Orbital polarization in layered t$_{2g}$ electron systems

Takashi Mizokawa
Department of Complexity Science and Engineering, University of Tokyo,
5-1-5 Kashiwanoha, Kashiwa, Chiba, Japan
E-mail: mizokawa@k.u-tokyo.ac.jp

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Abstract. By means of x-ray absorption spectroscopy and model Hartree–Fock calculations, we have investigated the electronic structure of layered t$_{2g}$ electron systems such as Ca$_{2-x}$Sr$_x$RuO$_4$ and Bi$_2$Sr$_2$Co$_2$O$_9$. For the hole-doped Co–O triangular lattice in Bi$_2$Sr$_2$Co$_2$O$_9$, the x-ray absorption spectral line shape indicates that the carriers in the t$_{2g}$ band mainly have the a$_{1g}$ symmetry. This result is supported by model Hartree–Fock calculations on the CoO$_2$ lattice model. In Ca$_{2-x}$Sr$_x$RuO$_4$, the interplay between the orbital ordering and the Mott transition is demonstrated by the x-ray absorption measurement. It is shown that the orbital ordering accompanied by the lattice distortion is important in describing the insulating state of Ca$_{2-x}$Sr$_x$RuO$_4$. This idea is also supported by model Hartree–Fock calculations on the RuO$_2$ lattice model.

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1. Introduction

Transition-metal oxides have been attracting much interest because of their rich and interesting physical properties such as the metal–insulator transition in V$_2$O$_3$, the high-temperature
superconductivity in cuprates, and the colossal magnetoresistance (CMR) in manganites [1]–[3]. The magnetic and electric properties of transition-metal oxides are governed by the transition-metal d electrons with the five-fold orbital degeneracy. Under a cubic crystal field, the d orbitals are further split into doubly degenerate eg orbitals and triply degenerate t2g orbitals. In general, the anisotropic orbital shape of the eg and t2g orbitals is important in describing the electronic structure of the transition-metal oxides since the d electrons tend to have an atomic character due to the strong Coulomb interaction between them [4]. In particular, the insulating transition-metal oxides such as La2CuO4 and LaMnO3, which have an integer number of d electrons per transition-metal site, can be viewed as Mott insulators. In Mott insulators with partially filled eg or t2g subshell, the eg or t2g electrons strongly couple with the Jahn–Teller distortion giving an interesting interplay between spin, orbital and lattice degrees of freedom [5]. Also in the anomalous metallic states realized in the doped Mott-insulators such as La2−xSrxCuO4 and La1−xSr1.5MnO3, the electron–lattice coupling is expected to play important roles. In the doped systems with mixed valence of transition-metal ions, instability to various ordered states are expected to compete with each other and couple with various local lattice distortions [6].

X-ray absorption spectroscopy (XAS) of the oxygen 1s and transition-metal 2p core levels is very useful for extracting information on the local electronic configuration including the orbital anisotropy. There is a variety of transition-metal oxides in which the electron–electron and electron–lattice interactions cause competition between various ordered states. In such systems, the local lattice distortions and the orbital anisotropy are expected to play important roles to control the relative stability of various phases. In this paper, we present XAS study of layered systems: a hole-doped CoO2 triangular lattice in Bi2Sr2Co2O9 and a quasi-two-dimensional Mott-transition system Ca2−xSr1xRuO4.

2. Orbital polarization in a hole-doped CoO2 triangular lattice

Recently, it has been found that the (Bi,Pb)-Sr-Co-O system has a misfit-layered structure with a two-dimensional CoO2 triangular lattice [7, 8]. The electronic structure of the CoO2 triangular lattice is interesting in the light of the large thermoelectric power found in the (Bi,Pb)-Sr-Co-O compounds, the NaCo2O4 compounds [9] and the Ca3Co4O9 compounds [10], all of which have the hole-doped CoO2 triangular lattice in common (see figure 1). The average valence of Co ions is expected to be +3.33 for (Bi,Pb)-Sr-Co-O [7, 8].

Figure 2 shows the O 1s XAS spectra of Bi-Sr-Co-O and (Bi,Pb)-Sr-Co-O taken at normal (θ = 0°) and off-normal (θ = 60°) incidence [11]. θ is the angle between the Poynting vector of circularly polarized light and the z direction that is normal to the cleaved surface and the CoO2 layer. Structures at ~528 and ~529 eV are given by the transitions from the O 1s core level to the O 2p states hybridized into the unoccupied Co t2g and eg states, respectively. As shown in figure 2, the intensity of the Co t2g structure is dramatically enhanced in going from normal to off-normal. The intensity ratio of the structure α at θ = 60° to that at θ = 0° is estimated to be 2.4 and 2.1 for Bi-Sr-Co-O and (Bi,Pb)-Sr-Co-O, respectively. Under the trigonal crystal field, the three t2g orbitals are split into the a1g orbital and the two eg′ orbitals. For na = 1 and ne = 0, the intensity ratio is calculated to be 2.1 which agrees well with the experimental value. On the other hand, the intensity ratio is 1.2 for na = ne = 0.5. (Here, na and ne are the number of holes in the a1g and eg′ states, respectively.) From the angular dependence, it is clearly shown that the holes are mainly located in the a1g orbital. If the Co4+ site has a high-spin or intermediate-spin
states, the $t_{2g}$ orbitals accommodate two or three holes. This means that some holes should be accommodated by the $e'_g$ states in case of high-spin or intermediate-spin states. Therefore, one can safely conclude that the Co$^{4+}$ site has the low-spin $t_{2g}^5$ configuration as shown in the inset of figure 2.

In the (Bi,Pb)-Sr-Co-O system, the $a_{1g}$ band dispersion is expected to be small since the $a_{1g}$ orbital is directed to the out-of-plane direction and, in the CoO$_2$ triangular lattice, the electron hopping between the neighbouring $a_{1g}$ orbitals is suppressed. In fact, the band-structure calculation for NaCo$_2$O$_4$ predicts that the $t_{2g}$ band width is very narrow in the CoO$_2$ triangular...
lattice [12]. In the CoO$_2$ triangular lattice, the $t_{2g}$ band width is small compared to the electron–
electron and electron–lattice interaction terms. Consequently, the effect of the electron–electron
and electron–phonon interactions would be very strong to give instability to some symmetry
breaking such as ferromagnetism, charge ordering and superconductivity.

We have studied this possibility by means of model Hartee–Fock calculations on the CoO$_2$
triangular lattice model [13]. We employ the multi-band d–p model in which the Co 3d and O 2p
orbitals of the CoO$_2$ triangular lattice are taken into account. The Hamiltonian is given by

$$H = H_d + \sum_{k,\sigma} \varepsilon_{k}^{p} p_{k,\sigma}^{+} + \sum_{k,i,m,\sigma} V_{k,m}^{pd} d_{i,m,\sigma}^{+} p_{k,\sigma} + H.c$$

and

$$H_d = \sum_{i,m,\sigma} \varepsilon_{i}^{d} d_{i,m,\sigma}^{+} d_{i,m,\sigma} + u \sum_{i,m,\sigma} d_{i,m,\uparrow}^{+} d_{i,m,\downarrow}^{+} d_{i,m,\downarrow} d_{i,m,\uparrow} + (u' - j) \sum_{i,m>m',\sigma} d_{i,m,\sigma}^{+} d_{i,m',\sigma}^{+} d_{i,m',\sigma} d_{i,m,\sigma} + u' \sum_{i,m \neq m'} d_{i,m,\uparrow}^{+} d_{i,m,\downarrow}^{+} d_{i,m',\downarrow} d_{i,m',\uparrow}

+ j' \sum_{i,m \neq m'} d_{i,m,\uparrow}^{+} d_{i,m,\downarrow}^{+} d_{i,m',\downarrow} d_{i,m',\uparrow} + j \sum_{i,m \neq m'} d_{i,m',\uparrow}^{+} d_{i,m,\uparrow} d_{i,m',\downarrow} d_{i,m,\downarrow},$$

where $d_{i,m,\sigma}^{+}$ are creation operators for the Co 3d electrons at site $i$. $p_{k,\sigma}^{+}$ are creation operators
for the O 2p electrons with wave vector $k$. The intra-atomic Coulomb interaction between the 3d
electrons is expressed using Kanamori parameters $u$, $u'$, $j$ and $j'$. The transfer integrals between
the Co 3d and O 2p orbitals $V_{k,m}^{pd}$ are given by Slater–Koster parameters ($p d\sigma$) and ($p d\pi$). Here,
the ratio $(p d\sigma)/(p d\pi)$ is $-2.16$. The charge transfer energy $\Delta$ is defined by $\Delta = \varepsilon^d - \varepsilon^p + 6U$, where
$\varepsilon^d$ and $\varepsilon^p$ are the energy of the bare Co 3d and O 2p orbitals and $U(=u - 20/9 f)$ is the multiplet-
averaged d–d Coulomb interaction. Using the Hartree–Fock approximation, we obtained the charge
ordering in the CoO$_2$ triangular lattice for Co$^{3+}$:Co$^{4+}$ to be 1:1, 1:2, and 2:1. In the present
work, $\Delta$, $U$ and $(p d\sigma)$ are 2, 6.5 and $-2.5$ eV, respectively. These values are typical for
low-spin Co$^{3+}$ oxides with CoO$_6$ octahedra.

Figure 3 shows possible spin and charge arrangements for hole concentration $x$ of 1/3,
1/2, and 2/3. For $x = 1/3$, the ratio of the Co$^{3+}$ and Co$^{4+}$ sites is 2:1. The model Hartee–Fock
calculation using a realistic parameter set (charge-transfer energy $\Delta = 2$ eV and multiplet-
averaged Coulomb interaction $U = 5.5$ eV) predicts that the most stable state is a Wigner-type
charge-ordered state in which the Co$^{4+}$ sites form a triangular lattice (see figure 3(a)). In the
Wigner-type charge ordering for $x = 1/3$, the magnetic coupling between the Co$^{4+}$ spin 1/2
states becomes ferromagnetic. On the other hand, the ratio between the Co$^{3+}$ and Co$^{4+}$ sites
is 1:2 for $x = 2/3$. In the model Hartee–Fock calculation for $x = 2/3$, the most stable state is
found to be another Wigner-type charge-ordered state in which the Co$^{4+}$ sites form a honeycomb
lattice (see figure 3(c)). In the Wigner-type charge ordering for $x = 2/3$, the Co$^{4+}$ spin 1/2 has
antiferromagnetic ordering in the honeycomb lattice. For $x = 1/2$, the frustration effect of the
triangular lattice gives the situation where various charge-ordered states are degenerate in energy.
Among them, a stripe-type charge ordering is indicated in figure 3(b) as an example. There are
a variety of zigzag-type charge orderings that can be degenerate in energy with the stripe-type
charge ordering. If the crystal-field splitting between the $a_{1g}$ and $e_g'$ levels changes its sign, one of
the two $e_g'$ orbitals is occupied by the hole. In such a case, orbital ordering in the $e_g'$ orbitals can
lift the degeneracy and can stabilize one of the stripe-type or zigzag-type charge orderings even.
Figure 3. (a) Wigner-type charge ordering pattern for $x = 1/3$. The open and shaded circles indicate the Co$^{4+}$ and Co$^{3+}$ sites respectively. The arrows indicate the spin 1/2 of the Co$^{4+}$ sites. (b) Stripe-type charge-ordering pattern for $x = 1/2$. (c) Wigner-type charge ordering pattern for $x = 2/3$.

Figure 4. Density of states obtained by the model Hartree–Fock calculations for $x = 1/3$, 1/2, and 2/3. For $x = 1/3$ and 2/3, the Wigner-type charge ordering is stable. The peak labelled as $a_{1g}$ is derived from the unoccupied $a_{1g}$ orbital. Peaks $e_{g}(4+)$ are the unoccupied $e_{g}$ levels of the Co$^{4+}$ sites.

for $x = 1/2$ [14]. The density of states for the three charge-ordered states are plotted in figure 4. The lowest unoccupied band is mainly derived from the $a_{1g}$ orbital supporting the observation by x-ray absorption spectroscopy. The intensity of the $a_{1g}$ band increases with the hole doping.
3. Orbital state and metal–insulator transition in Ca$_{2-x}$Sr$_x$RuO$_4$

The quasi-two-dimensional system Ca$_{2-x}$Sr$_x$RuO$_4$ has been attracting much interest because of the rich physical properties [15]. In Ca$_{2-x}$Sr$_x$RuO$_4$, four electrons (two holes) occupy the three nearly degenerate Ru $4d_{t_{2g}}$ orbitals as indicated in figure 5. The end material Ca$_2$RuO$_4$ is an antiferromagnetic insulator (AFI) below 110 K and a paramagnetic insulator (PI) between 110 and 350 K [15]–[17]. At about 350 K, Ca$_2$RuO$_4$ has a first-order metal–insulator (MI) transition and becomes a paramagnetic metal (PM). The substitution of Sr for Ca reduces the MI transition temperature as shown in figure 5. For $0.09 < x < 0.2$, Ca$_{2-x}$Sr$_x$RuO$_4$ is AFI at low temperatures and changes into PM at elevated temperatures.

In figure 6, the $t_{2g}$-derived O 1s XAS spectra of Ca$_{1.91}$Sr$_{0.91}$RuO$_4$ taken at 77 and 300 K are compared to those of Ca$_2$RuO$_4$ taken at 77, 300 and 370 K in figure 6 for $\theta = 0^\circ$, $15^\circ$ and $30^\circ$ [18]. The closed circles in the left panel of figure 5 indicate the temperature and Sr doping level for these XAS measurements. In the $t_{2g}$-derived region, the two peaks located at 528.5 and 529.3 eV (labelled as A and B, respectively) show a very distinct temperature and angle dependence. We can assign features A and B to transitions at the apical and in-plane oxygen sites, respectively. In the AFI phase of Ca$_2$RuO$_4$, the apical component (structure A) is intense compared to the in-plane component (structure B). The O 1s XAS spectra strongly depend on the angle $\theta$ between the surface normal and the Poynting vector of the incident light.

Comparison of the angle dependence with the model Hartree–Fock calculation indicates that the cooperation between the spin–orbit coupling and the small compression of the RuO$_6$ octahedron gives this orbital ordering in the insulating region. In going from AFI to PI of Ca$_2$RuO$_4$, the apical component gradually loses its intensity and the in-plane component gradually grows. This suggests that the orbital state is partially fluctuating even in the insulating phase and the orbital fluctuation increases with temperature. Also the intensity of the apical component is reduced and that of the in-plane component is enhanced by the Sr doping. This indicates that the Sr doping induces the orbital disorder in Ca$_{1.91}$Sr$_{0.91}$RuO$_4$ that is probably responsible for the reduction of the MI transition temperature. In the PM state of Ca$_2$RuO$_4$ and Ca$_{1.91}$Sr$_{0.91}$RuO$_4$, the intensity of the in-plane component becomes dominant. The O 1s XAS spectra of the PM phase is very similar to that of Sr$_2$RuO$_4$. The orbital population in the PM phase hardly changes with temperature.

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Figure 6. The upper panel shows the experimental arrangement. The lower panel shows the angle dependence of the O 1s XAS spectra of Ca$_{1.91}$Sr$_{0.09}$RuO$_4$ taken at 77 and 300 K and that of Ca$_2$RuO$_4$ taken at 77, 300 and 370 K. $\theta$ is the incidence angle.

Since the O 1s x-ray absorption spectrum is given by the transition from the O 1s core level to the unoccupied O 2p states mixed into the upper Hubbard band, it would be useful to compare the experimental result with the O 2p partial density of states obtained by the model Hartree–Fock calculation. The calculated O $p_x$, $p_y$ and $p_z$ components are multiplied by the transition matrix element that is sensitive to the polarization vector of the incoming soft x-ray. The O 1s x-ray absorption spectra thus estimated are plotted in the left panel of figure 7 for the compressed, regular, and elongated cases. The agreement between theory and experiment is satisfactory supporting the ferro-type orbital ordering predicted by the model calculation [18]–[20]. In the AFI state with the compressed octahedra, the $p_z$ component is dominant in the in-plane O site, indicating that the two holes are mainly located in the $yz$ and $zx$ orbitals. In going from the compressed case to the regular case, the $p_z$ component rapidly increases. This means that the holes are transferred from the $yz/zx$ orbital to the $xy$ orbital due to the reduction of the Jahn–Teller distortion. For the elongated case, the anisotropy is essentially the same as that for the regular case although the spectral line shape is very different. The present result shows that the $yz$/zx orbital polarization is already weakened in the insulating phase by increasing the temperature or Sr doping level.
Figure 7. Calculated O 1s XAS spectra using the model Hartree–Fock method for the AFI and PM states of Ca$_2$RuO$_4$. In the right panel, the O 2p density of states are decomposed into the p$_x$, p$_y$ and p$_z$ components.

4. Concluding remarks

For the hole-doped Co–O triangular lattice in Bi$_2$Sr$_2$Co$_2$O$_9$, the x-ray absorption spectroscopy reveals that holes are located in the a$_{1g}$ band with out-of-plane character. The effective band width becomes extremely narrow due to this orbital polarization. The model Hartree–Fock calculation with a realistic parameter set reproduces the orbital polarization and predicts that the Wigner-type charge ordering is stable for $x = 1/3$ and $2/3$. In Ca$_{2-x}$Sr$_x$RuO$_4$, the x-ray absorption spectrum changes dramatically as a function of temperature and Sr doping, indicating that the orbital ordering accompanied by the lattice distortion is important to explain the metal–insulator transition. The model Hartree–Fock calculation with ferro-type orbital ordering can explain the angle dependence of the x-ray absorption spectra. The present studies demonstrate that x-ray absorption spectroscopy is very powerful for studying orbital anisotropy in layered transition-metal oxides. In future, this technique should be applied to other interesting oxides such as NaTiO$_2$ and Sr$_2$VO$_4$ in order to explore exotic orbital states in two-dimensional $t_{2g}$ systems.

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References

[1] Goodenough J B 1963 Magnetism and the Chemical Bond (New York: Wiley)
[2] Mott N F 1990 Metal–Insulator Transition (London: Taylor & Francis)
[3] Imada M, Fujimori A and Tokura Y 1998 Rev. Mod. Phys. 70 1039
[4] Tokura Y and Nagaosa N 2000 Science 288 462
[5] Mizokawa T and Fujimori A 1995 Phys. Rev. B 51 12880
Mizokawa T and Fujimori A 1996 Phys. Rev. B 54 5368
[6] Saini N L, Oyanagi H, Lanzara A, Di Castro D, Agrestini S, Bianconi A, Nakamura F and Fujita T 2001 Phys. Rev. B 64 132510
[7] Yamamoto T, Tsukada I, Uchinokura K, Takagi M, Tsubone T, Ichihara M and Kobayashi K 2000 Japan. J. Appl. Phys. 39 L747
[8] Leligny H, Grebille D, Perez O, Masset A, Hervieu M, Michel C and Raveau B 1999 C. R. Acad. Sci. Paris, Serie II 2 409
[9] Terasaki I, Sasago Y and Uchinokura K 1997 Phys. Rev. B 56 R12685
[10] Masset A C, Michel C, Maignan A, Hervieu M, Toulemonde O, Studer F, Raveau B and Hejtmanek J 2000 Phys. Rev. B 62 166
[11] Mizokawa T, Tjeng L H, Steeneken P G, Brookes N B, Tsukada I, Yamamoto T and Uchinokura K 2001 Phys. Rev. B 64 115104
[12] Singh D J 2000 Phys. Rev. B 61 13397
[13] Hitsuda Y and Mizokawa T, unpublished
[14] Khomskii D I and Mizokawa T 2004 Preprint cond-mat/0407458
[15] Nakatsuji S and Maeno Y 2000 Phys. Rev. Lett. 84 2666
Nakatsuji S and Maeno Y 2000 Phys. Rev. B 62 6458
[16] Braden M, Andre G, Nakatsuji S and Maeno Y 1998 Phys. Rev. B 58 847
[17] Friedt O, Braden M, Andre G, Adelmann P, Nakatsuji S and Maeno Y 2001 Phys. Rev. B 63 174432
[18] Mizokawa T, Tjeng L H, Sawatzky G A, Ghiringhelli G, Tjernberg O, Brookes N B, Fukazawa H, Nakatsuji S and Maeno Y 2001 Phys. Rev. Lett. 87 077202
[19] Kurokawa K and Mizokawa T 2002 Phys. Rev. B 66 024434
[20] Mizokawa T, Tjeng L H, Lin H-J, Chen C T, Schuppler S, Nakatsuji S, Fukazawa H and Maeno Y 2004 Phys. Rev. B 69 132410