the anisotropy in the optical spectra and the proximity of the critical temperatures of magnetic and orbital transitions.

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