Distorted Perovskite with eg1 Configuration as a Frustrated Spin System

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Distorted perovskite with $e_g^1$ configuration as a frustrated spin system

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The evolution of spin- and orbital-ordered states has been investigated for a series of insulating perovskites $RMnO_3$ ($R$ = La, Pr, Nd, . . . ). $RMnO_3$ with a large GdFeO$_3$-type distortion is regarded as a frustrated spin system having ferromagnetic nearest-neighbor and antiferromagnetic (AF) next-nearest-neighbor (NNN) interactions within a MnO$_2$ plane. The staggered orbital order associated with the GdFeO$_3$-type distortion induces the anisotropic NNN interaction, and yields unique sinusoidal and up-up-down-down AF ordered states in the distorted perovskites with $e_g^1$ configuration.

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Common electronic characteristics exist in perovskite manganites $RMnO_3$ and nickelates $RNiO_3$ ($R$ = trivalent lanthanoids). On the Mn$^{3+}$ and Ni$^{3+}$ sites with the $e_g^{1/2}$ and $e_g^{3/2}$ configurations, respectively, the $e_g$ orbital is doubly degenerate and the $t_{2g}$ orbital degree of freedom is quenched. It is widely recognized that the layered-type (A-type) antiferromagnetic (AF) structure in LaMnO$_3$ is understood from the viewpoint of the anisotropic superexchange (SE) interaction under the directional order of orbital.1,2 On the other hand, the spin structure in nickelates ($R$ ≠ La) is distinct from the A-type AF; the so-called “up-up-down-down”-type one, where two Ni sites of “up” spins are followed by two sites of “down” spins along the principal axes in the cubic unit cell. Origin of this unusual magnetic order has been a long-standing question, as well as its relations to metal-insulator transition, orbital order (OO), and charge disproportionation.3-5 Recently, a similar spin structure, i.e., the up-up-down-down order in a MnO$_2$ plane ($E$-type AF order in the Wollan-Koehler notation6), is found in a manganite HoMnO$_3$ (Ref. 7) with a significantly distorted perovskite structure. This has to be a bridge between the well-understood A-type AF in manganites and the unique magnetic ground state in nickelates.

In this Communication, we examine systematically the magnetic and orbital structures in a series of $RMnO_3$ as a function of the ionic radius ($r_R$) of $R$. The most significant effect on the crystal structure by decreasing $r_R$ is an enhancement of the cooperative rotation of the MnO$_6$ octahedra (the GdFeO$_3$-type distortion) characterized by the increase of Mn-O-Mn bond angle $\phi$. Let us first summarize in Fig. 1 the orbital (a) and spin (b) ordering temperatures ($T_{OO}$ and $T_{N}$, respectively) on Mn sites of $RMnO_3$ as a function of $\phi$, which is based on both the present and the former studies.7–10 Here, we adopt the $\phi$ at room temperature.11 The $T_{OO}$ monotonically increases with decreasing $r_R$, while the magnetic transition occurs from the A-type AF to the $E$-type one through the incommensurate structure. We argue that the combination of OO and next-nearest-neighbor (NNN) SE interaction brings about a nontrivial effect on the magnetic ground state in the systems with the orbital degeneracy and the large GdFeO$_3$-type distortion. Microscopic calculation shows that the magnetism in this system is mapped onto the frustrated spin model which well reproduces the phase diagram of $RMnO_3$.

A series of $RMnO_3$ ($R$ = La-Dy) crystals were grown by the floating zone method. We made powder x-ray-diffraction
accordance with the cooperative Jahn-Teller anomaly was observed up to 1500 K. Thus, the OO state is confirmed that all the crystals show the measurements on the obtained crystals at room temperature, and confirmed that all the crystals show the $Pbnm$ orthorhombic structure. Magnetization at 0.5 T was measured with a superconducting quantum interference device magnetometer. Specific heat was measured using a relaxation technique. Resistivity measurements were made by a standard four-probe method in a flow of Ar gas up to $\sim 1200$ K.

Let us show in Fig. 2 the experimental data [temperature ($T$) profiles of (a) resistivity $\rho$, (b) magnetization $M$, and (c) specific heat divided by temperature $C/T$, for $R\text{MnO}_3$ crystals. Vertical arrows in (a) and (b) indicate $T_{OO}$ and $T_N$ for the Mn moment, respectively. The inset magnifies the $M$ of $R=$ Tb and Eu in the vicinity of $T_N$.

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As shown in Fig. 2(b), a steep rise of $M$ toward lower $T$ (indicated by vertical arrows) is observed in most of the crystals. The anomaly in $R=$ La-Nd crystals well corresponds to $T_N$ for the $A$-type AF order. The $T_N$ falls monotonically with decreasing $r_R$ from La to Gd. A similar jump of $M$ attributed to the spin ordering of Mn site is not observed in $R=$ Tb and Dy crystals with small $r_R$. (The anomaly in $M$ below 10 K is related to the ordering of $R$-site $f$ moment.) In $\text{TbMnO}_3$, however, the $M$ exhibits two sharp peaks at $\sim 42$ K and $\sim 27$ K [the inset of Fig. 2(b)]. Figure 2(c) shows the $C/T$ for crystals with smaller $r_R$. In $\text{SmMnO}_3$, the jump of $C/T$ at $\sim 59$ K nicely agrees with the steep rise of $M$, and can be assigned to the $A$-type AF ordering. A remarkable feature in the $C/T$ of $\text{EuMnO}_3$ is the sharp peak at $\sim 46$ K, as well as the jump at $\sim 51$ K. The sharp $46$ K peak is suggestive of the first-order phase transition. In crystals with smaller $r_R$ ($R=$ Gd-Dy), a rather broader peak is observed at $\sim 40$ K. In addition, another broad peak feature is evident in the $T$ region 18–26 K. Among them, the $T$ evolution of spin structure has been investigated for $\text{TbMnO}_3$ by neutron-diffraction measurements. The observed peaks in $C/T$ and $M$ at $\sim 42$ K for $\text{TbMnO}_3$ correspond to the onset of the sine-wave ordering of the Mn moments with the wave vector of $(0,k_s,0)$. The $k_s$ ($\sim 0.295$) at $T_N$ is incommensurate (IC) and decreases with decreasing $T$, and becomes nearly constant ($k_s=0.28$) below $\sim 30$ K. The anomalies in $C/T$ and $M$ at $\sim 27$ K are in good agreement with the $T$ where $k_s$ is locked at a constant value ($T_{lock}$). With further decreasing $r_R$, Muñoz et al. reported that in polycrystalline $\text{HoMnO}_3$ ($T_N=41$ K), the IC-to-commensurate (CM) magnetic phase transition takes place at $\sim 26$ K, where the wave vector is $(0,k_s,0)$ [0.4$\leq k_s < 0.5$ ($T$ dependent) for the IC phase and $k_s = \frac{1}{2}$ for the CM one].

As displayed in Fig. 1, $T_{OO}$ steeply increases with decreasing $\phi$, whereas $T_N$ for the $A$-type AF order monotonically decreases. With the suppression of the $A$-type AF order, the IC sinusoidal magnetic structure which propagates along the $b$ axis appears. With further decreasing $\phi$, the CM magnetic structure with the wave vector of $(0,\frac{1}{2},0)$ turns up at the ground state in $\text{HoMnO}_3$. The CM magnetic structure can be identified with the "up-up-down-down" spin structure within the $ab$ plane or the $E$-type AF structure. To visualize the modification of the crystallographic and magnetic structures by the decrease of $\phi$, we illustrate in Fig. 1(c) the projection of the fundamental crystal structure of $\text{LaMnO}_3$ and $\text{HoMnO}_3$ along the $c$ axis.

In $\text{R MnO}_3$ with a small GdFeO$_3$-type distortion, such as $\text{LaMnO}_3$, the staggered $[d_{3z^2-2y^2}/d_{3z^2-2y^2}]$-type OO is responsible for the $A$-type AF order. There are the ferromagnetic (FM) SE interaction between nearest-neighbor (NN) $e_g$ spins and the AF one ($J_e^{A2}_{NN}$) between NN $t_{2g}$ spins. The latter is superior along the $c$ axis. In $\text{R MnO}_3$ with significant GdFeO$_3$-type distortion (small $r_R$), the FM SE interaction is weakened due to reduction of the transfer intensity of an $e_g$ electron. However, such an argument based on the NN interactions is not enough to explain the $E$-type AF or sinusoidal magnetic order; the inversion symmetry of the spin alignment is broken in the $ab$ plane for the $E$-type AF structure, in
The crucial effect caused by the significant GdFeO₃-type distortion is the SE interaction between NNN Mn sites. It is schematically written as the constants, and ~Mn inequivalent; the interaction between Mn NNN SE interactions along the different directions become which is known to describe well the orbitally degenerate OO. The Hamiltonian adopted here is the spin-orbital model e.g., the O 2 orbitals occur through the O 2 orbitals. The effective electron transfer between Mn spins, respectively. Beyond the conventional spin-orbital model, the SE interactions between NNN Mn sites are considered in H.J. The effective electron transfer between Mn spins, respectively. The orbital part hₘ(\vec{T}, \vec{T}) is represented by the pseudospin orbital \vec{T} with a magnitude 1/2. H₈ and H₈,F in \H are the Hund coupling between e₉ and t₂g spins, and the AF interaction J₈,F between NN t₂g spins, respectively. The orbital part hₘ(\vec{T}, \vec{T}) is represented by the pseudospin orbital \vec{T} with a magnitude 1/2. H₈ and H₈,F in \H are the Hund coupling between e₉ and t₂g spins, and the AF interaction J₈,F between NN t₂g spins, respectively. Beyond the conventional spin-orbital model, the SE interactions between NNN Mn sites are considered in H.J. The effective electron transfer t_j'' between i and j Mn sites with \gamma and \gamma' (=3z^2-r^2-x^2-y^2) orbitals occurs through the O 2p orbitals. For example, for the Mn(1)-Mn(3) pair [see Fig. 1(c)], possible exchange paths are \[\text{[Mn(1)-O(1),O(4)-O(2),O(3)-Mn(3)].}\] Both the GdFeO₃-type and JT-type distortions are introduced in t_j'' through the Slater-Koster formulas. The magnetic phase diagram is calculated by the mean-field approximation at T=0 [Fig. 3(a)] (Refs. 15, 16) in the two-dimensional (2D) square lattice, since the AF spin alignment along the c axis due to J₈,F remains unchanged in a series of RMnO₃. The staggered OO with two sublattices is of the \[[\theta'-\theta]\]-type characterized by the mixing angle: \[\theta = \cos(\theta/2)(d_{x^2-y^2}) + \sin(\theta/2)(d_{z^2-r^2}).\] The \[\text{[d_{x^2-y^2},d_{z^2-r^2}]}\]-type OO corresponds to \[\theta=2\pi/3.\] Without the GdFeO₃-type distortion, the FM order in the ab plane, corresponding to the A-type AF order in the three-dimensional lattice, appears for \[\theta<1.75\pi.\] With decreasing \phi, the E-type AF phase of the present interest appears for \[1.75\pi<\theta<2.5\pi\] and \phi<143°. This result agrees semiquantitatively with the experiments. The remarkable change with
decreasing $\phi$ is seen in the SE interaction between Mn(1) and Mn(3) along the $b$ axis; it turns to a strong AF interaction from a weak FM one [see $J_2$ in the inset of Fig. 3(a)] as well as weakening of the NN FM one ($J_1$).\textsuperscript{17,18}

The essence of magnetic properties in this system is mapped onto the 2D frustrated Heisenberg model for $S = 2$ with FM NN interaction ($J_1$), AF NNN one along the $b$ axis ($J_2$), and weak FM NNN along the $a$ axis ($J_3$). The finite $T$ phase diagram is obtained by the mean-field approximation [Fig. 3(b)]. A periodicity $N$ of the spin structure is taken up to 20 along the $a$, $b$, and $a+b$ directions, and each phase is characterized by the wave number $q = M/N$. The phase diagram shows a similar topological structure to that in the axial next-nearest-neighbor Ising model,\textsuperscript{19,20} numerous long-range orders between the FM ($q = 0$) and up-up--down-down-type AF ($q = 1/4$) phases, which is the so-called Devil’s flower. The calculated results qualitatively reproduce the phase diagram of R MnO$_3$ in Fig. 1(b). (Note that the $A$-type AF state is regarded as the 2D FM state.) Further supporting evidence is needed to confirm the validity of the present scenario. However, it is difficult to investigate the spin structure by the neutron diffraction for compounds with Gd and Dy elements because of their large neutron-scattering cross sections. Hence, we overcome the problem by measurements of single-crystal x-ray diffraction. Figures 4(a)–4(c) show x-ray-diffraction scans along $(0, k, 3)$ at various $T$ for $R =$ Gd, Tb, and Dy crystals.\textsuperscript{21} For all the crystals, additional superlattice peaks appear at the wave vector $(0, k_f, 1)$ for integer $I$ below $T_N$. In TbMnO$_3$, the $k_f$ is $\sim 0.57$ at $T_N = 40$ K, decreases with decreasing $T$, and becomes nearly constant ($k_f \sim 0.55$) below $T_{lock} \sim 27$ K. The value of $T$-dependent $k_f$ is almost twice as large as that of $k_s$. It is well known that the crystallographic deformations at magnetic ordering are due to the exchange striction.\textsuperscript{22} The observed superlattice reflections due to the atomic displacement can be regarded as the second harmonic peaks magnetoelastically induced by sinusoidal AF order. Hence, a half value of $k_f$ could represent $k_s$. The $T$ profiles of the wave number $k_s = k_f/2$ obtained by experiments are compared with those calculated for the representative values of $J_2/(-J_1)$ [Figs. 4(d) and 4(e)]. The theoretical results are in quantitatively good agreement with experiments in terms of $T$ and $R$ dependence, which strongly suggests that the present modeling approach is proper for understanding the phase diagram of RMnO$_3$.

We examined the evolution of magnetic and orbital states in a series of RMnO$_3$ as a function of the ionic radii $r_R$ in $R$. The $T_N$ of the $A$-type AF order steeply decreases with the decrease of $r_R$. Eventually the up-up-down-down type ($E$-type) AF order appears in $R = Ho$ via the sinusoidal magnetic order in $R = Tb$. Such curious AF ordered states in RMnO$_3$ can be explained in a scenario of the spin frustration caused by the combination of the significant GdFeO$_3$ distortion and the staggered OO: the former enhances the NNN SE interaction, and the latter causes the anisotropy in the NNN SE interaction. This scenario can also be applicable to the up-up-down-down AF order observed in R NiO$_3$ with the distorted perovskite structure.

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