Orbital ordering and one-dimensional magnetic correlation in vanadium spinel oxides $A\text{V}_2\text{O}_4$ ($A = \text{Zn, Mg, or Cd}$)

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Abstract

We present our theoretical results on the mechanism of two transitions in vanadium spinel oxides $A\text{V}_2\text{O}_4$ ($A = \text{Zn, Mg, or Cd}$) in which magnetic V cations constitute a geometrically-frustrated pyrochlore structure. We have derived an effective spin-orbital-lattice coupled model in the strong correlation limit of the multiorbital Hubbard model, and applied Monte Carlo simulation to the model. The results reveal that the higher-temperature transition is a layered antiferro-type orbital ordering accompanied by tetragonal Jahn-Teller distortion, and the lower-temperature transition is an antiferromagnetic spin ordering. The orbital order lifts the magnetic frustration partially, and induces spatial anisotropy in magnetic exchange interactions. In the intermediate phase, the system can be considered to consist of weakly-coupled antiferromagnetic chains lying in the perpendicular planes to the tetragonal distortion.

Key words: vanadium spinel oxides, geometrical frustration, orbital ordering, antiferromagnetic ordering, Monte Carlo simulation

Vanadium spinel oxides $A\text{V}_2\text{O}_4$ with nonmagnetic cations $A = \text{Zn, Mg, or Cd}$ are one of the most typical geometrically-frustrated systems; the magnetic V cations constitute the pyrochlore lattice, which is a three-dimensional network of corner-sharing tetrahedra. The geometrical frustration strongly suppresses development of magnetic correlations, and the antiferromagnetic (AF) ordering sets in at a much lower temperature $\sim 40$K than the Curie-Weiss temperature $\sim 1000$K [1]. Besides the AF transition, at a slightly higher temperature $\sim 50$K, the system shows another phase transition with the structural change from high-temperature cubic to low-temperature tetragonal symmetry [1]. The origin of the two successive transitions is under debate. In particular, theories based on spin degree of freedom only or the spin-lattice coupling appear to be insufficient to describe the two transitions in a comprehensive manner [2].

In the present study, we focus on the $t_{2g}$ orbital degree of freedom in these vanadium spinels to understand the microscopic mechanism of the two successive transitions. Each $V^{3+}$ cation has two 3$d$ electrons in threefold $t_{2g}$ orbitals, and therefore the orbital degree of freedom is active. Starting from the standard multiorbital Hubbard model, we consider the perturbation in the strong correlation limit to describe the low-energy physics of these insulating materials, and derive the effective spin-orbital-lattice coupled model in the form [2]

$$H = H_{SO} + H_{JT},$$

$$H_{SO} = -J \sum_{\langle s,j \rangle} h_{ij} - J_3 \sum_{\langle \langle s,j \rangle \rangle} h_{ij},$$

where $h_{ij}$ and $h_{ij}$ are the hopping integrals between nearest and next-nearest neighbors, respectively. The parameters $J$ and $J_3$ represent the spin-exchange interactions in the $x$ and $y$ directions, respectively.
\( h_{ij} = (A + BS_i \cdot S_j)[n^\alpha_{ia(ij)}n^\beta_{ja(ij)} + n^\alpha_{ia(ij)}n^\beta_{ja(ij)}] + C(1 - S_i \cdot S_j)n^\alpha_{ia(ij)}n^\beta_{ja(ij)}, \)

\( H_{JT} = \sum_i Q_i e_i + \sum_{i,j} Q_i^2/2 - \lambda \sum_{i,j} Q_i Q_j, \)

where \( S_i \) is the \( S = 1 \) spin operator and \( n^\alpha_{ia} \) is the density operator for site \( i \) and orbital \( \alpha = 1 \) (\( d_y \)), 2 (\( d_x \)), 3 (\( d_{xy} \)). Here, \( n^\alpha_{ia} = 1 - n^\alpha_{ia} \) and \( e_i = n^1_{i1} + n^2_{i2} - 2n^3_{i3}; \) and we impose a local constraint \( \sum_{\alpha=1}^3 n^\alpha_{ia} = 2 \) at each site. The summations with \( \langle i,j \rangle \) and \( \langle i,j \rangle \) are taken over the nearest-neighbor (NN) sites and third-neighbor sites, respectively. Here, we take into account only the dominant \( \sigma \)-bond hopping integrals in the original multiorbital Hubbard model, which results in the orbital diagonal interaction in \( H_{SO} \); \( \alpha(ij) \) is the orbital which gives rise to the \( \sigma \)-bond between sites \( i \) and \( j \). \( H_{JT} \) describes the orbital-lattice coupling part, where \( \gamma \) is the electron-phonon coupling constant of the tetragonal Jahn-Teller (JT) mode, \( Q_i \) denotes the amplitude of local lattice distortion at site \( i \), and \( \lambda \) describes the interaction between NN JT distortions, which mimics the cooperative aspect of the JT distortion. The parameters in \( H_{SO} \) are given by the coupling constants in the starting multiorbital Hubbard Hamiltonian, and we use the reasonable estimates as \( J_{xy}/J = 0.02 \) with \( J \approx 200K, A = 1.21, B = 0.105 \), and \( C = 0.931 \). For the JT parameters, we take \( \gamma^2/J = 0.04 \) and \( \lambda/J = 0.15 \), which are typical values to reproduce the tetragonal distortion observed in experiments.

We have performed Monte Carlo (MC) simulation to investigate thermodynamic properties of the model (1), which is a classical simulation to avoid the negative sign problem due to the geometrical frustration. Since quantum nature exists only in the spin operators in \( H_{SO} \), we approximate them by classical vectors, and apply a standard metropolis MC algorithm. Details of MC calculations will be reported elsewhere [3].

MC results show that the model (1) exhibits two transitions: One is first order transition at \( T_O \approx 0.19J \) corresponding to the orbital ordering with the tetragonal JT distortion, and the other is at \( T_N \approx 0.115J \) with continuous growth of the AF spin ordering. The orbital order below \( T_O \) is a layered antiferro type; \( (d_y, d_{xy}) \) and \( (d_{xy}, d_{xz}) \)-occupied planes stack alternatively in the \( c \) direction (\( c \) is the axis of the tetragonal distortion). This orbital ordering plays a crucial role to reduce the magnetic frustration in the following way: Let us consider an effective spin Hamiltonian by replacing the orbital part in \( H_{SO} \) by its mean-field. The model has highly anisotropic spin exchanges; for instance, between NN sites, the strong AF interaction \( J_{xy} \approx 0.931J \) in the \( xy \) direction whereas the weak ferromagnetic interaction \( J_F \approx -0.105J \) in the \( yz \) and \( xz \) directions. Moreover, the weak ferromagnetic interactions \( J_F \) are completely frustrated between the AF \( xy \) chains due to the geometry of the pyrochlore structure. These anisotropic exchange interactions are shown in the inset of Fig. 1 in a tetrahedron unit. As a consequence, the magnetic correlation becomes highly anisotropic, and the system looks like a weakly-coupled AF chains.

Figure 1 shows the ratio between the staggered moments in the \( xy \) chains and in the \( yz \) chains. The orbital ordering temperature \( T_O \) and the antiferromagnetic spin ordering temperature \( T_N \) are shown. The system size is \( L^2 \times 16 \) sites. Inset: Anisotropic spin exchange interactions under the orbital ordering.

References

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