Alternating spin-orbital order in tetragonal Sr_2VO_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 Sr_2VO_4. The used parameters of the model Hamiltonian allow us 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.[1] 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.[2,3] If spin-orbit coupling competes with electron-phonon or exchange interactions even strong fluctuation regimes can arise.[4–6]

The system investigated here is the layered insulator Sr_2VO_4 with tetragonal symmetry, which early on has come into focus as an isostructural d^1 analog of La_2CuO_4.[7] Consequently, it was suggested that Sr_2VO_4 could become superconducting upon applying chemical pressure by doping or external pressure.[8,9] While the system could not be driven toward superconductivity, it turned out to be a model system for studying the interplay of orbital-lattice, spin-orbital, and superexchange interactions.[10–13]

In tetragonal Sr_2VO_4 with space group I_4/mmm,[14,15] the octahedrally coordinated 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.[11] 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 Sr_2VO_4 has been interpreted in terms of stripelike orbital and collinear AFM spin order[10] 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 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 V^{4+} ions we use the Hamiltonian $H = H_{si} + H_{ex}$, where H_{ex} describes the exchange coupling of neighboring ions and H_{si} contains the single-ion contributions in a tetragonal crystal field:

$$H_{si} = D\left[3l_z^2 - l(l+1)\right] + \lambda_c l_z s_z + \frac{\lambda_{a,b}}{2}(l_- s_+ + l_+ s_-). \quad (1)$$

Here D denotes the single-ion anisotropy and l the effective angular momentum $l = 1$ of the t_{2g} orbitals, which we describe using $|1\rangle = -\frac{1}{\sqrt{2}}[d_{yz} + i d_{xz}]$, $|-1\rangle = \frac{1}{\sqrt{2}}[d_{yz} - i d_{xz}]$, and $|0\rangle = d_{xy}$ as a basis.[2] Moreover, we use anisotropic spin-orbit coupling constants λ_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^1 systems in octahedral environment.[2,20]

The superexchange coupling between 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

$$t_{1,1} = t_{-1,-1} = \tfrac{1}{2}(t_{xz,xz} + t_{yz,yz}), \quad (2)$$

$$t_{1,-1} = t_{-1,1} = \tfrac{1}{2}(t_{xz,xz} - t_{yz,yz}), \quad (3)$$

$$t_{0,0} = t_{xy,xy}. \quad (4)$$

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, $|t_{1,-1}| > |t_{1,1}|$. This observation allows us to deduce the most likely ordering of the V states in the ground state.

Using the reported crystal structure of Sr_2VO_4 one finds that $D < 0$ and, therefore, the possible ground states of the V^{4+}

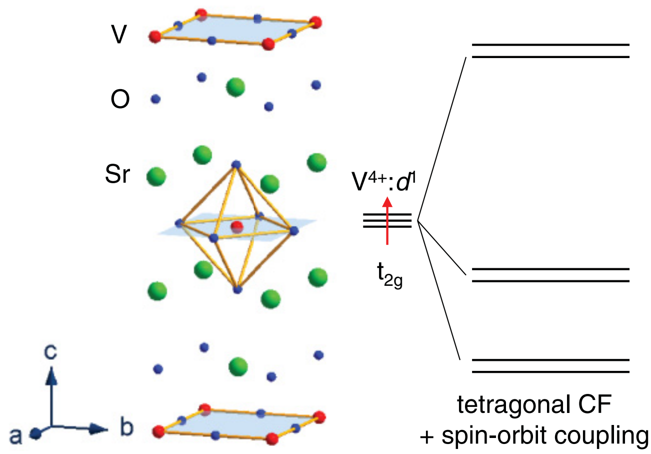

FIG. 1. (Color online) Left: Unit cell of tetragonal Sr_2VO_4 with symmetry *I4/mmm* (Ref. 15) highlighting the VO_2 planes and the octahedral coordination of the V ions. Right: Splitting of the V^{4+} t_{2g} levels due the tetragonal crystal field and spin-orbit coupling.

ions are $|\pm1,\pm1/2\rangle$. The AFM superexchange coupling (see below) yields an additional gain in energy when $|-1,\pm1/2\rangle$ states are surrounded by $|1,\mp1/2\rangle$, 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 Sr_2VO_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 ($s_z = \pm1/2$) and angular ($l_z = \mp1$) 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 $m_z/\mu_B = 2s_z - \kappa l_z$ is almost completely muted, when the the covalency reduction factor κ 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

$$J_a = 4\frac{t_{xz,xz}^2 + t_{yz,yz}^2}{U}, \tag{5}$$

$$J_{\rm int} = -8\frac{t_{xz,xz}t_{yz,yz}}{U}, \tag{6}$$

where U denotes the on-site Coulomb repulsion. The signs of the transfer integrals $t_{xz,xz}$ and $t_{yz,yz}$ are different and, therefore, the cross term $J_{\rm int}$ 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

$$H_{ex}(1) = \frac{J_a}{8}\left(\mathbf{s}_i\mathbf{s}_j - \frac{1}{4}\right)\left(2l_{iz}^2l_{jz}^2 + l_{i+}^2l_{j+}^2 + l_{i-}^2l_{j-}^2\right) - \frac{J_{int}}{4}\left(\mathbf{s}_i\mathbf{s}_j - \frac{1}{4}\right)l_{iz}l_{jz}. \tag{7}$$

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

$$J_f = J_p - 2\frac{I_f}{U^2}\left(t_{xy,xy}^2 + t_{xz,xz}^2\right) \quad \text{and} \tag{8}$$

$$J_f' = J_p' - 2\frac{I_f}{U^2}\left(t_{xz,xz}^2\right), \quad \text{with} \qquad I_f = \langle d_{xy},d_{xz}|\frac{e^2}{r_{12}}|d_{xz},d_{xy}\rangle. \tag{9}$$

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 Hunds-coupling parameter in Ref. 12.

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

$$H_{ex}(2_x) = \left(\mathbf{s}_i\mathbf{s}_j + \frac{3}{4}\right)\left[J_f\left(-2 + l_{ix}^2 + l_{jx}^2 + l_{iz}^2l_{jy}^2 + l_{iy}^2l_{jz}^2\right) + J_f'\left(l_{ix}^2 + l_{jx}^2 - 2l_{ix}^2l_{jx}^2\right)\right]. \tag{10}$$

The effective Hamiltonian for a pair along the y axis can be obtained by a permutation of indices $x \longrightarrow y$ and $y \longrightarrow x$. 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 $|\vartheta\rangle = \cos\vartheta/2|1,1/2\rangle + \sin\vartheta/2|-1,-1/2\rangle$ with $\vartheta = \vartheta_i$ and is surrounded by four V ions of sublattice j with $\vartheta = \vartheta_j$.[23] Using the effective exchange operator $H_{ex} = \sum[H_{ex}(1) + H_{ex}(2_x) + H_{ex}(2_y)]$ 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:

$$\varepsilon_{1,2} = D + \frac{\lambda_c}{2} - \frac{J_a + J_{\rm int}}{4} + \frac{3J_f'}{2} \pm\frac{1}{4}[(J_a + J_{\rm int} + 2J_f')u^2 + (J_a - J_f')^2v^2]^{\frac{1}{2}}, \tag{11}$$

$$\varepsilon_{3,4} = -\frac{D}{2} - \frac{\lambda_c}{4} + \frac{J_a - J_{int}}{8}(u-1) + \frac{J_f}{4}(3-u) + \frac{3J_f'}{2} \pm\frac{1}{2}\left[\left(3D - \frac{\lambda_c}{2} + \frac{J_a - J_{\rm int}}{4}(u-1) - \frac{J_f}{2}(3-u) + J_f'u\right)^2 + 2\lambda_{a,b}^2\right]^{\frac{1}{2}}, \tag{12}$$

$$\varepsilon_{5,6} = -\frac{D}{2} - \frac{\lambda_c}{4} - \frac{J_a - J_{\rm int}}{8}(u+1) + \frac{J_f}{4}(3+u) + \frac{3J_f'}{2} \pm\frac{1}{2}\left[\left(3D - \frac{\lambda_c}{2} - \frac{J_a - J_{\rm int}}{4}(u+1) - \frac{J_f}{2}(3+u) - J_f'u\right)^2 + 2\lambda_{a,b}^2\right]^{\frac{1}{2}}. \tag{13}$$

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 ε_1. A minimum in energy of this level will occur at $\vartheta = \pm\pi/2$ only if $3|J_f^{'}| > J_{\rm int}$. If $J_{\rm int} > 3|J_f^{'}|$ 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.[13] 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 co-workers the energy cost for moving a $3d$ electron between V ions in Sr_2VO_4 is about $U \simeq$ 11 eV and the effective transfer integrals $t_{xz,xz} \simeq -0.2$ eV and $t_{yz,yz} \simeq 0.05$ meV.[10] Therefore, we estimate $J_a \simeq 15$ meV, $J_{\rm int} \simeq 7.5$ 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.[2,12] Using these values we plot the energy levels as $\varepsilon_i(\vartheta) - \varepsilon_1(\vartheta = 0,\pi)$ in Fig. 2(a) as a function of the orbital-mixing angle ϑ. Note that $\varepsilon_1(\vartheta)$ is not constant but becomes minimal for $\vartheta = 0$ and π. 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. 2(a).[13,19]

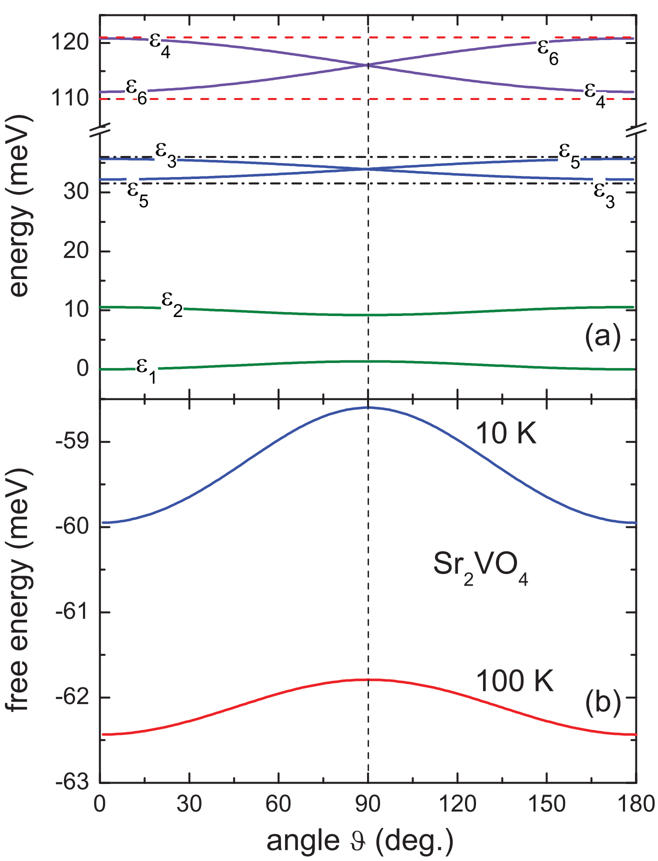

FIG. 2. (Color online) (a) Calculated energy levels as a function of the orbital mixing angle ϑ using Eqs. (13)–(15) and parameters $\lambda_c = -30$ meV, $\lambda_{ab} = -28$ meV, $D = -33$ meV, $J_a = -15$ meV, $J_f = -9.3$ meV, $J_f' = -0.7$ meV, and $J_{\rm int} = 7.5$ meV. Excitation energies observed by neutron scattering (Ref. 13) and optical spectroscopy (Ref. 19) are shown as dashed and dash-dotted lines, respectively. (b) Free energy as a function of ϑ calculated with the same parameters 10 K and 100 K.

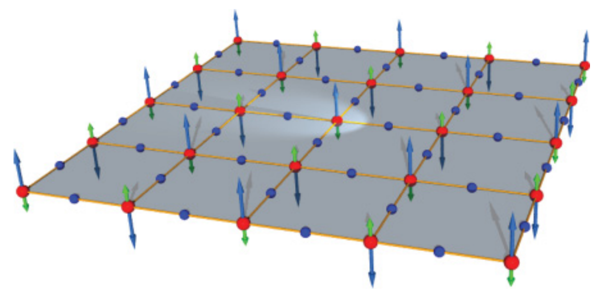

FIG. 3. (Color online) Sketch of the proposed alternating spin-orbital order in the ab plane of tetragonal Sr_2VO_4. Short and long arrows correspond to spin and orbital moments of the V ions, respectively.

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 ϑ using the values for the exchange constants estimated above:

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

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 ϑ can be expected. We estimate these fluctuations by $\overline{\Delta\vartheta^2} = k_B T(\partial^2 F/\partial\vartheta^2)^{-1} \simeq (\pi/5)^2$ 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,[13] 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 meV corresponds nicely to the optical excitation observed for $T > 80$ K, but given the strong fluctuations expected for this temperature range the interval $(\varepsilon_3 + \varepsilon_5)/2 - (\varepsilon_2 + \varepsilon_1)/2 \sim 29$ 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_2VO_4. The proposed scenario and parameter values allow one to obtain a consistent picture of the low-temperature excitation spectrum of Sr_2VO_4, which was recently reported by neutron and optical experiments.

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