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In many transition-metal compounds the orbital degrees of freedom play a decisive role in determining the ground-state properties of materials such as manganites, titanates, or vanadates.1 When contributions of the orbital moment state properties of materials such as manganites, titanates, and superexchange interactions.10–13

In tetragonal $\text{Sr}_2\text{VO}_4$ with space group $I_4/mmm$, the octahedrally coordinated $\text{V}^{4+}$ ions occupy a square lattice in the $ab$ plane (see Fig. 1). The magnetic ground state has been claimed to be antiferromagnetic with transition temperatures in the range 10–100 K determined from susceptibility measurements, but long-range order has remained evasive on the basis of neutron-diffraction studies.14,16,17 Recent studies have established the occurrence of a magnetostructural phase transition extending over a temperature range from 94 K to 122 K. Both the high-temperature and the low-temperature structure are tetragonal and reportedly coexist within this range.13 Specific heat data have revealed two distinct broad maxima occurring at 98 K and 127 K mirroring the borders of the two-phase regime.18,19

The disappearance of the high-temperature phase is accompanied by a significant drop in the susceptibility at about 100 K, which has been attributed to the onset of long-range antiferromagnetic (AFM) and orbital order.11 Theoretically, the ground state of $\text{Sr}_2\text{VO}_4$ has been interpreted in terms of stripelike orbital and collinear AFM spin order10 or an ordering of magnetic octupoles.12 Inelastic neutron scattering has revealed two excitations at about 120 meV, which have been assigned to the highest lying doublet of the $\text{V}^{4+}$ $t_{2g}$ levels.13 Recent optical experiments have reported excitations at 31 meV (visible for $T > 80$ K) and 36 meV (visible for $T < 120$ K) and a two-peak structure at 100 meV and 108 meV, which remains visible from 13 K to room temperature.19

To elucidate the nature of the ground state and to understand the observed excitation spectrum we consider the effects of spin-orbit coupling, crystal field, and superexchange on the energy levels of the vanadium ions. The resulting free energy points toward a novel alternating spin-orbital order in the ground state.

To describe the system of $\text{V}^{4+}$ ions we use the Hamiltonian $H = H_{\text{ex}} + H_{\text{eff}}$, where $H_{\text{ex}}$ describes the exchange coupling of neighboring ions and $H_{\text{eff}}$ contains the single-ion contributions in a tetragonal crystal field:

$$H_{\text{ex}} = D[3l^2 - l(l + 1)] + \lambda_x l_x s_z + \lambda_{ab} (l_x s_y + l_y s_x).$$  (1)

Here $D$ denotes the single-ion anisotropy and $l$ the effective angular momentum $l = 1$ of the $t_{2g}$ orbitals, which we describe using $|1\rangle = -\frac{1}{\sqrt{2}}[d_{yz} + i d_{zx}], |0\rangle = -\frac{1}{\sqrt{2}}[d_{yz} - i d_{zx}]$, and $|0\rangle = d_{xy}$ as a basis.2 Moreover, we use anisotropic spin-orbit coupling constants $\lambda_x$ and $\lambda_{ab}$ parallel and perpendicular to the $c$ direction. Anisotropic spin-orbit coupling can arise due to covalency effects and has been observed in several $d^1$ systems in octahedral environment.2,20 The superexchange coupling between $\text{V}$ ions via oxygen ions in the $ab$ plane is usually described via the corresponding hopping integrals,21 which in our case are given by

$$t_{1,0} = t_{xy,xz},$$  (4)

From the spatial distributions of the $d_{xz}$ and $d_{yz}$ orbitals it is clear that the signs of the transfer integrals $t_{xz,xz}$ and $t_{yz,yz}$ are different and, therefore, $|t_{1,0}| > |t_{1,1}|$. This observation allows us to deduce the most likely ordering of the $\text{V}$ states in the ground state.

Using the reported crystal structure of $\text{Sr}_2\text{VO}_4$ one finds that $D < 0$ and, therefore, the possible ground states of the $\text{V}^{4+}$...
ions are \(\pm 1/2\). The AFM superexchange coupling \(J_{\text{AF}}\) (see below) yields an additional gain in energy when \(-1, \pm 1/2\) states are surrounded by \(1, \mp 1/2\), or vice versa. Then, keeping in mind that the spin-orbit coupling parameter \(\lambda_c < 0\), we arrive at a configuration in the \(ab\) plane of Sr2VO4 where each vanadium ion in the state \(\pm 1/2\) is surrounded by vanadium ions in the \(-1, -1/2\) state and vice versa. According to the third Hund rule, spin \((s_c = \pm 1/2)\) and angular \((l_c = \mp 1)\) momentum of the \(V^{\pm 1}\) ground state configuration are in opposition. The corresponding combined spin-angular moment per site therefore possesses the peculiarity that the magnetic moment \(m_c/\mu_B = 2s_c - kl_c\) is almost completely muted, when the the covalency reduction factor \(\kappa\) is close to 1.2 The resulting ordering scheme can be described as an alternating order of spin and orbital moments on each site.

First, we introduce the superexchange parameters

\[
J_u = 4\frac{t_{x,z}^2 + t_{y,z}^2}{U},
J_{\text{int}} = -8\frac{t_{x,z}t_{y,z}}{U},
\]

where \(U\) denotes the on-site Coulomb repulsion. The signs of the transfer integrals \(t_{x,z,z}\) and \(t_{x,z,y}\) are different and, therefore, the cross term \(J_{\text{int}}\) is positive. This parameter describes the quantum interference effect in superexchange coupling. The part of the effective exchange Hamiltonian containing these parameters is written as

\[
H_{\text{ex}}(1) = \frac{J_u}{8} \left( \langle s_s s_j \rangle - \frac{1}{4} \right) \left( 2l_{x,z}^2l_{y,z}^2 + l_{x,y}^2l_{y,z}^2 + l_{x,y}^2l_{y,z}^2 \right) - \frac{J_{\text{int}}}{4} \left( \langle s_s s_j \rangle - \frac{1}{4} \right) l_{x,z}l_{y,z}.
\]

The ferromagnetic contributions to the superexchange interaction comprise two exchange integrals \(J_f\) and \(J'_f\), which for a pair of V ions along the \(x\) axis can be denoted as

\[
J_f = J_p - 2\frac{J_f}{U^2} (t_{x,y} + t_{y,z})
\]

\[
J'_f = J'_p - 2\frac{J_f}{U^2} (t_{y,z}),
\]

with

\[
I_f = \langle d_{s,y}, d_{z,l} \rangle \frac{e^2}{r_{12}} |d_{z,s}, d_{x,y} |.
\]

Here \(I_f\) is an exchange integral, which can be estimated via Racah parameters as \(3B + C = 0.9\) eV and \(J_p\) and \(J'_p\) correspond to potential exchange contributions. In Eq. (9) the potential exchange parameter \(J'_p\) is expected to be small and is neglected in the following. Note that \(J'_f\) is called the Hund’s coupling parameter in Ref. 12.

In momentum representation for \(l = 1\) and \(s = 1/2\), this part of the exchange Hamiltonian is written as

\[
H_{\text{ex}}(2) = \frac{3}{4} \left( s_s s_j + \frac{1}{4} \right) \left( J_f(-2 + l_{x,z}^2 + l_{x,y}^2 + l_{x,y}^2 + l_{x,y}^2) + J'_f(l_{x,y}^2 - 2l_{x,y}^2) \right).
\]

The effective Hamiltonian for a pair along the \(y\) axis can be obtained by a permutation of indices \(x \rightarrow y\) and \(y \rightarrow x\). For a detailed discussion of the differences in spin-dependent factors of ferromagnetic and AFM exchange terms we refer to Ref. 22. Let us consider now a two-sublattice configuration in which each V ion of sublattice \(i\) is described by the wave function \(|\psi_i\rangle = \cos \theta / 2 |1, 1/2\rangle + \sin \theta / 2 |1, -1/2\rangle\) with \(\theta = \vartheta\), and is surrounded by four V ions of sublattice \(j\) with \(\vartheta = \vartheta^\prime\). Using the effective exchange operator \(H_{\text{ex}} = \sum_i (H_{\text{ex}}(1) + H_{\text{ex}}(2) + H_{\text{ex}}(3) + H_{\text{ex}}(4))\) and assuming that only the ground states of the surrounding V ions are populated, we arrive at the following energy spectrum of the vanadium ions:

\[
\varepsilon_{1,2} = D + \frac{\lambda_c}{2} - \frac{J_u + J_{\text{int}}}{4} + \frac{3J_f}{4},
\]

\[
\pm \frac{1}{4} (J_u + J_{\text{int}} + 2J'_f) u^2 + (J_u - J'_f)^2 v^2 + \frac{3}{4} J'_f u^2 v^2.
\]

\[
\varepsilon_{3,4} = -\frac{D}{2} - \frac{\lambda_c}{4} + \frac{J_u - J_{\text{int}}}{8} (u - 1) + \frac{J_f}{4} (3 - u) + \frac{3J'_f}{2},
\]

\[
\pm \frac{1}{4} \left( 3D - \frac{\lambda_c}{2} - \frac{J_u - J_{\text{int}}}{4} (u - 1) - \frac{J_f}{2} (3 - u) + \frac{3J'_f}{2} \right),
\]

\[
\varepsilon_{5,6} = \frac{D}{2} - \frac{\lambda_c}{4} + \frac{J_u - J_{\text{int}}}{8} (u + 1) + \frac{J_f}{4} (3 + u) + \frac{3J'_f}{2},
\]

\[
\pm \frac{1}{4} \left( 3D - \frac{\lambda_c}{2} - \frac{J_u - J_{\text{int}}}{4} (u + 1) + \frac{J_f}{2} (3 + u) + \frac{3J'_f}{2} \right),
\]

Here we have introduced \(u = \cos \vartheta\) and \(v = \sin \vartheta\). From the expressions for \(\varepsilon_{3,4}\) and \(\varepsilon_{5,6}\) one finds that at \(\vartheta = \pm \pi/2\) the excited states are degenerate doublets, i.e., \(\varepsilon_3 = \varepsilon_5\) and \(\varepsilon_4 = \varepsilon_6\). However, this choice of \(\vartheta = \pm \pi/2\) cannot explain the
observed splitting of the highest-lying doublet $\epsilon_{d,6}$ which was observed by neutron scattering and optical spectroscopy.\textsuperscript{13,19}

Now let us turn to the ground state $\epsilon_1$. A minimum in energy of this level will occur at $\vartheta = \pm \pi/2$ only if $3|J_f| > |J_{int}|$. If $|J_{int}| > 3|J_f|$ the minimum will occur at $\vartheta = 0$ or $\vartheta = \pi$. At these angles the excited states are split due to the exchange-molecular field in agreement with experiment.\textsuperscript{13}

Using the experimentally observed splitting\textsuperscript{13} of the highest doublet of about 10 meV we estimate the value $|J_f + J'_f| \simeq 10$ meV. Following Imai and co-workers the energy cost for moving a 3d electron between V ions in Sr$_2$VO$_4$ is about $U \simeq 11$ eV and the effective transfer integrals $t_{1x,1z} \simeq -0.2$ eV and $t_{2x,1z} \simeq 0.05$ meV.\textsuperscript{10} Therefore, we estimate $J_a \simeq 15$ meV, $J_{int} \simeq 7.5$ meV, $J'_f = -(3B + C)/2U \approx J_a \simeq -0.7$ meV, and $J_f \simeq -9.3$ meV. The values $D = -33$ meV, $\lambda_c = -30$ meV, and $\lambda_{ab} = -28$ meV are in agreement with conventional estimates.\textsuperscript{2,12} Using these values we plot the energy levels as $\epsilon_1(\vartheta) - \epsilon_i(\vartheta = 0, \pi)$ in Fig. 2(a) as a function of the orbital-mixing angle $\vartheta$. Note that $\epsilon_1(\vartheta)$ is not constant but becomes minimal for $\vartheta = 0$ and $\pi$. The estimated excitation energies $\epsilon_4 - \epsilon_1 = 121$ meV, $\epsilon_6 - \epsilon_1 = 111$ meV, and $\epsilon_3 - \epsilon_1 = 36$ meV for $\vartheta = 0$ (or corresponding values for $\vartheta = \pi$) are in agreement with the transitions observed by optical (dash-dotted lines) and neutron scattering experiments (dashed lines) at low temperatures shown in Fig. 2(a).\textsuperscript{13,19}

In Fig. 2(b) we compare the free energy per vanadium site at 10 K and 100 K (close to $T_N$) as a function of the parameter $\vartheta$ using the values for the exchange constants estimated above:

$$F(T, \vartheta) = -k_B T \ln \sum \exp \left( \frac{\epsilon_i(\vartheta)}{k_B T} \right). \quad (14)$$

There is a minimum at $\vartheta = 0$ and $\vartheta = \pm \pi$ in both cases and the energy difference with respect to $\vartheta = \pm \pi/2$ decreases from 1.5 to 0.5 meV, respectively. Hence, one can anticipate that with increasing temperature considerable fluctuations of $\vartheta$ can be expected. We estimate these fluctuations by $\Delta \vartheta^2 = k_B T (\partial^2 F/\partial \vartheta^2)^{-1} \simeq (\pi/5)^2$ and $(\pi/3)^2$ for 10 K and 100 K, respectively. Certainly, the proposed spin-orbital ordered state as depicted in Fig. 3 will be destabilized at high temperatures. However, the splitting of the highest-lying doublet remains almost unchanged across the Neel temperature,\textsuperscript{13} and it is reasonable to expect the exchange splitting of $\epsilon_{3,5}$ to survive as well, even though the exchange parameters might be somewhat reduced. We would like to mention that the value $\epsilon_5 - \epsilon_1 = 31$ meV corresponds nicely to the optical excitation observed for $T > 80$ K, but given the strong fluctuations expected for this temperature range the interval $(\epsilon_3 + \epsilon_5)/2 - (\epsilon_2 + \epsilon_1)/2 \sim 29$ meV might provide a more suitable estimation of the high-temperature optical excitation.

In summary, we calculated the level scheme for the energy levels of the vanadium ions and proposed an alternating spin-orbital ordering with almost muted magnetic moment as the ground state for Sr$_2$VO$_4$. The proposed scenario and parameter values allow one to obtain a consistent picture of the low-temperature excitation spectrum of Sr$_2$VO$_4$, which was recently reported by neutron and optical experiments.

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23. Note that the orbital mixing angle $\theta$ used in our approach is different from the notation introduced in Ref. 12.