Spin and charge frustration in magneto-dielectric material

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Abstract. Electronic, dielectric and magnetic properties in exotic dielectrics, $R$Fe$_2$O$_4$ ($R$: rare-earth metal ion), are investigated. By analyzing the effective Hamiltonian for Fe 3$d$ electrons, spin and charge correlation functions and electric polarization are calculated by the Monte-Carlo technique. Electric polarization is strongly reinforced below magnetic ordering temperature and is controlled by applying magnetic field. Observed unique magneto-dielectric phenomena are attributed to frustration in a spin-charge coupled system.

1. Introduction
It is widely recognized that geometrical frustration brings about a variety of non-trivial exotic phenomena in correlated electron system. One of the recent topics in this research field are multiferroic phenomena, i.e. a coexistence of ferro(ferri)magnetic and ferroelectric long-range orders. Because of spin frustration, localized spins tend to show a non-collinear magnetic order with long-periodicity such as spiral, helical and cycloidal structures. In order to gain the anti-symmetric exchange interaction, so-called the Dzyloshinskii-Moriya interaction, a spontaneous lattice distortion without inversion symmetry is induced under the non-collinear spin structure. In this point of view, a series of the multiferroic materials are recognized to be spin driven ferroelectric materials.

On the other hand, in some classes of materials, an electronic charge order without inversion symmetry generates the electric polarization. This is termed electronic ferroelectricity. The layered iron oxide $R$Fe$_2$O$_4$ ($R$: rare-earth metal ion) of the present interest is one of this class of materials [1]. The crystal structure consists of a pair of the Fe triangle planes stacked along the c axis, as shown in Fig. 1. Electric and magnetic properties in this material are governed by the Fe 3$d$ electrons. A nominal valence of Fe ion is +2.5, and a charge ordered (CO) state of Fe$^{2+}$ and Fe$^{3+}$ is confirmed below $T_{CO} = 320K$ by the electron diffraction experiments [2]. Electron configurations in Fe$^{2+}$ and Fe$^{3+}$ are $d^6$ and $d^5$ respectively, and the doubly degenerate orbital degree of freedom is active in Fe$^{2+}$. The ferrimagnetic long-range order of Fe spins is confirmed below $T_N = 250K$ [3, 4]. A variety of dielectric anomalies are observed around $T_{CO}$, and several magneto-dielectric phenomenal are also reported experimentally [5]. These observations indicate that the electric polarization and low-energy dielectric properties are responsible for the electronic charge of Fe 3$d$ orbital and strong coupling between charge and spin degrees of freedom.

In this paper, the electronic, magnetic and dielectric properties in exotic dielectrics, $R$Fe$_2$O$_4$, are examined. Based on the derived effective Hamiltonian for charge, spin and orbital, we
calculate the electric polarization by the Monte-Carlo technique. We find that the polarization
is strongly enhanced below the magnetic ordering temperature, and is controlled by applying
magnetic field. These unique nature is attributed to the spin-charge coupling on a geometrical
frustration.

2. Model and method
We start from the model Hamiltonian which describes the electronic structure in a paired triangle
lattice of $RFeO_4$. The main electronic interactions in a paired triangle lattice for Fe 3$d$ electrons
are the long-range Coulomb interaction and the exchange one. The Hamiltonian is given by
\[ \mathcal{H} = \mathcal{H}_V + \mathcal{H}_J. \]
The first term is for the Coulomb interaction and is represented by the pseudo-spin operator for
the charged degree of freedom. This is given by
\[ \mathcal{H}_V = \sum_{(ij)} V_{ij} Q_i Q_j, \]
where $Q_i$ takes 1/2 for Fe$^{3+}$, and -1/2 for Fe$^{2+}$. We introduce the largest three interactions
in a paired triangle layer, i.e. the interplane NN interaction ($V_{cNN}$), the intraplane NN one
($V_{abNN}$), and the interplane next NN one ($V_{cNNNN}$). The exchange Hamiltonian is derived
from the generalized $pd$ model where the five Fe 3$d$ orbitals and the O 2$p$ orbitals are taken
into account. By the canonical transformation in the perturbational procedure, we obtain the
effective exchange Hamiltonian for the NN Fe ions. The exchange interactions depend on the
valences of Fe ions which occupy a given NN Fe bond. The Hamiltonian is divided by a sum of
them given by $\mathcal{H}_J = \mathcal{H}_{22} + \mathcal{H}_{23} + \mathcal{H}_{23}$ where $\mathcal{H}_{nm}$ is the term for a Fe$^{n+}$-Fe$^{m+}$ bond. Details
of the Hamiltonian are presented in Ref. [6, 7]. One of the dominant terms of $\mathcal{H}_{22}$ and $\mathcal{H}_{23}$ are
given by
\[ \mathcal{H}_{22}^{(1)} = J_{22}^{(1)} \sum_{(ij)} \left( \frac{\vec{T}_i \cdot \vec{T}_j}{2} + 6 \right) \left( \frac{1}{2} - 2\tau_i^l \tau_j^l \right) \left( \frac{1}{2} - Q_i \right) \left( \frac{1}{2} - Q_j \right), \]
and
\[ \mathcal{H}_{23}^{(1)} = J_{23}^{(1)} \sum_{(ij)} \left( \frac{\vec{J}_i \cdot \vec{J}_j}{2} + \frac{15}{2} \right) \left( \frac{1}{2} - \tau_j^l \right) \left( \frac{1}{2} + Q_i \right) \left( \frac{1}{2} - Q_j \right), \]
where $\vec{T}_i$ and $\vec{J}_i$ are the spin operators for Fe$^{2+}$ and Fe$^{3+}$ at site $i$ with amplitude of 2 and
5/2, respectively. The pseudo-spin operator $\tau_i^l$ for the orbital degree of freedom is defined by
$\tau_i^l = \cos(2\pi n_l/3) T_i^l + \sin(2\pi n_l/3) T_i^z$ with $n_l = (1, 2, 3)$ where $l$ indicates the three Fe-O NN
bond directions in a triangle plane. The operator $\vec{T}_i$ is given by the electronic operator as
$\vec{T}_i = \frac{1}{2} \sum_{lts} d_{lts}^d (\vec{\sigma})_{lt} d_{lt}^d s$ where $d_{lts}$ is the electron annihilation operator for Fe 3$d$ electron with
spin $s(=\uparrow, \downarrow)$, orbital $l(=x^2-y^2, xy)$ at site $i$, and $\vec{\sigma}$ are the Pauli matrices [8]. The exchange
constants are represented by the on-site Coulomb interaction at a Fe site and the transfer integral
between the NN Fe 3$d$ and O 2$p$ orbitals.

In order to analyze the model Hamiltonian given above, we adopt the classical Monte-Carlo
(MC) method in a finite size cluster system. The multi-canonical MC method is utilized to avoid
trapping of the simulation in local minima. Finite size cluster of $L \times L \times 2$ ($L = 6$ and 12) sites
with the periodic boundary condition in a plane is utilized. In the simulation, $6 \times 10^6$MC steps
are spent for generating a histogram in the multi-canonical MC method, and $16 \times 10^6$ MC steps
are for measurements. Energy parameter value is chosen to be $V_{cNN}/V_{abNN} = 1.2$. Numerical
values for the on-site Coulomb interactions, the electron-transfer integral, and the charge-transfer
gap, to estimate the exchange constants, are obtained from the experimental analyses. In the
following simulation, products of the orbital pseudo-spin operators, $\tau_i^l \tau_j^l$, in the Hamiltonian
Eqs. (2) and (3) are taken to be zero. This may be justified from our supplementary simulation;
we obtain by the MC simulation that the characteristic temperature for orbital degree of freedom is much lower than charge and spin ordering ones.

3. Numerical results

Figure 1. Crystal structure of the paired triangle lattice and a schematic view of the CO structure characterized by $\vec{q} = (1/3, 1/3)$ accompanied with electric polarization. Open and filled circles represent Fe$^{2+}$ and Fe$^{3+}$ respectively.

Numerical results of the electric polarization $P$, the charge correlation function $N(\vec{q})$, and spin correlation one $S(\vec{q})$ at $\vec{q} = (1/3, 1/3)$ are presented in Fig. 2. These are defined by $P = \sqrt{\langle p^2 \rangle}$ with $p = N^{-1}(\sum_i^u - \sum_i^l)Q_i$, $N(\vec{q}) = (2N^2)^{-1}\sum_{ij} \langle Q_i Q_j \rangle e^{-i\vec{q} \cdot (\vec{r}_i - \vec{r}_j)}$, and $S(\vec{q}) = (2N^2)^{-1}\sum_{ij} \langle K_i^z K_j^+ \rangle e^{-i\vec{q} \cdot (\vec{r}_i - \vec{r}_j)}$. Symbols $\sum_i^u$ and $\sum_i^l$ represent summations of sites in the upper and lower triangle layers, respectively, and $K_i^z = J_i^z$ for Fe$^{3+}$ and $I_i^z$ for Fe$^{2+}$. A small peak structure in $N(\vec{q})$ around $T/V_{abNN} = 0.2$ corresponds to the CO temperature at momentum $\vec{q} = (1/3, 1/3)$ associated with electric polarization. The Néel temperature for the ferrimagnetic spin ordering is identified from a sharp increase of $S(\vec{q})$ around $T/V_{abNN} = 0.1$. It is shown that the electric polarization $P$ starts to increase around the CO temperature and furthermore enhances below the Néel temperature. These results imply that the electric polarization accompanied by the CO is stabilized by the spin ordering through the charge-spin coupling in the exchange Hamiltonian. Below the Néel temperature, the Fe spins are ordered partially; directions of $N/3$ spins, $N$ is a total number of sites, are not uniquely determined due to spin frustration. This spin structure is realized on the polar CO structure accompanied with the electric polarization. In other-types of CO states with no polarization, which compete with the present polar CO state, spin degeneracy is much lower than that in the present case. As a result, this spin fluctuation contributes to the entropy gain at finite temperature and stabilizes the polar CO state.

Now we show the magneto-electric response in the present spin-charge coupled frustrated system. In Fig. 3, the magnetic field dependence of the electric polarization is presented. When we take $V_{abNN} = 1$ eV, $H = 0.05$ corresponds to about 50T. It is shown that, with applying the magnetic field, the electric polarization is gradually decreases. This is because the entropy gain due to the spin fluctuation, explained above, is reduced by the magnetic field. In Fig. 4, the numerical results in another parameter set are presented. At $V_{cNNN}/V_{abNN} = 0.61$, the following sequential magnetic phase-transition occurs with decreasing temperature; the paramagnetic phase to the polar CO characterized by a momentum $\vec{q} = (1/3, 1/3)$ at $T/N_{abNN} = 0.125$,
and to another CO with a momentum $\vec{q} = (1/2, 1/2)$ at $T/V_{\text{abNN}} = 0.02$. This is confirmed by the $P - T$ curve at $H = 0$ in Fig. 3 where a small dip around $T/V_{\text{abNN}} = 0.125$ and a large reduction of $P$ at $T/V_{\text{abNN}} = 0.02$ appear. By applying the magnetic field, in the polar CO state in the intermediate temperature range, the polarization is gradually decreased. On the other hand, at the lowest temperature CO phase, the magnetic field enhances the electric polarization. In the low temperature CO state with a momentum $\vec{q} = (1/2, 1/2)$, a stable magnetic structure is the antiferromagnetic order. Under the magnetic field, this spin structure becomes unstable in comparison with the ferrimagnetic one realized in the polar charge order with $\vec{q} = (1/3, 1/3)$.

In summary, we examine the electronic, magnetic and dielectric properties in exotic dielectrics, $\text{RFe}_2\text{O}_4$. Based on the effective model Hamiltonian derived from the generalized $pd$ model, we calculate the spin and charge correlation functions and electric polarization by the Monte-Carlo technique. It is found that the polarization is strongly enhanced below the magnetic ordering temperature and is controlled by applying magnetic filed. We show that a geometrical frustration in the spin-charge coupling plays crucial roles in the magneto-dielectric phenomena.

![Figure 3. Magnetic field dependence of electric polarization. Parameter is chosen to be $V_{c\text{NNN}}/V_{\text{abNN}} = 0.6$.](image1)

![Figure 4. Magnetic field dependence of electric polarization. Parameter is chosen to be $V_{c\text{NNN}}/V_{\text{abNN}} = 0.61$.](image2)

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References
[1] Kimizuka N, Takayama-Muromachi E, and Shiratori K 1990 in *Handbook on the Physics and Chemistry of Rare Earth* vol 13 ed Gshneider Jr. K A, and Eyring L, (Amsterdam; Elsevier) p 283
[2] Yamada Y, Kitsuda K, Nohdo S, and Ikeda N 2000 *Phys. Rev. B* 62, 12167
[3] Akimitsu J, Inada Y, Shiratori K, Shindo I, and Kimizuka N 1979 *Sol. Stat. Comm.* 32, 1065
[4] Funahashi S, Akimitsu J, Shiratori K, Kimizuka N, Tanaka M, and Fujishita H 1984 *J. Phys. Soc. Jpn.* 53, 2688
[5] Ikeda N, Ohsumi Y, Ohwada K, Ishii K, Inami T, Kakurai K, Murakami Y, Yoshii K, Mori S, Horibe Y, and Kito Y 2005 *Nature* 436, 1136
[6] Nagano A, Naka M, Nasu J, and Ishihara S 2007 *Phys. Rev. Lett.* 99, 217202
[7] Naka M, Nagano A and Ishihara S 2008 *Phys. Rev. B* 77, 224441
[8] Nasu J, Nagano A Naka M, and Ishihara S 2008 *Phys. Rev. B* 78 024416