Orbital ordering and fluctuation in perovskite titanates

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Abstract

We study the orbital ordering and fluctuation in perovskite titanates where the three t_{2g} orbitals are degenerate at each Ti site. The orbital correlation function is calculated by using the random-phase approximation. It is proposed that the successive phase transition for the orbital ordering occurs. This is caused by the multi-components of the orbital order parameters. The characteristic feature of the momentum dependence of the orbital correlation function near the orbital ordering temperature is expected to be observed by the resonant x-ray scattering.

Key words: Strongly correlated electrons, orbital ordering, phase transition, titanates

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The orbital degrees of freedom in a transition-metal ion have been recently attracted much attention since the discovery of the colossal magnetoresistance in perovskite manganites. The perovskite titanates $\mathrm{RTiO_3}$, where R indicates a trivalent rare-earth cation, is known to be another class of materials where the orbital degrees of freedom govern the electrical and magnetical properties. The nominal charge valence of a Ti ion in these compounds is 3+ and one electron occupies the triply degenerate t_{2g} orbitals. Recently resonant x-ray scattering method (RXS) [1] is developed as a probe to detect the orbital ordering (OO) and was applied to the perovskite manganites and titanates [2]. There are several different aspects between the t_{2g} and e_g orbital systems ; in the t_{2g} orbital systems, the three-fold orbital degeneracy, no electron transfer between the different orbitals in the nearest neighboring (NN) sites, a weak Jahn-Teller coupling, the orbital angular momentum and so on. In order to clarify the mechanism of OO in perovskite titanates and its difference from that in manganites, we study, in this paper, the orbital correlation functions as well as the order parameters. We propose that the orbital fluctuation is observed by RXS as a diffuse scattering.

We calculate the scattering cross section of RXS from the orbital fluctuation. We derived the scattering cross section by using the group theoretical analyses where the microscopic mechanism of the scattering is not identified. The cross section is given by [3]

$$\frac{d\sigma}{d\Omega} = A \sum_{\Gamma\gamma\Gamma'\gamma'} I_{\Gamma'} I_{\Gamma} S_{\Gamma'\gamma'} S_{\Gamma\gamma} \langle O_{l'\Gamma'\gamma'} O_{l\Gamma\gamma} \rangle e^{-i\boldsymbol{K}\cdot\boldsymbol{R}}, \quad (1)$$

with $\boldsymbol{R} = \boldsymbol{r}_{l'} - \boldsymbol{r}_l$. $\mathrm{O}_{l\Gamma\gamma}$ is the orbital operator with symmetry Γ and γ at site l where Γ and γ indicate the irreducible representation and its basis in the O_h group, respectively ($(\Gamma\gamma) = (E_u, E_v)$, (T_{1x}, T_{1y}, T_{1z}) and (T_{2x}, T_{2y}, T_{2z})). I_Γ is the coupling constant between orbital and x-ray and is not determined by the group theoretical analyses. $\boldsymbol{K}$ is the scattering vector of x-ray, $S_{\Gamma\gamma}$ is the polarization part of the cross section including information of the polarization of incident and scattered x-rays, and A is a constant. We note that the cross section is written by the correlation function of the orbital operators.

The orbital correlation function in Eq.(1) is calculated based on the effective Hamiltonian for orbitals derived previously [3]. This model is obtained from the tight-binding Hamiltonian for the Ti ions. By using the perturbational calculation with respect to (the electron transfer)/(the on-site Coulomb interaction), the

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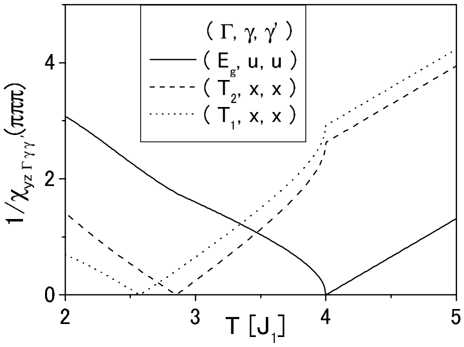

Fig. 1. Temperature dependence of the inverse of the orbital correlation functions. Bold, broken and dotted lines are $\chi^{-1}_{E_u E_u}(\pi\pi\pi)$, $\chi^{-1}_{T_{2x} T_{2x}}(\boldsymbol{k})$, and $\chi^{-1}_{T_{1x} T_{1x}}(\boldsymbol{k})$, respectively.

effective Hamiltonian is given by

$$H = \sum_{g=T_{2g},T_{1g},E_g,A_{1g}} J_g K_g^S K_g^O. \qquad (2)$$

J_g's are the exchange constants where the intermediate states in the exchange process are classified by g. K_g^S and K_g^O are the spin and orbital parts given by

$$K_g^S = (A_g + B_g \boldsymbol{S}_i \cdot \boldsymbol{S}_j), \qquad (3)$$

and

$$K_g^O = \sum_{\Gamma\gamma\gamma' <i,j>} G_{i,j,g}^{\Gamma\gamma\Gamma\gamma'} O_{i\Gamma\gamma} O_{j\Gamma\gamma'}, \qquad (4)$$

respectively. $\boldsymbol{S}_i$ is the spin operator at site i, $G_{i,j,g}^{\Gamma\gamma\Gamma\gamma'}$ is the coupling constant between the NN orbital operators, and A_g and B_g are the coupling constants of the spin interactions.

By using the random-phase approximation, we calculate the orbital correlation functions defined by $\chi_{\Gamma\gamma\Gamma\gamma'}(\boldsymbol{k}) \equiv \langle O_{\boldsymbol{k}\Gamma\gamma} O_{-\boldsymbol{k}\Gamma\gamma'} \rangle$. Here $O_{\boldsymbol{k}\Gamma\gamma}$ is the orbital operator in the momentum space. The spin state is assumed to be paramagnetic. Among several kinds of the orbital correlation functions, the temperature dependence of $\chi^{-1}_{E_u E_u}(\boldsymbol{k})$, $\chi^{-1}_{T_{2x} T_{2x}}(\boldsymbol{k})$, and $\chi^{-1}_{T_{1x} T_{1x}}(\boldsymbol{k})$ at $k = (\pi, \pi, \pi)$ are plotted in Fig. 1. It is shown that the successive phase transitions for the orbital orderings occur; $\chi^{-1}_{EuEu}(\pi\pi\pi)$ becomes zero at $T = 4J_1$ ($\equiv T_{oo1}$) with $J_1 \equiv (9J_{T_{1g}} + 3J_{T_{2g}} - 4J_{E_g} - 2J_{A_{1g}})/18$. At the same temperature, $\chi^{-1}_{E_v E_v}$ and $\chi^{-1}_{E_u E_v}$ also become zero. The second transition occurs at $T = 2.85J_1$ ($\equiv T_{oo2}$) where the T$_{2g}$ components of the order parameters appear. With decreasing temperature furthermore, the T$_{1g}$ components of the order parameters appear at $T = 2.59J_1$. This successive phase transition for the orbital orderings is characteristic of the t_{2g} orbital systems such as the perovskite titanates. This is attributed to the three fold-orbital degeneracy which causes the multi components of the orbital order parameters with different symmetries, that is, E$_g$, T$_{2g}$ and T$_{1g}$. On the other hand, in the e_g orbital systems, the orbital order parameter with the E$_g$ symmetry and the octopole order parameter with A_{2g} are possible to appear. The latter may not appear in an insulating state without doping of holes [4]. We note that, below T_{oo1}, the cubic symmetry in the system is broken by the E$_g$-type orbital order parameters. Then, the correlation functions for the three components of the T$_{2g}$ orbital operators, i.e. $\chi_{T_{2l}T_{2l}}$ $(l = x, y, z)$, are not equivalent.

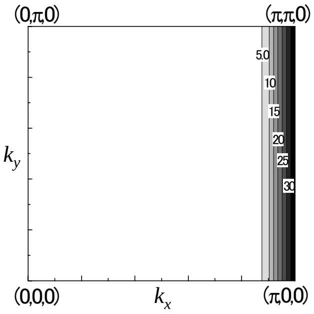

Fig. 2. A contour plot of the the orbital correlation function $\chi_{T2xx}(k_x, k_y, 0)$ at $T = 1.1T_{oo2}$.

The contour map of the orbital correlation function $\chi_{T_{2x}T_{2x}}(\boldsymbol{k})$ at $T = 1.1T_{oo2}$ is presented in Fig. 2. We assume the (yz/zx)-type orbital ordered state at this temperature where the two kinds of the orbital sublattice exist and the d_{yz} and d_{zx} orbitals are occupied by electrons in each sublattice. It is shown that this component of the correlation function diverges in the region of (π, k_y, k_z) with any values of k_y and k_z. This characteristic feature is caused by the fact that there is no interaction between the $O_{T_{2x}}$ operators at the NN site along the y and z directions [3]. This characteristic feature is related to the large degeneracy of the mean-field orbital order parameters in the ground state obtained by our previous calculations [3]. Although, in the actual compounds, a certain small interaction between orbitals termed J, which are not taken into account in the present calculations, may stabilize a certain type of the orbital ordered state, the large orbital fluctuations shown here are expected above $T_{oo2} + J$ and may be observed by RXS.

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