Alternating spin-orbital order in tetragonal \( \text{Sr}_2\text{VO}_4 \)

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Considering spin-orbit coupling, the tetragonal crystal-field, and all relevant superexchange processes including quantum interference, we derive expressions for the energy levels of the vanadium ions in tetragonal \( \text{Sr}_2\text{VO}_4 \). The used parameters of the model Hamiltonian allow to describe well the excitation spectra observed in neutron scattering and optical experiments at low temperatures. The free energy exhibits a minimum which corresponds to a novel alternating spin-orbital order with strong thermal fluctuation of the orbital mixing parameter.

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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. When contributions of the orbital moment and spin-orbit coupling are not negligible a separation between spin and orbital degrees of freedom is not adequate anymore and the system is better described by an effective total angular momentum. Spin-orbit coupling competes with electron-phonon or exchange interactions even strong fluctuation regimes can arise.

The system investigated here is the layered insulator \( \text{Sr}_2\text{VO}_4 \) with tetragonal symmetry, which early or has come into focus as an isostructural \( d^4 \) analogue of \( \text{La}_2\text{CuO}_4 \). Consequently, it was suggested that \( \text{Sr}_2\text{VO}_4 \) could become superconducting upon applying chemical pressure by doping or external pressure. While the system could not be driven towards superconductivity, it turned out to be a model system for studying the interplay of orbital-lattice, spin-orbital and superexchange interactions.

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 remained elusive on the basis of neutron-diffraction studies. Recent studies established the occurrence of a magneto-structural phase transition extending over a temperature range from 94 - 122 K. Both the high-temperature and the low-temperature structure are tetragonal and reportedly coexist within this range. Specific heat data revealed two distinct broad maxima occurring at 98 and 127 K mirroring the borders of the two-phase regime.

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 AFM and orbital order. Theoretically, the ground state of \( \text{Sr}_2\text{VO}_4 \) has been interpreted in terms of stripe-like orbital and collinear AFM spin order or an ordering of magnetic octupoles. Inelastic neutron scattering revealed two excitations at about 120 meV, which were assigned to the highest lying doublet of the \( \text{V}^{4+} \) levels due the tetragonal crystal field and spin-orbit coupling.

![FIG. 1. Left: Unit cell of tetragonal \( \text{Sr}_2\text{VO}_4 \) with symmetry \( I_4/mmm \) (Ref. 13) highlighting the \( \text{VO}_2 \) planes and the octahedral coordination of the V ions. Right: Splitting of the \( \text{V}^{4+} \) levels due the tetragonal crystal field and spin-orbit coupling.](image-url)
tonian $H = H_{si} + H_{ex}$ where $H_{si}$ describes the exchange coupling of neighbouring ions and $H_{si}$ contains the single-ion contributions in a tetragonal crystal field:

$$H_{si} = D[3l^2 - l(l + 1)] + \lambda_c l_z s_z + \frac{\lambda_{a,b}}{2} (l_+ s_+ + l_- s_-)$$  \hspace{0.5cm} (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 $|1\rangle = -\frac{1}{\sqrt{2}} [d_{yz} + id_{x^2 - y^2}]$, $|-1\rangle = \frac{1}{\sqrt{2}} [d_{yz} - id_{x^2 - y^2}]$, and $|0\rangle = d_{xy}$ as a basis. Moreover, we use anisotropic spin-orbit coupling constants $\lambda_c$ and $\lambda_{a,b}$ parallel and perpendicular to the $c$-direction. Anisotropic spin-orbit coupling can arise due to covalency effects and has been observed in several $d^3$ systems in octahedral environments.

The superexchange coupling between $V$ ions via oxygen ions in the $ab$ plane is usually described via the corresponding hopping integrals, which in our case are given by:

$$t_{1,1} = t_{-1,-1} = \frac{1}{2} (t_{xz,zz} + t_{yz,yz}) \hspace{0.5cm} (2)$$

$$t_{1,-1} = t_{-1,1} = \frac{1}{2} (t_{xz,zz} - t_{yz,yz}) \hspace{0.5cm} (3)$$

$$t_{0,0} = t_{xy,xy} \hspace{0.5cm} (4)$$

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

Using the reported crystal structure of Sr$_2$VO$_4$ one finds that $D < 0$, and, therefore, the possible ground states of the $V^{4+}$ ions are $|\pm 1, \pm 1/2\rangle$. The antiferromagnetically superexchange coupling (see below) will yield an additional gain in energy when $|\pm 1, \pm 1/2\rangle$-states are surrounded by $|1, \mp 1/2\rangle$, or vice versa. Then, keeping in mind that the spin-orbit coupling parameters $\lambda_c < 0$, we arrive at a configuration in the $ab$ plane of Sr$_2$VO$_4$ where each vanadium ion in the state $|1,1/2\rangle$ is surrounded by vanadium ions in the $|-1,-1/2\rangle$ state and vice versa. According to the third Hund rule, spin $(s_z = \pm 1/2)$ and angular $(l_z = \mp 1)$ momentum of the $V^{4+}$ ground state configuration are in opposition. The corresponding combined spin-angular moment per site therefore possesses the peculiarity that the magnetic moment $m_{sz} = 2s_z - kl_z$ is almost completely muted, when the the covalency reduction factor $\kappa$ is close to one.

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

$$J_a = 4t_{xz,zz}^2 + t_{yz,yz}^2$$  \hspace{0.5cm} (5)$$

$$J_{int} = -8 \frac{t_{xz,zz}t_{yz,yz}}{U},$$  \hspace{0.5cm} (6)

where $U$ denotes the onsite Coulomb repulsion. The signs of the transfer integrals $t_{xz,zz}$ and $t_{yz,yz}$ are different and, therefore, the cross term $J_{int}$ 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

$$H_{ex} = \frac{J_a}{8} (s_is_j - \frac{1}{4}) (2l_{z}^2 + 2l_{+}^2 + 2l_{-}^2) - \frac{J_{int}}{4} (s_is_j - \frac{1}{4}) l_z l_{jz}.$$  \hspace{0.5cm} (7)

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

$$J_f = J_p - \frac{2}{U} \left( t_{xy,xy}^2 + t_{xz,zz}^2 \right)$$  \hspace{0.5cm} and \hspace{0.5cm} (8)$$

$$J_f' = J_p' - \frac{2}{U} \left( t_{xz,zz}^2 \right)$$  \hspace{0.5cm} with \hspace{0.5cm} (9)$$

$$I_f = \langle d_{xy}, d_{xz} \rangle \frac{e^2}{r_{12}^3} |d_{xz}, d_{xy}|.$$  \hspace{0.5cm} (10)

Here $I_f$ is an exchange integral, which can be estimated via Racah parameters as $3B + C = 0.9$ eV and $J_{p}, J_{p}'$ correspond to potential exchange contributions. In Eq. (4) the potential exchange parameter $J_{p}'$ is expected to be

\[\text{FIG. 2. (a) Calculated energy levels as a function of the orbital mixing angle } \vartheta \text{ using Eqs. (13)-(15) and parameters } \lambda_c = -30 \text{ meV, } \lambda_{ab} = -28 \text{ meV, } D = -33 \text{ meV, } J_a = -9.3 \text{ meV, } J_f = -0.7 \text{ meV, and } J_{int} = 7.5 \text{ meV. Excitation energies observed by neutron scattering (Ref. 13) and optical spectroscopy (Ref. 16) are shown as dashed and dash-dotted lines, respectively. (b) Free energy as a function of } \vartheta \text{ calculated with the same parameters 10 and 100 K.}\]
The effective Hamiltonian for a pair along the $y$-axis can be obtained by a permutation of indices $x \rightarrow y$, $y \rightarrow x$. For a detailed discussion of the differences in spin dependent factors of ferro- and antiferromagnetic exchange terms we refer to Ref. [24]. Let us consider now a two-sublattice configuration in which each V ion of sublattice $i$ is described by the wave function $|\vartheta\rangle = \cos \vartheta/2|1,1/2\rangle + \sin \vartheta/2| -1,-1/2\rangle$ with $\vartheta = \vartheta_j$ is surrounded by four V ions of sublattice $j$ with $\vartheta = \vartheta_j$ [23].

Using the effective exchange operator $H_{ex} = \sum [H_{ex}(1) + H_{ex}(2x) + H_{ex}(2y)]$ and assuming that only the ground states of surrounding V ions are populated we arrive at the following energy spectrum of the vanadium ions:

$$H_{ex}(2x) = \left( s_i s_j + \frac{3}{4} \right) \left[ J_f ( -2 + l_i^2 + l_j^2 + l_i^2 l_j^2 + l_i^2 l_j^2 ) + J'_f ( l_i^2 + l_j^2 - 2l_i^2 l_j^2 ) \right]$$

(10)

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$$\varepsilon_{1,2} = D + \frac{\lambda_c}{2} \frac{J_a + J_{int}}{4} + \frac{3J_f}{2} + \frac{1}{4} \left[ (J_a + J_{int} + 2J'_f)u^2 + (J_a - J'_f)^2v^2 \right]^{1/2}$$

(11)

$$\varepsilon_{3,4} = D - \frac{\lambda_c}{4} \frac{J_a - J_{int}}{8} (u - 1) + \frac{J_f}{4} (3 - u) + \frac{3J'_f}{2} \pm \frac{1}{2} \left[ \left( 3D - \frac{\lambda_c}{2} \frac{J_a - J_{int}}{4} (u - 1) - \frac{J_f}{2} (3 - u) \right)^2 + 2\lambda_{ab}^2 \right]^{1/2}$$

(12)

$$\varepsilon_{5,6} = D - \frac{\lambda_c}{4} \frac{J_a - J_{int}}{8} (u + 1) + \frac{J_f}{4} (3 + u) + \frac{3J'_f}{2} \pm \frac{1}{2} \left[ \left( 3D - \frac{\lambda_c}{2} \frac{J_a - J_{int}}{4} (u + 1) - \frac{J_f}{2} (3 + u) \right)^2 + 2\lambda_{ab}^2 \right]^{1/2}$$

(13)

Here we have introduced $u = \cos \vartheta_j$ and $v = \sin \vartheta_j$. 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 $\varepsilon_{4,6}$ which was observed by neutron scattering and optical spectroscopy [13,19].

Now let us turn to the ground state $\varepsilon_1$. 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 [23]. Using the experimentally observed splitting [13] of the highest doublet of about 10 meV we estimate the value $|J_f + J'_f| \simeq 10$ meV. Following Imai and coworkers the energy cost for moving a 3d-electron between V ions in Sr$_2$VO$_4$ is about $U \approx 11$ eV and the effective transfer integrals $t_{xx,zz} \simeq -0.2$ eV and $t_{yz,yz} \simeq 0.05$ meV [20]. Therefore, we estimate $J_a \simeq 15$ meV, $J_{int} \simeq 7.5$ meV, $J'_f = -(3B + C)/2U * J_a \simeq -0.7$ 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 [24]. Using these values we plot the energy levels as $\varepsilon_1(\vartheta) - \varepsilon_1(\vartheta = 0, \pi)$ in Fig. 2a) as a function of the orbital-mixing angle $\vartheta$. Note that $\varepsilon_1(\vartheta)$ is not constant but becomes minimal for $\vartheta = 0, \pi$. The estimated excitation energies $\varepsilon_4 - \varepsilon_1 = 121$ meV, $\varepsilon_6 - \varepsilon_1 = 111$ meV, and $\varepsilon_3 - \varepsilon_1 = 36$ 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. 2a) [13,19].

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

$$F(T, \vartheta) = -k_B T \ln \sum \exp \left( -\frac{\varepsilon_i(\vartheta)}{k_B T} \right)$$

(14)
one can anticipate that with increasing temperature decreases from 1.5 meV to 0.5 meV, respectively. Hence, these fluctuations by \( \vartheta \) and the energy difference with respect to the splitting of the highest-lying doublet remains almost unchanged across the Neel temperature and it is reasonable to expect the exchange splitting of \( \varepsilon_{3,5} \) to survive as well, even though the exchange parameters might be somewhat reduced. We would like to mention that the value \( \varepsilon_5 - \varepsilon_1 = 31 \text{ meV} \) corresponds nicely to the optical excitation observed for \( T > 80 \text{ K} \), but given the strong fluctuations expected for this temperature range the interval \( (\varepsilon_3 + \varepsilon_5)/2 - (\varepsilon_2 + \varepsilon_1)/2 \sim 29 \text{ meV} \) 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 propose an alternating spin-orbital ordering with almost muted magnetic moment as the ground state for \( \text{Sr}_2\text{VO}_4 \). The proposed scenario and parameter values allow to obtain a consistent picture of the low-temperature excitation spectrum of \( \text{Sr}_2\text{VO}_4 \), which was recently reported by neutron and optical experiments.

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