Charge dynamics of electronic ferroelectricity in geometrically frustrated lattice

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Abstract. Charge dynamics in electronic ferroelectric materials, where electronic charge order is responsible for the electric polarization, is studied. Motivated from the layered iron oxide LuFe$_2$O$_4$ with a frustrated geometrical lattice, we introduce the spin-less fermion V-t model in a paired triangular lattice. This model is analyzed by utilizing the exact diagonalization method with the Lanczos algorithm in finite-size clusters. In particular, we focus on frustration effects on the charge dynamics. In the calculation of the ground state phase diagram, the non-polar two-fold charge order (CO) and the polar three-fold CO appear. In the optical conductivity spectra in the polar three-fold CO phase, multiple-peak structures appear in a wide energy range, in contrast to the spectra in the non-polar two-fold CO phase. This is originated from the non-equivalent two sublattices in the three-fold CO phase. The dynamical charge correlation function in the non-polar two-fold CO phase shows low-energy excitation at the wave vectors which correspond to the three-fold CO. This feature becomes remarkable near the phase boundary between the two-fold and three-fold CO phases. These precursor effects are attributed to the frustrated charge ordered system.

1. Introduction
Ferroelectricity and related phenomena have widely attracted much attention since discovery of the gigantic multiferroic phenomena in rare-earth manganese oxides. It is recently revealed that in the multiferroic materials, the electric polarization is driven by the inverse Dzyaloshinsky-Moriya interaction and/or the exchange striction mechanism under the non-collinear spin structures in the frustrated spin system. This is recognized to be a spin-driven ferroelectricity where the non-collinear spin order is the primary order parameter and the ferroelectric polarization is the secondary one, that is, the improper ferroelectricity. Recently, another type of the ferroelectricity is suggested theoretically and experimentally: the electronic charge order (CO) without the inversion symmetry is responsible for the electric polarization. This is termed the electronic ferroelectricity or the charge-driven ferroelectricity [1, 2, 3]. This is seen in some transition-metal oxides, e.g. LuFe$_2$O$_4$, and the charge-transfer organic salts such as $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$. These materials are the so-called the 1/4 filling system where the electron per site is 0.5, and are the charge ordered insulator. This is in contrast to the spin-driven type ferroelectric materials, which are the Mott insulators of the 1/2 filling, and most of the displacive-type ferroelectric materials which are the band insulators.

As an example, we introduce the electronic structure and the dielectric properties in LuFe$_2$O$_4$. The crystal structure of the system consists of the Fe-O double layers and the Lu-O ones stacked
along the c axis. The electric and magnetic properties are responsible for the Fe-O paired-triangular lattices which are termed the W-layer. The double triangular lattice is schematically shown in Fig. 1. The nominal valence of the Fe ions are 2.5+ which implies a coexistence of the Fe$^{2+}$ and Fe$^{3+}$ with equal amount. The three-dimensional CO of Fe ions occurs around 320K where large dielectric anomalies are observed in the dielectric constant. The 3-fold charge ordered state is confirmed by the resonant x-ray scattering experiments at the Fe K-edge. It is thought that the charge order pattern in the W-layer are mainly determined by the interactions inside of the W-layer, and the stacking pattern of the charge order along the c axis is described by the weak inter-W-layer interactions. Therefore, it is widely expected that the electric polarization is attributed to the CO in the W-layer without the inversion symmetry.

As well as the CO, the charge fluctuation in the electronic ferroelectric materials has much attention. Several characteristic charge dynamics is suggested experimentally. The relaxor-like dielectric fluctuations are observed in LuFe$_2$O$_4$ and κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ [4]. The optical absorption experiments in LuFe$_2$O$_4$ indicate that large charge fluctuation remains far below the charge ordering temperature [5]. A drastic change in the charge ordered patterns by introducing small amount of the oxygen deficiency is observed in rare-earth iron oxides. From the theoretical view points, the present authors and co-workers suggest that the polar three-fold charge ordered phase is stabilized by the thermal and quantum charge fluctuation [6, 7, 8, 9]. It is required to reveal origin of such characteristic charge dynamics in electronic ferroelectric materials.

Motivated from these recent experimental and theoretical results in the electronic ferroelectric materials, we study dynamical properties in the geometrically frustrated charge ordered system. We analyzed the extended V-t model in the paired triangular lattice by utilizing the exact diagonalization method. The optical conductivity spectra and the dynamical charge correlation function are calculated in a paired triangular lattice beyond the previous studied in the single-triangular lattice [10, 11]. It is shown that the multiple peak structure in the polar charge ordered phase is due to the two-sublattice structure in this charge ordered structure. This is directly related to origin of the electric polarization in this system. Near the phase boundary between different charge ordered phases, the low-energy charge excitations are observed in several momentum. Relation between the obtained results and the recent resonant x-ray scattering experiments is discussed.

2. Model and Method
Motivated from the crystal and electronic structure of the layered iron oxide LuFe$_2$O$_4$, we consider the double triangular lattices stacked along the c axis. As a minimal model to study the CO and dynamics in this crystal lattice, we adopt the half-filled extended V-t model for spinless fermions. The electron transfer and the long-range Coulomb interactions are introduced in the double triangular lattice. The model Hamiltonian is defined by

$$\hat{H}_{Vt} = \hat{H}_t + \hat{H}_V,$$

where the first term is for the electron transfers given by

$$\hat{H}_t = -t_{ab} \sum_{\langle ij \rangle} c_i^\dagger c_j - t_c \sum_{\langle ij \rangle} c_i^\dagger c_j + H.c.,$$

and the second term is for the Coulomb interactions given by

$$\hat{H}_V = V_{abNN} \sum_{\langle ij \rangle} n_i n_j + V_{NN} \sum_{\langle ij \rangle} n_i n_j + V_{cNN} \sum_{[ij]} n_i n_j.$$ 

Here, $c_i$ and $n_i$ ($\equiv c_i^\dagger c_i$) represent the annihilation operator and the number operator of a fermion,
respectively. A schematic view of the crystal lattice and the interactions are shown in Fig. 1 where the large and small circles represent the sites in the upper and lower planes, respectively. We consider the inter-site Coulomb interactions between the in-plane NN sites \(V_{abNN}\), those between the inter-plane NN sites \(V_{cNN}\) and NNN sites \(V_{cNNN}\). The symbols \(\sum_{(ij)}\), \(\sum_{(ij)}\) and \(\sum_{(ij)}\) represent summation for the pairs corresponding to \(V_{abNN}\), \(V_{cNN}\) and \(V_{cNNN}\), respectively. As for the electron transfer term \(H_t\), the transfer integral between the in-plane NN sites \(t_{ab}\) and that between the inter-plane NN site \(t_c\) are taken into account. The optical conductivity and the dynamical charge correlation functions are calculated by using the exact diagonalization method based on the Lanczos procedure. We adopt the finite size cluster of \(4 \times 3 \times 2 = 24\) sites with the periodic boundary condition along the \(x\) and \(y\) directions (see Fig. 1), and the fermion number \(N_e = 12\).

3. Results of Calculation
First we show the phase diagram in the plane of \(V_{cNN}/V_{abNN}\) and \(t/V_{abNN}\) in Fig 2. The parameter sets are chosen to be \(V_{cNN} = 1.2V_{abNN}\) and \(t = t_{ab} = t_{c}\). The dynamical charge correlation functions are calculated in parameter values indicated by black circles (see the text).
Figure 3. Schematic charge ordered structures of CO$_{1/3}$ in (a) and CO$_{1/2}$ in (b). The black and white circles are for the charge rich and poor sites, respectively. Symbols A and B represent the two kinds of the sublattices (see the text).

i.e. the three-fold CO (CO$_{1/3}$) and the two-fold one (CO$_{1/2}$) as schematically shown in Fig. 3(a) and (b), respectively, where black and white circles represent charge-rich and poor sites. The maximum values of $N(q)$ for $q = (1/3,1/3)$ in CO$_{1/3}$ and that for $q = (1/2,1/2)$ in CO$_{1/2}$ are 0.11 and 0.25, respectively. In $t/V_{\text{abNN}} = 0.005$, we obtain $N(q) = 0.10$ for $q = (1/3,1/3)$ and $N(q) = 0.25$ for $q = (1/2,1/2)$ at $V_{\text{NNNN}}/V_{\text{abNN}} = 0.6$ and 0.7, respectively. Since the total charge in the upper and lower planes are different, a finite electric polarization exists in CO$_{1/3}$. At $t = 0$, where the present model is the classical charge model, it is exactly shown that the polar CO$_{1/3}$ phase is degenerated with the CO$_{1/2}$ phase at $V_{\text{NNNN}}/V_{\text{abNN}} = 0.6$. This point is recognized as a frustration point. When the finite electron transfer is introduced at the frustration point, the CO$_{1/3}$ phase is stabilized. In a region of large $t$, both the charge correlation $N(q)$ for the CO$_{1/3}$ phase and the Drude component in the optical conductivity spectra are observed. Thus, this phase is identified as a mixed phase of CO$_{1/3}$ and metal, although further studies are required to understand detailed character of this phase. The topological feature of the obtained phase diagram is consistent with the previous result where the present Hamiltonian of Eqs. (1), (2) and (3) are analyzed by utilizing variational Monte Carlo method in Ref. [8, 9].

Stability of the polar CO$_{1/3}$ phase is attributed to the large quantum charge fluctuation in the paired triangular lattice. A key issue is the two-sublattice structure in this charge ordered structure, as shown in Fig. 3(a). Each charge-poor site in the upper plane is surrounded by the six NN charge-rich sites in the same plane. Thus, the Coulomb potential, acting on these sites are strong, and the charge fluctuation hardly occurs. On the other hand, each charge-poor site in the lower plane is surrounded by three charge-rich sites and three charge-poor sites in the same plane. The Coulomb potentials at these sites from the in-plane NN sites are canceled out, and the charges easily fluctuate at these site. These two sublattices are termed A and B from now on. Therefore, in the case of finite electron transfer, there is large kinetic energy gain due to charge fluctuation. This is a unique character in the CO$_{1/3}$ phase. In the CO$_{1/2}$ phase, all sites are equivalent.

Now we introduce the dynamical properties in the V-t model in a paired triangular lattice. We calculate the optical conductivity spectra and the dynamical charge correlation function defined by

$$
\sigma_{\mu}(\omega) = -\frac{e^2}{N\omega} \text{Im}(\langle j^\dagger_\mu j_\mu \rangle) \frac{1}{\omega - \mathcal{H} + E_0 + i\eta},
$$

and

$$
N(q,\omega) = -\text{Im}(\langle n(q) \rangle) \frac{1}{\omega - \mathcal{H} + E_0 + i\eta} \langle n(-q) \rangle,
$$

respectively. Here, $|0\rangle$ and $E_0$ are the ground state and the ground state energy, respectively.
We define the current operator as \( j_\mu = \sum_{i,j} t_{ij} (r_{ij} c_i^\dagger c_j + r_{ji} c_j^\dagger c_i) \) for the \( \mu = (x, z) \) direction where \( r_{ij} \) is a unit vector connecting site \( i \) and site \( j \). We introduce an infinite decimal constant \( \eta \) for the recursion procedure in the Lanczos calculation.

In Fig. 4, we show the numerical results of the optical conductivity \( \sigma_\mu(\omega) \) in the CO\(_{1/2}\) [Fig. 4(a)] and CO\(_{1/3}\) [Fig 4(b)] phases. Parameter values are chosen to be \( V_{\text{NNN}}/V_{\text{abNN}} = 0.6 \) in Fig. 4(a) and \( V_{\text{NNN}}/V_{\text{abNN}} = 0.7 \) in Fig. 4(b). In the CO\(_{1/2}\) phase, the spectra in both the \( x \) and \( z \) show simple peak structure. These peaks correspond to the charge excitations from the charge rich sites to the poor sites in the CO\(_{1/2}\) structure. On the other hand, in the CO\(_{1/3}\) phase, the multiple-peak structures are shown in a wide energy range. These structures are attributed to various excitation energies due to the sublattice structure of the CO\(_{1/3}\) phase explained above. For example, the lowest (highest) energy peak is due to the charge fluctuation between the sublattice B(A).

The calculated dynamical charge correlation function spectra \( N(\mathbf{q}, \omega) \) in the CO\(_{1/2}\) phase are
shown in Fig. 5. The parameter values of the electron transfer are chosen to be \( t/V_{abNN} = 0.05 \) (broken lines) and 0.15 (solid lines) which correspond to the symbols in Fig. 2. The wave vectors are defined in the Brillouine zone of the triangular lattice and the phase between the upper and lower planes is taken to be \( \pi \). In the case of \( t/V_{abNN} = 0.05 \), a large peak structure appears around \( \omega = 0 \) at \( q = (-1/2, 1/2) \). This reflects the CO of the CO\(_{1/2}\) structure. Other peak structures observed in the region of \( \omega/V_{abNN} = 1.7 \sim 1.9 \) are not remarkable. On the other hand, in the case of \( t/V_{abNN} = 0.15 \), which is close to the phase boundary between the CO\(_{1/2}\) and the mixed phase of CO\(_{1/3}\) and metal, the peaks in \( N(q, \omega) \) at the wave vectors \( q = (1/3, 1/3) \) and \( q = (-1/3, 2/3) \) are prominent in a low energy range. This is interpreted as a precursor of the phase transition from the CO\(_{1/2}\) phase to the CO\(_{1/3}\) one, and is resulted from the charge frustration.

4. Summary and discussion

Recently, the charge dynamics in LuFe\(_2\)O\(_4\) is studied by the resonant inelastic x-ray scattering (RIXS) experiments [12]. The scattering intensity of RIXS is approximately given by the loss function as \( I(q, \omega) \sim -\text{Im}[1/\varepsilon(q, \omega)] \). It is shown that above the charge ordering temperature, the peak structures are observed in the several wave vectors correspond to the two-fold, three-fold and four-fold COs. This is in contrast to the results in other charge ordered systems such as Sr\(_{14}\)Cu\(_2\)O\(_4\) where the spectra appear at the wave vector corresponding to the CO pattern. This may be related to the present calculated results in the dynamical charge correlation function presented in Fig. 5 where the peak structure appears at CO\(_{1/3}\) even in the two-fold CO structure near the phase boundary. Further comparisons between theoretical and experimental results are required to reveal characteristic charge dynamics in electronic ferroelectricity.

In summary, we study the charge dynamics in the electronic ferroelectricity motivated from the layered iron oxides. It is shown that the multiple peak structure in the polar charge ordered phase is due to the two-sublattice structure in this charge ordered structure. This is directly related to the origin of the electric polarization in this system. Near the phase boundary between different charge ordered phases, the low-energy charge excitations are observed in several momentum. This is a precursor of the phase transition due to the charge frustration. The obtained results and the recent resonant x-ray scattering experiments are discussed.

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6. References

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