Interplay among Spin, Orbital and Lattice Degrees of Freedom in $t_{2g}$ Electron Systems with Edge-Sharing Network of Octahedra

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Transition metal oxides whose lattice structure has edge-sharing network of octahedra constitute a diverse group of intriguing materials besides compounds with corner-sharing octahedra such as perovskites. We present a theoretical investigation of the interplay among spin, orbital and lattice degrees of freedom in these materials. We focus on $t_{2g}$ electron systems where a keen competition among those degrees of freedom is expected to emerge under a relatively weak Jahn-Teller coupling. We study the interplay between spin and orbital degrees of freedom in vanadium spinels and titanium pyroxenes. We clarify the important role of the strong anisotropy in the orbital interactions due to the edge-sharing geometry. We also discuss the interplay between spin and lattice in chromium spinels focusing on the magnetization process under the external magnetic field.

§1. Introduction

Transition metal oxides, in many cases, consist of the basic unit of octahedron where a metal is surrounded by six oxygens. One of the famous families is the perovskite such as high-$T_c$ cuprates and CMR manganites, in which octahedra form two-dimensional (2D) or three-dimensional (3D) network by sharing oxygens at their corner. Another typical geometry is the edge-sharing network of octahedra. An old but still intriguing example is the spinel in which octahedra form 3D edge-sharing network. A 2D example is found in the sodium cobaltite which has a triangular lattice of Co cations. There, a large thermoelectric effect or superconductivity is recently attracting much interest.

In this paper, we present our recent theoretical efforts to understand remarkable properties in several edge-sharing materials with focusing on a keen competition among spin, orbital and lattice degrees of freedom. In the octahedral coordinate, the fivefold energy levels of $d$ electrons of transition metals split into lower threefold $t_{2g}$ levels and higher twofold $e_g$ levels. Here, we consider the systems in which electrons in the $t_{2g}$ levels play a central role. In the $t_{2g}$ electron systems, it is known that the Jahn-Teller interaction is rather weak compared to the $e_g$ systems.
Therefore, it is expected that the energy scales in spin, orbital and lattice degrees of freedom become closer to each other and that a keen competition among them seriously affects physical properties of the system.

This paper is organized as follows. In §2, we mainly address the interplay between spin and orbital degrees of freedom. In §2.1, we discuss the mechanism of lifting the degeneracy due to the geometrical frustration in vanadium spinels. We remark how the magnetic ordering pattern is changed depending on the sign of the third-neighbor spin coupling. In §2.2, we discuss the non spin-Peierls mechanism of the spin-singlet formation in titanium pyroxenes. We observe an interesting phase competition between different spin-orbital orderings. In §3, we discuss the interplay between spin and lattice degrees of freedom in chromium spinels to understand the unusual magnetization process under the external magnetic field.

§2. Interplay between spin and orbital

2.1. Vanadium spinels

Vanadium spinels $AV_2O_4$ with nonmagnetic $A$ cations such as Zn, Mg or Cd have 3D edge-sharing network of $VO_6$ octahedra, and consequently, magnetic V cations form the geometrically frustrated pyrochlore lattice. In general, the geometrical frustration results in (nearly) degenerate ground states and suppresses a long-range ordering. Nevertheless, these compounds exhibit two successive transitions at low temperatures: One is the structural transition at $T_{c1} \approx 50$ K from high-temperature cubic phase to low-temperature tetragonal phase, and the other is the antiferromagnetic (AF) transition at $T_{c2} \approx 40$ K. The issue is the microscopic mechanism of these two transitions, that is, how the frustration is reduced and how the long-range orders are stabilized.

We have studied this problem by taking into account the orbital degree of freedom of $t_{2g}$ electrons, because $V^{3+}$ cation has two $d$ electrons in threefold $t_{2g}$ levels. The important point is the spatial anisotropy of the $t_{2g}$ orbitals. In the edge-sharing configuration of $VO_6$ octahedra, the most relevant contribution in the hopping integrals is given by the overlap between the same orbitals lying in the same plane, that is, the so-called $\sigma$-bond. We derived an effective spin-orbital coupled model in the strong correlation limit with considering only the $\sigma$-bond contribution in the perturbation for the multiorbital Hubbard model. We found that the effective model shows the strong anisotropy (three-state Potts type) in the orbital intersite interactions. This strong anisotropy plays a crucial role in the keen competition between spin and orbital, and finally reduces the frustration. That is, the degeneracy is lifted in the orbital sector first, accompanied by the tetragonal lattice distortion. This explains well the structural transition at $T_{c1}$ in experiments.

The mechanism of the magnetic transition at $T_{c2}$ is also interesting. In the orbital ordered state, $d_{xy}$ orbital is singly occupied at every V site. On the other hand, $d_{yz}$ and $d_{zx}$ orbitals are occupied in the staggered way in the $z$ direction. The uniform occupation of $d_{xy}$ orbitals leads to a large enhancement of the AF spin correlation along one-dimensional (1D) chains lying in the $xy$ planes. Thus, the magnetic
Fig. 1. Magnetic ordering structure predicted in the effective spin-orbital coupled model for vanadium spinels with (a) antiferromagnetic $J_3'$ and (b) ferromagnetic $J_3'$.

frustration is partially lifted by the orbital ordering. However, the relative angles of the staggered moments between different $xy$ chains are not yet determined because of the pyrochlore structure. We proposed that the third-neighbor spin exchange $J_3'$ as well as thermal and/or quantum fluctuations can lift the remaining degeneracy and establish the 3D magnetic long-range order.\(^2\),\(^3\)

The 3D magnetic ordering pattern is hence determined by the way of stacking the 1D AF $xy$ chains in the $z$ direction, and strongly depends on the sign of $J_3'$. When $J_3'$ is AF as in our effective model, the spin configuration is up-up-down-down-\(\cdots\) (four-times period) along the $yz$ and $zx$ chains as shown in Fig. 1 (a). This pattern is consistent with the neutron scattering results by Niziol\(^4\) and Lee et al.\(^5\) On the other hand, if we suppose the ferromagnetic $J_3'$, the primitive unit cell (four-site tetrahedra) corresponds to the magnetic unit cell, and hence a different spin configuration may be obtained; up-down-up-down-\(\cdots\) in the $yz$ (or $zx$) chains and ferromagnetic in the others as shown in Fig. 1 (b). However, we note that it is rather difficult to obtain the ferromagnetic $J_3'$ by the perturbation for the multiorbital Hubbard model and that the latter spin ordering may lead to further lowering of lattice symmetry through the spin-lattice coupling. Thus, theoretical predictions depend on the sign of the small energy scale $J_3'$, but the spin configuration in Fig. 1 (a) is the most likely within our theoretical model. The point to be stressed is that the small coupling $J_3'$ becomes crucial only when the frustration is reduced by the orbital ordering.

2.2. Titanium pyroxenes

Titanium pyroxenes $ATiSi_2O_6$ ($A=$Na or Li) are other typical compounds with edge-sharing octahedra where the orbital degree of freedom may play a crucial role. These materials have quasi 1D structure in which the octahedra share their edges alternatively to form zig-zag chains. Due to this peculiar structure, threefold $t_{2g}$ levels split into a lower doublet and a higher singlet. Ti$^{3+}$ cation has one $d$ electron in the lower twofold levels. The compounds show a phase transition at $T_c \simeq 200$ K.
where the magnetic susceptibility suddenly drops and the lattice structure is dimerized along the 1D zig-zag chains.\textsuperscript{6,7} The temperature dependence of the magnetic susceptibility as well as the estimate of the spin gap compared to $T_c$ suggests that the transition cannot be understood by the usual spin-Peierls mechanism.\textsuperscript{6}

We have considered the mechanism of this peculiar transition by taking account of the twofold orbital degeneracy explicitly. As in the case of V spinels, the spatial anisotropy of the $t_{2g}$ orbitals and the edge-sharing geometry play an important role, resulting the Ising-type orbital interaction in the effective spin-orbital model. We found that the model exhibits two different ground states; one is the spin-dimer and orbital-ferro state and the other is the spin-ferro and orbital-antiferro state. The transition between them can be controlled by the Hund’s-rule coupling $J_H$ and/or the external magnetic field $h$. For the realistic values of parameters, the ground state is the former one. The obtained temperature dependence of the magnetic susceptibility explains the experimental result semiquantitatively.\textsuperscript{8}

Let us focus on the spin-orbital phase competition in the parameter space of $J_H$ and/or $h$. A schematic phase diagram is shown in Fig. 2. In the multicritical regime (the hatched area in Fig. 2), the competition becomes conspicuous; both spin and orbital correlations are suppressed as the temperature decreases. This severe competition suppresses $T_c$ in the multicritical regime, and enables us to see effects of the competition more clearly above $T_c$. The details will be reported elsewhere.\textsuperscript{9}

In order to observe the intrinsic effects of the spin-orbital competition, it is desired to realize an experimental situation in the vicinity of the multicritical point.

§3. Interplay between spin and lattice: Chromium spinels

Chromium spinels $ACr_2O_4$ with nonmagnetic $A$ cations show only one phase transition\textsuperscript{10} in contrast to the two transitions in V spinels in §2.1 nevertheless the lattice structures are isomorphic. The difference is in the orbital state: because Cr$^{3+}$ has three $d$ electrons in threefold $t_{2g}$ orbitals, the orbital degree of freedom is

Fig. 2. Schematic multicritical phase diagram of the effective spin-orbital model for titanium pyroxenes. The hatched area shows the multicritical competing regime.
inactive in Cr spinels. At the transition temperature, an AF spin ordering occurs simultaneously with the structural change from cubic to tetragonal. The origin of this transition has been discussed in terms of the spin Jahn-Teller mechanism: the geometrical frustration is reduced by the lattice distortion which gains the magnetic exchange energy.\textsuperscript{11,12}

Very recently, the compounds with $A=$Hg or Cd are found to exhibit the half-magnetization plateau, which is unusually stable, under the external magnetic field.\textsuperscript{13,14} This plateau phenomenon has been also discussed by using the AF Heisenberg model with the spin-lattice coupling.\textsuperscript{15} The plateau is well reproduced by the mean-field results in the ground state for finite spin-lattice couplings.

Following this idea, we have extensively studied finite-temperature properties of the spin-lattice coupled model on the pyrochlore lattice under the magnetic field by using the Monte Carlo simulation. We found that the half-magnetization plateau remains robust at finite temperatures, and that the temperature dependence of the magnetization curve is favorably compared with the experimental results.\textsuperscript{16} We also found that the plateau phase is induced by thermal fluctuations even in the absence of the spin-lattice coupling. The details of the results and the comparison with the experimental results will be reported elsewhere.\textsuperscript{17}

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