Theory of Anomalous X-Ray Scattering in Orbital-Ordered Manganites

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(Received 11 November 1997)

We study the theory of the anomalous x-ray scattering in relation to its role as a detector of the orbital orderings and excitations in perovskite manganites. The scattering matrix is given by virtual electron excitations in Mn from the $1s$ level to the unoccupied $4p$ level. We find that the orbital dependence of the Coulomb interaction between $3d$ and $4p$ electrons is essential to the anisotropy of the scattering factor near the K edge. The calculated results in MnO_6 clusters explain the forbidden reflections observed in $La_{0.5}Sr_{1.5}MnO_4$ and $LaMnO_3$. The possibility of observing orbital waves with x-ray scattering is discussed as well. [S0031-9007(98)05782-2]

PACS numbers: 71.10.–w, 71.90.+q, 75.90.+w, 78.70.Ck

The discovery of high T_c cuprates has stimulated intensive study of transition-metal oxides (TMO) from the new theoretical and experimental viewpoints. One of the key factors in studying the electronic structures in TMO is the orbital degrees of freedom in $3d$ transition-metal ions. In particular, the orbital degrees in perovskite manganites and related compounds bring about a lot of fruitful and dramatic phenomena [1–5]. The electron configuration in a Mn^{3+} ion is $(e_g)^1(t_{2g})^3$ with parallel spins due to the strong Hund coupling. In the cubic oxygen octahedral cage, the two e_g levels are degenerate. Thus, an e_g electron has the orbital degrees of freedom as well as charge and spin. In order to reveal the unique magnetotransport phenomena in manganites, it is essential to study the nature of the orbital degrees and their correlation with spin and lattice. However, the experimental techniques directly detecting the orbital ordering have been limited [6].

Recently, Murakami *et al.* have applied the anomalous x-ray scattering in order to observe the orbital ordering in the single layered manganites $La_{0.5}Sr_{1.5}MnO_4$ [7]. By studying a $(3/4, 3/4, 0)$ reflection, which would be forbidden were the anomalous part of the scattering factor isotropic [8,9], they observed a sharp reflection near the Mn^{3+} K edge. This experimental result implies the following [7]: (i) There exist two nonequivalent Mn^{3+} ions in the MnO_2 plane, which exhibit an alternating orbital ordering. The ordering is called "antiferro-type" hereafter. (ii) The electric dipole ($E1$) transition in Mn from the $1s$ core level to the unoccupied $4p$ level causes the anomalous scattering. This method was also applied to the undoped manganite $LaMnO_3$ [10] where the $(3, 0, 0)$ forbidden reflection suggesting the antiferro-type orbital ordering was observed. The new experimental technique not only confirms the orbital ordering in the two manganites, but has a great potential for applications to study the nature of the orbital in a variety of TMO.

In this Letter, we study theoretically the anomalous x-ray scattering in relation to its role as a detector of the orbital ordering in manganites. We identify the origin of the anisotropy of the scattering factor in the orbital ordered state. The orbital dependence of the Coulomb interactions between $3d$ and $4p$ electrons is dominant on the anisotropy of the scattering factor. We also discuss the possibility of detecting orbital waves by the inelastic x-ray scattering.

First, we briefly mention the general formula of the x-ray scattering factor. In the x-ray scattering process, the structure factor is defined by the scattering amplitude divided by (e^2/mc^2). By the second-order perturbational calculation with respect to the electron-photon interaction, the anomalous part of the scattering factor for the ith ion in the unit cell is given by [11,12]

$$\Delta f_i(k', k'')_{\alpha\beta} = \frac{m}{e^2} \sum_l \left\{ \frac{\langle f|j_{i\alpha}(-\vec{k}')|l\rangle\langle l|j_{i\beta}(\vec{k}'')|0\rangle}{\varepsilon_0 - \varepsilon_l - \omega_{k''} - i\delta} + \frac{\langle f|j_{i\beta}(\vec{k}'')|l\rangle\langle l|j_{i\alpha}(-\vec{k}')|0\rangle}{\varepsilon_0 - \varepsilon_l + \omega_{k'} - i\delta} \right\}, \quad (1)$$

where the electronic system is excited from the initial state $|0\rangle$ with energy ε_0 to the intermediate one $|l\rangle$ with ε_l, and is finally relaxed to the final state $|f\rangle$ with ε_f. Here, α and β represent the polarization of photons, $\omega_{k'(k'')}$ is the incident (scattered) photon energy with momentum $k'(k'')$, and δ is a small constant. The current operator describing the $1s \rightarrow 4p$ $E1$ transition is given by $j_{i\alpha}(\vec{k}) = \frac{eA_\alpha(\vec{k})}{m} \sum_\sigma P^\dagger_{i\alpha\sigma} s_{i\sigma}$, where $P^\dagger_{i\alpha\sigma}$ and $s_{i\sigma}$ are the creation operator of the Mn $4p$ electron and the annihilation of the Mn $1s$ core one, respectively, with spin σ and Cartesian coordinate α. $A_\alpha(\vec{k})$ is the coupling constant given by $A_\alpha(\vec{k}) = \int d\vec{r}\, e^{-i\vec{k}\vec{r}} \phi_{4p_\alpha}(\vec{r})^*(-i\nabla_\alpha)\phi_{1s}(\vec{r})$, where $\phi_m(\vec{r})$ $(m = 1s, 4p)$ is the atomic wave function. The quadrupole transition is ruled out in Eq. (1), since it is expected to be weak near the K edge in manganites [13,14].

Concerning the anomalous part of the structure factor, it is worth noting the following: (i) By utilizing the fact

that Δf_i is the second rank tensor with respect to photon polarization, we can directly detect the anisotropy of the microscopic electronic structure [8], i.e., the microscopic birefringence and dichroism due to the orbital order. (ii) The imaginary part of Δf_i, $\Delta f_i''$, with $|0\rangle = |f\rangle$ is written as $(\pi m/e^2)\sum_l \delta(\varepsilon_0 - \varepsilon_l + \omega_k)\,|\langle 0|j_{i\alpha}(\vec{k})|l\rangle|^2$ near the K edge. For the uniform ordering of orbitals, which we call ferro-type, this is proportional to the intensity of the Mn $1s$ x-ray absorption spectra (XAS) or x-ray fluorescence spectra.

As mentioned above, the anomalous scattering is dominated by the $1s \rightarrow 4p$ $E1$ transition. In this case, how do the $3d$ orbital orderings reflect on the anisotropy of the anomalous scattering factor? In order to study the problem, let us consider the electronic structure in the MnO_6 octahedron, since the local electronic excitation dominates Δf_i. In the Mn ion, a minimal set of orbitals is $\{1s, 3d_\gamma\ (\gamma = \gamma_{\theta+}, \gamma_{\theta-}), 4p_\gamma\ (\gamma = x, y, z)\}$, where $|3d_{\gamma_{\theta+}}\rangle = \cos(\theta/2)\,|3z^2 - r^2\rangle + \sin(\theta/2)\,|x^2 - y^2\rangle$ and $|3d_{\gamma_{\theta-}}\rangle$ is its counterpart. Six O $2p$ orbitals, which contribute to the σ bond with the Mn orbitals, are recombined by the symmetry in the O_h group as $\{2p_{\gamma_{\theta+}}, 2p_{\gamma_{\theta-}}, 2p_x, 2p_y, 2p_z, 2p_{r^2}\}$, where x, etc. represent the bases of the irreducible representation in the group. When we consider only the electron hybridization between Mn $3d$ and O $2p$ orbitals and between the Mn $4p$ and O $2p$ orbitals, $3d$ and $4p$ orbitals are decoupled, and the $3d$ orbital ordering does not reflect on $4p$ orbitals. It is concluded that the electron hybridizations do not result in the anisotropy of the scattering factor.

One of the promising origins of the anisotropy of the scattering factor is the Coulomb interactions between Mn $3d$ and $4p$ electrons. When we consider that one of the e_g orbitals $3d_{\gamma_{\theta+}}$ is occupied, the electron-electron interaction in the orbital ordered state breaks the cubic symmetry and thus lifts the degeneracy of Mn $4p$ orbitals. The interaction between Mn $3d$ and $4p$ electrons is represented as

$$V(3d_{\gamma_{\theta+}}, 4p_\gamma) = F_0 + 4F_2 \cos\left(\theta + m_\gamma \frac{2\pi}{3}\right), \quad (2)$$

where $m_x = +1$, $m_y = -1$, and $m_z = 0$. F_n is the Slater integral between $3d$ and $4p$ electrons. The explicit formula of F_n is given by $F_0 = F^{(0)}$ and $F_2 = \frac{1}{35}F^{(2)}$ with $F^{(n)} = \int dr\, dr'\, r^2 r'^2 R_{3d}(r)^2 R_{4p}(r')^2 \frac{r_<^n}{r_>^{n+1}}$, where $r_<$ ($r_>$) is the smaller (larger) one between r and r'. When the $d_{3z^2-r^2}$ orbital is occupied ($\theta = 0$), the energy in the $4p_z$ orbital is higher than that of the $4p_{x(y)}$ orbital by $6F_2$. As a result, $(\Delta f_i)_{xx(yy)}$ dominates the anomalous scattering near the edge in comparison with $(\Delta f_i)_{zz}$.

The interatomic Coulomb interaction between Mn $4p_\gamma$ electron and O $2p_{\gamma_{\theta-}}$ hole also provides an origin of the anisotropy of the scattering factor through the Mn $3d$–O $2p$ hybridization. The interaction is represented by $V(2p_{\gamma_{\theta-}}, 4p_\gamma) = -\varepsilon + \frac{\varepsilon\rho^2}{5}\cos(\theta + m_\gamma \frac{2\pi}{3})$, where the definition of m_γ is the same as that in Eq. (2). $\varepsilon = Ze^2/a$ and $\rho = \langle r_{4p}\rangle/a$, where $Z = 2$, a is the Mn-O bond length, and $\langle r_{4p}\rangle$ is the average radius of the Mn $4p$ orbital. Although the above two interactions cooperate to bring about the anisotropy of the scattering factor, it seems likely that the magnitude of $V(2p_{\gamma_{\theta-}}, 4p_\gamma)$ is much reduced by the screening effects, in comparison with $V(3d_{\gamma_{\theta+}}, 4p_\gamma)$.

The lattice distortion in the oxygen octahedron also lifts the degeneracy of Mn $4p$ orbitals. The difference of the energy between Mn $4p_{x(y)}$ and Mn $4p_z$ orbitals is given by $V(4p_{x(y)}) - V(4p_z) = \varepsilon\rho^2 \frac{18}{5}(\frac{\delta a}{a})$ with $\delta a = a_z - a_{x(y)}$, where a_α is the Mn-O bond length in the α direction. In $La_{2-x}Sr_xCuO_4$ and $La_{2-x}Sr_xNiO_4$ [15–18], this contribution seems to dominate the anisotropy in XAS. On the other hand, in $La_{1-x}Sr_{1+x}MnO_4$ at $x \sim 0.5$, it is confirmed that the noted lattice distortion in the MnO_6 octahedron is not observed experimentally [10]. Therefore, the mechanism based on Eq. (2) mainly provides the origin of the anisotropy of the scattering factor. In $LaMnO_3$ where $\delta a/a$ is about 13% [19], the contribution from the lattice distortion weakens the anisotropy caused by the intra-atomic and interatomic Coulomb interactions.

In order to confirm the mechanism of the anisotropy of the scattering factor discussed above, we calculate the anisotropy of Δf_i in a MnO_6 cluster. The following Hamiltonian is adopted in the calculation [20,22]: $H = H_0 + H_t + H_{\text{core}} + H_{3d-4p} + H_{3d-3d}$. H_0 and H_t describe the energy level and the electron transfer between Mn $3d_\gamma$ and O $2p_\gamma$ orbitals, respectively. The core hole potential is introduced in H_{core}. H_{3d-4p} represents the Coulomb interaction between Mn $3d$ and $4p$ electrons shown in Eq. (2), where F_n are treated as parameters by considering the screening and correlation effects. H_{3d-3d} includes the Coulomb and exchange interactions in e_g orbitals and the Hund coupling between e_g and t_{2_g} spins [4]. The interatomic Coulomb interaction $V(2p_{\gamma_{\theta-}}, 4p_\gamma)$ is not included in the model, in accordance with the previous discussion. Being based on the Hamiltonian, the imaginary part of the scattering factor $[(\Delta f_i'')_{xx(zz)}m/\pi|A_{x(z)}|^2]$ is calculated by the configuration interaction method. In order to check the adequacy of the several parameters, we also calculate the photoemission, inverse photoemission, and the optical spectra in the Hamiltonian.

The calculated $(\Delta f_i'')_{\alpha\alpha}$ near the K edge is shown in Fig. 1(a), where the $3d_{3z^2-r^2}$ orbital is occupied. It is noted that the edge of the lowest main peak corresponds to the Mn K edge. The detailed structure away from the edge may become broad and be smeared out in the experiments by overlapping with other peaks which are not included in the calculation. In the figure, the clear anisotropy is shown near the edge where the scattering intensity is governed by $(\Delta f_i'')_{xx}$. Owing to the core hole potential, the main and satellite peaks are attributed to the transition from the ground state, which is mainly dominated by the $|3d^1_{\gamma_{\theta+}}\rangle$ state, to the

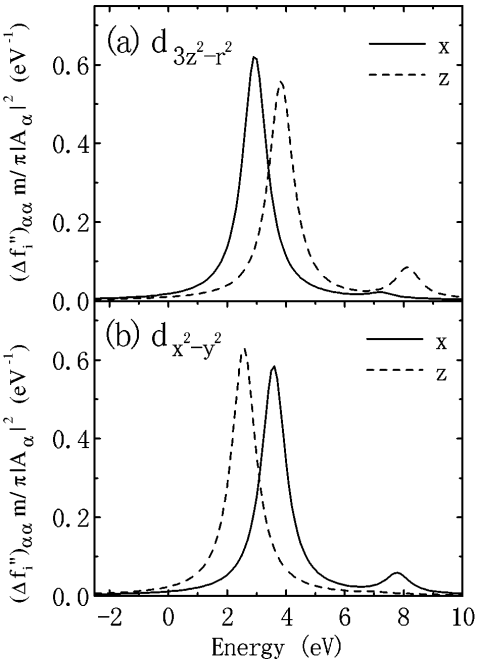

FIG. 1. The imaginary part of the scattering factor $[(\Delta f_i'')_{xx(zz)} m/\pi |A_{x(z)}|^2]$ in the case where the following orbital is occupied: (a) $\theta = 0$ $(d_{3z^2-r^2})$ and (b) $\theta = \pi$ $(d_{x^2-y^2})$. The straight and broken lines show $(\Delta f_i'')_{xx}$ and $(\Delta f_i'')_{zz}$, respectively. The value of δ in Eq. (1) is chosen to be 0.5 eV. The origin of the energy is taken to be arbitrary.

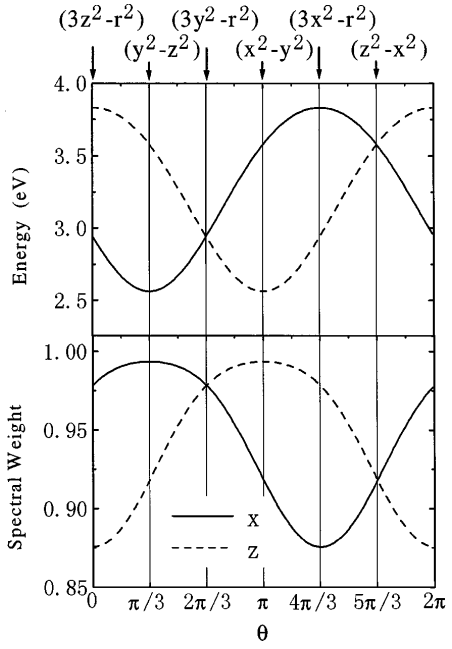

FIG. 2. The amplitudes and energy position of the main peak in the scattering factor $[(\Delta f_i'')_{xx(zz)} m/\pi |A_{x(z)}|^2]$ as functions of θ. The straight and broken lines show $(\Delta f_i'')_{xx}$ and $(\Delta f_i'')_{zz}$, respectively. The origin of the energy is taken to be arbitrary.

$|\underline{1s}\, 3d^1_{\gamma_{\theta+}} 3d^1_{\gamma_{\theta-}} 4p^1_{x(z)}\, \underline{2p_{\gamma_{\theta-}}}\rangle$ and $|\underline{1s}\, 3d^1_{\gamma_{\theta+}} 4p^1_{x(z)}\rangle$ excited states, respectively, where the underlines show the states occupied by a hole, although the two excited states strongly mix with each other. Therefore, the anisotropy in the main peak is caused by $V(3d_{\gamma_{\theta+}}, 4p_\gamma)$ through the Mn $3d$–O $2p$ hybridization. As a comparison, the results in the case where the $d_{x^2-y^2}$ orbital is occupied are shown in Fig. 1(b). In the figure, the anisotropy near the edge is entirely opposite to that in Fig. 1(a); i.e., the scattering factor near the edge is governed by $(\Delta f_i'')_{zz}$, owing to the positive value of $V(3d_{x^2-y^2}, 4p_x) - V(3d_{x^2-y^2}, 4p_z)$. In the general case where the occupied orbital is $d_{\gamma_{\theta+}}$, the amplitude and energy position of the main peak in $(\Delta f_i'')_{xx(zz)}$ are shown as functions of θ in Fig. 2. At $\theta = 2\pi/3$ $(3d_{3y^2-r^2})$ and $5\pi/3$ $(3d_{z^2-x^2})$, $(\Delta f_i'')_{xx}$ and $(\Delta f_i'')_{zz}$ are identical, as expected. It is noted that the anisotropy at $\theta = 0$ $(d_{3z^2-r^2})$ is almost the same as that at $\theta = \pi/3$ $(d_{y^2-z^2})$, although the peak is slightly pushed up in the higher energy region in the former case. This is due to the fact that $V(3d_{3z^2-r^2}, 4p_z) - V(3d_{3z^2-r^2}, 4p_x) = V(3d_{y^2-z^2}, 4p_z) - V(3d_{y^2-z^2}, 4p_x) = 6F_2$.

Murakami *et al.* analyzed their experimental results in $La_{0.5}Sr_{1.5}MnO_4$ phenomenologically [7]. In the $[d(x, y, z)/d(y, x, z)]$-type orbital ordering which they assumed, the intensity of the forbidden reflection is proportional to the difference of the scattering factor $|(\Delta f)_{xx} - (\Delta f)_{yy}|^2$. It is concluded in the present study that the observed sharp intensity corresponds to the anisotropy of the scattering factor at the edge shown in Fig. 1(a). However, even by the present microscopic calculation, it is difficult to determine which orbital ordering, $(d_{3x^2-r^2}/d_{3y^2-r^2})$ or $(d_{z^2-x^2}/d_{y^2-z^2})$, exists, as mentioned above. It is necessary to perform the experiments which determine the tensor elements $[(\Delta f_i)_{\alpha\alpha}]$ of the structure factors where α is perpendicular to the MnO_2 plane in $La_{0.5}Sr_{1.5}MnO_4$.

The anomalous x-ray scattering may also detect the orbital excitations in the orbital ordered states, that is, the orbital waves [4]. The mechanism of the observation is analogous to the Raman scattering to detect the two orbital waves [23]. Let us start from the antiferro-type orbital ordered state described by $|3d^1_{\gamma_{\theta+}}\rangle_i |3d^1_{\gamma_{\theta-}}\rangle_j$, where i and j denote the nearest neighbor (NN) Mn sites. As mentioned above, the excited state in the anomalous x-ray scattering is mainly dominated by the state where a hole is located in the oxygen site between two Mn sites. This state mixes with $|\underline{1s}\, 3d^1_{\gamma_{\theta+}} 3d^1_{\gamma_{\theta-}} 4p^1_{x(z)}\rangle_i$ through the electron transfer between j and the oxygen sites. After the $4p$ electron fills up the $1s$ hole, one $3d$ electron at the i site comes back to the j site. As a result, the system is relaxed to the final state represented as $|3d^1_{\gamma_{\theta-}}\rangle_i |3d^1_{\gamma_{\theta+}}\rangle_j$, where the orbital state at i and j sites is exchanged; that is, two orbital waves are emitted by the x ray. Since the $E1$ transition in the present case is local, the intermediate state accompanied with the charge transfer from the O $2p$ orbital to the Mn $3d$ orbital promotes the orbital exchange process. In this case, photons with the polarization x bring about the exchange process between $\vec{i}$ and $\vec{i} \pm \hat{y}(\hat{z})$ sites, where $\hat{y}$ is the unit vector in the y direction, as well as $\vec{i}$

and $\vec{i} \pm \hat{x}$ sites. This is in contrast to the conventional Raman process, where photons with polarization α only exchange the orbital states between $\vec{i}$ and $\vec{i} \pm \hat{\alpha}$ sites. Because the spin states in NN sites are also exchanged in this process, in the $(d_{3x^2-r^2}/d_{3y^2-r^2})$ orderings with the A(layer)-type antiferromagnetic structure realized in $LaMnO_3$, the orbital and spin couple and contribute to the inelastic x-ray scattering. The orbital wave in $LaMnO_3$, which has an excitation gap in the same order of the bandwidth, is expected to be observed in the region of the order of 100 meV [4].

Furthermore, when there are low-lying fluctuations in the orbital degrees of freedom, it is possible to detect them by the diffuse scattering in the anomalous x-ray scattering. It is expected that near the orbital ordering temperature in $LaMnO_3$ and $La_{0.5}Sr_{1.5}MnO_4$ the diffuse scattering owing to the $(d_{3x^2-r^2}/d_{3y^2-r^2})$-type orbital fluctuation becomes remarkable as the critical scattering around $(3/4, 3/4, 0)$ and $(3, 0, 0)$, respectively. Another candidate is the orbital fluctuation with $d_{x^2-y^2}$, $d_{y^2-z^2}$, and $d_{z^2-x^2}$ characters in the ferromagnetic metallic phase in $La_{1-x}Sr_xMnO_3$. The flat dispersions of the orbital fluctuation along the Γ-X and other equivalent directions in the Brillouin zone is predicted in this phase [5]. These characteristic dispersions imply the two dimensional character of the orbital fluctuation and will provide the strong anisotropic shape of the diffuse scattering around the fundamental reflection points.

In summary, we have derived the theory of the anomalous x-ray scattering in perovskite manganites and applied to the recent experiments. The dipole transition in Mn from the $1s$ level to the $4p$ level causes the anomalous scattering. The electron-electron interaction in the orbital ordered state is identified as the main mechanism of the anisotropy of the scattering factor. The anomalous x-ray scattering is promising as a probe to study the orbital degrees of freedom in not only manganites but other transition metal oxides.

The authors thank Y. Endoh for suggesting this study and encouragement at every stage of the work, Y. Murakami for providing the experimental data prior to publication, and W. Koshibae for valuable discussions. This work was supported by Priority Areas Grants from the Ministry of Education, Science and Culture of Japan, and CREST (Core Research for Evolutional Science and Technology Corporation) Japan.

[1] J. B. Goodenough, Phys. Rev. **100**, 564 (1955).
[2] J. Kanamori, J. Phys. Chem. Solids **10**, 87 (1959).
[3] K. I. Kugel and D. I. Khomskii, JETP Lett. **15**, 446 (1972).
[4] S. Ishihara, J. Inoue, and S. Maekawa, Physica (Amsterdam) **263C**, 130 (1996); Phys. Rev. B **55**, 8280 (1997).
[5] S. Ishihara, M. Yamanaka, and N. Nagaosa, Phys. Rev. B **56**, 686 (1997).
[6] Y. Ito and J. Akimitsu, J. Phys. Soc. Jpn. **40**, 1333 (1976).
[7] Y. Murakami, H. Kawada, H. Kawata, M. Tanaka, T. Arima, H. Moritomo, and Y. Tokura, Phys. Rev. Lett. **80**, 1932 (1998).
[8] D. H. Templeton and L. K. Templeton, Acta Crystallogr. Sect. A **38**, 62 (1982); **41**, 133 (1985).
[9] V. E. Dmitrienko, Acta Crystallogr. Sect. A **39**, 29 (1983).
[10] Y. Murakami (private communication).
[11] A. V. Kolpakov, V. A. Bushuev, and R. N. Kuz'min, Sov. Phys. Usp. **21**, 959 (1978).
[12] M. Blume, J. Appl. Phys. **57**, 3615 (1985).
[13] M. Croft, D. Sills, M. Greenblatt, C. Lee, S.-W. Cheong, K. V. Ramanujachary, and D. Tran, Phys. Rev. B **55**, 8726 (1997).
[14] M. Fabrizio, M. Altarelli, and M. Benfatto, Phys. Rev. Lett. (to be published).
[15] A. Sahiner, M. Croft, S. Guha, I. Perez, Z. Zhang, M. Greenblatt, P. A. Metcalf, H. Jahns, and G. Liang, Phys. Rev. B **51**, 5879 (1995).
[16] J. M. Tranquada, S. M. Heald, W. Kunnmann, A. R. Moodenbaugh, S. L. Qiu, Y. Xu, and P. K. Davies, Phys. Rev. B **44**, 5176 (1991).
[17] H. Tolentino, M. Medarde, A. Fontaine, F. Baudelet, E. Dartyge, D. Guay, and G. Tourillon, Phys. Rev. B **45**, 8091 (1992).
[18] In Ref. [17], the anisotropy in the Cu K edge XAS in high T_c cuprates, where the spectra for the z polarization are more conspicuous near the edge, was attributed to the interference between charge transfer from Mn $3d$ to O $2p$ and the photoelectron. Our theory, however, shows that the $1s \rightarrow 4p_{x(y)}$ transition dominates spectra near the edge in the case where the $3d_{3z^2-r^2}$ orbital is occupied, if the lattice effect is neglected.
[19] H. Kawano, R. Kajimoto, M. Kubota, and H. Yoshizawa, Phys. Rev. B **53**, R14 709 (1996).
[20] In the numerical calculation, the parameter values in the Hamiltonian are as follows: the differences of the energy in the orbital $\varepsilon(\text{Mn } 4p) - \varepsilon(\text{Mn } 3d) = 13.0$ eV and $\varepsilon(\text{O } 2p) - \varepsilon(\text{Mn } 3d) = 2.5$ eV, the electron transfer between Mn $3d$ and O $2p$ orbitals $t_{pd\sigma} = 1.2$ eV, the core hole potential between Mn $1s$ and Mn $3d$ (Mn $4p$) electrons $V_{3d-1s} = V_{4p-1s} = 7.0$ eV, the Coulomb interaction between Mn $3d$ and $4p$ electrons $F_0 = 5.0$ eV and $F_2 = 0.3$ eV, the intraorbital and interorbital Coulomb interactions in the Mn e_g orbitals $U = 8.5$ eV and $U' = 6.5$ eV, respectively, the interorbital exchange interaction $K = (U - U')/2$, and the Hund coupling between t_{2g} and e_g spins $J_H = 1.0$ eV. By using these parameters, the d-d Coulomb interaction and the charge transfer energy with respect to the lowest multiplet are estimated to be $U_{\text{eff}} = 5.5$ eV and $\Delta_{\text{eff}} = 1.5$ eV, respectively, and the ground state consists of $\sim 70\%$ d^4 and $\sim 30\%$ $d^5\underline{L}$ [21].
[21] T. Saitoh, A. E. Bocquet, T. Mizokawa, H. Namatame, A. Fujimori, M. Abbate, T. Takeda, and M. Takano, Phys. Rev. B **51**, 13 942 (1995).
[22] The electron transfer between Mn $4p$ and O $2p$ orbitals is not considered in the Hamiltonian, because it is not important for the anisotropy of Δf_i, as mentioned in the text.
[23] J. Inoue, S. Okamoto, S. Ishihara, W. Koshibae, Y. Kawamura, and S. Maekawa, Physica (Amsterdam) **237B–238B**, 51 (1997).