

Chapter 1

Introduction

1.1 Overview

Transition-metal oxides (TMO) have a wide range of interesting physical phenomena, such as high-temperature superconductivity [1], colossal magnetoresistance [2, 3], metal-to-insulator transition [4], half-metallicity [5], and non-Fermi liquid behavior, *etc.* An electron in a solid has three attributes: charge, spin, and orbital. The orbital degree of freedom determines the shape of the electron cloud or the electron's probability-density distribution in solids. These three attributes determine the physical properties of solids. One, therefore, can modify the physical properties by controlling the doping, pressure, and external magnetic field. The richness of these physical insights is intimately associated with strong coupling among charge, spin, orbital and lattice degrees of freedom.

The Coulomb interaction between the electrons in a solid, known as the electron-correlation effect, is responsible for a rich variety physical phenomena. The electron-correlation effect has been a long-standing research topic in

condensed-matter physics, and is the key ingredient for understanding many unusual physical properties such as high-temperature (high- T_c) superconductivity and colossal magnetoresistance (CMR). Particularly after the discovery of high- T_c copper oxides, another interesting subject is the physics of doped Mott insulator. An insulator with an energy gap determined by the correlation effects is called the Mott Insulator. The doping might yield many fascinating physical phenomena. For example, a metal-to-insulator transition could be induced.

Another example is the high-temperature superconductivity, CuO_2 sheets in high- T_c oxides by the doping are separated from each other by ionic blocking layers. Although it has conduction electron or hole per Cu site, each CuO_2 sheet of the undoped cuprates is insulating because of the large on-site Coulomb energy. When holes are doped into the CuO_2 layers, change in the number of conduction leads to the superconductivity. Another correlated-electron systems in widespread interesting is the colossal magnetoresistant phenomenon in which the resistance is gigantically decreased by application of a magnetic field. The phase changes in CMR manganites arise from the interplay between three electron attributes and their interaction with the lattice. To control the electronic and magnetic phases of correlated-electron materials in unconventional ways could provide an opportunity for future novel electronics.

1.2 Electron Correlations

1.2.1 Mott-Hubbard Insulators

In the Mott-insulating state of a transition-metal oxide, the d -electrons are almost entirely localized on the atomic site. The electrons cannot hop to other sites when the kinetic energy gain is smaller than the on-site Coulomb repulsion energy (U). The fundamental idea of the electron correlations was first developed by Mott [6] and Hubbard [7]. Mott took the first important step for understanding how the electron-electron correlations could explain the insulating state; such a state is called as the Mott insulator. He considered a single electronic orbital on each lattice site. Without the electron correlation effect, the overlap of each orbital can form a single band, and the band becomes full when two electrons occupy each lattice site. If these two electrons sitting on the same site, they will feel a large Coulomb repulsion. The Coulomb repulsion will split one band into two. The lower band is formed from electrons that occupied one empty site.

A simple one-dimension lattice, as shown in Figure 1.1, is a brief introduction to the concept of Mott insulator. Considering the electron-electron interaction, the Coulomb repulsion energy of two electrons sitting on the same site i can be described as

$$U = \int dr_1 \int dr_2 |\phi(r_1)|^2 \frac{e^2}{|r_1 - r_2|} |\phi(r_2)|^2. \quad (1.1)$$

The Coulomb repulsion decreases the probability for the two electrons on the same site, so this U will reduce the electron hopping. Including both

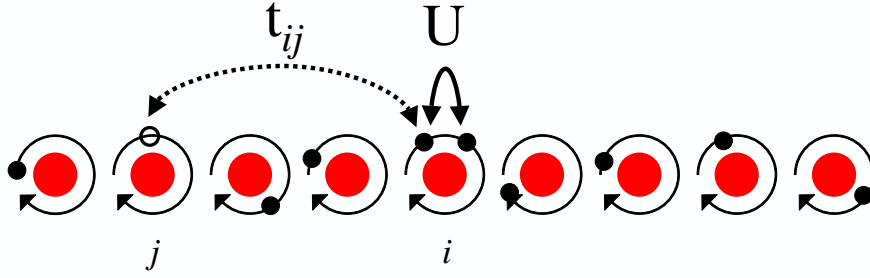


Figure 1.1: A simple 1D electron system with antiferromagnetic coupling.

hybridization and on-site Coulomb repulsion, the simplest Hamiltonian was proposed by Hubbard and written as:

$$H = \varepsilon \sum_{i\sigma} \hat{n}_{i\sigma} - \sum_{\langle ij \rangle, \sigma} t_{ij} (c_{\sigma i}^\dagger c_{\sigma j} + c_{\sigma j}^\dagger c_{\sigma i}) + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}, \quad (1.2)$$

$$N \equiv \sum_{i,\sigma} n_{i\sigma}, \quad (1.3)$$

where the $c_{i\sigma}^\dagger$ creates an electron on site i with spin σ . The number operator is $n_{i\sigma} \equiv c_{i\sigma}^\dagger c_{i\sigma}$. The transfer matrix element, $t_{i,j} = \langle i|H|j \rangle$, describes the hopping between two neighbors, also named as hopping integral. The second term is the kinetic-energy operator, which is obtained from the overlap of two atomic orbitals. And the third term describes the Coulomb repulsion of two electrons on the same site, as shown in Equation 1.1.

Let us consider the simplest case where the system is a half filled band, i.e., the number of electrons is equal to the number of sites in this system. If $U \ll t$, the system is metallic because the band is half filled. On the other hand, in the opposite limit of $U \gg t$, it is unfavorable for two electrons to be on the same site, i.e., there are no double occupied sites in the ground state. Because of $U \gg t$, moving an electron to another site will cost the Coulomb

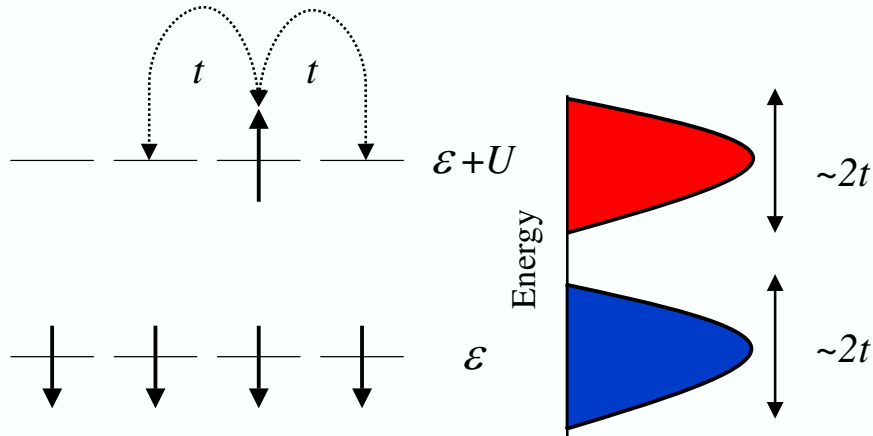


Figure 1.2: **Left:** Energy diagram of a n -electrons system in the Hubbard model. The ground state energy of n -electrons is ε while that of $(n + 1)$ th electron on site i is $\varepsilon + U$. **Right:** Schematic representation of the origin of Hubbard sub-bands. The hopping of an spin-up electron on the background of spin-down electrons gives rise to a band width $\sim 2t$ centering on $\varepsilon + U$. Similarly, the motion of a spin-down hole leads to the lower sub-band.

energy U . Each site is forced to be occupied by exactly one electron and each electron can not move to other sites. The electrons are fully localized and the system becomes insulating. Despite the simplicity, Hubbard model implies that a metal-insulator transition by a function of U/t . It tells us that the ratio of the Coulomb integral to the bandwidth is one important parameter. This is very interesting feature of the Hubbard model suggesting that an insulator to metal might be expected when U is reduced to values comparable or even smaller than the bandwidth.

In the limit case, that the lattice distances approach infinite, there is no orbital hybridization between sites. The Hamiltonian can be written as:

$$H = \varepsilon \sum_{\sigma} \hat{n}_{i\sigma} + U \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}. \quad (1.4)$$

The energy of electron occupying on site i is ε . When a second electron is

added on the same site, the energy $\varepsilon + U$ should be added to the system, and the total energy of the system is $2\varepsilon + U$. The two-level spectrum of the 1-D system is shown in Figure 1.2. In the case that there are \downarrow -spin electrons occupying in the lower level ε and one \uparrow -spin electron with an energy $\varepsilon + U$, the hopping of the \uparrow -spin electron broadens the upper energy level into a band with a bandwidth $\sim 2t$. In other words, two bands of states are with a bandwidth $\sim 2t$ at the central atomic levels energy of ε and $\varepsilon + U$, and known as the Hubbard sub-bands. The energy gap is $U - W$, where W is the band width which is the order of t .

The drastic simplification in the Hubbard model is only consider electrons in a single orbit, say s -orbit. However, the transition-metal oxides are d -electron systems, and orbital degeneracy is an important and unavoidable property of complicated behavior. The effects of orbital fluctuations and orbital symmetry breaking play important roles in d -electron systems. Another aspect is the overlap of the d -band in transition metals with the p -band of oxygen. The ligand atoms play important roles which bridge transition metals in oxides. This part of discussion will be described later.

1.2.2 Zaanen-Sawatzky-Allen scheme

An important assumption in the Hubbard model is that the oxygen does not introduce an extra degree of freedom. For a late transition-metal elements such as copper in high-temperature superconductors, the charge gap of the Mott insulator cannot be accounted for solely with d -electrons;

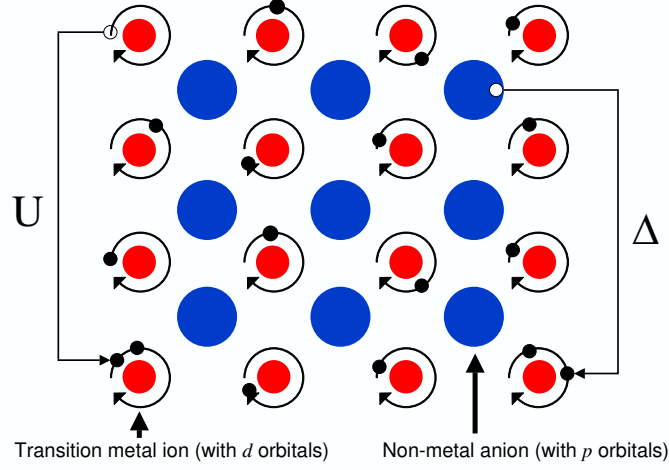


Figure 1.3: Anderson lattice model or $p-d$ model in transition-metal compounds based on the on-site Coulomb interaction U and the charge transfer energy Δ . The on-site Coulomb energy: $U = E(d^{n+1}) + E(d^{n-1}) - 2E(d^n)$, and the charge transfer energy: $\Delta = E(d^{n+1}\underline{L}) - E(d^n)$

oxygen p -electrons degrees of freedom need to be considered. The importance of the charge transfer energy as a fundamental parameter determining the properties of transition-metal compounds was first realized by Fujimori and Minami [8], Sawatzky and Allen [9]. Shortly after, Zaanen, Sawatzky and Allen [10] proposed a classification scheme for transition-metal compounds based on the on-site Coulomb interaction U and the charge transfer energy Δ .

The Anderson lattice model (or $p-d$ model) is shown in Fig. 1.3, the on-site Coulomb interaction U can be conveniently defined as the energy cost in the charge fluctuations of $d^n d^n \rightarrow d^{n+1} d^{n-1}$, written as

$$U = E(d^{n+1}) + E(d^{n-1}) - 2E(d^n), \quad (1.5)$$

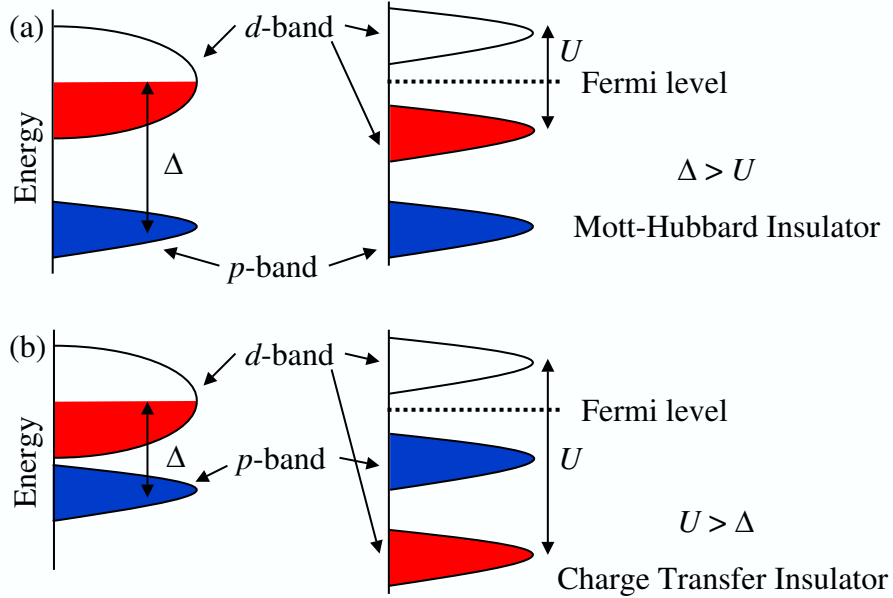


Figure 1.4: Schematic illustration of energy levels of (a) a Mott-Hubbard insulator and (b) charge-transfer insulator.

where the $E(d^{n+1})$, $E(d^{n-1})$ and $E(d^n)$ are the energies of electron ionization, affinity, and the ground state of the system, respectively. This formula describes the energy change in removing an electron from one site in solids and then putting back to another atomic site. In addition, the charge transfer energy (Δ) is defined as the energy cost for removing an electron from O $2p$ band and putting into transition metal $3d$ orbitals:

$$\Delta = E(d^{n+1}\underline{L}) - E(d^n), \quad (1.6)$$

where \underline{L} denotes a hole in the ligand band.

For transition metals with an open $3d$ shell, we could regard the Hubbard model as a description of a d -band only. A singly occupied d -band is called the

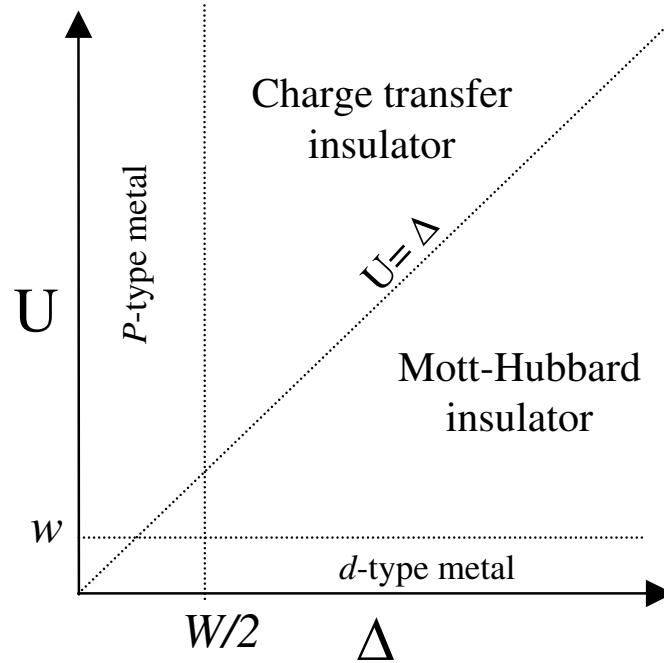


Figure 1.5: Zaanen-Sawatzky-Allen classification scheme for transition metal compounds based on the on-site Coulomb interaction U and the charge transfer energy Δ . (from Ref. [10])

lower Hubbard band, and the upper Hubbard band is a doubly occupied d -band (with spin up and down). The charge-excitation gap is formed between the lower and upper Hubbard band. As shown in Fig. 1.4(a), if $\Delta > U$, the $d^n \underline{L}$ configuration would lie below the d^{n-1} configuration and leading to a $d-d$ band gap. This $d-d$ type band gap in the original Hubbard picture is called a Mott-Hubbard gap and the corresponding compound is called a Mott-Hubbard insulator. On the other hand, for $U > \Delta$, the p band is located between the upper and lower Hubbard bands; the band gap is of the $p-d$ type and called a charge-transfer gap, as shown in Fig 1.4(b). The corresponding

compound is called a charge-transfer insulator. The term "Mott insulator" is used in a broad sense which covers both types.

In the Zaanen-Sawatzky-Allen scheme, as shown in Fig 1.5, two parameters U and Δ roughly divide the transition-metal compounds into a charge transfer ($U > \Delta$) or a Mott-Hubbard ($U < \Delta$) insulator. Furthermore, even for $U \rightarrow \infty$, we can get a p -type metallic ground state if $\Delta < W/2$. And a d -band metal appear when $U < w$ even for $U < \Delta$. Here w and W denote, respectively, the bandwidth of the transition-metal $3d$ and oxygen $2p$ bands.

1.3 Exchange Interaction

In strongly correlated materials, the presence of local moments is associated to the strong Hund's rule of atomic exchange energy. Usually below a certain critical temperature, the local moments of the strongly correlated magnetic insulators show a long range magnetic order because of strong inter-atomic exchange interactions. These interactions are from the chemical bonding between atoms and the Pauli exclusion principle.

The inter-atomic exchange interactions dependent on the hybridization and Coulomb interactions could be considered as a two-site Hubbard model. If $t \ll U$, the inter-atomic exchange energy J can be approximated as:

$$J \approx -\frac{2t^2}{U}, \quad (1.7)$$

where J is the energy difference of the lowest triplet state and singlet state. The negative sign of J means that the local magnetic moments with anti-

ferromagnetically aligned make the lowest energy. This indicates that the antiparallel is more favourable because the electron hopping back and forth between sites could gain kinetic energy. But in the parallel configuration, Pauli exclusion principle does not allow the electron hopping. However, for understanding the exchange mechanism on the magnetic properties, one must take into account the spin and orbital degrees of freedom. Because the magnitude and the sign of exchange interactions depend on the orbital occupation, both ferromagnetic and antiferromagnetic might occur.

The study of manganite perovskites started from Wollan and Koehler [11] on $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ in the 1955. Immediately, Goodenough [12] announced a theoretical treatise on using the ideas of superexchange and double exchange, which have been successful in explaining the magnetic arrangements.

1.3.1 Superexchange

The indirect interaction involving two metal atoms with an intervening oxygen is known as superexchange. The superexchange interactions with mediating oxygens are important if the bond angles of metal-oxygen are close to 180° , like in many perovskite structures. The spins at the neighboring metal ions are antiparallel because antiferromagnetic ground state has the lowest energy, like shown in Fig. 1.6(a). An electron hops from O to M_1 and another from M_2 to O form a virtual excitations like in Fig. 1.6(b). In figure 1.6(c), two oxygen electrons hop to M_1 and M_2 . In Fig. 1.6(b), it can be seen as one of the excited configurations involving with the Hubbard

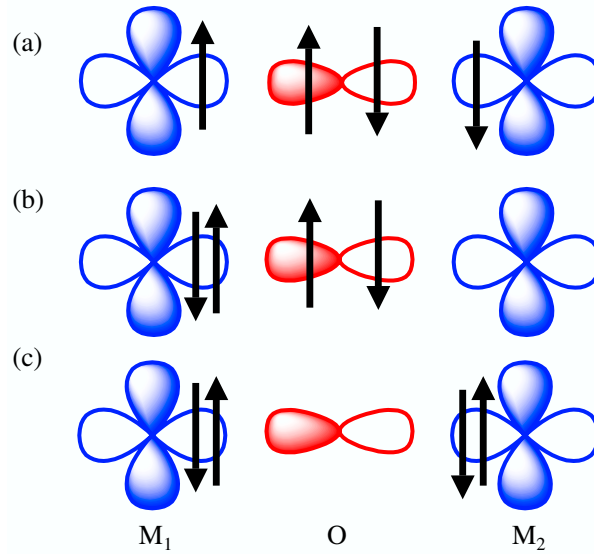


Figure 1.6: Antiferromagnetic superexchange interaction in a metal-oxygen-metal arrangement. Electron configuration of the ground state (a) can mix with two types of excited configuration (b) and (c).

energy U ; Fig. 1.6(c) depends on the charge-transfer gap between valence (O $2p$) band and empty $3d$ band. This leads to an effective superexchange interaction including charge-transfer energy E_{CT} is

$$J \approx -2t^2 \left[\frac{1}{U} + \frac{1}{E_{CT}} \right]. \quad (1.8)$$

This is a simple way to understand the superexchange interaction. Goodenough-Kanamori rules [22] could be used to predict the situation in simple cases.

1.3.2 Double Exchange

In some mixed-valent transition-metal oxides, ferromagnetism associated with high spin electronic conductivity is known as double exchange mechanism. Double exchange mechanism is based on the fact that the electron hopping does not flip the spin, i.e., coherent tunnelling of electrons between

atoms with spin conservation. Both metallic behavior and especially ferromagnetism are rare in oxides. Most of them are anti-ferromagnetic or ferrimagnetic with dominating anti-ferromagnetic interactions. Certain special conditions have to meet to stabilize ferromagnetism. One of the main mechanisms invoked to explain ferromagnetic ordering in these systems is the *double exchange mechanism* [16]. This was stimulated by the study of the colossal magnetoresistance manganites $\text{La}_{1-x}(\text{Ca,Sr})_x\text{MnO}_3$. The undoped compound ($x = 0$, LaMnO_3) is an anti-ferromagnetic insulator. The system with a nominal doping ($0.2 < x < 0.5$) causes a paramagnetic to ferromagnetic transition and accompanies with a large decrease in resistance. In ionic picture, the effect of substituting a 2+ cation for a 3+ cation at the La site is to force a nearby Mn to change from 3+ to 4+ ionic valence. In Hund's rule, each Mn ion is of Mn^{3+} ($t_{2g}^3 e_g^1$) and Mn^{4+} (t_{2g}^3) configuration. In shortly, the doping of 2+ cation changes the valence of Mn from 3+ to 4+ and introduces an hole in the e_g -state. The lowest energy of the system corresponds to a parallel alignment of the spins of the two sites. The state reached after the electron hopping ($\text{Mn}^{4+}\text{-O}^{2-}\text{-Mn}^{3+}$) is degenerate in energy with the initial state before the hopping ($\text{Mn}^{3+}\text{-O}^{2-}\text{-Mn}^{4+}$). Therefore, in the case of ferromagnetic alignment, electrons can freely and coherently hopping from site to site without flipping the spin.

1.4 Jahn-Teller Distortion

The Jahn-Teller effect describes the geometrical distortion of the electron cloud in a molecule under certain situations. Sometimes, this effect is also known as Jahn-Teller distortion, and plays an important role in the description of transition-metal oxides.

For a transition-metal ion (M^+) surrounded by six oxygen ions (O^{2-}) to form a MO_6 octahedron in a perovskite-structure crystal, as shown in Fig. 1.7, the oxygen ions give rise to a crystal-field potential which partly lifts the degeneracy of the d -electron of the transition-metal ion into two groups with t_{2g} and e_g symmetries. The wavefunctions of d -electrons pointing toward O^{2-} ions are called the e_g orbitals, including $d_{x^2-y^2}$ and $d_{3z^2-r^2}$. The wavefunctions pointing between two adjoined oxygen ions are called the t_{2g} orbitals, including d_{xy} , d_{yz} , and d_{zx} . The ground state energy of the e_g orbitals are higher than the t_{2g} orbitals, because of the Coulomb repulsion between electrons. Such an energy difference is the crystal field splitting, called the $10Dq$.

When the energy $10Dq$ is greater than the exchange energy, the spin of the d -orbitals is minimized, typically forming a low-spin state. In such a low-spin state, the t_{2g} orbitals will be occupied before the e_g orbitals are occupied. On the other hand, if crystal-field splitting energy is smaller than the exchange energy, the spin of the d -orbitals is maximized to form a high-spin state.

In addition, any structure distortion will further remove the degeneracy

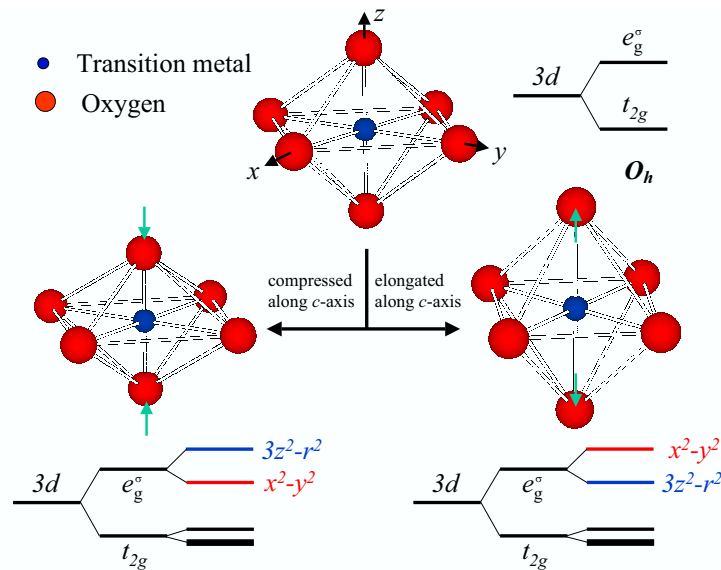


Figure 1.7: The d -electron orbital symmetry of a transition metal with an octahedron of oxygen. The lattice distortion changes the electronic structure.

of the e_g and the t_{2g} states, as shown in Fig. 1.7. In the MO_6 octahedron structure, if the crystal has a lattice distortion with an elongation of the distance between the transition-metal ion and oxygen ion along the z -axis, $d_{3z^2-r^2}$ in the e_g orbitals has an energy lower than that of $d_{x^2-y^2}$, because of the Coulomb repulsion along the z -axis is smaller than that in xy -plane. In contrast, if the MO_6 octahedron is with a contraction of the bond length along the z -axis, the ground-state energy of $d_{x^2-y^2}$ is lower than that of $d_{3z^2-r^2}$. In an octahedral structure, the Jahn-Teller effect is mostly observed when an odd number of electrons occupy the e_g orbitals. The Jahn-Teller distortion of a high-spin d^4 -system in Mn^{3+} compounds is frequently observed. In this thesis, we studied the Jahn-Teller effect of manganese oxides.

1.5 Charge and Orbital Ordering

For doping manganese oxide by the substitution of trivalent rare earth elements with divalent alkaline earth elements (such as Ca, Sr, Pb) to, holes are doped in the MnO_2 layers and the tetravalent Mn^{4+} is distributed among the trivalent Mn^{3+} lattice. The mixed-valent manganites are typically considered as disordered compounds, in which Mn^{3+} and Mn^{4+} cations randomly distribute in the lattice. However, in certain condition such as chemical pressure or temperature, these cations order coherently over long distances and form a charge-ordered lattice.

It was first proposed the possibility of *ion ordering* in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ by Wollan and Koehler [11]. They realized that the magnetic scattering intensities of this antiferromagnetic were very sensitive to the coherent ordering of Mn^{3+} and Mn^{4+} cations. This observation of insulating behavior at low temperature also led Goodenough [12] to suggest that the migration of electron from Mn^{3+} to Mn^{4+} ions makes it possible for ordering of the Mn^{3+} and Mn^{4+} ions, forming the charge ordering.

Neutrons scattering does not detect the electronic charge but senses the lattice distortion or spin ordering as a result of the charge ordering. Charge ordering cannot be detected by neutrons, but x-ray or electron diffraction could explore the charge ordering directly. Chen and Cheong [13] reported direct evidence of charge ordering for $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ with electron diffraction. And charge ordering has been also reported in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ [14]

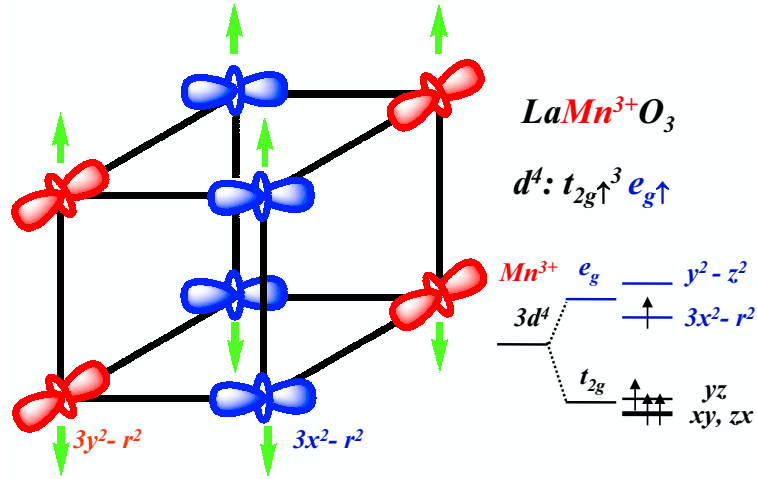


Figure 1.8: The orbital and spin ordering of d -electrons in $LaMnO_3$. The e_g orbitals ($d_{3x^2-r^2}$ and $d_{3y^2-r^2}$) stagger in the xy -plane.

and $Pr_{0.5}Ca_{0.5}MnO_3$ [15], similar to that found in $La_{0.5}Ca_{0.5}MnO_3$. All of these compounds are half-doped and exhibit the CE-type antiferromagnetic structure. However, not all the half-doped manganese compounds will have charge ordering behavior. For example, $Pr_{0.5}Sr_{0.5}MnO_3$ has a A-type antiferromagnetic insulating ground state and also has equal amounts of Mn^{3+} and Mn^{4+} cations, but does not have a charge ordering characteristic.

The ordering of either charges or orbitals associated with the crystal distortion is very important for comprehension of the physics of condensed matters. $LaMnO_3$, for example, has parallel spin moments in the xy -plane, but spins between the adjacent xy -planes are antiparallel as antiferromagnets. The spin ordering structure is layered-type or so-called A-type antiferromagnetic. In this Mn^{3+} compounds, the Mn sites have four d -electrons, and show an

electronic configuration of $t_{2g}^3 e_g^1$. As mentioned above, the Jahn-Teller distortion lifts the orbital degeneracy and favors the occupation of either $d_{3z^2-r^2}$ or $d_{x^2-y^2}$ orbitals. In addition, $d_{3x^2-r^2}$ and $d_{3y^2-r^2}$ orbitals of the e_g state occupy alternately in xy -plane with a transition temperature around 800 K [20]. This A-type antiferromagnetic state with alternating $d_{3x^2-r^2}$ and $d_{3y^2-r^2}$ in LaMnO_3 is attributed to the anisotropic superexchange interactions and Jahn-Teller distortion [21].

The phenomena of spin and orbital ordering in the transition-metal oxides has been understood by means of the Goodenough-Kanamori rules [22, 23]. If there is a large overlap between the partly occupied orbitals at two magnetic ions, the antiferromagnetic between them is superexchange interactions because of the Pauli exclusion principle. And ferromagnetic is due to the overlap of partly occupied and unoccupied orbitals because of the Hund's exchange.

In the typical case of 180° bonds through a ligand ion, the spin and orbital ordering become interdependent. The ferro-orbital ordering supports antiferromagnetic spin order, and the alternating orbital ordering supports ferromagnetic spin order. As in the LaMnO_3 , ferromagnetic spin correlations in the ab -planes are accompanied by alternating orbital order. On the other hand, along the c -axis, the antiferromagnetic correlations are accompanied by ferro-orbital order.

Goodenough-Kanamori rules have been successful in explaining the magnetic and orbital structures in a wide range of transition-metal oxides. Sur-

prisingly, they assumed that the orbital occupation is static. In the partly filled d -electron system, orbitals are degenerate and the degrees of freedom of spin and orbital should be considered as dynamic quantum variables [24]. Generally in e_g orbitals, the Goodenough-Kanamori rules could still work well because the Jahn-Teller coupling of degenerate orbitals to lattice fixes the orbital occupations well. However, for the t_{2g} orbitals, such as the perovskite titanates [25, 26] and vanadates [27], the Goodenough-Kanamori rules can not satisfy this condition.

Transition-metal oxides have a long history of research and have as materials with variety of interesting properties, such as magnetic, optical and transport properties. It is true that many basic ingredients responsible for these phenomena have been proposed such as double exchange [16, 17], Jahn-Teller effect, charge ordering [11, 12] and orbital ordering [18, 19]. Because these different mechanisms would be able to cause similar phenomena, it still difficultly to identify the real controlling mechanism of each phenomenon clearly. Here, we mainly present the studies of orbital physics in $\text{La}_{1-x}\text{Sr}_{1+x}\text{MnO}_4$, $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ and Na_xCoO_2 by using soft x-ray absorption spectroscopy.

Reference

- [1] J. G. Bednorz and K. A. Muller, *Z. Phys. B* **64**, 189 (1986).
- [2] S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and L. H. Chen, *Science* **264**, 413 (1994).

- [3] Yoshinori Tokura. *Colocssal Magnetoresistive*, volume 2 of *Advances in Condensed Matter Science*. Gordon and Breach Science Publishers, (2000).
- [4] N. F. Mott. *Metal-Insulator Transitions*. Taylor and Francis, 2nd edition, (1990).
- [5] R. A. de Groot, F. M. Mueller, P. G. van Engen, and K. H. J. Buschow, *Phys. Rev. Lett.* **50**, 2024 (1983).
- [6] N. F. Mott, *Proc. Phys. Soc. London, Sect. A* **62**, 416 (1949); *Can. J. Phys.* **34**, 1356 (1956).
- [7] J. Hubbard, *Proc. Phys. Soc. London, Sect. A* **276**, 238 (1963); *ibid A* **277**, 237 (1964).
- [8] A. Fujimori and F. Minami, *Phys. Rev. B* **30**, 957 (1984).
- [9] G. A. Sawatzky and J. W. Allen, *Phys. Rev. Lett.* **53**, 2339 (1984).
- [10] J. Zaanen, G. A. Sawatzky, and J. W. Allen, *Phys. Rev. Lett.* **55**, 418 (1985).
- [11] E. O. Wollan and W. C. Koehler, *Phys. Rev.* **100**, 545 (1955).
- [12] J. B. Goodenough, *Phys. Rev.* **100**, 564 (1955).
- [13] C. H. Chen and S.-W. Cheong, *Phys. Rev. Lett.* **76**, 4042 (1996).
- [14] H. Kawano, R. Kajimoto, H. Yoshizaw, Y. Tomioka, H. Kuwahara and Y. Tokura, *Phys. Rev. Lett.* **78**, 4253 (1997).
- [15] Z. Jirak, S. Krupicka, Z. Simsa, M. Dlouha and S. Vratislav, *J. Magn. Mat.* **53**, 153 (1985).
- [16] C. Zener, *Phys. Rev.* **82**, 403 (1951).
- [17] P. W. Anderson and H. Hasegawa, *Phys. Rev.* **100**, 675 (1955).
- [18] Y. Ito and J. Akimitsu, *J. Phys. Soc. Jpn.* **40**, 1333 (1976).
- [19] J. Akimitsu and Y. Ito, *J. Phys. Soc. Jpn.* **40**, 1621 (1976).
- [20] J. Rodriguez-Carvajal, M. Hennion, F. Moussa, A. H. Moudden, L. Pinsard, and A. Revcolevschi, *Phys. Rev. B* **57**, R3189 (1998).
- [21] J. Kanamori, *J. Appl. Phys.* **31**, S14 (1960).

- [22] J. B. Goodenough, *Magnetism and the Chemical Bond*, Interscience, New York (1963).
- [23] J. Kanamori, *J. Phys. Chem. Solids* **10**, 87 (1959).
- [24] Y. Tokura and N. Nagaosa, *Science* **288**, 462 (2000).
- [25] B. Keimer, D. Casa, A. Ivanov, J. W. Lynn, M. v. Zimmermann, J. P. Hill, D. Gibbs, Y. Taguchi and Y. Tokura, *Phys. Rev. Lett.* **85**, 3946 (2000).
- [26] C. Ulrich, G. Khaliullin, S. Okamoto, M. Reehuis, A. Ivanov, H. He, Y. Taguchi, Y. Tokura and B. Keimer, *Phys. Rev. Lett.* **89**, 167202 (2002).
- [27] C. Ulrich, G. Khaliullin, J. Sirker, M. Reehuis, M. Ohl, S. Miyasaka, Y. Tokura and B. Keimer, *Phys. Rev. Lett.* **91**, 257202 (2003).

