Photoemission study of Cu oxides related to high Tc superconductors

Master Thesis

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January 1992
## Contents

abstract  
1

Chapter 1. Introduction  
2

Chapter 2. Experiments  
10
  1. Sample Preparation  
10
  2. Photoemission Experiments  
11

Chapter 3. Methods of Model Calculations  
12
  1. General Formulation  
12
  2. Models  
15
  3. Configuration-Interaction Cluster Model Calculation  
18
  4. Anderson Single-Impurity Model Calculation  
21

Chapter 4. Experimental Results and Analysis  
24
  1. XPS of NaCuO₂  
24
  2. XPS of LaCuO₃  
35
  3. Comparison of the Photoemission Spectra  
38
    of NaCuO₂, LaCuO₃, La₄BaCu₅O₁₃ and La₂₋ₓCa₁₊ₓCu₂O₆₊₅

Chapter 5. Discussions and Concluding Remarks  
46
  1. Charge-Transfer Energies and Other Parameters  
46
  2. Origin of the Band Gap of NaCuO₂  
47
  3. Electronic Structure of Metallic Copper Oxides  
60

Acknowledgments  
62

Appendix A.  
63

Appendix B.  
69
abstract

It is shown by photoemission spectroscopy that 3d transition-metal oxides with unusually high formal valences are characterized by their very small or even negative ligand-to-metal charge transfer energies. One of the formally Cu$^{3+}$ insulating oxides NaCuO$_2$ has been studied in detail. It is shown that the $d^8 \rightarrow d^9L$ ($L$: ligand hole) charge-transfer energy is negative and the ground state is dominated by the $d^9L$ configuration. The band gap is mainly determined by the charge fluctuation $d^9L + d^9L \rightarrow d^9 + d^9L^2$. The magnitude of the gap is strongly affected by the geometrical arrangement of the metal-oxygen local units, giving a natural explanation for the difference between insulating NaCuO$_2$ and metallic LaCuO$_3$. The electronic structures of Fe$^{4+}$ and Ni$^{3+}$ oxides, which are expected to resemble those of Cu$^{3+}$ oxides, are also discussed.

In the photoemission spectra of the metallic copper oxides LaCuO$_3$, La$_4$BaCu$_5$O$_{13}$ and La$_{1.82}$Ca$_{1.18}$Cu$_{2}$O$_{6+δ}$, the intensity just below the Fermi level is very small and the satellite structures are observed. Such features of the spectra resemble those of the Cu-oxide superconductors and are common to the metallic copper oxides including those made metallic both by carrier doping and by gap collapse. The satellite structures are similar to those of Cu$^{2+}$ charge-transfer insulators, indicating that the Cu d-d Coulomb interaction is still large in these metallic Cu-oxides.
Chapter 1  Introduction

Introduction

Since the discovery of high Tc copper oxides [1.1], there has been increasing interest in the electronic properties of 3d transition-metal compounds, where electron correlation plays an important role. Recently, much work has been done on the 3d transition-metal compounds following the new interpretation of photoemission spectroscopy data [1.2,3] and shown that photoemission spectroscopy is a powerful tool to investigate the electronic structure of these compounds. In order to fundamentally understand the properties of high Tc superconductors, it is important to study the electronic structure of related materials such as metallic but non-superconducting copper oxides and formally Cu$^{3+}$ oxides. In this thesis, we have studied the electronic states of copper oxides related to high Tc superconductors, NaCuO$_2$ [1.5, 6], LaCuO$_3$ [1.7,8] and La$_4$BaCu$_5$O$_{13}$ [1.9,10] as well as La$_{2-x}$Ca$_{1+x}$Cu$_2$O$_{6+δ}$ which had been thought to be non-superconducting until recently [1.11,12].

According to the classification scheme proposed by Zaanen, Sawatzky and Allen (ZSA) [1.3], transition-metal compounds can be classified into two regimes by the relative magnitude of the ligand-to-metal charge-transfer energy $\Delta$ and d-d Coulomb energy $U$ [1.1]. In the Mott-Hubbard regime, $\Delta > U$, the band gap corresponds to charge fluctuations of a d-d type, $d^n+d^n \rightarrow d^{n+1}+d^{n-1}$ and its magnitude is essentially given by $\sim U$. [fig. 1(a)] In the charge-transfer regime, $\Delta < U$, charge fluctuations of the type $d^n+d^n \rightarrow d^{n+1}+d^{n}L$ constitute a p-d type
band gap, whose magnitude is $-\Delta$. [Fig. 1(b)] In Fig. 2, we have plotted the $\Delta-U$ values of various 3d transition-metal compounds determined by the analysis of the transition-metal 2p core-level photoemission spectra (so-called ZSA plot) [1.8]. Systematics found in various 3d transition-metal compounds suggest that $\Delta$ is decreased with increasing valence of the transition-metal ion and becomes very small or negative for compounds with unusually high valences such as Cu$^{3+}$, Ni$^{3+}$, Fe$^{4+}$ etc. According to the above picture, it is expected that the charge-transfer type band gap collapses in these compounds leading to metallic behavior, but actually many high valence compounds exist as insulators.

Fig. 1. Schematic representation of the single-particle density of state (DOS) for the (a) Mott-Hubbard, (b) charge-transfer, and (c) negative-\(\Delta\) insulators. The shaded and open areas represent the Cu 3d- and ligand p-derived DOS, respectively. The dashed curves in (c) indicate the opening of a p-p type band gap.
Fig. 2. Zaanen-Sawatzky-Allen Δ-U plot determined from the analysis of the transition-metal 2p core-level photoemission spectra. Since the ratio of the 3d-3d Coulomb energy $U$ to the 2p-3d Coulomb energy $Q$ is assumed to be $\sim 0.83$ in this analysis (the ratio is assumed to be $\sim 0.7$ in the text), the values of the parameters for NaCuO$_2$ are somewhat different from those obtained in the text. The charge-transfer energy $\Delta$ decreases by $\sim 3$ eV for a unit increase of the valence. (from Ref. 1.8)
One of the formally 3+ copper compounds NaCuO$_2$ is an insulator and consists of CuO$_2^-$ chains as shown in Fig. 3 [1.5]. This compound has been studied as a reference Cu$^{3+}$ compound in discussing the existence of Cu$^{3+}$ species in the high T$_c$ copper oxide superconductors [1.6], but its electronic structure has not been studied in detail so far. On the other hand, LaCuO$_3$ is also a formally Cu$^{3+}$ compound and have metallic behavior. LaCuO$_3$ has a rombohedrally-distorted perovskite structure and the distortion from the perovskite is very small [1.7,8]. The perovskite structure is shown in Fig. 4(a) and (b).

There are interesting issues concerning the electronic structures of the formally Cu$^{3+}$ oxides including both insulating NaCuO$_2$ and metallic LaCuO$_3$. One is whether the ground states of these compounds are d$^8$ (real Cu$^{3+}$) or d$^9$L (formally Cu$^{3+}$ but actually Cu$^{2+}$ plus an oxygen p hole L). In the theoretical scheme of charge-transfer insulators, the charge-transfer energy of 2+ copper oxides $\Delta$(d$^9$→d$^{10}$L) is 1-3 eV, and since this $\Delta$ value is smaller than the d-d Coulomb energy U, doped holes go into oxygen p orbitals. Therefore, it is possible that the charge-transfer energy of formally 3+ copper oxides $\Delta$(d$^8$→d$^9$L) - ($\Delta$(d$^9$→d$^{10}$L)-U) is negative, or that the d$^9$L configuration is dominant in the ground state. Another issue is what makes the difference between the insulating NaCuO$_2$ and the metallic LaCuO$_3$. It is important to reveal the origin of the band gap of NaCuO$_2$.

In a strongly correlated electron system, the wave function is sensitively dependent on the number of particles. The electronic state of an insulating system, where the electron correlation is strong, is drastically changed when the system is made metallic by changing the occupation number. Many insulating 3d transition-metal oxides both in the Mott-Hubbard regime and in the charge-transfer regime can be made metallic by carrier doping. But the carrier doping is carried out
Fig. 3. Crystal structure of NaCuO$_2$ (distorted KCuO$_2$-type structure). A copper ion is coordinated square-planerly by four oxygen ions and the Cu-O distance is ~ 1.84 Å. (from ref. 1.5)

NaCuO$_2$

triclinic (distorted KCuO$_2$ structure)
\[a=2.749 \text{ Å}, \ b=6.671 \text{ Å}, \ c=3.460 \text{ Å}\]
\[\alpha=76.25^\circ, \ \beta=113.41^\circ, \ \gamma=128.28^\circ\]
square-planer CuO$_4$ Cu-O 1.84Å

KCuO$_2$ structure
Fig. 4. (a) Unit cell of the perovskite LaCuO$_3$ and the arrangement of the CuO$_6$ octahedrons and CuO$_5$ pyramids in the (b) perovskite LaCuO$_3$ (romboedral distortion is neglected) (c) oxygen-deficient perovskite La$_4$BaCu$_5$O$_{13}$ and (d) layered perovskite La$_{2-x}$Ca$_{1+x}$Cu$_2$O$_6$. (from ref. 1.10)

The Cu-O distances are listed.

(a) CuO$_6$ octahedron

(b) LaCuO$_3$ (ref. 1.7)
CuO$_6$ Cu-O 1.94 Å
CuO$_5$ Cu-O (apex) 2.31 Å
Cu-O (plane) 1.911 Å

(c) La$_4$BaCu$_5$O$_{13}$ (ref. 1.9)
CuO$_6$ Cu-O (apex) 1.930 Å
Cu-O (plane) 2.039 Å
CuO$_5$ Cu-O (apex) 2.272 Å
Cu-O (plane) 1.935 Å, 1.875 Å

(d) La$_{2-x}$Ca$_{1+x}$Cu$_2$O$_{6+δ}$
(x=0.15, at 2000 atom, ref. 1.11)
CuO$_5$ Cu-O (apex) 2.31 Å
Cu-O (plane) 1.911 Å
by substituting metal ions or introducing excess oxygens or vacancies in many real compounds and the effects of impurity potential cannot be excluded. La$_4$BaCu$_5$O$_{13}$ is an oxygen-deficient-perovskite compound composed of CuO$_5$ pyramids and CuO$_6$ octahedra and Ba$^{2+}$ ions and oxygen vacancies are regularly arranged as shown in Fig. 4(c) [1.9,10]. Therefore, we can investigate the electronic structure of hole doped Cu oxides without the effect of impurities. La$_4$BaCu$_5$O$_{13}$ is metallic but non-superconducting. The formal valence of copper is +2.4 and this value corresponds to the overdoped region of high Tc copper oxides. La$_2$-$x$Ca$_{1+x}$Cu$_2$O$_{6+δ}$ is a layered-perovskite compound, where CuO$_5$ pyramids are connected to form two dimensional Cu-O planes as shown in Fig. 4(d) [1.11,12]. Although La$_{2-x}$Ca$_{1+x}$Cu$_2$O$_{6+δ}$ synthesized under low oxygen pressure is metallic but non-superconducting, La$_{2-x}$Ca$_{1+x}$Cu$_2$O$_{6+δ}$ synthesized under high pressure shows superconductivity [1.11,12]. It is interesting to investigate the electronic structures of the metallic copper oxides La$_4$BaCu$_5$O$_{13}$ and La$_{2-x}$Ca$_{1+x}$Cu$_2$O$_{6+δ}$ and to compare them with those of other superconducting oxides.

Parts of the results about NaCuO$_2$ and La$_4$BaCu$_5$O$_{13}$ have been published. [1.13,14]

References


1. Sample Preparation

Polycrystalline samples of NaCuO$_2$ were prepared by sintering a mixture of CuO and Na$_2$O$_2$ powders at 500$^\circ$C for 24 hours in O$_2$ gas flow. (by Koichi Akeyama and Hiroshi Kondoh, Department of Chemistry) Since the samples are highly hygroscopic, the synthesis and subsequent handlings were carried out in a glove box filled with Ar, except for a short time exposure ($< 10$ sec) during transfer to the spectrometer.

Polycrystalline samples of La$_4$BaCu$_5$O$_{13}$ were synthesized by the spray-dry method. La$^{3+}$, Ba$^{2+}$, Cu$^{2+}$ were dissolved in acetic acid in appropriate proportions. After the solution was dried at 400$^\circ$C for 5 hours, the residue was fired at 800$^\circ$C for 5 hours and pressed into pellets. The pellets were fired at 1000$^\circ$C for 50 hours in O$_2$ gas flow. (by Dr. Hiroshi Eisaki, Department of Applied Physics)

Polycrystalline samples of LaCuO$_3$ were prepared by the following procedure. The mixture of La$_2$O$_3$ and CuO was pressed into pellets and fired at 850$^\circ$C for 2-3 hours in air. The product was milled and pressed into pellets again. After firing at 1000$^\circ$C in air for 24 hours, LaCuO$_{2.5}$ was obtained. The sample was further fired at 800$^\circ$C and 200 atom for 48 hours and at 400$^\circ$C and 400-500 atom for 3-4 days in O$_2$ gas flow. (by Prof. Y. Takeda, Department of Chemistry, Mie University)

Polycrystalline samples of La$_{1.82}$Ca$_{1.18}$Cu$_2$O$_{6+\delta}$ were synthesized from La$_2$O$_3$, CaCO$_3$ and CuO powders. The mixed power was pressed into pellets and sintered in air or O$_2$ gas flow. The products were sintered
again at 1050-80°C in 20% O₂ + 80% Ar at a pressure between 50 and 2000 atom using a furnace for hot isostatic pressing. (by Dr. Kyoichi Kinoshita, NTT Basic Research Laboratories [1.11] ) Spectra of a non-superconducting sample synthesized under low pressure were successfully measured and studied.

2. Photoemission Experiments

A Mg Kα source ( hv=1253.6 eV ) were used for x-ray photoemission spectroscopy (XPS). The XPS spectra were corrected for the Mg Kα₃,₄ ghost. A He resonance lamp (hv=21.2 eV for He I and 40.8 eV for He II) were used for ultraviolet photoemission spectroscopy (UPS). Photoelectrons were collected with a PHI double-pass cylindrical-mirror analyzer. The resolutions including both source broadening and instrumental broadening were about 1.0 eV, 0.35 eV and 0.25 eV for XPS, He I and He II, respectively. USP spectra were also measured for resonant photoemission at beamline BL-2 of Synchrotron Radiation Laboratory, Institute for Solid State Physics, University of Tokyo and at beamline BL-11D of Photon Factory, National Laboratory for High Energy Physics. In order to prevent possible loss of oxygens from the surface, the samples were cooled to liquid-nitrogen temperature during the measurements. Electron-energy-loss spectroscopy (EELS) measurements were also performed by using 1.7 keV incidental electrons. In order to obtain fresh, clean surfaces, the samples were scraped in situ with a diamond file until the O 1s core-level spectrum became a single peak, which is an indication of good sample quality (Figs. 5 and 18). The base pressure in the spectrometer was in the low 10⁻¹⁰-torr range for NaCuO₂ and La₄BaCu₅O₁₃, and was about 1×10⁻⁹ torr for LaCuO₃ and La₁.₈₂Ca₁.₁₈Cu₂O₆₊₅.
Chapter 3 Methods of Model Calculations

1. General Formulation

We consider the photoemission process from a many electron system following the formulation by Kotani [3.1] and Gunnarsson [3.2]. The system of electrons can be divided into three sub-systems, outer electrons, a core hole and a photoelectron. The Hamiltonian can be described by

\[ H = H_m + \sum_c V_c a_c^\dagger a_c^\dagger + \sum_c (-\varepsilon_c) a_c a_c^\dagger + \sum_k V_{ka} a_k^\dagger a_k + \sum_k \varepsilon_k a_k^\dagger a_k \]  

(1-1)

where \( a_c \) and \( a_k^\dagger \) are creation operators of a core hole and a photoelectron. The first, third and fifth terms represent systems of outer electrons, a core hole and a photoelectron, respectively. The second term describes an interaction between a core hole and outer electrons. The forth term describe an interaction between a photoelectron and outer electrons ( + a core hole ). We define there are N outer electrons in the initial state. The eigen value and eigen function of the initial state can be denoted by \( E_0(N) \) and \( |E_0(N)\rangle \). In the final states of valence band photoemission, we have N-1 outer electrons and a photoelectron. Therefore, if we neglect the interaction between outer electrons ( + a core hole ) and a photoelectron, namely, if we neglect the forth term of eq. (1-1) (this is called a sudden approximation), the eigen values and the wave functions of the final states can be given by \( \varepsilon_k + E_n(N-1) \) and \( |k\rangle |E_n(N-1)\rangle \), where \( \varepsilon_k \) and \( |k\rangle \) are the eigen values and eigen functions of
the photoelectron and $E_n(N-1)$ and $|E_n(N-1)>$ are the eigen values and
the states of $H_m$ including $N-1$ electrons. On the other hand, we have $N$
outer electrons, a core hole and a photoelectron in the final states of
core-level photoemission. If we use the sudden approximation, the eigen
values and the wave functions of the final states are given by $e_k -$
$\varepsilon_c + E'_n(N)$ and $|k> |c> |E'_n(N)>$, where $-\varepsilon_c$ and $|c>$ are the eigen values and
eigen functions of the core hole and $E'_n(N)$ and $|E'_n(N)>$ are the eigen
values and the states of the system of $N$ outer electrons interacting with
a core hole described by the Hamiltonian $H_m + V_c$. We introduce an
operator representing the photoexcitation process,

$$M_i^\dagger = \sum_k T_{ki} a_k^\dagger a_i \quad (1-2)$$

where $T_{ki}$ is an matrix element of the dipole operator between the one-
particle state $|i>$ and $|k>$. 

In the valence band photoemission, from the golden rule, the
number of electron with the energy $\varepsilon$ is proportional to

$$I(\varepsilon) = \sum_i I_i(\varepsilon) =$$

$$\sum\sum_i k, n |<E_n(N-1)|<k|M_i^\dagger |E_0(N)>|^2 \delta(\varepsilon - \varepsilon_k) \delta(\varepsilon - \hbar \nu + E_n(N-1) - E_0(N)) \quad (1-3)$$

where $\varepsilon$ is the kinetic energy of the detected electron and $\hbar \nu$ is energy
of incidental photon. $|E_0(N)>$ in (1-3) includes the vacuum of the
photoelectron subspace. If we assume that there is no interference
between different values of $i$, namely if we assume $\sum T_{ki}^* T_{kj} = \Sigma |T_{ki}|^2 \delta_{ij}$,
\[ I(\epsilon) = \sum_i I_i(\epsilon) = \sum_i \sum_k |T_{ki}|^2 \delta(\epsilon-\epsilon_k) \langle E_n(N-1)|a_i|E_0(N)\rangle \langle \epsilon^2 \delta(\epsilon-\epsilon_0+H_{m}-E_0(N)) \rangle. \] (1-4)

Since the energy dependence of \( \Sigma |T_{ki}|^2 \delta(\epsilon-\epsilon_k) \) is negligible, \( I_i(\epsilon) \) is proportional to the spectral function of photoemission,

\[ q_i^{\text{PES}}(\epsilon-\epsilon_0) = \sum_n |\langle E_n(N-1)|a_i|E_0(N)\rangle|^2 \delta(\epsilon-\epsilon_0+E_n(N-1)-E_0(N)) \]. (1-5)

Eq. (1-5) is transformed through the relation \( 1/(x + i0) = P1/x - i\pi \delta(x) \),

\[ q_i^{\text{PES}}(\epsilon-\epsilon_0) = -\frac{1}{\pi} \text{Im} \langle E_0(N)|a_i^\dagger \frac{1}{\epsilon-\epsilon_0+H_{m}-E_0(N)} a_i|E_0(N)\rangle. \] (1-6)

In the case of inverse photoemission process, the spectral function is given by

\[ q_i^{\text{IPES}}(\epsilon-\epsilon_0) = -\frac{1}{\pi} \text{Im} \langle E_0(N)|a_i^\dagger \frac{1}{\epsilon-\epsilon_0-H_{m}+E_0(N)} a_i|E_0(N)\rangle, \] (1-7)

where \( \epsilon \) is the kinetic energy of the incident electron and \( \epsilon_0 \) is the energy of the detected photon. The spectral functions of photoemission and inverse photoemission are related to the retarded Green's function at zero temperature,

\[ G_i(z) = -i \int_0^\infty \theta(t) \langle E_0(N)|a_i|a_i^\dagger|E_0(N)\rangle e^{itz} dt = \langle E_0(N)|a_i^\dagger \frac{1}{z+H-E_0(N)} a_i|E_0(N)\rangle + \langle E_0(N)|a_i \frac{1}{z-H+E_0(N)} a_i^\dagger|E_0(N)\rangle, \] (1-8)

where \([ , ]_+\) is an anticommutator. Therefore, we obtain the relation
\[ q_i^{\text{PES}}(\epsilon-h\nu) + q_i^{\text{PES}}(\epsilon-h\nu) = -\frac{1}{\pi} \text{Im} G_i(\epsilon-h\nu+i0). \] (1-9)

In the core-level photoemission, the number of electron with the energy \( \epsilon \) is proportional to

\[ I_c(\epsilon) = \sum_{k,n} |<E'_n(N)|<k>M_i^\dagger|E_0(N)>|^2 \delta(\epsilon-\epsilon_k) \delta(\epsilon-h\nu-\epsilon_c+E'_n(N)-E_0(N)), \] (1-10)

where we neglect the interference between photoemission processes from different core levels, namely we assume \( \Sigma T_{kc}^* T_{kc'} = \Sigma |T_{kc}|^2 \delta_{cc'} \).

\(|E_0(N)>\) in (1-10) include the vacuum of the photoelectron and core hole subspaces.

\[ I_c(\epsilon) = \sum_k |T_{kc}|^2 \delta(\epsilon-\epsilon_k) |<E'_n(N)|E_0(N)>|^2 \delta(\epsilon-h\nu-\epsilon_c+E'_n(N)-E_0(N)). \] (1-11)

Since the energy dependence of \( \Sigma |T_{kc}|^2 \delta(\epsilon-\epsilon_k) \) is negligible, \( I_c(\epsilon) \) is proportional to the spectral function of core-level photoemission,

\[ q_c(\epsilon-h\nu) = \sum_n |<E'_n(N)|E_0(N)>|^2 \delta(\epsilon-h\nu-\epsilon_c+E'_n(N)-E_0(N)). \] (1-12)

2. Models

The Anderson lattice model has been considered to be a good model to describe the system where localized orbitals hybridize with extended orbitals, such as Ce compounds. The Hamiltonian of the Anderson lattice model is given by (2-1) - (2-4).

\[ H = H_d + H_L + H_h \] (2-1)
\[ H_d = \sum_i \sum_m \varepsilon_{d_{i,m}} d_{i,m}^\dagger + \sum_i \sum_{m1,m2,m3,m4} U_{m1,m2,m3,m4} d_{i,m1}^\dagger d_{i,m2}^\dagger d_{i,m3}^\dagger d_{i,m4} \quad (2-2) \]

\[ H_L = \sum_k \varepsilon_{L_k} c_k^\dagger c_k \quad (2-3) \]

\[ H_h = \sum_i \sum_k V_{k,m} c_k^\dagger d_{i,m} + \text{h.c.} \quad (2-4) \]

where \( i \) is a site index and \( m \) is an orbital and spin index of the localized states and \( k \) denotes the wave vector of the extended states. The second term in the Hamiltonian \( H_d \) represents the on-site Coulomb interactions, which is described by the Slater integrals [3.7]. The Hamiltonian \( H_h \) describes the hybridization between the localized states and the extended states. When we consider the 3d transition-metal oxides, the localized orbitals and the extended states correspond to the atomic 3d orbitals and the Bloch states constructed from the O 2p orbitals, respectively. In this case, we can use the Racah A, B and C parameters instead of the Slater integrals [3.8]. The transfer integrals \( V_{k,m} \) are described in terms of the Slater-Koster parameters \( (pd\sigma) \) and \( (pd\pi) \) [3.9,10].

Since the Anderson lattice model is very difficult to solve not only analytically but also numerically, much work has been limited to the Anderson impurity model, where localized orbitals at only one site are taken into account and the translational symmetry of the localized orbitals is neglected. The Hamiltonian of the Anderson single-impurity model is given by replacing (2-2) and (2-4) by

\[ H_d = \sum_m \varepsilon_{d_m} d_m^\dagger d_m + \sum_{m1,m2,m3,m4} U_{m1,m2,m3,m4} d_{m1}^\dagger d_{m2}^\dagger d_{m3}^\dagger d_{m4} \quad , \quad (2-5) \]
\[ H_h = \sum_k V_{k,m} c_k^d d_m + \text{h.c.} \quad (2-6) \]

In stead of solving this Hamiltonian, we make the transformation

\[ |V_m(\varepsilon)|^2 = \sum_k |V_{k,m}|^2 \delta(\varepsilon - \varepsilon_k) . \quad (2-7) \]

The Hamiltonian of the Anderson single-impurity model is given by (2-1), (2-5), (2-8) and (2-9).

\[ H_L = \int d\varepsilon \, c_\varepsilon^t c_\varepsilon \quad (2-8) \]

\[ H_h = \int d\varepsilon \, V_m(\varepsilon) c_\varepsilon^t d_m + \text{h.c.} \quad (2-9) \]

Historically, many calculations using the Anderson impurity model have been performed on Ce mixed-valence compounds and show that the model can reproduce the photoemission spectra and can describe the electronic structures of the 4f mixed-valence compounds. Recently, Zaanen and Sawatzky have applied the impurity model to 3d transition-metal compounds and have shown that the model works well.

It is still hard to solve the Anderson single-impurity model numerically including both the intra-atomic multiplet effect of localized 3d orbitals and the finite band width of extended orbitals. When it is more important to take into account the multiplet effect than the finite band width, we can limit the calculation to a cluster including only one transition-metal site and nearest neighbor ligand sites and neglect the
band width. The Hamiltonian of the cluster type model is given by replacing (2-8) and (2-9) by

\[ H_L = \sum_m \varepsilon_m c_m^\dagger c_m, \quad (2-10) \]

\[ H_h = \sum_m V_m c_m^\dagger d_m + \text{h.c.}, \quad (2-11) \]

where \( c_m^\dagger \) is a creation operator of an electron in a ligand molecular orbital with spin and orbital symmetry \( m \). The \( m \) dependence of \( V_m \) is presented in Appendix A in detail for the octahedral and the square-planer clusters.

3. Configuration-Interaction Cluster Model Calculation

In order to obtain valence [3.4,5] and [3.3,11] core-level photoemission spectra, (1-5) and (1-12) should be calculated under a given Hamiltonian. We have performed configuration-interaction (CI) calculation using a square-planer \( (\text{Cu}^{3+}\text{O}_4)^5^- \) cluster model \( (D_{4h} \text{ symmetry}) \) for \( \text{NaCuO}_2 \) and a octahedral \( (\text{Cu}^{3+}\text{O}_6)^9^- \) cluster model \( (O_h \text{ symmetry}) \) for \( \text{LaCuO}_3 \). [3.3,4,5] If we neglect the intra-atomic multiplet coupling and the anisotropy of the hybridization, the wave function of the ground state of an \( N \)-electron system is given by

\[ \Psi_g = a_0 d^8 > + a_1 d^9 L_2 > + a_2 d^{10} L_2^2 >, \quad (3-1) \]

where \( L_2 \) denotes a ligand hole. The Hamiltonian is
\[
H = \begin{pmatrix}
E_8 & V_1 & 0 \\
V_1 & E_8 + \Delta & V_2 \\
0 & V_2 & E_8 + 2\Delta + U
\end{pmatrix}
\]  

(3-2)

where \(E_8 = \langle d^8 | H | d^8 \rangle\), \(\Delta = \langle d^9_{L} | H | d^9_{L} \rangle - \langle d^8 | H | d^8 \rangle\) is the charge-transfer energy, \(U = \langle d^7 | H | d^7 \rangle + \langle d^9_{L} | H | d^9_{L} \rangle - 2\langle d^8 | H | d^8 \rangle\) is the repulsive d-d Coulomb interaction energy, \(V_1 = \langle d^8 | H | d^9_{L} \rangle\) and \(V_2 = \langle d^9_{L} | H | d^{10}_{L,2} \rangle\) are effective transfer integrals. The energy of the ground state \(E_0(N)\) is obtained by diagonalizing the Hamiltonian (3-2). The final states of 3d photoemission, namely, the eigen states of \((N-1)\)-electron system, are given by

\[
\Psi_f = b_0 \langle d^7 \rangle + b_1 \langle d^8_{L} \rangle + b_2 \langle d^9_{L,2} \rangle + b_3 \langle d^{10}_{L,3} \rangle .
\]  

(3-3)

The Hamiltonian is

\[
H = \begin{pmatrix}
E_7 & V_1' & 0 & 0 \\
V_1' & E_7 + U & V_2' & 0 \\
0 & V_2' & E_7 + 2U & V_3' \\
0 & 0 & V_3' & E_7 + 3\Delta
\end{pmatrix}
\]  

(3-4)

where \(E_7 = \langle d^7 | H | d^7 \rangle\), \(V_1' = \langle d^7 | H | d^8_{L} \rangle\), \(V_2' = \langle d^8_{L} | H | d^9_{L,2} \rangle\) and \(V_3' = \langle d^9_{L,2} | H | d^{10}_{L,3} \rangle\). The energies and wave functions of the final states are obtained by diagonalizing the Hamiltonian (3-4). The lowest energy level of the final states is the first ionization level and the energy is denoted by \(E_0(N-1)\). The 3d photoemission intensity is given by eq. (3-5) in the sudden approximation.

\[
I_f \propto |a_0b_0 + a_1b_1 + a_2b_2|^2
\]  

(3-5)
The Hamiltonian of the \((N+1)\)-electron system can be constructed in the same way. The lowest energy level of the \((N+1)\)-electron system is the affinity level and the energy is denoted by \(E_0(N+1)\). The magnitude of the conductivity gap in the cluster approximation is given by

\[
E_{\text{gap}} = E_0(N-1) + E_0(N+1) - 2E_0(N). \quad (3-6)
\]

In the calculation of the valence band spectra, we have included both the intra-atomic multiplet coupling and the anisotropy of hybridization. In that case, we have to consider the splitting of the Cu 3d orbitals into \(\text{e}_g\) and \(\text{t}_{2g}\) orbitals for \(\text{O}_h\) symmetry and into \(\text{a}_{1g}, \text{b}_{1g}, \text{b}_{2g}\) and \(\text{e}_g\) orbitals for \(\text{D}_{4h}\) symmetry by the crystal field and the anisotropic hybridization between these 3d orbitals and ligand orbitals. At the same time, the multiplet splitting of the \(d^7\) and \(d^8\) configurations due to intra-atomic Coulomb and exchange interactions have to be taken into account. In the case of \(\text{NaCuO}_2\), the ground state is found to have the symmetry of \(^1\text{A}_{1g}\) and the symmetry of final states is \(^2\text{A}_{1g}, ^2\text{B}_{1g}, ^2\text{B}_{2g}\) and \(^2\text{E}_g\). The basis functions and matrix elements are listed in Appendix B.

Final states of core-level photoemission are given by

\[
\Psi_f = c_0|\text{d}^8> + c_1|\text{d}^9\text{L}> + c_2|\text{d}^{10}\text{L}^2>, \quad (3-7)
\]

where \(\zeta\) denotes a core hole. The Hamiltonian is

\[
H = \begin{pmatrix}
E_c & V''_1 & 0 \\
V''_1 & E_c + \Delta Q & V''_2 \\
0 & V''_2 & E_c + 2\Delta Q + U
\end{pmatrix}, \quad (3-8)
\]
where \( E_c = \langle \psi_d^8 | H | \psi_d^8 \rangle \), \( Q \) is the attractive Coulomb interaction energy between the core hole and the 3d electron, \( V_1'' = \langle \psi_d^8 | H | \psi_d^9 L \rangle \) and \( V_2'' = \langle \psi_d^9 L | H | \psi_d^{10} L \rangle \) are effective transfer integrals. The 2p core level photoemission intensity is given by

\[
I_f = |a_0 c_0 + a_1 c_1 + a_2 c_2|^2. \tag{3-9}
\]

4. Anderson Single-Impurity Model Calculation

In order to check the effect of the finite width of the ligand band, we have studied a simplified Anderson impurity model for a Cu\(^{3+}\) ion embedded in the filled oxygen p band. It is still hard to solve the Anderson single-impurity model numerically including both the intra-atomic multiplet effect of the localized 3d orbitals and the finite width of the ligand band, and therefore we neglect the intra-atomic multiplet coupling and the anisotropy of hybridization. The energy dependence of \( |V(\epsilon)\|^2 \) is assumed to be proportional to the semi-ellipsoid with an appropriate width \( W \).

If we follow the formulation by Zaanen [3.3,6], the wave function of the ground state of the N-electron system is given by

\[
\Psi_g = \alpha \langle \psi_d^8 | + \int_{-W/2}^{W/2} d\epsilon \beta(\epsilon) \psi_d^9 L(\epsilon) | + \int_{-W/2}^{W/2} d\epsilon d\epsilon' \gamma(\epsilon, \epsilon') \psi_d^{10} L(\epsilon) L(\epsilon') |, \tag{4-1}
\]

where \( L(\epsilon) \) denotes a ligand hole with energy \( \epsilon \). The matrix elements between \( \psi_d^9 L(\epsilon) \) and \( \psi_d^{10} L(\epsilon) L(\epsilon') \) are approximated by \( \sqrt{2} V(\epsilon') \). If we operate \( \psi_d^8, \psi_d^9 L(\epsilon) \), and \( \psi_d^{10} L(\epsilon) L(\epsilon') \) from the left side of the Schrödinger equation \( H \Psi_g = E \Psi_g \), we obtain (4-2) - (4-4).
\[
\alpha ( E_8 + \sqrt{2} \int_{-W/2}^{W/2} \, \text{d} \beta(e) V(e) \big) = \alpha \, E \tag{4-2}
\]

\[
\sqrt{2} \alpha \, V(e) + \alpha \beta(e) E_9(e) + \sqrt{2} \alpha \int_{-W/2}^{W/2} \, \text{d} e' \gamma(e,e')V(e') = \alpha \, \beta(e) \, E \tag{4-3}
\]

\[
\sqrt{2} \, \beta(e) \, V(e') + \alpha \gamma(e,e') E_{10}(e,e') = \alpha \gamma(e,e') \, E \tag{4-4}
\]

where \( E_8 = \langle d_8 | H | d_8 \rangle \), \( E_9(e) = \langle d_9 L(e) | H | d_9 L(e) \rangle \) = \( E_8 + \Delta + \epsilon \) and \( E_{10}(e,e') = \langle d_{10} L(e) L(e') | H | d_{10} L(e) L(e') \rangle \) = \( E_8 + 2\Delta + U + \epsilon + \epsilon' \). \( \Delta \) is the charge-transfer energy and \( U \) is repulsive d-d Coulomb interaction energy. If we define \( \delta = E - E_8 \), we get (4-5) from (4-2) - (4-4).

\[
\delta = 2 \int_{-W/2}^{W/2} \text{d} e \frac{|V(e)|^2}{\delta - \Delta - \epsilon - 2} \int_{-W/2}^{W/2} \text{d} e' \frac{|V(e')|^2}{\delta - 2\Delta - U - \epsilon - \epsilon'} \tag{4-5}
\]

Since we can neglect the \( d_{10} \) configurations in the large \( U \) limit, the denominator of the integrated function in (4-5) becomes \( \delta - \Delta - \epsilon \). We can integrate the right-hand side of (4-5) analytically and can obtain the energy of the ground state \( E_0(N) \). Otherwise, we solve the Anderson impurity model numerically by replacing the continuous band states by a set of discrete states. \( E_0(N-1) \) and \( E_0(N+1) \) can be obtained by the same procedure and we can calculate the conductivity gap by (3-6).
References


Chapter 4 Experimental Results and Analysis

1. XPS of NaCuO$_2$

The XPS spectra of the O 1s and Cu 2p core levels and the valence band are compared with those of CuO (Cu$^{2+}$) and Cu$_2$O (Cu$^+$) (by Ghijsen et al. [4.1]) in Figs. 5, 6 and 7, respectively. Since NaCuO$_2$ is a good insulator, the samples were charged up during the XPS measurements, so absolute binding energies could not be obtained. Therefore the spectra of NaCuO$_2$ are tentatively calibrated so as to align the top of the valence band with those of CuO and Cu$_2$O. Core-level binding energies thus determined are listed in Table I. The binding energy of the Cu 2p$_{3/2}$ main peak is 0.4 eV lower than CuO, and that of the O 1s peak is 0.4 eV higher than CuO. The Na 2s core-level XPS spectrum is shown in Fig. 8. The binding energy of the Na 2s level is ~ 61.9 eV. From the EELS measurements, the band gap is estimated to be 1-2 eV (Fig. 9). Therefore, all the binding energies may be 1-2 eV higher than the present values if the Fermi level is located at the bottom of the conduction band, and do not necessarily contradict with Steiner et al.'s results, [4.2] in which the binding energy of the Cu 2p$_{3/2}$ main peak of NaCuO$_2$ is 1.3 eV higher than that of CuO. The full width at half maximum (FWHM) of the Cu2p$_{3/2}$ main peak is ~ 2.2 eV, which is much smaller than that of the Cu$^{2+}$ compounds ~ 3.2 eV. If a broadening by charge up is taken into account, the width is also consistent with Steiner et al.'s measurements, in which the FWHM of Cu 2p$_{3/2}$ main peak is ~ 1.6 eV. [4.2]
Table I. Core-level binding energies. The absolute energies for NaCuO$_2$ have no significance as described in the text.

<table>
<thead>
<tr>
<th></th>
<th>Cu 2p$_{3/2}$ (main)</th>
<th>O 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Binding Energy</td>
<td>FWHM</td>
</tr>
<tr>
<td>Cu$_2$O$^a$</td>
<td>932.4 eV</td>
<td>530.2 eV</td>
</tr>
<tr>
<td>CuO$^a$</td>
<td>933.2 eV</td>
<td>529.2 eV</td>
</tr>
<tr>
<td>La$_4$BaCu$<em>5$O$</em>{13}$</td>
<td>932.8 eV</td>
<td>3.4 eV</td>
</tr>
<tr>
<td>LaCuO$_3$</td>
<td>933.9 eV</td>
<td>3.4 eV</td>
</tr>
<tr>
<td>NaCuO$_2$</td>
<td>932.7 eV</td>
<td>2.2 eV</td>
</tr>
</tbody>
</table>

$^a$ Ghijsen et al.(ref. 4.1)

Fig. 5. O 1s XPS spectrum of NaCuO$_2$ compared with those of Cu$_2$O, CuO (Ghijsen et al. [4.1]). Ghijsen et al.'s spectra have been taken using monocromatized Al K$\alpha$ radiation and their resolution is 0.3-0.4 eV higher than ours. The spectra of NaCuO$_2$ have been corrected for the Mg K$\alpha$ satellites.
Fig. 6. Cu 2p XPS spectrum of NaCuO$_2$ compared with those of Cu$_2$O, CuO (Ghijsen et al. [4.1]). The spectrum of NaCuO$_2$ is compared with the result of CI cluster calculation (bottom). The main peaks have mainly $\epsilon d^{10}L^2$ character and the satellites have $\epsilon d^9L$ character. Features dominated by $d^8$ character are very week.
Fig. 7. XPS valence band spectrum of NaCuO$_2$, compared with those of Cu$_2$O, CuO (Ghijsen et al. [4.1]). The spectra of NaCuO$_2$ is compared with the result of CI cluster calculation (bottom). Both d$^8$L and d$^9$L$^2$ configurations are contained in the main bands (0-5 eV), and d$^8$L is dominant in the satellite structure (> 6 eV).
Fig. 8. Na 2s core-level XPS spectrum of NaCuO₂.

![Na 2s XPS spectrum](image)

Fig. 9. EELS spectrum of NaCuO₂.

![EELS spectrum](image)
We have analyzed the Cu 2p and 3s core level spectra using a cluster model with configuration interaction (CI) following the same procedure as that of Ni$^{2+}$ compounds by Zaanen, Westra and Sawatzky. [3.3] The wave function of the ground state can be described by a linear combination of the $d^8$, $d^9L$, $d^{10}L^2$ configurations. The wave functions of the final states are given by linear combinations of the $\zeta d^8$, $\zeta d^9L$, $\zeta d^{10}L$, where $\zeta$ denotes a core hole. The intensities of the final states are calculated in the sudden approximation, and the line spectra thus obtained are broadened in order to compare with the experimental spectrum. The calculated Cu 2p spectrum is shown in Fig. 10. There are four parameters in our model, namely, the charge-transfer energy from $d^8$ to $d^9L\Delta$, the d-d Coulomb repulsive interaction U, the p-d transfer integral $T\ [T=\sqrt{3}(pd\sigma), V_1=V_2=\sqrt{2}T]$ and the Coulomb attractive interaction between the core hole and the 3d electron Q. In calculating the Cu 2p core level spectrum, Q is assumed to be ~ U/0.7. [3.3,12] With U and Q being fixed to 7 eV and 10 eV, respectively, the best fit has been obtained with $\Delta=\pm 1$ eV and $T=2.9\pm 0.2$ eV. The $2p_{3/2}$ main peak at ~ 932.7 eV has mainly $\zeta d^{10}L^2$ character and the satellite at ~ 941.5 eV has $\zeta d^9L$ character. It should be noted that it was not possible to reproduce the experimental spectrum with a positive $\Delta$ as this lead to two distinct peaks in the satellite region. The value of the 3s-3d Coulomb attractive energy should be close to that of 3d-3d Coulomb repulsive energy U since both orbitals have the same principal quantum number $n=3$. Actually, we can reproduce the Cu 3s spectrum by changing the value of Q from U/0.7 to U with the other parameters hardly changed from those of the Cu 2p case (Fig. 11). The Cu 3p spectrum also have a satellite structure as Cu 2p and Cu 3s spectra as shown in Fig. 12. Since the multiplet coupling is strong between a 3p core hole and 3d electrons, the Cu 3p spectrum cannot be fitted by the
Fig. 10. **Upper panel:** Cu 2p core-level spectrum of NaCuO$_2$ calculated by using the CI cluster model. **Lower panel:** Decomposition of line spectra into final-state configurations.

![Cu 2p core-level spectrum of NaCuO$_2$](image1)

- $d^8$
- $d^9_L$
- $d^{10}_{L^2}$

Fig. 11. **Upper panel:** Cu 3s core-level spectrum of NaCuO$_2$ calculated by using the CI cluster model. **Lower panel:** Decomposition of the line spectra into final-state configurations.

![Cu 3s core-level spectrum of NaCuO$_2$](image2)

- $d^8$
- $d^9_L$
- $d^{10}_{L^2}$
Fig.12. Upper panel: Cu 3p core-level spectrum of NaCuO$_2$ calculated by using the CI cluster model. Lower panel: Decomposition of the line spectra into final-state configurations.

![Cu 3p core-level spectrum of NaCuO$_2$](image)

Fig.13. Upper panel: Cu 2p core-level XAS spectrum of NaCuO$_2$ (top, from ref. 4.3) is compared with that obtained from the CI cluster calculation (bottom).

![Cu 2p XAS spectrum of NaCuO$_2$](image)
simple method neglecting the multiplet effect. If we try to reproduce the Cu 2p X-ray absorption spectrum by Sarma et al. [4.3] with the same parameters except for the fine structures due to $2p_3d^9$ multiplet splitting, the intensity of the satellite structure becomes too small. In order to make the intensity larger, we have to decrease the value of $T$ and increase the value of $|\Delta-Q+U|$. For example, the spectrum calculated with the parameters $\Delta=-1.0$ eV, $U=7.0$ eV, $T=2.0$ eV and $Q=13.0$ eV is shown in Fig. 13. This discrepancy is probably due to neglecting the multiplet coupling between 3d electrons and a 2p core hole and due to excluding the change of the transfer integrals by the core-hole potential and the increase of the 3d electrons in the final states. Recently, calculations of the Cu 2p XPS and XAS spectra including multiplet effects have been performed by Okada and Kotani.[4.4]

In calculating the valence band photoemission spectrum of NaCuO$_2$, we have done a CI calculation including multiplet structures, using a square-planer CuO$_4^{5-}$ cluster model.[3.4,5] If $\Delta$ is negative, the ground state is found to have $^1A_{1g}$ symmetry (Fig. 14(a),(b)), where a d hole ($d^9$) with $x^2-y^2$ symmetry and a ligand hole with the same symmetry form a spin singlet (so-called "local singlet") [4.5,6]. The symmetry of the final states are $^2A_{1g}$, $^2B_{1g}$, $^2B_{2g}$, $^2E_g$, and can be described by linear combinations of $d^7$, $d^{8L}$, $d^{9L^2}$ and $d^{10L^3}$ configurations. The basis functions and the Hamiltonians of $d^7$, $d^{8L}$ and $d^{9L^2}$ are listed in Appendix B. The Racah B, C parameters are fixed to the free-ion values. The ratio $(pd\sigma)/(pd\pi)$ is assumed to be $\sim -2.2$, which was evaluated from the band structure calculation. [3.10,4.8] Therefore, we have three adjustable parameters, $\Delta$, $U$ and $(pd\sigma)$. When we neglect the overlap integrals between the 3d orbitals and the ligand 2p orbitals, no set of the parameters in the reasonable range cannot reproduce the satellite structures as shown at the top of Fig. 15. Since the overlap integrals
Fig. 14. Energies of the \( ^1A_{1g} \) (crosses) and \( ^3B_{1g} \) (solid line) states for the square-planer \((\text{CuO}_4)^5^-\) cluster as a function of \( \Delta \) for appropriate values of \( \langle \text{pd}\sigma \rangle \) and \( U \) \((\text{pd}\sigma) = -1.5 \text{ eV}, U = 7.5 \text{ eV}\) (a) including the non-orthogonality between \( \text{Cu} \) 3d and \( \text{O} \) 2p orbitals and (b) excluding the non-orthogonality. When the non-orthogonality is included, the point, where the curves of \( ^1A_{1g} \) and \( ^3B_{1g} \) cross, is shifted to left by \(-0.4 \text{ eV}\). This corresponds to the ligand field due to non-orthogonality. (see Appendix A) Also shown are energies of the \( ^1A_{1g} \) and \( ^1E_g \) (crosses) and \( ^3A_{2g} \) (solid line) states for the octahedral \((\text{CuO}_6)^9^-\) cluster as a function of \( \Delta \) for the appropriate values of \( \langle \text{pd}\sigma \rangle \) and \( U \). \((\text{pd}\sigma) = -1.5 \text{ eV}, U = 7.5 \text{ eV}\) (c) including the non-orthogonality between \( \text{Cu} \) 3d orbitals and \( \text{O} \) 2p orbitals and (d) excluding the non-orthogonality. States with the other symmetries are omitted.
Fig.15. Upper panel: Valence band XPS spectra of NaCuO$_2$ calculated by using the CI cluster model excluding the non-orthogonality (top) and including the non-orthogonality (bottom) compared with the experimental result (middle). Lower panel: Decomposition of the line spectra into final-state configurations.

![Graph of NaCuO$_2$ valence band XPS spectra](image)

Binding Energy (eV)

Intensity (arb. units)

- $d^7$
- $d^8_{\text{L}}$
- $d^9_{\text{L}}$
- $d^9_{\text{L}}^2$

- $^{2}B_1$
- $^{2}A_1$
- $^{2}B_1$
- $^{2}E$
- $^{2}B_2$
- $^{2}A_1$
- O$_2$p
Sσ ~ 0.06 and Sπ ~ -0.03 were also evaluated from the band structure calculation for the transition-metal monoxides by Mattheiss [4.8], the effect of non-orthogonality can be taken into account without additional parameters. When we include the effect of the overlap integrals, the spectrum is well reproduced with Δ = -0.5 eV, U = 7.0 eV, (pðσð) = -1.5 eV as shown at the bottom of Fig. 15. These parameters are consistent with those obtained from the Cu 2p and 3s core-level XPS spectra. In analyzing the core-level spectra, the model is so simplified that the effect of non-orthogonality is not clear. The ground state is a mixture of 21% d8, 52% d9L, and 5% d10L2 configurations with an overlap population 22%. When the overlap integrals are neglected with the other parameters fixed, the ground state has 27% d8, 65% d9L, and 8% d10L2 characters, which is in good agreement with ab initio calculations (Hartree-Fock+Cl) by Akeyama and Kosugi (32.5% d8, 61.7% d9L, 3.4% d10L2). [4.7] In the final states, both d8L and d9L2 configurations are dominant in the main band at 0 - 6 eV, and d8L is dominant in the satellite region (>6 eV). The symmetry of the first ionization state is 2A1g. The satellite structure at ~ 12 eV is mainly d8L(2B1g) whose intensity is enhanced by the effect of non-orthogonality reflecting its antibonding character.

2. XPS of LaCuO3

The Cu 2p core-level photoemission spectrum of LaCuO3 has a satellite structure. Although LaCuO3 is metallic, it is assumed that the cluster-type model can be applied to this system. The spectrum is reproduced by the CI cluster method as shown in Fig. 16 with Δ = -2.0 eV, T = 2.7 eV, U = 7.0 eV Q = 10.0 eV. The value of T is reduced from that of NaCuO2. The reduction of the effective transfer integral probably
Fig. 16. Upper panel: Cu 2p core-level spectrum of LaCuO₃ calculated by using the CI cluster model compared with the experimental result. Lower panel: Decomposition of the line spectra into final-state configurations.

Fig. 17. The valence band XPS spectrum of LaCuO₃ calculated by using the CI cluster model.
reflects that the Cu-O distance of LaCuO₃ is ~ 0.1 Å larger than that of NaCuO₂. The parameters obtained from the analysis are compared with those for NaCuO₂ in Table II. The CI cluster-type calculation have also been performed for the valence band spectra just as for NaCuO₂. The ground state of the cubic (Cu³⁺O₆)⁹⁻ cluster has 3A₂g symmetry (Fig. 14 (c),(d)). The symmetry of the final states are 4T₁g, 4E₉, 2T₁g, 2E₉ and the first ionization state has 2E₉ symmetry. The spectrum calculated with Δ = -2.0 eV, U = 5.0 eV and (pdσ) = -1.0 eV is compared with the the valence band XPS spectrum in Fig. 17. We can reproduce the spectrum to some extent by reducing the value of U from 7 eV, which was obtained from the photoemission studies of the other Cu oxides. [3.5,4.1,9] However, agreement with the experimental result is still poor, indicating the limitation of the cluster model.

Table II. Parameters obtained from the analysis by using the CI cluster model. Δₑffective is the charge-transfer energy defined with respect to the lowest term of each multiplet as described in Chap. 5. Δₑffective = Δ + (-14/9B+7/9C) + 8B for LaCuO₃ (3A₂g for Øh symmetry) and Δₑffective = Δ + (-14/9B+7/9C) - 4B - 2C for NaCuO₂ (1A₁g for D₄h symmetry).

<table>
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<tr>
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<th>Δ (eV)</th>
<th>Δₑffective (eV)</th>
<th>U (eV)</th>
<th>(pdσ) (eV)</th>
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<td>7.0</td>
<td>-1.55±0.12</td>
</tr>
</tbody>
</table>
3. Comparison of the Photoemission Spectra of NaCuO$_2$, LaCuO$_3$, La$_4$BaCu$_5$O$_{13}$ and La$_{2-x}$Ca$_{1+x}$Cu$_2$O$_{6+δ}$

The XPS spectra of the O 1s, Cu 2p and valence band of NaCuO$_2$, LaCuO$_3$ and La$_4$BaCu$_5$O$_{13}$ are shown in the Figs. 18, 19 and 20. The binding energies and the FWHM's of the O 1s and Cu 2p core-levels are listed in Table I. The Cu 2p binding energy of the perovskite LaCuO$_3$ is ~1 eV higher than that of the oxygen deficient perovskite La$_4$BaCu$_5$O$_{13}$. Although both LaCuO$_3$ and La$_4$BaCu$_5$O$_{13}$ seem to be normal metals, [1.7,10] the spectral weight just below Fermi level in the valence band spectra is very small and the satellite structures are clear in the Cu 2p spectra. Such features of the spectra have also been observed in high Tc cooper oxides. [4.9]

Fig.18. O 1s core-level spectra of NaCuO$_2$, LaCuO$_3$ and La$_4$BaCu$_5$O$_{13}$. 

![O1s XPS spectra of NaCuO$_2$, LaCuO$_3$, and La$_4$BaCu$_5$O$_{13}$](image-url)
Fig. 19. Cu 2p core-level spectra of NaCuO$_2$, LaCuO$_3$ and La$_4$BaCu$_5$O$_{13}$.

Fig. 20. Valence band XPS spectra of NaCuO$_2$, LaCuO$_3$ and La$_4$BaCu$_5$O$_{13}$. 
The Cu LVV Auger spectra of NaCuO$_2$, LaCuO$_3$ and La$_4$BaCu$_5$O$_{13}$ are shown in Fig. 21. and the Cu 3p spectra of NaCuO$_2$ and La$_4$BaCu$_5$O$_{13}$ are shown in Fig. 22. The spectra of NaCuO$_2$ is broadened by the charging effect. The Cu 3p spectrum of NaCuO$_2$ has a satellite structure at 5 - 20 eV higher binding energy region from the main peak. The satellite of the Cu 3p spectrum of La$_4$BaCu$_5$O$_{13}$ is hidden by the Ba 4d peaks. The La 3d spectra of LaCuO$_3$ and La$_4$BaCu$_5$O$_{13}$ are shown in Fig. 23. Each of the La 3d$_{5/2}$ and 3d$_{3/2}$ peaks has satellite structures through the final state effect of the ligand to La 4f charge-transfer type. When the surface of the sample is degraded, the splitting between the main peak and the satellite peak becomes unclear.

Fig.21. Cu LVV Auger spectra of NaCuO$_2$, LaCuO$_3$ and La$_4$BaCu$_5$O$_{13}$. 

![Cu LVV Auger spectra](image-url)
Fig. 22. Cu 3p spectra of NaCuO$_2$ and La$_4$BaCu$_5$O$_{13}$.

Fig. 23. La 3d core-level spectra of LaCuO$_3$ and La$_4$BaCu$_5$O$_{13}$.
The valence band UPS and XPS spectra of La$_4$BaCu$_5$O$_{13}$ are shown in Fig. 24. The valence band UPS spectra of La$_4$BaCu$_5$O$_{13}$ and La$_{1.82}$Ca$_{1.18}$Cu$_2$O$_{6+\delta}$ are compared with those of the insulating La$_2$CuO$_4$ and superconducting La$_{1.85}$Sr$_{0.15}$CuO$_4$ [4,9,10] in Fig. 25. The intensity just below the Fermi level is very small compared with that of the main band in the metallic and non-superconducting La$_4$BaCu$_5$O$_{13}$ and La$_{1.82}$Ca$_{1.18}$Cu$_2$O$_{6+\delta}$. Such valence band spectra resemble that of the Cu-oxide superconductor La$_{1.85}$Sr$_{0.15}$CuO$_4$, indicating that the electronic structures of La$_4$BaCu$_5$O$_{13}$ and La$_{1.82}$Ca$_{1.18}$Cu$_2$O$_{6+\delta}$ are similar to that of high-Tc superconductors. Based on the photon-energy dependence of photoionization crosssections, the center of the O 2p band of La$_4$BaCu$_5$O$_{13}$ is located at ~ 2.5 eV, which is 1-2 eV lower than in the other copper oxides. The resonant photoemission spectra of La$_4$BaCu$_5$O$_{13}$ and La$_{1.82}$Ca$_{1.18}$Cu$_2$O$_{6+\delta}$ are shown in Figs. 26 and 27. The satellite structures enhanced at $h\nu=74$ eV are observed.

Fig.24. valence band XPS and UPS spectra of La$_4$BaCu$_5$O$_{13}$. 

![Image of spectra](https://example.com/fig24.png)
Fig. 25. Valence band UPS spectra of La$_2$CuO$_4$, La$_{1.85}$Sr$_{0.15}$CuO$_4$, La$_4$BaCu$_5$O$_{13}$ and La$_{1.82}$Ca$_{1.18}$Cu$_2$O$_{6+\delta}$.
Fig. 26. Valence band UPS spectra of \( \text{La}_4\text{BaCu}_5\text{O}_{13} \). The spectra were taken on resonance (\( h\nu = 74 \text{ eV} \)) and off resonance (\( h\nu = 70 \text{ eV} \)) at the Cu 3p threshold.

![La4BaCu5O13 UPS spectra](image)

Fig. 27. Valence band UPS spectra of \( \text{La}_{1.82}\text{Ca}_{1.18}\text{Cu}_2\text{O}_{6+\delta} \). The spectrum taken at \( h\nu = 74 \text{ eV} \) is on resonance and the spectrum \( h\nu = 70 \text{ eV} \) is off resonance at the Cu 3p threshold.

![La1.82Ca1.18Cu2O6+ delta UPS spectra](image)
References


4.4 K. Okada and A. Kotani, B. T. Tole, and G. A. Sawatzky, Solid State Commun. 77, 835 (1991). Their definition of $\Delta = E(d^{10}L^2) - E(d^9L)$ is different from ours [$\Delta = E(d^9L) - E(d^8) \equiv E(d^{10}L^2) - E(d^9L) - U$].


4.7 K. Akeyama and N. Kosugi, unpublished.


Chapter 5 Discussions and Concluding Remarks

1. Charge-Transfer Energies and Other Parameters

From the analysis of the Cu 2p and the valence band XPS, the charge-transfer energy of NaCuO$_2$ is $\sim -1 \pm 1$ eV and that of LaCuO$_3$ is $\sim -2 \pm 1$, or the d$^9$L configuration is found to be dominant in the ground state of these Cu$^{3+}$ compounds. In the case of Fe oxide, the $\Delta$ of Fe$^{2+}$ is estimated $\sim 6.5$ eV [5.1] and the $\Delta$ of Fe$^{3+}$ is $\sim 3.0$ eV [5.2] from the valence band XPS and the $\Delta$'s are estimated $\sim 6.0$ eV, 3.5 eV and 0.0 eV for FeO, Fe$_2$O$_3$ and SrFeO$_3$, respectively, from the Fe 2p XPS [1.4,5.3]. The $\Delta$ decreases by $\sim 3 - 4$ eV for a unit increase of the valence. Therefore, the value for NaCuO$_2$ and LaCuO$_3$ is reasonable, because the $\Delta$ of Cu$^{2+}$ is $1 - 3$ eV. According to the parameter estimation on the simple ionic model, [1.3] $\Delta(2+) = \Delta V_M(2+) - I_{TM}(2) - A_L(2)$, $U = I_{TM}(3) - I_{TM}(2)$ and $\Delta(3+) = \Delta V_M(3+) - I_{TM}(3) - A_L(2) = \Delta(2+) - U + \Delta V_M(3+) - \Delta V_M(2+)$, where $\Delta V_M(2+)$ and $\Delta V_M(3+)$ are the Madelung potential difference between the transition-metal site and the oxygen site for the 2+ and 3+ compounds, respectively. $\Delta V_M$ is considerably reduced from the purely ionic value by a change of charge distribution due to covalency. $I_{TM}(n)$ is the n-th ionization potential of the transition metal and $A_L(n)$ is the n-th electron affinity of oxygen. They are reduced from the free-ion values by screening effects. In general, $\Delta V_M(3+)$ is larger than $\Delta V_M(2+)$ and therefore $\Delta(3+)$ is larger than $\Delta(2+) - U$ by $\Delta V_M(3+) - \Delta V_M(2+)$. The reduction of $\Delta V_M$ due to covalency is probably larger than in Cu oxides than in Fe oxides and it is expected that the difference between $\Delta(2+)$ and $\Delta(3+)$ is larger in Cu oxides than in Fe oxides. The reduction of $\Delta V_M$
due to covalency should be determined in a self-consistent way. If we assume that $\Delta V_M(3+) - \Delta V_M(2+)$ of Fe oxides is larger by $\sim 1$ eV than that of Cu oxides, the rough estimation of parameter have qualitative agreement with the value obtained from the analysis.

The parameters $\Delta$ and $U$ are defined as follows, $\Delta = E(d^{n+1}L) - E(d^n)$, $U = E(d^{n-1}) + E(d^{n+1}) - 2E(d^n)$, where $E(d^nL^m)$ is the center of the multiplet of the configuration $d^nL^m$. In this definition, the multiplet effect is excluded and the cation systematics of $\Delta$ becomes clear as shown in Fig. 2. [1.8] The charge-transfer energy and the d-d Coulomb interaction can be defined with respect to the lowest term of each multiplet [1.3] and we denote them as $\Delta_{\text{eff}}$ and $U_{\text{eff}}$. The parameter $\Delta_{\text{eff}}$ and $U_{\text{eff}}$ should be used when we classify the transition-metal compounds due to the character of the band gap. In the case of Cu$^{3+}$ (d$^8$), $\Delta_{\text{eff}} = \Delta + (-14/9B + 7/9C) + 8B$ for high spin ground state ($^3A_2$g for O$_h$ symmetry and $^3B_1$g for D$_{4h}$ symmetry) and $\Delta_{\text{eff}} = \Delta + (-14/9B + 7/9C) - 4B - 2C$ for low spin ground state ($^1A_1$g for D$_{4h}$ symmetry). Therefore, the $\Delta_{\text{eff}}$ of NaCuO$_2$ is smaller than $\Delta$ by $\sim 1.5$ eV and is $\sim -2.5 \pm 1$ eV. On the other hand, the $\Delta_{\text{eff}}$ of LaCuO$_3$ is larger by $\sim 1$ eV than $\Delta$ and is $\sim -1 \pm 1$ eV. The $\Delta_{\text{eff}}$ of NaCuO$_2$ is smaller than that of LaCuO$_3$ and the d$^9$L character is more dominant in NaCuO$_2$ than in LaCuO$_3$. In the case of high spin Fe$^{4+}$ (d$^4$), $\Delta_{\text{eff}}$ is smaller than $\Delta$ by $5(-14/9B + 7/9C) + 14B \sim 3$ eV. The $\Delta$ of SrFe$^{4+}$O$_3$ is estimated to be $\sim 0$ eV and the $\Delta_{\text{eff}} \sim -3$ eV. Therefore, SrFeO$_3$ belongs to the negative-$\Delta$ (negative-$\Delta_{\text{eff}}$) regime.

2. Origin of the Band Gap of NaCuO$_2$

According to the picture of charge-transfer insulators and metals in the impurity model neglecting hybridization between different configurations,[1.3] if $\Delta$ is smaller than half of the width of the ligand
band, the charge-transfer gap collapses and the compound is expected to be metallic. We consider in two steps the reason why the negative-Δ compound NaCuO₂ is insulating in the picture of the Anderson impurity model.

First, the ground state has to be a discrete state (separated by a finite energy from exited states) for a system to be an insulator. The ground state of the negative-Δ compound is the d⁹L configuration which is originally a continuum. But if the effect of strong hybridization is taken into account, a discrete state is split off from the continuum in the impurity limit. It is known that the first ionization state of Cu²⁺ oxides is a d⁹L-like state and is split off from the d⁹L continuum with ¹A₁g symmetry. [4.5,6] In the ground state of NaCuO₂, a d⁹L like discrete state is split off from the d⁹L continuum through the strong hybridization with d⁸ located above the d⁹L continuum. In order to examine this point we studied a simplified the Anderson impurity model for a Cu³⁺ ion embedded in the filled oxygen band (an ellipsoid with an appropriate band width). As shown in Fig 28, we indeed found a discrete d⁹L like split-off state with ¹A₁g symmetry, i.e. a local singlet, is formed 1.2 eV and 1.5 eV below the lower edge of the d⁹L continuum for the analytical and numerical calculations, respectively, using the same Δ_eff and T (T² is assumed to be equal to ʃ|V(e)|² de) as those obtained from the valence band XPS spectrum. We also have to examine whether the local singlets continue to be stable when the translational symmetry of the 3d states is included. NaCuO₂ consists of edge sharing CuO₄ planer units with Cu-O-Cu bonds forming nearly 90⁰ angles and the wave function of the local singlets d⁹L(¹A₁g) split off from the continuum are nearly orthogonal to those of the nearest neighbor Cu sites. Therefore, interaction between neighboring local singlets is weak and the local singlets remain localized even in the periodic lattice. It has also been pointed out that the
Fig. 28. Formation of a split-off state in the ground state of NaCuO₂. From the Anderson impurity model neglecting the d¹⁰_L² configurations.

\[ \delta = 2 \int_{-W/2}^{W/2} \frac{d\varepsilon |V(\varepsilon)|^2}{\delta - \Delta - \varepsilon} \]  

where \( \Delta \) is the charge-transfer energy from \( d^8 \) to \( d^9_L \) and \( \delta \) is the relative energy from the center of \( d^9_L \). If the shape of the ligand band is approximately assumed to be semi-ellipsoid, this equation is analytically solved and the result is shown at the top panel. The numerical results are shown in the middle (neglecting the \( d^{10}_L² \) configuration) and at the bottom (including the \( d^{10}_L² \) configuration) by replacing the continuum band states by a set of 20 discrete states. The parameters used for the calculations are as follows. \( \Delta_{\text{eff}} = -2.0 \text{ eV}, \) the square of the effective transfer integral \( T^2 = 6.75 \text{ eV}^2 \) (\( |V(\varepsilon)|^2 d\varepsilon = 6.75 \text{ eV}^2 \)), \( U = 7.0 \text{ eV} \) and the ligand band width \( W = 3.0 \text{ eV} \).
Fig. 29. Energy levels for the (N-1)-, N and (N+1)-electron systems calculated by using the simplified Anderson impurity model. In the N-electrons system (middle), a $d^9_{\text{L}}$-like discrete state is split off from the bottom of the continuum. The continuum ligand band is replaced by 15 discrete states. The parameters used for calculation are as follows. $\Delta_{\text{eff}} = -2.0$ eV, the square of the effective transfer integral $T^2 = 6.75$ eV$^2$, $U = 7.0$ eV and the ligand band width $W = 3.0$ eV.
geometrical arrangement of the CuO$_4$ units influences the dispensional band width of the extra hole (local singlet) in Cu$^{2+}$ oxides. [5.4]

Second, the magnitude of the band gap or the conductivity gap has to be finite, which is the minimum energy to create a well separated electron-hole pair, $E_{N+1} + E_{N-1} - 2E_N$. In general, a band gap cannot open if the ground state of the impurity model is a continuum, but it is not clear whether a band gap will open or not if the ground state is a discrete state in the impurity model. Using the above parameter values, the magnitude of the band gap is calculated to be 1.2 eV for the cluster model and 0.8 eV for the simplified impurity model, consistent with the EELS result. The gap is mainly determined by the charge fluctuation $d^9L + d^9L \rightarrow d^9 + d^9L^2$, and the character of the gap can be called p-p type. Namely, the lowest affinity level corresponds to the unoccupied ligand 2p state (hybridizing with $d_{x^2-y^2}$ state) and the lowest ionization level corresponds to the occupied ligand 2p state (hybridizing with $d_{3z^2-r^2}$ state), as shown in Fig.1 (c). The origin of this gap is the strong hybridization between ligand 2p states and localized 3d states, or the gap is opened due to the stabilization of the local singlet, which lowers the ground state energy $E_N$ through the strong hybridization between the $d^9L$ and $d^8$ configurations. Because of the p-p nature of the band gap, the Coulomb interaction at the oxygen site $U_{pp}$ may somewhat increase the band gap from the predicted value. On the other hand, the band gap in the periodic lattice is smaller than that predicted for the impurity model by dispensional widths of occupied [(N-1)-electron or extra-hole] and unoccupied [(N+1)-electron or extra-electron] states. However both widths are expected to be small for NaCuO$_2$ with edge sharing CuO$_4$ units for the same reason as stated above and the band gap will remain large even in the periodic lattice.
Such an argument naturally explains the metallic behavior of another Cu$^{3+}$ oxide LaCuO$_3$, which consists of corner sharing CuO$_6$ octahedra and has 180$^\circ$ Cu-O-Cu bonds. With the corner sharing geometry, the split-off d$^9$ state formed in the impurity limit strongly overlap with those of nearest neighbor clusters and will become extended state. Namely the formation of split-off state is frustrated in the corner sharing CuO$_4$ lattice. The band gap will also collapse due to the large dispersional width of the (N-1)-electrons and (N+1)-electrons states arising from the corner sharing geometry.

In the case of Fe$^{4+}$ oxides ($\Delta \sim 0$ eV, $\Delta_{\text{eff}} \sim -3$ eV), it is reported that SrFeO$_3$ is metallic and CaFeO$_3$ is semiconducting.[5.5] The cubic perovskite SrFeO$_3$ has 180$^\circ$ Fe-O-Fe bonds. On the contrary, CaFeO$_3$ is distorted from the cubic perovskite and Fe-O-Fe bond angle may be ~150 - 160$^\circ$. [5.5] It is possible that the band gap opens in CaFeO$_3$ just as NaCuO$_2$, although the magnitude may be rather small. It is interesting that CaFeO$_3$ is proposed to undergo the transition to a CDW state through the charge disproportionation $2\text{Fe}^{4+} \to \text{Fe}^{3+} + \text{Fe}^{5+}$ from Mössbauer spectroscopy. [5.5] If CaFeO$_3$ belongs to the negative-$\Delta$ (negative-$\Delta_{\text{eff}}$) regime, this charge disproportionation corresponds to the charge fluctuation d$^5$L$^+$+d$^5$L$^-$ $\to$ d$^5$+d$^5$L$^2$ which determine the magnitude of the band gap and the magnitude is so small that a small lattice distortion can make the energy of d$^5$+d$^5$L$^2$ state lower than that of d$^5$L$^+$+d$^5$L$^-$ state.

The above discussion can also be applied to the electronic structure of Ni$^{3+}$ compounds, namely, insulating LiNiO$_2$ [5.6] and metallic LaNiO$_3$. [5.7] The $\Delta$ of Ni$^{2+}$ is estimated to be ~4 eV [3.4,5.8] and therefore the $\Delta$ of Ni$^{3+}$ is expected to be 0 - 1 eV. In this case, d$^7$ and d$^8$L$^-$ are nearly degenerate and are strongly hybridized with each other, leading to the formation of a split-off state in the ground state. The split-off state will be still localized and the gap persists in LiNiO$_2$ which has the NaCl
structure with alternating Ni and Li (111) layers and has 90° Ni-O-Ni bonds. On the other hand, the split-off state is delocalized or the gap collapses in the perovskite structure LaNiO₃, where the angle of Ni-O-Ni bonds is close to 180°. Distorted Ni perovskites such as PrNiO₃-NdNiO₃, etc, indeed show insulating gaps. [5.9]

Here, it should be noted that the magnitude of the p-p band gap, is related neither to U nor to Δ in a direct way. The band gap opens when the local (intracluster) p-d hybridization is strong and the extended (intercluster) hybridization is weak. Therefore the magnitude of the band gap is sensitively dependent on the geometrical arrangement of the metal-oxygen local units. Now that the band gap of NaCuO₂ is largely due to the p-d hybridization in the ground state, it is interesting to ask whether the band gap is correctly predicted by the density functional theory with local-density approximation (LDA). A recent LDA band-structure calculation by Karlsson et al. [5.10] has yielded a band gap of ~ 0.8 eV comparable to our result but the states forming the gap has strongly hybridized p-d character rather than p-dominant. Also, the highest occupied x²-y² symmetry states in the LDA calculation are close to the top of the valence band whereas our cluster model fit yields them to be ~ 2.5 eV from the first ionization level. That is, the gap between the occupied and unoccupied x²-y² symmetry states is considerably underestimated in LDA. According to the another band structure calculation by M. Czyzyk, a band gap of ~ 1 eV also opens.[5.11]

In the ground state of a negative-Δ insulator, the insulating state is stabilized by the formation of a chemical bond between the dⁿ+¹ configuration and a ligand hole within the local cluster in a way analogous to the formation of a Heitler-London state. In this sense, the negative-Δ insulator is a "valence bond insulator", which is contrasted with the basically ionic Mott-Hubbard and charge-transfer insulators.
The compound becomes a metal when the local valence-bond formation is frustrated, e.g., due to metal-ligand-metal bonds forming angles much different from 90°.

The magnitude of the band gap is sensitive to the relative strength of the intracluster and intercluster hybridization in the negative-Δ (negative-Δ_{eff}) regime. Within the impurity limit, the effect of the intercluster hybridization can be taken into account to some extent through the increase of the width of the ligand band. In Fig. 30, we have plotted the magnitude of the band gaps calculated by using the simplified Anderson impurity model versus the charge-transfer energy (-10 - 10 eV) for the various sets of U (1 - 8 eV), T^2 (3.00 and 6.75 eV^2) and W (1.0, 2.0, 3.0 and 4.0 eV). In the Mott-Hubbard regime, the magnitude of the band gap E_g is proportional to the d-d Coulomb interaction U. In the charge-transfer regime, the magnitude of the band gap E_g is proportional to the charge-transfer energy Δ. As the width of the ligand band W becomes smaller or the effective transfer integral T becomes larger, the band gap tends to open in the negative-Δ region. In this region, the magnitude of the band gap is proportional neither to Δ nor U. In order to show the tendency of the band gap, we plot in Fig. 31 sets of U_{eff} and Δ_{eff} values which give E_g = 0.4 eV in the Δ_{eff}-U_{eff} diagram. As W becomes smaller or T becomes larger, the line shifts into the negative-Δ_{eff} region. If we assume the line is the "metal-insulator" phase boundary, the right-hand side of the line is the "insulating" region (E_g>0.4 eV) and the left-hand side of the line is the "metallic" region (E_g<0.4 eV). When the width of the ligand band W is much larger than the effective transfer integral T (for example, W=4.0 eV and T^2=3.0 eV^2), the phase boundary is close to that of the typical ZSA phase diagram.

In conclusion, it is found that the Δ_{eff} of NaCuO_2 is -2 eV and the d^9\text{L} configuration is dominant in the ground state from XPS experiment.
Fig. 30. Magnitude of band gaps calculated by the simplified Anderson impurity model. The magnitude of the band gaps are plotted for various $\Delta$ (-10 - 10 eV) and $U$ (1 - 8 eV) values. The band width $W$ and the square of the effective transfer integrals $T^2$ ($\langle |V(\epsilon)|^2 d\epsilon \rangle = 6.75 \text{ eV}^2$) used for calculations are (a) $W=2.0 \text{ eV}$ and $T^2 = 6.75 \text{ eV}^2$, (b) $W=3.0 \text{ eV}$ and $T^2 = 6.75 \text{ eV}^2$, (c) $W=4.0 \text{ eV}$ and $T^2 = 6.75 \text{ eV}^2$, (d) $W=1.0 \text{ eV}$ and $T^2 = 3.00 \text{ eV}^2$, (e) $W=2.0 \text{ eV}$ and $T^2 = 3.00 \text{ eV}^2$, (f) $W=3.0 \text{ eV}$ and $T^2 = 3.00 \text{ eV}^2$, (g) $W=4.0 \text{ eV}$ and $T^2 = 3.00 \text{ eV}^2$
**Charge-Transfer Energy (eV)**

(b) $T^2 = 6.75 \text{ eV}^2$

- $W = 3.0 \text{ eV}$
- $U = 8.0 \text{ eV}$
- $U = 7.0 \text{ eV}$
- $U = 6.0 \text{ eV}$
- $U = 5.0 \text{ eV}$
- $U = 4.0 \text{ eV}$
- $U = 3.0 \text{ eV}$
- $U = 2.0 \text{ eV}$
- $U = 1.0 \text{ eV}$

(c) $T^2 = 6.75 \text{ eV}^2$

- $W = 4.0 \text{ eV}$
- $U = 8.0 \text{ eV}$
- $U = 7.0 \text{ eV}$
- $U = 6.0 \text{ eV}$
- $U = 5.0 \text{ eV}$
- $U = 4.0 \text{ eV}$
- $U = 3.0 \text{ eV}$
- $U = 2.0 \text{ eV}$
- $U = 1.0 \text{ eV}$
\[ T^2 = 3.00 \text{ eV}^2 \]
\[ W = 1.0 \text{ eV} \]

\[ \begin{align*}
\times U &= 8.0 \text{ eV} \\
\times U &= 7.0 \text{ eV} \\
\ast U &= 6.0 \text{ eV} \\
\times U &= 5.0 \text{ eV} \\
+ U &= 4.0 \text{ eV} \\
\square U &= 3.0 \text{ eV} \\
\diamondsuit U &= 2.0 \text{ eV} \\
\times U &= 1.0 \text{ eV}
\end{align*} \]

\[ T^2 = 3.00 \text{ eV}^2 \]
\[ W = 2.0 \text{ eV} \]

\[ \begin{align*}
\times U &= 8.0 \text{ eV} \\
\times U &= 7.0 \text{ eV} \\
\ast U &= 6.0 \text{ eV} \\
\times U &= 5.0 \text{ eV} \\
+ U &= 4.0 \text{ eV} \\
\square U &= 3.0 \text{ eV} \\
\diamondsuit U &= 2.0 \text{ eV} \\
\times U &= 1.0 \text{ eV}
\end{align*} \]
Fig. 31. Modified ZSA phase diagram. The solid and dotted lines are the "metal-insulator" phase boundaries on which the band gap $E_g$ in the impurity model calculation is equal to 0.4 eV. The ligand band width $W$ and the square of the effective transfer integrals $T^2$ ($T^2 = \int |V(\epsilon)|^2 d\epsilon$) used for calculations are $W=2.0, 3.0, 4.0$ eV for $T^2 = 6.75$ eV$^2$ and $W=1.0, 2.0, 3.0, 4.0$ eV for $T^2 = 3.00$ eV$^2$. The right-hand side of the line is the "insulating" ($E_g > 0.4$ eV) region and the left-hand side of the line is the "metallic" ($E_g < 0.4$ eV) region. When the width of the band $W$ is much larger than the effective transfer integral $T$, the diagram is close to the typical ZSA phase diagram. As the band width $W$ becomes smaller or the effective transfer integral $T$ becomes larger, the phase boundary shifts into the negative-$\Delta_{\text{eff}}$ region.
and subsequent cluster model calculation with CI. The band gap is of the p-p type, and the relative strengths of the intracluster and intercluster hybridization is a key factor controlling the metallic versus insulating behaviors of negative-Δ compounds. In order to fully understand the electronic structure of NaCuO₂ and LaCuO₃ as well as those of other Cu³⁺ compounds, the translational symmetry of the 3d states must be taken into account more appropriately beyond the impurity limit.

3. Electronic Structures of Metallic Copper Oxides

As mentioned in Chapter 1, LaCuO₃, which has an integer formal valence, should be essentially discriminated from the La₄BaCu₅O₁₃ and high Tc copper oxides, which are made metallic by carrier doping. However, the spectra of LaCuO₃ resemble those of La₄BaCu₅O₁₃ and high Tc copper oxides, which indicates that the electronic structure of LaCuO₃ is not much different from those of high Tc copper oxides and non-superconducting copper oxide La₄BaCu₅O₁₃. The satellite structures in the XPS spectra of the Cu 2p core-level and in the resonant photoemission spectra of the valence band are similar to those of Cu²⁺ charge-transfer insulators such as CuO and La₂CuO₄, which suggests that the Cu d-d Coulomb interaction is still large in these metallic Cu-oxides. Although the satellite structure can be reproduced by the cluster calculation to some extent, the main band within ~ 6 eV of the Fermi level is difficult to study using the cluster model. It is necessary to study the model which can explain both the considerably reduced spectral weight near the Fermi level and the satellite structure.
References


5.9 J. B. Torrance et. al preprint


5.11 M. Czyzyk, unpublished.
Acknowledgments

The author would like to thank Prof. A. Fujimori and Dr. H. Namatame for their stimulation to the subject and helpful advice. The author is grateful to H. Kondoh, K. Akeyama, Prof. H. Kuroda and Prof. N. Kosugi for the collaboration in the study of NaCuO$_2$, and Dr. H. Eisaki, T. Ito, Dr. H. Takagi, Prof. S. Uchida for providing the La$_4$BaCu$_5$O$_{13}$ samples, Prof. M. Takano and Prof. Y. Takeda for providing the LaCuO$_3$ samples, Dr. K. Kinoshita for providing the La$_{2-x}$Ca$_{1+x}$Cu$_2$O$_{6+\delta}$ samples. The author is also grateful to the members of Fujimori laboratory and SOR, ISSP, T. Saitoh, K. Shimada, I. Hase, M. Nakamura, K. Yamaguchi, S. Nohara, I. Inoue, A. E. Bocquet, Dr. S. Ogawa, H. Matsubara and Prof. S. Suga. We would also like to thank Dr. O. Gunnarsson, Prof. J. C. Fuggle, Prof. G. A. Sawatzky, Prof. A. Kotani, and Dr. K. Okada for useful discussions and Dr. D. D. Sarma for valuable comments and the staff of Synchrotron Radiation Laboratory, Institute for Solid State Physics and BL-11D, Photon Factory, National Laboratory for High Energy Physics for technical support. All the calculations in this work were performed by using the VAX/VMS in Faculty of Science, University of Tokyo. The present work is supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.
Appendix A. CuO$_4$ and CuO$_6$ Cluster Models

We consider a cluster including only one transition-metal ion and nearest neighbor anions. The Hamiltonian of the cluster model is given by (A-1) - (A-4) as described in the text.

$$H = H_d + H_L + H_h$$  \hspace{1cm} (A-1)

$$H_d = \sum_m \epsilon_m d_m^\dagger d_m + \sum_{m_1,m_2,m_3,m_4} U_{m_1,m_2,m_3,m_4} d_{m_1}^\dagger d_{m_2}^\dagger d_{m_3} d_{m_4}$$ \hspace{1cm} (A-2)

$$H_L = \sum_m \epsilon_{L_m} c_m^\dagger c_m$$ \hspace{1cm} (A-3)

$$H_h = \sum_m V_m c_m^\dagger d_m + \text{h.c.} \hspace{1cm} (A-4)$$

where $c_m^\dagger$ and $d_m^\dagger$ are creation operators of an electron in a ligand molecular orbital and an atomic Cu 3d orbital, respectively, with spin and orbital symmetry $m$. The ligand molecular orbitals are constructed from the atomic O 2p orbitals. The transfer integrals $V_m$ are described in terms of the Slater-Koster parameters (pd$\sigma$) and (pd$\pi$) [3.9,10].

1. square-planer CuO$_4^{5-}$ cluster

Since the square-planer CuO$_4$ cluster has the point group symmetry $D_{4h}$, its eigen states are labeled by irreducible representations $a_{1g}$, $a_{2g}$, $b_{1g}$, $b_{2g}$, $e_g$, $a_{1u}$, $a_{2u}$, $b_{1u}$, $b_{2u}$, $e_u$. [A.3] The 3d orbitals are reduced into the orbitals with $e_g$ (yz, zx), $b_{2g}$ (xy), $a_{1g}$ ($3z^2-r^2$) and $b_{1g}$ ($x^2-y^2$) symmetries. These 3d orbitals can hybridize with the ligand molecular orbitals labeled by the same irreducible
representations. The ligand molecular orbitals with eg, b2g, a1g and b1g symmetries are constructed from the O 2p orbitals as listed below. For example, |P_x(1)> represents the O 2p_x orbital of the site 1. (see Fig. A.1)

e_g symmetry

|L_yz> = 1/2{-|p_z(3)> + |p_z(4)>}

|L_zx> = 1/2{|p_z(1)> + |p_z(2)>}

b_2g symmetry

|L_xy> = 1/2{-|p_y(1)> + |p_y(2)> - |p_x(3)> + |p_x(4)>}

a_1g symmetry

|L_{3z^2-r^2}> = 1/2{|p_x(1)> - |p_x(2)> + |p_y(3)> - |p_y(4)>}

b_1g symmetry

|L_{x^2-y^2}> = 1/2{|p_x(1)> - |p_x(2)> - |p_y(3)> + |p_y(4)>}

![CuO_4 square planer cluster](image)

**CuO_4 square planer cluster**

Fig. A.1. Square-planer CuO_4 cluster. The numbers 1-4 represent the ligand sites.
The transfer and overlap integrals for $e_g$, $b_{2g}$, $a_{1g}$ and $b_{1g}$ symmetries are listed below. The transfer integral $V_{b1}$ is noted as $T$ in the text.

**transfer integrals**

\[ V_e = \langle L_{yz}|H_h|d_{yz} \rangle = \langle L_{zx}|H_h|d_{zx} \rangle = r^2(p^d_\pi) \]
\[ V_{b2} = \langle L_{xy}|H_h|d_{xy} \rangle = 2(p^d_\pi) \]
\[ V_{a1} = \langle L_{3z^2-r^2}|H_h|d_{3z^2-r^2} \rangle = -(p^d_\sigma) \]
\[ V_{b1} = \langle L_{x^2-y^2}|H_h|d_{x^2-y^2} \rangle = -\sqrt{3}(p^d_\sigma) \]

**overlap integrals**

\[ S_e = \langle L_{yz}|d_{yz} \rangle = \langle L_{zx}|d_{zx} \rangle = r^2S_x \]
\[ S_{b2} = \langle L_{xy}|d_{xy} \rangle = 2S_x \]
\[ S_{a1} = \langle L_{3z^2-r^2}|d_{3z^2-r^2} \rangle = -S_\sigma \]
\[ S_{b1} = \langle L_{x^2-y^2}|d_{x^2-y^2} \rangle = -\sqrt{3}S_\sigma \]

2. octahedral CuO$_6^{9-}$ cluster

Since the octahedral CuO$_6$ cluster has the point group symmetry $O_h$, its eigen states are labeled by irreducible representations $a_{1g}$, $a_{2g}$, $e_g$, $t_{1g}$, $t_{2g}$, $a_{1u}$, $a_{2u}$, $e_u$, $t_{1u}$, $t_{2u}$. [A.3] The 3d orbitals are reduced into the orbitals with $t_{2g}$ ($yz$, $zx$, $xy$) and $e_g$ ($3z^2-r^2$, $x^2-y^2$) symmetries. The ligand molecular orbitals with $t_{2g}$ and $e_g$ symmetries are constructed from the O 2p orbitals as follows. [A.1] The transfer and overlap integrals for $t_{2g}$ and $e_g$ symmetries are also listed.
\text{t}_{2g} \text{ symmetry}

\begin{align*}
|L_{yz}> &= \frac{1}{2}\{-|p_y(5)> + |p_y(6)> - |p_z(3)> + |p_z(4)>\} \\
|L_{zx}> &= \frac{1}{2}\{-|p_z(1)> + |p_z(2)> - |p_x(5)> + |p_x(6)>\} \\
|L_{xy}> &= \frac{1}{2}\{-|p_y(1)> + |p_y(2)> - |p_x(3)> + |p_x(4)>\}
\end{align*}

\text{e}_g \text{ symmetry}

\begin{align*}
|L_{3z^2-r^2}> &= \frac{1}{\sqrt{2}}\{-|p_x(1)> + |p_x(2)> - |p_y(3)> + |p_y(4)> + 2|p_z(5)> - 2|p_z(6)>\} \\
|L_{x^2-y^2}> &= \frac{1}{2}\{|p_x(1)> - |p_x(2)> - |p_y(3)> + |p_y(4)>\}
\end{align*}

\text{CuO}_6 \text{ octahedral cluster}

Fig. A.2. Octahedral CuO$_6$ cluster. The numbers 1-6 represent the ligand sites.
transfer integrals

\( V_{t2} = <L_{yz}|H_{h}|d_{yz}> = <L_{zx}|H_{h}|d_{zx}> = <L_{xy}|H_{h}|d_{xy}> = 2(p\delta) \)

\( V_{e} = <L_{x2-y2}|H_{h}|d_{x2-y2}> = <L_{3z^2-r2}|H_{h}|d_{3z^2-r2}> = -\sqrt{3}(p\sigma) \)

overlap integrals

\( S_{t2} = <L_{yz}|d_{yz}> = <L_{zx}|d_{zx}> = <L_{xy}|d_{xy}> = 2S_{x} \)

\( S_{e} = <L_{x2-y2}|d_{x2-y2}> = <L_{3z^2-r2}|d_{3z^2-r2}> = -\sqrt{3}S_{\sigma} \)

3. ligand field due to non-orthogonality

If we use the atomic orbitals to construct the molecular orbitals without orthogonalizing procedures, the overlap integrals of the orbitals on the adjacent sites cannot be neglected. When we consider the overlap integrals between the transition-metal 3d orbitals and the ligand 2p orbitals, the ligand field due to non-orthogonality [A.1,2,4.8] is evaluated in terms of the overlap integrals and the transfer integrals as listed below, using the relation \(<0|c_{m}d_{m}H_{h}d_{m}^{\dagger}c_{m}^{\dagger}|0> = -2V_{m}S_{m} \). It should be noted that the signs of the transfer and overlap integrals depend on the definitions [Here, \((p\delta)<0, (p\pi)>0, S_{\sigma}>0, S_{\pi}<0]. [A.2]

Square-planer CuO4 cluster

\(<d_{x2-y2}|L_{x2-y2}|H_{h}|d_{x2-y2}> = <d_{3z^2-r2}|L_{3z^2-r2}|H_{h}|d_{3z^2-r2}> = -2(S_{b1}V_{b1}-S_{a1}V_{a1}) > 0 \)
\[ <d_{xy}L_{xy}|H_{h}|d_{xy}L_{xy}> - <d_{yz}L_{yz}|H_{h}|d_{yz}L_{yz}> = -2(S_{b2}V_{b2} - S_{e}V_{e}) > 0 \]

\[
\frac{1}{2}(d_{x^2-y^2}L_{x^2-y^2}|H_{h}|d_{x^2-y^2}L_{x^2-y^2}) + \frac{1}{3}(d_{yz}L_{yz}|H_{h}|d_{yz}L_{yz}) + \frac{1}{3}(d_{zx}L_{zx}|H_{h}|d_{zx}L_{zx}) + \frac{1}{3}(d_{xy}L_{xy}|H_{h}|d_{xy}L_{xy}) - 2\{\frac{1}{2}(S_{b1}V_{b1} + S_{a1}V_{a1}) - \frac{1}{3}(S_{b2}V_{b2} + 2S_{e}V_{e})\} > 0
\]

Octahedral CuO$_6$ cluster

\[ <d_{x^2-y^2}L_{x^2-y^2}|H_{h}|d_{x^2-y^2}L_{x^2-y^2}> - <d_{yz}L_{yz}|H_{h}|d_{yz}L_{yz}> = -2(S_{e}V_{e} - S_{t2}V_{t2}) > 0 \]

References


Appendix B. Basis functions and Hamiltonians for square-planer $(\text{Cu}^{3+}\text{O}_4)^{5-}$ cluster

Basis functions and Hamiltonians for the ground state ($^1A_{1g}$) and the final states ($^2A_{1g}, ^2B_{1g}, ^2B_{2g}, ^2E_g$). The basis functions for the ground state consist of 12 terms of the $d^8$, $d^9L$ and $d^{10}L^2$ configurations. The basis for the final states are the $d^7$, $d^8L$ and $d^9L^2$ configurations. $^2A_{1g}, ^2B_{1g}$ and $^2B_{2g}$ contain 37 basis, respectively. The basis $\phi_1 - \phi_5$ are the $d^7$ configuration and the basis $\phi_6 - \phi_{20}$ and $\phi_{36}$ are the $d^8L$ configuration. The basis functions $\phi_6 - \phi_{20}$ hybridize with those of the $d^7$ configuration and the basis functions $\phi_{36}$ dose not. $^2E_g$ has 72 basis. The matrix elements are described in terms of the charge-transfer energy $\Delta$, d-d Coulomb energy $U$, the Racah B, C parameters and the transfer integrals ($V_e, V_{b2}, V_{a1}, V_{b1}$). The definitions of the parameters are listed at the end of the table.

<table>
<thead>
<tr>
<th>ground state</th>
<th>$^1A_{1g}$ symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi_1=l_{a1}^{2\rangle}$, $\phi_2=l_{b1}^{2\rangle}$, $\phi_3=l_{b2}^{2\rangle}$, $\phi_4=l_{e}^{2\rangle}$, $\phi_5=l_{a1L_{a1}}$, $\phi_6=l_{b1L_{b1}}$, $\phi_7=l_{b2L_{b2}}$, $\phi_8=l_{eLe}$, $\phi_9=l_{L_{a1}^{2\rangle}}$, $\phi_{10}=l_{L_{b1}^{2\rangle}}$, $\phi_{11}=l_{L_{b2}^{2\rangle}}$, $\phi_{12}=l_{Le}^{2\rangle}$</td>
<td></td>
</tr>
<tr>
<td>$h_{1,1}=h_{2,2}=h_{3,3}=E(d^8)-5E(d^8)-38B+24C$, $h_{4,4}=E(d^8)-5E(d^8)-35B+25C$, $h_{5,5}=h_{6,6}=h_{7,7}=h_{8,8}=E(d^8)+\Delta-5E(d^8)$, $h_{9,9}=h_{10,10}=h_{11,11}=h_{12,12}=E(d^8)+2\Delta+U-5E(d^{10})$</td>
<td></td>
</tr>
<tr>
<td>$h_{1,2}=h_{1,3}=4B+C$, $h_{1,4}=\sqrt{2}(B+C)$, $h_{2,3}=C$, $h_{2,4}=h_{3,4}=\sqrt{2}(3B+C)$, $h_{1,5}=\sqrt{2}V_{a1}$, $h_{2,6}=\sqrt{2}V_{b1}$, $h_{3,7}=\sqrt{2}V_{b2}$, $h_{4,8}=\sqrt{2}V_{e}$, $h_{5,9}=\sqrt{2}V_{a1}$, $h_{6,10}=\sqrt{2}V_{b1}$, $h_{7,11}=\sqrt{2}V_{b2}$, $h_{8,12}=\sqrt{2}V_{e}$</td>
<td></td>
</tr>
</tbody>
</table>
**final states**

\(^{2}A_1\) symmetry

<table>
<thead>
<tr>
<th>(\phi_1)</th>
<th>(\phi_2)</th>
<th>(\phi_3)</th>
<th>(\phi_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(l_{a1}b_{1}^{2})</td>
<td>(l_{a1}b_{2}^{2})</td>
<td>(l_{a1}e^{2}(1A_{1}))</td>
<td>(l_{b1}e^{2}(1B_{1}))</td>
</tr>
<tr>
<td>(l_{b2}^{2}(1B_{2}))</td>
<td>(l_{b1}^{2}L_{a1})</td>
<td>(l_{a1}b_{1}(1B_{1})L_{b1})</td>
<td>(l_{a1}b_{1}(3B_{1})L_{b1})</td>
</tr>
<tr>
<td>(l_{b2}^{2}L_{a1})</td>
<td>(l_{a1}b_{2}(1B_{2})L_{b2})</td>
<td>(l_{a1}b_{2}(3B_{2})L_{b2})</td>
<td>(l_{a1}b_{2}(1B_{1}))</td>
</tr>
<tr>
<td>(l_{e}^{2}(1A_{1})L_{a1})</td>
<td>(l_{a1}e(1E)L_{e})</td>
<td>(l_{a1}e(3E)L_{e})</td>
<td>(l_{a1}e(3E)L_{e})</td>
</tr>
<tr>
<td>(l_{b1}e(1E)L_{e})</td>
<td>(l_{b1}e(3E)L_{e})</td>
<td>(l_{b2}e(1E)L_{e})</td>
<td>(l_{b2}e(1E)L_{e})</td>
</tr>
</tbody>
</table>

\[ h_{1,1} = h_{2,2} = E(d^{7}) - 3E(d^{7}) - 36B + 18C, \]
\[ h_{3,3} = E(d^{7}) - 3E(d^{7}) - 16B + 18C, \]
\[ h_{4,4} = E(d^{7}) - 3E(d^{7}) - 34B + 17C, \]
\[ h_{6,6} = E(d^{7}) + 3E(d^{8}) + 38B + 24C, \]
\[ h_{7,7} = E(d^{7}) + 3E(d^{8}) + 38B + 24C, \]
\[ h_{8,8} = E(d^{7}) + 3E(d^{8}) + 42B + 23C, \]
\[ h_{11,11} = E(d^{7}) + 3E(d^{8}) + 42B + 23C, \]
\[ h_{12,12} = E(d^{7}) + 3E(d^{8}) + 50B + 21C, \]
\[ h_{13,13} = E(d^{7}) + 3E(d^{8}) + 35B + 25C, \]
\[ h_{14,14} = E(d^{7}) + 3E(d^{8}) - 1B + 21C, \]
\[ h_{16,16} = h_{19,19} = E(d^{7}) + 3E(d^{8}) - 41B + 23C, \]
\[ h_{17,17} = E(d^{7}) + 3E(d^{8}) - 47B + 21C, \]
\[ h_{21,21} = E(d^{7}) + 3E(d^{8}) - 41B + 23C, \]
\[ h_{1,2} = C, \]
\[ h_{1,3} = h_{2,3} = \sqrt{2}(3B + C), \]
\[ h_{1,4} = h_{2,5} = \sqrt{6}B, \]
\[ h_{3,4} = h_{3,5} = 5\sqrt{3}B, \]
\[ h_{4,5} = -3B, \]
\[ h_{5,6} = h_{6,8} = h_{6,9} = 4B + C, \]
\[ h_{12,36} = \sqrt{2}(3B + C) \]

\[ h_{7,21} = h_{7,22} = h_{10,24} = -h_{11,25} = h_{13,27} = -h_{14,28} = -1/2V_{a1}, \]
\[ h_{8,21} = h_{8,22} = h_{11,24} = -h_{10,25} = -h_{14,27} = -h_{13,28} = -\sqrt{3}/2V_{a1}, \]
\[ h_{6,21} = h_{7,23} = \sqrt{2}/2V_{b1}, \]
\[ h_{16,30} = h_{17,31} = -1/2V_{b1}, \]
\[ h_{9,24} = h_{10,26} = -\sqrt{2}/2V_{b2}, \]
\[ h_{19,33} = -h_{20,34} = -1/2V_{b2}, \]
\[ h_{12,27} = h_{13,29} = h_{15,30} = h_{16,32} = h_{18,33} = h_{19,35} = -\sqrt{2}/2V_{e}, \]
\[ h_{12,28} = h_{14,29} = h_{15,31} = h_{17,32} = h_{18,34} = h_{20,35} = -\sqrt{6}/2V_{e}, \]
\[ h_{36,37} = V_{a1} \]
2B\(_1\) symmetry

\[\begin{align*}
\phi_1 &= \phi_4 = l_{1A}^2 \phi_1 >, \\
\phi_2 &= l_{1A}^2 \phi_2 >, \\
\phi_3 &= l_{1E}^2 \phi_3 >, \\
\phi_4 &= l_{1E}^2 \phi_4 >, \\
\phi_5 &= l_{2B}^2 (3A_2) >, \\
\phi_6 &= l_{1A}^2 l_{B_1} >, \\
\phi_7 &= l_{1B}^2 (3E) >, \\
\phi_8 &= l_{1B}^2 (3B_2) >, \\
\phi_9 &= l_{2B}^2 \phi_9 >, \\
\phi_{10} &= l_{2B}^2 \phi_{10} >, \\
\phi_{11} &= l_{2B}^2 (3A_2) >, \\
\phi_{12} &= l_{2A}^2 \phi_{12} >, \\
\phi_{13} &= l_{2A}^2 \phi_{13} >, \\
\phi_{14} &= l_{2A}^2 \phi_{14} >, \\
\phi_{15} &= l_{2B}^2 (3B_1) >, \\
\phi_{16} &= l_{2B}^2 (3B_1) >, \\
\phi_{17} &= l_{2B}^2 (3B_1) >, \\
\phi_{18} &= l_{2B}^2 (3B_1) >, \\
\phi_{19} &= l_{2B}^2 (3B_1) >, \\
\phi_{20} &= l_{2B}^2 (3B_1) >, \\
\phi_{21} &= l_{2B}^2 (3B_1) >, \\
\phi_{22} &= l_{2B}^2 (3B_1) >, \\
\phi_{23} &= l_{2B}^2 (3B_1) >, \\
\phi_{24} &= l_{2B}^2 (3B_1) >, \\
\phi_{25} &= l_{2B}^2 (3B_1) >, \\
\phi_{26} &= l_{2B}^2 (3B_1) >, \\
\phi_{27} &= l_{2B}^2 (3B_1) >, \\
\phi_{28} &= l_{2B}^2 (3B_1) >, \\
\phi_{29} &= l_{2B}^2 (3B_1) >, \\
\phi_{30} &= l_{2B}^2 (3B_1) >, \\
\phi_{31} &= l_{2B}^2 (3B_1) >, \\
\phi_{32} &= l_{2B}^2 (3B_1) >, \\
\phi_{33} &= l_{2B}^2 (3B_1) >, \\
\phi_{34} &= l_{2B}^2 (3B_1) >, \\
\phi_{35} &= l_{2B}^2 (3B_1) >, \\
\phi_{36} &= l_{2B}^2 (3B_1) >, \\
\phi_{37} &= l_{2B}^2 (3B_1) >, \\
\phi_{38} &= l_{2B}^2 (3B_1) >.
\end{align*}\]

h\(_{1,1}\) = E(d\(_7\)) - E(d\(_7\)) - 36B + 18C,

h\(_{2,2}\) = E(d\(_7\)) - E(d\(_7\)) - 36B + 18C,

h\(_{3,3}\) = E(d\(_7\)) - E(d\(_7\)) - 28B + 19C,

h\(_{4,4}\) = E(d\(_7\)) - E(d\(_7\)) - 24B + 17C,

h\(_{5,5}\) = E(d\(_7\)) - E(d\(_7\)) - 34B + 17C,

h\(_{6,6}\) = E(d\(_7\)) - E(d\(_7\)) - 38B + 24C,

h\(_{7,7}\) = E(d\(_7\)) - E(d\(_7\)) - 38B + 24C,

h\(_{8,8}\) = E(d\(_7\)) - E(d\(_7\)) - 4B + 23C,

h\(_{9,9}\) = E(d\(_7\)) - E(d\(_7\)) - 3B + 23C,

h\(_{10,10}\) = E(d\(_7\)) - E(d\(_7\)) - 3B + 23C,

h\(_{11,11}\) = E(d\(_7\)) - E(d\(_7\)) - 3B + 23C,

h\(_{12,12}\) = E(d\(_7\)) - E(d\(_7\)) - 3B + 23C,

h\(_{13,13}\) = E(d\(_7\)) - E(d\(_7\)) - 3B + 23C,

h\(_{14,14}\) = E(d\(_7\)) - E(d\(_7\)) - 3B + 23C,

h\(_{15,15}\) = E(d\(_7\)) - E(d\(_7\)) - 3B + 23C,

h\(_{16,16}\) = E(d\(_7\)) - E(d\(_7\)) - 3B + 23C,

h\(_{17,17}\) = E(d\(_7\)) - E(d\(_7\)) - 3B + 23C,

h\(_{18,18}\) = E(d\(_7\)) - E(d\(_7\)) - 3B + 23C,

h\(_{19,19}\) = E(d\(_7\)) - E(d\(_7\)) - 3B + 23C,

h\(_{20,20}\) = E(d\(_7\)) - E(d\(_7\)) - 3B + 23C,

h\(_{21,21}\) = ... = h\(_{35,35}\) = h\(_{37,37}\) = E(d\(_7\)) + 2\(\Delta\) - E(d\(_9\)),
$2B_2$ symmetry

\begin{align*}
\phi_1 &= \text{lal}^2 b_2^2, \quad \phi_2 = \text{lb}^2 b_2^2, \quad \phi_3 = \text{lal}e^2(B^2)\text{l}, \quad \phi_4 = \text{lb}e^2(3A_2)\text{l}, \\
\phi_5 &= \text{lb}^2 e^2(A_1)\text{l}, \quad \phi_6 = \text{la}^2 L b_2, \quad \phi_7 = \text{la} b_2(B_2)\text{l}_a, \quad \phi_8 = \text{la} b_2(3B_2)\text{l}_a, \\
\phi_9 &= \text{lb} b_2 L b_2, \quad \phi_{10} = \text{lb}^2 b_2(A_2)\text{l}_b, \quad \phi_{11} = \text{la} b_2(3A_2)\text{l}_b, \\
\phi_{12} &= \text{le}^2(B_2)\text{l}_a, \quad \phi_{13} = \text{la} e^2(1E)\text{le}, \quad \phi_{14} = \text{la} e^2(3E)\text{le}, \quad \phi_{15} = \text{le}^2(3A_2)\text{l}_b, \\
\phi_{16} &= \text{lb} e^2(1E)\text{le}, \quad \phi_{17} = \text{lb} e^2(3E)\text{le}, \quad \phi_{18} = \text{le}^2(A_1)\text{l}_b, \quad \phi_{19} = \text{lb} e^2(1E)\text{le}, \\
\phi_{20} &= \text{lb} e^2(1E)\text{le}, \quad \phi_{21} = \text{la} a_1 L b_2(1B_2), \quad \phi_{22} = \text{la} a_1 L b_2(3B_2), \\
\phi_{23} &= \text{lb}^2 a_1^2, \quad \phi_{24} = \text{lb}^2 b_2 L b_2(1A_2), \quad \phi_{25} = \text{lb}^2 b_2 L b_2(3A_2), \\
\phi_{26} &= \text{lb} b_2 L b_2^2, \quad \phi_{27} = \text{le} a_1 L e(1E), \quad \phi_{28} = \text{le} a_1 L e(3E), \quad \phi_{29} = \text{la} a_2(1B_2), \\
\phi_{30} &= \text{le} b_2 L e(1E), \quad \phi_{31} = \text{le} b_2 L e(3E), \quad \phi_{32} = \text{le} b_2(3A_2), \\
\phi_{33} &= \text{le} b_2 L e(1E), \quad \phi_{34} = \text{le} b_2 L e(3E), \quad \phi_{35} = \text{le} b_2 L e(1A_1), \quad \phi_{36} = \text{lb}^2 L b_2, \\
\phi_{37} &= \text{lb}^2 L b_2^2, \\
\h_{1,1} &= E(d^7) - 5E(d^7) - 36B + 18C, \quad h_{2,2} = E(d^7) - 5E(d^7) - 16B + 19C, \\
\h_{3,3} &= E(d^7) - 5E(d^7) - 24B + 17C, \quad h_{4,4} = E(d^7) - 5E(d^7) - 34B + 17C, \\
\h_{5,5} &= E(d^7) - 5E(d^7) - 28B + 19C, \quad h_{6,6} = h_{9,9} = h_{15,15} = h_{36,36} = E(d^7) + \Delta-U-5E(d^9) - 38B + 24C, \quad h_{7,7} = h_{10,10} = E(d^7) + \Delta-U-5E(d^9) - 42B + 23C, \\
\h_{8,8} &= h_{11,11} = E(d^7) + \Delta-U-5E(d^9) - 50B + 21C, \quad h_{12,12} = E(d^7) + \Delta-U-5E(d^9) - 35B + 25C, \quad h_{13,13} = E(d^7) + \Delta-U-5E(d^9) - 39B + 23C, \\
\h_{14,14} &= E(d^7) + \Delta-U-5E(d^9) - 41B + 21C, \quad h_{15,15} = h_{18,18} = h_{19,19} = E(d^7) + \Delta-U-5E(d^9) - 41B + 21C, \quad h_{17,17} = E(d^7) + \Delta-U-5E(d^9) - 47B + 21C, \\
\h_{20,20} &= E(d^7) + \Delta-U-5E(d^9) - 47B + 21C, \quad h_{21,21} = \ldots = h_{35,35} = h_{37,37} = E(d^7) + 2\Delta-U-5E(d^9), \\
\h_{1,2} &= 4B+C, \quad h_{1,3} = -3\sqrt{6}B, \quad h_{1,5} = \sqrt{2}(B+C), \quad h_{2,4} = -3\sqrt{6}B, \\
\h_{2,5} &= h_{12,36} = \sqrt{2}(3B+C), \quad h_{3,4} = \sqrt{3}B, \quad h_{3,5} = -5\sqrt{3}B, \quad h_{4,5} = -3\sqrt{3}B, \\
\h_{6,36} &= 4B+4C, \quad h_{9,36} = C, \\
\h_{1,6} &= h_{2,9} = h_{5,18} = V_{b_2}, \\
\h_{1,7} &= -\sqrt{2}/2 V_{a_1}, \quad h_{1,8} = \sqrt{6}/2 V_{a_1}, \quad h_{3,12} = V_{a_1}, \\
\h_{2,10} &= -\sqrt{2}/2 V_{b_1}, \quad h_{2,11} = \sqrt{6}/2 V_{b_1}, \quad h_{4,15} = V_{b_1}, \\
\h_{3,13} &= h_{4,17} = h_{5,19} = -\sqrt{2}/2 V_{e}, \quad h_{3,14} = -h_{4,16} = h_{5,20} = -\sqrt{6}/2 V_{e}, \\
\h_{6,9} &= 4B+C, \quad h_{6,12} = \sqrt{2}(B+C), \quad h_{9,12} = \sqrt{2}(3B+C), \quad h_{7,15} = -2\sqrt{3}B, \quad h_{11,18} = 6B, \\
\h_{13,16} &= h_{16,19} = -\sqrt{3}B, \quad h_{13,19} = -3B, \quad h_{14,17} = h_{14,20} = -\sqrt{3}B, \quad h_{17,20} = 3B, \\
\h_{7,21} &= h_{7,22} = h_{10,24} = -h_{11,25} = h_{19,33} = -h_{20,34} = -1/2 V_{b_2}, \\
\h_{8,21} &= h_{8,22} = h_{11,24} = h_{10,25} = -h_{20,33} = -h_{19,34} = -\sqrt{3}/2 V_{b_2}, \\
\h_{6,21} &= h_{7,23} = -\sqrt{2}/2 V_{a_1}, \quad h_{6,22} = h_{8,23} = -\sqrt{6}/2 V_{a_1}, \\
\h_{11,32} &= h_{14,28} = -1/2 V_{a_1}, \quad h_{14,27} = -h_{13,28} = -\sqrt{3}/2 V_{a_1}, \\
\h_{9,24} &= h_{10,26} = -\sqrt{2}/2 V_{b_1}, \quad h_{9,25} = h_{11,26} = \sqrt{6}/2 V_{b_1}, \\
-h_{16,30} &= h_{17,31} = -1/2 V_{b_1}, \quad h_{17,30} = h_{16,31} = -\sqrt{3}/2 V_{b_1}, \\
\h_{12,27} &= h_{13,29} = h_{15,31} = h_{17,32} = h_{18,33} = h_{19,35} = -\sqrt{2}/2 V_{e}, \\
\h_{12,28} &= h_{14,29} = -h_{15,30} = h_{16,32} = h_{18,34} = h_{20,35} = -\sqrt{6}/2 V_{e}, \\
\h_{36,37} &= V_{b_2}
\end{align*}
\[ \begin{align*}
2E \text{ symmetry} \\
\phi_1 &= l a_1^2 e >, \ \phi_2 = l a_1 b_1 (1B_1) e >, \ \phi_3 = l a_1 b_2 (3B_1) e >, \ \phi_4 = l a_1 b_2 (1B_2) e >, \\
\phi_5 &= l a_1 b_2 (3B_2) e >, \ \phi_6 = l b_1^2 e >, \ \phi_7 = l b_1 b_2 (1A_2) e >, \ \phi_8 = l b_1 b_2 (3A_2) e >, \\
\phi_9 &= l b_2^2 e >, \ \phi_{10} = l e^{3E}, \ \phi_{11} = l a_1^2 L e >, \ \phi_{12} = l a_1 e (1E) L a_1 >, \ \phi_{13} = l a_1 e (1E) L a_1 >, \\
\phi_{14} &= l a_1 b_1 (1B_1) L e >, \ \phi_{15} = l a_1 e (1E) L b_1 >, \ \phi_{16} = l a_1 e (3E) L b_1 >, \\
\phi_{17} &= l b_1 e (1E) L a_1 >, \ \phi_{18} = l b_1 e (1E) L a_1 >, \ \phi_{19} = l a_1 b_1 (3B_1) L e >, \\
\phi_{20} &= l a_1 b_2 (1B_2) L e >, \ \phi_{21} = l a_1 e (1E) L b_2 >, \ \phi_{22} = l a_1 e (3E) L b_2 >, \\
\phi_{23} &= l b_2 e (1E) L a_1 >, \ \phi_{24} = l b_2 e (3E) L a_1 >, \ \phi_{25} = l a_1 b_2 (3B_2) L e >, \ \phi_{26} = l b_1^2 L e >, \\
\phi_{27} &= l b_1 e (1E) L b_1 >, \ \phi_{28} = l b_1 e (3E) L b_1 >, \ \phi_{29} = l b_1 b_2 (1A_2) L e >, \\
\phi_{30} &= l b_1 e (1E) L b_2 >, \ \phi_{31} = l b_2 e (3E) L b_1 >, \ \phi_{32} = l b_2 e (1E) L b_1 >, \\
\phi_{33} &= l b_2 e (3E) L b_1 >, \ \phi_{34} = l b_1 b_2 (3A_2) L e >, \ \phi_{35} = l b_2^2 L e >, \ \phi_{36} = l b_2 e (1E) L b_2 >, \\
\phi_{37} &= l b_2 e (3E) L b_2 >, \ \phi_{38} = l e^2 (1A_1) L e >, \ \phi_{39} = l e^2 (1B_1) L e >, \ \phi_{40} = l e^2 (1B_2) L e >, \\
\phi_{41} &= l e^2 (3A_2) L e >, \ \phi_{42} = l a_1 L a_1 L e (1E) >, \ \phi_{43} = l a_1 L a_1 L e (3E) >, \ \phi_{44} = l e L a_1^2 >, \\
\phi_{45} &= l a_1 b_1 L e (1E) >, \ \phi_{46} = l a_1 b_1 L e (3E) >, \ \phi_{47} = l b_1 L a_1 L e (1E) >, \\
\phi_{48} &= l b_1 L a_1 L e (3E) >, \ \phi_{49} = l e L a_1 b_1 (1B_1) >, \ \phi_{50} = l e L a_1 b_1 (3B_1) >, \\
\phi_{51} &= l a_1 b_2 L e (1E) >, \ \phi_{52} = l a_1 b_2 L e (3E) >, \ \phi_{53} = l b_2 L a_1 L e (1E) >, \\
\phi_{54} &= l b_2 L a_1 L e (3E) >, \ \phi_{55} = l e L a_1 b_2 (1B_2) >, \ \phi_{56} = l e L a_1 b_2 (3B_2) >, \\
\phi_{57} &= l b_1 L a_1 L e (1E) >, \ \phi_{58} = l b_1 b_1 L e (3E) >, \ \phi_{59} = l e L b_1^2 >, \\
\phi_{60} &= l b_1 L b_2 L e (1E) >, \ \phi_{61} = l b_1 L b_2 L e (3E) >, \ \phi_{62} = l b_2 b_1 L e (1E) >, \\
\phi_{63} &= l b_2 b_1 L e (3E) >, \ \phi_{64} = l e L b_1 b_2 (1A_2) >, \ \phi_{65} = l e L b_1 b_2 (3A_2) >, \\
\phi_{66} &= l b_2 b_2 L e (1E) >, \ \phi_{67} = l b_2 b_2 L e (3E) >, \ \phi_{68} = l e L b_2^2 >, \ \phi_{69} = l e L e^2 (1A_1) >, \\
\phi_{70} &= l e L e^2 (1B_1) >, \ \phi_{71} = l e L e^2 (1B_2) >, \ \phi_{72} = l e L e^2 (3A_2) >, \\
\end{align*} \]
h_{1,2}=\frac{5}{2}\sqrt{6}B, \ h_{3,4}=h_{5,10}=h_{6,7}=-\frac{3}{2}\sqrt{2}B, \ h_{1,5}=h_{7,10}=-\frac{9}{2}\sqrt{2}B,
\ h_{1,6}=h_{4,10}=-\sqrt{6}/2B, \ h_{1,9}=4B+C, \ h_{1,10}=B+C, \ h_{2,3}=\sqrt{3}B,
\ h_{2,4}=h_{3,5}=h_{5,7}=3/2B, \ h_{2,5}=h_{3,8}=h_{5,8}=-3/2\sqrt{3}B, \ h_{2,7}=\sqrt{3}/2B,
\ h_{2,8}=-9/2B, \ h_{2,10}=\sqrt{6}/2B, \ h_{3,4}=h_{4,5}=h_{7,8}=3/2\sqrt{3}B, \ h_{3,6}=3/2\sqrt{2}B,
\ h_{3,7}=h_{4,8}=-3/2B, \ h_{4,7}=\frac{5}{2}\sqrt{3}B, \ h_{4,9}=-\sqrt{6}B, h_{5,9}=h_{7,9}=-3\sqrt{2}B,
\ h_{6,8}=h_{8,10}=-3/2\sqrt{6}B, \ h_{6,9}=C, \ h_{6,10}=h_{9,10}=3B+C
\ h_{1,11}=h_{2,14}=h_{3,19}=h_{4,20}=h_{5,25}=h_{6,26}=h_{7,29}=h_{8,33}=h_{9,35}=V_e,
\ h_{1,12}=-\sqrt{2}/2V_a, \ h_{2,17}=-h_{3,18}=h_{4,33}=-1/2V_a, \ h_{1,13}=\sqrt{6}/2V_a, h_{2,18}=h_{3,17}=h_{4,24}=-\sqrt{6}/2V_a,
\ h_{2,15}=h_{3,16}=h_{7,32}=-h_{8,33}=-1/2V_b, h_{6,27}=-\sqrt{2}/2V_b, \ h_{2,16}=h_{3,15}=-h_{7,33}=h_{8,32}=-\sqrt{3}/2V_b, h_{6,28}=\sqrt{6}/2V_b,
\ h_{4,21}=h_{5,22}=h_{7,30}=h_{8,31}=-1/2V_b, \ h_{9,36}=-\sqrt{2}/2V_b, \ h_{4,22}=h_{5,21}=h_{7,31}=h_{8,30}=\sqrt{3}/2V_b, h_{9,37}=\sqrt{6}/2V_b,
\ h_{11,12}=h_{11,35}=4B+C, \ h_{11,38}=\sqrt{3}(B+C), h_{26,35}=C, \ h_{26,38}=\sqrt{3}(3B+C), h_{14,39}=-2\sqrt{3}B, \ h_{20,40}=2\sqrt{3}B, h_{34,41}=6B,
\ h_{12,17}=h_{12,23}=h_{15,27}=h_{21,30}=h_{21,32}=-3\sqrt{3}B, \ h_{17,23}=h_{27,32}=h_{30,36}=-3B,
\ h_{13,18}=h_{13,24}=h_{16,32}=h_{16,33}=h_{22,31}=h_{22,37}=-3\sqrt{3}B,
\ h_{18,24}=h_{28,37}=h_{31,37}=3B,
\ h_{12,42}=h_{13,43}=h_{15,45}=h_{16,46}=-h_{17,47}=h_{18,48}=-h_{21,51}=h_{22,52}=-h_{23,53}=-h_{24,54}=-h_{27,57}=-h_{28,58}=-h_{30,64}=-h_{31,61}=h_{32,62}=-h_{33,63}=-h_{36,66}=-h_{37,67}=-h_{38,69}=-h_{39,69}=-h_{40,69}=-h_{40,70}=-h_{40,71}=-h_{40,71}=h_{41,72}=1/2V_e,
\ h_{13,42}=-h_{12,43}=-h_{15,46}=-h_{16,47}=-h_{17,48}=-h_{18,48}=-h_{22,52}=-h_{21,51}=-h_{24,54}=-h_{23,55}=-h_{27,58}=-h_{28,58}=-h_{31,60}=-h_{30,61}=h_{33,62}=-h_{32,63}=-h_{36,67}=-h_{37,66}=-h_{41,69}=-h_{41,71}=-h_{38,72}=-h_{39,72}=-h_{40,72}=\sqrt{3}/2V_e,
\ h_{11,42}=h_{12,44}=-\sqrt{2}/2V_a, h_{11,43}=-h_{13,44}=\sqrt{6}/2V_a,
\ h_{14,47}=h_{15,49}=h_{19,48}=h_{16,50}=-h_{20,53}=-h_{21,55}=-h_{25,54}=-h_{22,56}=-h_{21,56}=-\sqrt{3}/2V_a,
\ h_{26,57}=-h_{27,58}=-\sqrt{2}/2V_b, h_{26,58}=-h_{25,54}=\sqrt{6}/2V_b,
\ h_{14,45}=-h_{17,49}=-h_{19,46}=-h_{18,50}=-h_{29,62}=-h_{30,64}=h_{34,63}=h_{31,65}=1/2V_b, h_{14,46}=-h_{14,46}=-h_{17,45}=-h_{19,45}=-h_{17,50}=-h_{29,63}=h_{31,64}=-h_{34,62}=-h_{30,65}=-h_{32,65}=\sqrt{3}/2V_b,
\ h_{35,66}=-h_{36,68}=-\sqrt{2}/2V_b, h_{35,67}=-h_{37,68}=\sqrt{6}/2V_b,
\ h_{20,51}=-h_{23,55}=-h_{25,52}=-h_{24,56}=-h_{29,60}=-h_{32,64}=h_{34,61}=-h_{33,65}=1/2V_b, h_{20,52}=-h_{24,55}=-h_{25,51}=-h_{23,56}=-h_{29,61}=-h_{33,64}=-h_{34,60}=-h_{32,65}=\sqrt{3}/2V_b,
Parameters

$E(d^7), E(d^8)$: center of gravity of the $d^7, d^8$ multiplets

$\delta E(d^n) = n(n-1)/2(-14/9B + 7/9C)$

$\Delta = E(d^9_L) - E(d^8)$

$U = E(d^7) + E(d^9) - 2E(d^{10}) = A + (-14/9B + 7/9C)$

$V_e = 2(pd\pi), V_{b2} = 2(pd\pi), V_{a1} = -(pd\sigma), V_{b1} = -\sqrt{3}(pd\sigma)$