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Spin–charge–orbital structures and frustration in multiferroic RFe_2O_4

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Abstract

We examine theoretically the spin, charge and orbital states in a frustrated system RFe_2O_4 . We suggest that the orbital degree of freedom is active in an Fe^{2+} ion. To describe the spin, charge and orbital states, the effective Hamiltonian for the electronic state is derived. By utilizing the Monte Carlo simulation in a finite-size cluster, we investigate the charge, spin and orbital structures. It is shown that the obtained charge and spin states are consistent with experimental results in RFe_2O_4 . The numerical simulation for the effective orbital model does not show the conventional orbital order. We discuss possible orbital states at low temperatures.

1. Introduction

It is commonly known that the frustration plays a key role in elucidating a large amount of exotic phenomena in correlated electron systems. One of the attractive examples is the so-called multiferroics, the coexistence of (anti)ferroelectricity and magnetism, recently discovered in the rare-earth manganites with perovskite structure RMnO_3 (R: rare-earth ion). At low temperatures, the electric polarization associated with the magnetic ordering of long periodicity appears and is controlled by the magnetic field. It is supposed that this coexistence is caused by the spin frustration based on the orbital order.

Layered iron oxide RFe_2O_4 , studied in the present paper, is another class of the exotic ferroelectric materials where the frustration may play important roles for the electric and magnetic orderings. This compound shows a layered crystal structure where the Fe–O double layers and the R–O layers are stacked along the c axis, and Fe ions in a Fe–O layer consist of the two-dimensional triangular lattice. The electronic structure has been examined by electron and neutron diffraction experiments. In LuFe_2O_4 , the streak-type diffuse intensity in the electron diffraction appears along the $(1/3, 1/3)$ direction below 500 K, and, inside the streak, the peak appears around $(1/3, 1/3, m + 1/2)$ below about 320 K. Because the nominal valence of an Fe ion is +2.5, this is interpreted to be the two- and three-dimensional charge orderings (CO) of the Fe^{2+} and Fe^{3+} ions [1]. The magnetic order characterized by a

momentum $(1/3, 1/3)$ is confirmed by the neutron diffraction experiments [2–4]. Through the macroscopic measurements [5, 6], it is revealed that the electric polarization starts to appear around 350 K and its magnitude increases at around 260 K. Since these temperatures are close to the three-dimensional CO temperature and the magnetic ordering temperature, these results suggest key roles of CO and magnetic order in the electric polarization.

In this paper, we examine theoretically the electronic structure, in particular the spin, charge and orbital states, in the frustrated system RFe_2O_4 as a fundamental study of the ferroelectricity and multiferroics. We suggest that the orbital degree of freedom is active in an Fe^{2+} ion. To describe the spin, charge and orbital states, we derive the effective Hamiltonian for the electronic state. By utilizing the Monte Carlo simulation in a finite-size cluster, we investigate CO, magnetic structure and orbital structure. The calculated charge and spin states are consistent with some experimental results in RFe_2O_4 . We examine the orbital state at low temperatures, where the charge and spin degrees are frozen. The numerical simulation does not show the conventional orbital ordering. We discuss possible orbital states at low temperatures.

2. Orbital degree of freedom and model Hamiltonian

Let us first pay attention to the orbital degree of freedom in an Fe ion. In the RFe_2O_4 crystal, an Fe ion is surrounded by the five nearest-neighbour (NN) O ions: three ions in a two-dimensional triangular lattice within the plane and two along the c -axis. We calculate the crystal-field splitting of the Fe 3d orbitals in a FeO_5 cluster by utilizing the experimental data of the crystal structure [7]. We assume a valence of O ions of 2– and the atomic-wavefunction for the Fe 3d orbitals. It is found that the five-fold orbital degeneracy is lifted to the two sets of the doubly degenerate orbitals, $(d_{xy}, d_{x^2-y^2})$ and (d_{yz}, d_{xz}) , and the non-degenerate $d_{3z^2-r^2}$ orbitals, and the $(d_{xy}, d_{x^2-y^2})$ orbitals have the lowest energy for an electron. Since the Fe ion is confirmed to take a high-spin state, in an Fe^{3+} ion with the d^5 configuration, five 3d orbitals are occupied by one electron per orbital. On the other hand, in an Fe^{2+} ion with the d^6 configuration, one hole occupies one of the d_{xy} and $d_{x^2-y^2}$ orbitals. That is, the orbital degree of freedom is active in an Fe^{2+} ion.

In order to describe the orbital degree of freedom theoretically, the orbital pseudo-spin operator with a magnitude of $1/2$ is introduced;

$$\vec{T}_i = \frac{1}{2} \sum_{s,\gamma,\gamma'} d_{i\gamma s}^\dagger \vec{\sigma}_{\gamma,\gamma'} d_{i\gamma' s}, \quad (1)$$

where $d_{i\gamma s}$ is the annihilation operator for a Fe 3d electron with orbital γ ($=d_{x^2-y^2}, d_{xy}$), spin s ($=\uparrow, \downarrow$) at site i , and $\vec{\sigma}$ is the Pauli matrices. In an FeO plane, an Fe ion is surrounded by three O ions, and there are three kinds of Fe–O bonds, denoted by l ($=\alpha, \beta, \gamma$). It is convenient to redefine the pseudo-spin operator for each bond as

$$\tau_i^l = \cos\left(\frac{2\pi n_l}{3}\right) T_i^z + \sin\left(\frac{2\pi n_l}{3}\right) T_i^x, \quad (2)$$

with $(n_\alpha, n_\beta, n_\gamma) = (1, 2, 3)$. This implies a mixing of the $d_{x^2-y^2}$ and d_{xy} orbitals, and the electronic wavefunction corresponding to $\tau_i^l = +1/2(-1/2)$ is directed (avoided) to a Fe–O bond with l direction.

Now we construct the model Hamiltonian to describe the electronic structure in RFe_2O_4 . Among several interactions, we consider that the long-range Coulomb interaction and the exchange interactions play dominant roles in the spin, charge and orbital degrees of freedom. These are described by the first and second terms of the following Hamiltonian, respectively:

$$\mathcal{H} = \mathcal{H}_V + \mathcal{H}_J. \quad (3)$$

The first term is given explicitly by

$$\mathcal{H}_V = \sum_{(ij)} V_{ij} n_i n_j, \quad (4)$$

where n_i is the number operator of the 3d electron at site i . The second term is derived by the generalized p-d Hamiltonian:

$$\begin{aligned} \mathcal{H}_{\text{pd}} = & \sum_{i,\gamma,\sigma} \varepsilon_\gamma^d d_{i\gamma\sigma}^\dagger d_{i\gamma\sigma} + \sum_{i,\{\gamma\},\{\sigma\}} U_{\{\gamma\},\{\sigma\}}^d d_{i\gamma_1\sigma_1}^\dagger d_{i\gamma_2\sigma_2}^\dagger d_{i\gamma_3\sigma_3} d_{i\gamma_4\sigma_4} \\ & + \sum_{i,\alpha,\sigma} \varepsilon_\alpha^p p_{i\alpha\sigma}^\dagger p_{i\alpha\sigma} + \sum_{i,\{\alpha\},\{\sigma\}} U_{\{\alpha\},\{\sigma\}}^p p_{i\alpha_1\sigma_1}^\dagger p_{i\alpha_2\sigma_2}^\dagger p_{i\alpha_3\sigma_3} p_{i\alpha_4\sigma_4} \\ & + \sum_{(ij),\gamma,\alpha,\sigma} t_{\gamma,\alpha}^{\text{pd}} d_{i\gamma\sigma}^\dagger p_{j\alpha\sigma} + \text{H.c.}, \end{aligned} \quad (5)$$

where $p_{i\alpha\sigma}$ is the annihilation operator of an O 2p electron with orbital α and spin σ at site i . ε_d (ε_p) indicates the orbital level energy and $U_{\{\gamma\},\{\sigma\}}^d$ ($U_{\{\alpha\},\{\sigma\}}^p$) describes the on-site Coulomb interaction for the d (p) electrons. For simplicity, sets of γ_i (α_i) and σ_i for $i = 1-4$ are described by $\{\gamma\}$ ($\{\alpha\}$) and $\{\sigma\}$, respectively. The last term expresses the electron transfer between the NN Fe and O sites where the $d_{x^2-y^2}$ and d_{xy} orbitals are only considered for γ . We derive the exchange Hamiltonian through the fourth-order perturbation processes with respect to $t_{\gamma\alpha}^{\text{pd}}$. This Hamiltonian is divided into the following three parts:

$$\mathcal{H}_J = \mathcal{H}_{2-2} + \mathcal{H}_{3-3} + \mathcal{H}_{2-3}, \quad (6)$$

where \mathcal{H}_{n-m} indicates the exchange interaction between Fe^{+n} and Fe^{+m} ions. Each term is expressed by a sum of the terms classified by the electron configuration in the intermediate states. As an example, an explicit form of the dominant term in \mathcal{H}_{2-2} is given by

$$\mathcal{H}_{2-2}^{\text{dd1}} = -J_{2-2}^{\text{dd1}} \sum_{(ij)} \left(\frac{3}{5} + \frac{1}{10} \vec{I}_i \cdot \vec{I}_j \right) \left(\frac{1}{4} - \tau_i^{l_{ij}} \tau_j^{l_{ij}} \right) \left(\frac{1}{2} - Q_i^z \right) \left(\frac{1}{2} - Q_j^z \right), \quad (7)$$

where \vec{I}_i is the spin operator with a magnitude of 2, and Q_i^z is the pseudo-spin operator for charge which takes $1/2$ for Fe^{3+} ion and $-1/2$ for Fe^{2+} one. $\tau^{l_{ij}}$ is defined in equation (2), where l is a function of sites i and j . A magnitude of the exchange interaction is given by $J_{2-2}^{\text{dd1}} = \frac{(t^{\text{pd}})^4}{\Delta^2 \Delta E}$ with the charge transfer excitation energy Δ from O to Fe, and the energy difference $\Delta E = E(d^7) + E(d^5) - 2E(d^6)$ between the intermediate state and the ground state of the Fe^{2+} ion. On the same footing, one term in \mathcal{H}_{2-3} is given by

$$\mathcal{H}_{2-3}^{\text{dd2}} = -J_{2-3}^{\text{dd2}} \sum_{(ij)} \left(\frac{3}{20} - \frac{3}{100} \vec{I}_i \cdot \vec{J}_j \right) \left(\frac{1}{2} + \tau_i^{l_{ij}} \right) \left(\frac{1}{2} - Q_i^z \right) \left(\frac{1}{2} + Q_j^z \right), \quad (8)$$

where Fe^{2+} and Fe^{3+} ions are assumed to be located at sites i and j , respectively. \vec{J}_i is the spin operator with a magnitude of $5/2$ for Fe^{3+} ion, and J_{2-3}^{dd2} is the exchange interaction. In both the terms in equations (7) and (8), the Hamiltonians are represented by products of the spin, orbital and charge parts.

3. Numerical results

We first show the numerical results for the charge state. The Coulombic term of the Hamiltonian \mathcal{H}_V in equation (3) is applied to a pair of the two-dimensional double triangle layers. We consider, in the Hamiltonian, three of the largest Coulomb interactions, i.e. the in-plane Coulomb interaction between the NN Fe sites, $V_{ab-\text{NN}}$, the inter-plane interaction between the NN sites, $V_{c-\text{NN}}$, and that between the next NN sites, $V_{c-\text{NNN}}$. We analyse the Hamiltonian

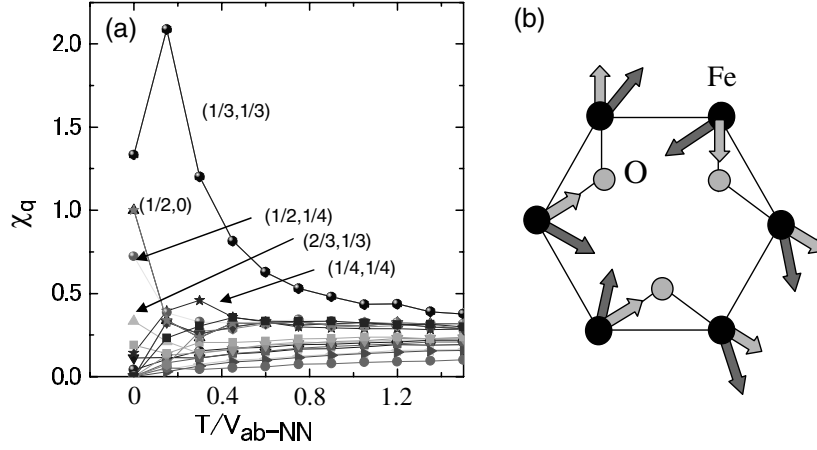


Figure 1. (a) Temperature dependence of the charge correlation function for several momenta; (b) a schematic picture of the pseudo-spin alignment and its projection component along Fe–O bonds.

by utilizing the classical Monte Carlo simulation in a 6×6 -size cluster with the periodic boundary condition. 100 000 steps are used for thermalization and 100 000 steps are used for the measurements. The Kawasaki algorithm is used to preserve charge conservation. We present in figure 1(a) the calculated temperature dependence of the charge correlation functions for several momenta \vec{q} defined by $\chi_{\vec{q}} = \frac{1}{N} \sum_{i,j} \langle n_i n_j \rangle e^{i\vec{q} \cdot (\vec{r}_i - \vec{r}_j)}$. Parameters are chosen to be $V_{c-NN}/V_{ab-NN} = 1.2$ and $V_{c-NNN}/V_{ab-NN} = 0.5$. With decreasing temperature, $\chi_{\vec{q}}$ at $\vec{q} = (1/3, 1/3)$ increases around $T = V_{ab-NN}$. This behaviour is consistent with the electron diffraction experiments where the streak-type diffuse intensity appears along the $(1/3, 1/3)$ direction. Below about $T = 0.2 V_{ab-NN}$, $\chi_{\vec{q}}$ s at other \vec{q} grow up and $\chi_{\vec{q}=(1/3, 1/3)}$ is reduced. It indicates that, in the ground state, several charge alignments seem to be nearly degenerate, as is known in the antiferromagnetic Ising model in a triangular lattice. Actually, in our mean field calculation, it is shown that, around $V_{c-NNN}/V_{c-NN} = 0.5$, the charge alignments with $\vec{q} = (1/3, 1/3)$, $(1/2, 1/2)$ and $(1/4, 1/4)$ are degenerate at $T = 0$, and the $(1/3, 1/3)$ state with a finite polarization along the c -axis stabilizes at finite temperature. This will be reported elsewhere in more detail [8].

Next we introduce the results calculated in $\mathcal{H}_V + \mathcal{H}_J$. Here, we assume that, below the CO temperature, the system consists of a pair of the $2\text{Fe}^{2+}-\text{Fe}^{3+}$ and $\text{Fe}^{2+}-2\text{Fe}^{3+}$ layers. At a temperature below the CO temperature, a sharp peak appears in the temperature dependence of the specific heat. This corresponds to the ferrimagnetic spin ordering with $\vec{q} = (1/3, 1/3)$, and the obtained spin structure is consistent with the neutron diffraction experiments [2–4].

Here, we show the orbital state at low temperature, where the charge and spin degrees of freedom are frozen. Let us consider the orbital state in the $2\text{Fe}^{2+}-\text{Fe}^{3+}$ layer (orbital-rich layer) where a Fe^{3+} ion with spin down is surrounded by the six NN Fe^{2+} ions with spin up. It is easily shown that, due to the six-fold symmetry, the orbital interaction in a $\text{Fe}^{2+}-\text{Fe}^{3+}$ bond is irrelevant to determining the orbital state. Then, when we focus on the Fe^{2+} sublattice, the orbital state is described by the following model in a honeycomb lattice:

$$\mathcal{H}_{\text{orbital}} = -J_{\text{orbital}} \sum_{\langle ij \rangle} \left(\frac{1}{4} + \tau_i^{l_{ij}} \tau_j^{l_{ij}} \right), \quad (9)$$

where J_{orbital} is the effective orbital interaction, which is negative. We performed a Monte Carlo simulation for this model in a finite-size cluster. It is shown that the temperature dependence of

the specific heat shows a weak cusp at around $T = 0.2J_{\text{orbital}}$. We calculate the correlation functions of the pseudo-spin operators defined by $S_q^{lm} = \frac{1}{N} \sum_{i,j} \langle T_i^l T_j^m \rangle e^{iq \cdot (\vec{r}_i - \vec{r}_j)}$ for all possible momenta \vec{q} in a cluster. However, S_q^{lm} s do not show the remarkable enhancement at low temperatures and their values are less than 10% of the maximum values. On the other hand, the so-called Edwards–Anderson parameter defined by $q_{\text{EA}} = \frac{1}{N} \sum_i (T_i^{z^2} + T_i^{x^2})$ increases at around $T = 0.2J_{\text{orbital}}$ and takes its maximum. The orbital-alignment patterns at low temperatures depend on a simulation, and seem to be random. A schematic picture of the pseudo-spin alignment in a cell is shown in figure 1(b), where the alignment of \vec{T} , as well as the projection component of the pseudo-spin along the bond, i.e. τ_i^{ij} , are plotted. It is seen that three of six τ s are directed inside the cell and other three are outside the cell and, at low temperatures, this rule is found in all cells. Although the definite orbital state is not identified at the present stage, we expect that possible orbital states are orbital-glass or-disordered states. This come from the orbital interaction depending on the bond direction, and the frustration between the three bonds connecting NN Fe ions.

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