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Kyoto University
First-principles multielectron calculations of Ni L_{2,3} NEXAFS and ELNES for LiNiO_{2} and related compounds

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A technique to compute 3d transition-metal L_{2,3}-edge near-edge x-ray-absorption fine structure (NEXAFS) and electron energy-loss near-edge structure (ELNES) is adopted to predict and interpret spectra from NiO, LiNiO_{2}, and NiO_{2}. Multielectron wave functions were obtained as a linear combination of Slater determinants. The Slater determinants were constructed using all Ni-2p- and Ni-3d-based molecular orbitals, instead of atomic orbitals, obtained by solving the Dirac equation within the local density approximation for NiO_{6}^{m-} clusters (m=10, 9, and 8). The O-2p contributions through covalency can therefore be included automatically without any other scheme. Experimental ELNES for the three compounds were satisfactorily reproduced by the present calculations, which unambiguously shows that Ni atoms are Ni(III) with a low-spin state in LiNiO_{2}, and Ni(IV) with a low-spin state in NiO_{2}. The origin of satellite peaks in the spectra is also clarified. The present method is based on the robust multielectron quantum theory, which could be applied to the analysis and prediction of L_{2,3}-edge spectra of other transition-metal compounds.

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I. INTRODUCTION

Both near-edge x-ray-absorption fine structure (NEXAFS) and electron energy-loss near-edge structure (ELNES) are powerful techniques to observe electronic structures of selected elements. When measured using transmission electron microscopy, ELNES is identical to NEXAFS. We will hereafter refer only to NEXAFS. However, the same discussion can be made for ELNES. L_{2,3} NEXAFS of a 3d transition-metal element mainly corresponds to electric dipole transition from its 2p core levels to 3d orbitals. Minor contributions because of electric dipole transitions from 2p to ns (n=4, 5,...) and the electric quadrupole transition are negligible. Hence, the spectra directly reflect electronic structure of the 3d orbitals of the selected element. In spite of its potential usefulness, the L_{2,3}-edge is less used than the K-edge. One of the reasons is the difficulty of interpreting the measured spectra.

It has been demonstrated that most of K NEXAFS can be reproduced by a standard first-principles method within the one-electron approximation if the effect of a core hole is properly taken into account.\(^1-6\) On the other hand, the L_{2,3} NEXAFS of 3d transition-metal compounds cannot be reproduced using such methods. It is sometimes misunderstood that the L_{2,3} NEXAFS of 3d transition-metal compounds can be obtained simply by overlaying the spectrum by the one-electron calculations with proper L_{3}-L_{2} splitting and L_{3}/L_{2} intensity ratio. However, strong correlation among spatially localized 3d electrons and that between the core-hole and the excited electron entirely changes the spectral shape. The 3d electrons show widely spread multiplet structures even without a 2p core hole because of the strong correlation. The presence of the 2p core hole introduces further complexity into the spectra. Therefore, one-electron calculations are useless for L_{2,3} NEXAFS, in general. Recently, theoretical methods to explicitly include correlation between the core hole and the excited electron have been reported.\(^7,8\) However, none of them computed the multiplet structures because of the strong correlation among 3d electrons.

Multielectron structures of isolated atoms were well studied both by experiment and theory. Crystal field effects have been incorporated into an atomic multiplet program using group theoretical formalism, which is called the crystal-field atomic multiplet program.\(^9,10\) Although this approach has been successful in reproducing multiplet structures of many transition-metal compounds, it employs a number of adjustable parameters and therefore cannot be used to predict multiplet structures \textit{a priori}. Another problem of this approach resides in the treatment of ligand orbitals. Contribution of ligand orbitals as a result of covalent bonding can only be indirectly included in the crystal-field theory. Establishment of a first-principles method beyond the one-electron approximation that takes into account the multielectron interactions is, therefore, highly desirable. In order to treat the electronic
transition from a core orbital, relativistic effects should also be considered. One part of the relativistic effects is known as spin-orbit coupling. It can be automatically included by solving Dirac equation instead of Schrödinger equation.

By this group of the authors, a different calculation technique, which can deal directly with both the multielectron problem and the relativistic effect, has been developed. Electronic correlations among 3d electrons and a 2p core hole were rigorously accounted for by taking multiple Slater determinants composed of molecular orbitals. The technique can be used to predict $L_{2,3}$-edge spectra quantitatively without any adjustable parameters. In the present work, the method is applied to the Ni $L_{2,3}$ NEXAFS of three kinds of nickel oxides, i.e., NiO, LiNiO$_2$, and NiO$_2$ (Li-extracted LiNiO$_2$). Then we show a method to investigate the origin of satellite peaks in the spectra in terms of symmetry and electronic configurations. LiNiO$_2$ and NiO$_2$ are both important in lithium-ion batteries as cathode materials. Changes in the electronic structure due to lithium extraction (such as valency and spin-state of nickel ions) are therefore very interesting, not only from a fundamental viewpoint, but also for development of new materials. Ni $L_{2,3}$ NEXAFS should be an ideal tool to investigate them since it provides direct information of the Ni-3d states.

II. COMPUTATIONAL PROCEDURE

The crystal structures of the three compounds are known by experiments. Ni ions are coordinated by six O ions. The model clusters of NiO$_6^{m-}$, which are composed of a Ni ion and six nearest-neighbor O ions, were used. The total number of electrons in the cluster was obtained from formal charges, thus $m=10$, 9, and 8 for NiO [Ni(II)], LiNiO$_2$ [Ni(III)], and NiO$_2$ [Ni(IV)], respectively. The cluster model of NiO shows $O_{h}$ symmetry, while those of LiNiO$_2$ and NiO$_2$ show $D_{4h}$ symmetry. The Ni-O bond lengths were 0.2090, 0.1967, and 0.1861 nm in NiO, LiNiO$_2$, and NiO$_2$, respectively. In order to take account of effective Madelung potential, an array of point charges was set at the external atomic sites in the calculations.

The computational procedure of multielectron calculations that we are going to explain is equivalent to the “configuration interaction” calculations that are popular in quantum chemistry. However, in order to avoid misunderstanding and confusion, we do not use the words “configuration interaction” because these words sometimes have different meanings between quantum chemistry and atomic physics. Before presenting a detailed description of our procedures, let us explain our terminology.

We use density-functional calculations to obtain molecular orbitals (MO). Atomic orbitals (AO) are used as basis functions for the MO calculations. Slater determinants are constructed using these MO as components. Multielectron eigenstates can be computed by diagonalizing the multielectron Hamiltonian to be given in Eq. (1). Multielectron wave functions are formed by a linear combination of Slater determinants, which will be given in Eq. (3). When we use the term “state,” such as in initial state and final state, it corresponds to individual multielectron eigenstates. In quantum chemistry, the term “configuration” corresponds to each of the Slater determinants. In atomic physics, on the other hand, the term “configuration” corresponds to a set of Slater determinants that have the same number of electrons in the atomic orbitals, such as $(2p)^5(3d)^2$ and $(2p)^6(3d)^2$. We adopt the latter way to define configuration.

In the present study, fully relativistic MO calculations were carried out by solving Dirac equations with the local density approximation (LDA) using the code that was originally described in Ref. 14. Recently the code has been modified and successful in calculations of optical spectra of many laser crystals. In this code, four-component relativistic molecular orbitals are expressed as linear combination of AO (LCAO). The numerically generated four-component relativistic AO (1s to 4p for Ni and 1s to 2p for O) were used as basis functions for MO. After one-electron calculations of relativistic MO, we made multielectron calculations.

Only Ni 2p orbitals and MO mainly composed of Ni 3d orbitals (as will be described by $\phi_{3d}$, or by $t_{2g}$ and $e_g$) were considered explicitly for the multielectron calculation, since inclusion of all $N$ electrons in the cluster requires a prohibitive amount of computational time and resources. An effective multielectron Hamiltonian is expressed as

$$H = \sum_{i=1}^{n} h(r_i) + \sum_{i=1}^{n} \sum_{j=i+1}^{n} \frac{1}{|r_i - r_j|},$$

where $n$ is the number of electrons in the selected MO. The one-electron operator $h(r_i)$ is given by

$$h(r_i) = c \alpha \beta \frac{Z_e}{r_i} + c^{-2} \beta - \sum_{\nu} \frac{Z_{\nu}}{|r_i - R_{\nu}|} + V'(r_i),$$

where $\alpha, \beta$ are Dirac matrices, $c$ is the velocity of light, $p_i$ is the momentum operator, $Z_e$ is the charge of $\nu$th nucleus, and $V'(r_i)$ is the potential from the other ($N-n$) electrons. In this approach, the Coulomb interaction and exchange-correlation interaction among the selected $n$ electrons are considered explicitly, whereas those interactions between the selected $n$ electrons and the remaining ($N-n$) electrons are expressed as an effective potential of $V'(r_i)$. The explicit form of $V'(r_i)$ as derived by Watanabe and Kamimura was adopted.

As basis functions to diagonalize the multielectron Hamiltonians shown in Eq. (1), all possible Slater determinants for given configurations that are related to Ni $L_{2,3}$ NEXAFS were used. The multielectron wave functions were then expressed as a linear combination of those Slater determinants,

$$\Psi_i = \sum_{j=1}^{M} C_{i\mu} \Phi_{\mu},$$

where $\Psi_i$ is the $i$th multielectron wave function, $\Phi_{\mu}$ is the $\mu$th Slater determinant, and $C_{i\mu}$ is the coefficient. Ni $L_{2,3}$ NEXAFS of NiO is due to the transitions from $(2p)^6(3d)^8$ to $(2p)^5(3d)^9$, where $\phi_{3d}$ denotes the MO mainly composed of Ni 3d orbitals. The number of possible Slater determinants for $(2p)^6(3d)^8$ is $45 (=5c_8 \times 10C_5$) and that for $(2p)^5(3d)^9$ is $60 (=6C_5 \times 10C_5)$. Thus 105 Slater determinants were used as bases for multielectron wave functions. For LiNiO$_2$
[Ni(III)], Ni $L_{2,3}$ NEXAFS corresponds to the transitions from $(2p)^6(3d)_g^3$ to $(2p)^6(3d)_g^8$. The number of Slater determinants for $(2p)^6(3d)_g^7$ is 120 $(\pi_n C_6 \times 10 C_7)$ and that for $(2p)^6(3d)_g^8$ is 270 $(\pi_n C_5 \times 10 C_8)$. Therefore, there were 390 Slater determinants used. In the case of NiO$_2$ [Ni(VI)], Ni $L_{2,3}$ NEXAFS corresponds to the transitions from $(2p)^6(3d)_g^8$ to $(2p)^6(3d)_g^8$. The number of determinants is 210 $(\pi_n C_6 \times 10 C_6)$ for $(2p)^6(3d)_g^8$ and 720 $(\pi_n C_5 \times 10 C_7)$ for $(2p)^6(3d)_g^7$, thus, 930 in total.

The oscillator strength of the electric dipole transition averaged over all directions is given by

$$ I_{if} = \frac{2}{3}(E_f - E_i) \left| \left\langle \Psi_f \left| \sum_{i=1}^{n} \mathbf{r}_i \right| \Psi_i \right\rangle \right|^2 $$

where $\Psi_i$ and $\Psi_f$ are multielectron wave functions for the initial state and the final state, while $E_i$ and $E_f$ are their energies. This procedure was pointed out to overestimate the absolute transition energy typically by $<$1%. In Ref. 11, the transition energy was corrected by taking the orbital-energy difference between single-electron orbitals for the Slater’s transition state as a reference. We have adopted the same procedure in the present study.

III. RESULTS AND DISCUSSION

A. Initial states

First, we made relativistic molecular-orbital calculations within LDA. The MO obtained by LDA calculations were used as components of Slater determinants in the multielectron calculations. It is generally accepted that the magnitude of covalent bonding between the 3d orbital of the transition element and 2p orbital of oxygen increases with the increase of the formal charge of the transition element. In order to quantify the trend, Mulliken’s population analysis has been made. We found that the atomic-orbital population of O-2p is 3.3%, 7.2%, and 17.6% in $t_{2g}$ for NiO, LiNiO$_2$, and NiO$_2$, respectively. The population is greater in $e_g$ than in $t_{2g}$, i.e., 14.3%, 30.3%, and 34.8% for NiO, LiNiO$_2$, and NiO$_2$, respectively. The substantial mixing of O-2p in these compounds clearly implies the superiority of using MO instead of AO as components of Slater determinants. Contribution of covalency can be thereby included automatically without implementation of any other scheme. It should be noted that the expressions $t_{2g}$ and $e_g$ are not rigorously right within the relativistic theory (see Fig. 1). Instead, the representations of the double group, such as $e_{g_{2g}}$ and $g_{3g}$, should be employed. They are equivalent to $\gamma_{2g}$ ($\gamma_{g}$) and $\gamma_{8g}$ ($\gamma_{8}$) using the Bethe symbol. Furthermore, $t_{2g}$ and $e_g$ orbitals split because of the trigonal distortion of the crystal field, since the point group symmetry of the cluster models for LiNiO$_2$ and NiO$_2$ is reduced to $D_{3d}$ symmetry from $O_3$ symmetry. However, the energy splitting in $t_{2g}$ and $e_g$ orbitals because of relativistic effects and trigonal distortion is one-tenth the order of the energy splitting between $t_{2g}$ and $e_g$, i.e., 10$\Delta q$. Therefore, the expressions $t_{2g}$ and $e_g$ will be adopted in the following part of this paper for simplicity.

Using the relativistic MO, multielectron calculations were carried out. First, we show the result for the initial states.

\[ \text{TABLE I. Compositions of configurations in the multielectron wave functions that correspond to the initial state of Ni } L_{2,3} \text{ NEXAFS} \]

\begin{tabular}{|c|c|c|}
\hline
\text{Configurations} & \text{Composition} & \text{($\%$)} \\
\hline
\text{NiO} & $(2p_{1/2})^2(2p_{3/2})^4(t_{2g})^4(e_g)^0$ & 96.7 \\
 & $(2p_{1/2})^2(2p_{3/2})^2(t_{2g})^6(e_g)^4$ & 1.8 \\
 & $(2p_{1/2})^2(2p_{3/2})^4(t_{2g})^4(e_g)^4$ & 1.5 \\
\hline
\text{LiNiO$_2$} & $(2p_{1/2})^2(2p_{3/2})^2(t_{2g})^6(e_g)^4$ & 98.1 \\
 & $(2p_{1/2})^2(2p_{3/2})^4(t_{2g})^4(e_g)^2$ & 0.4 \\
 & $(2p_{1/2})^2(2p_{3/2})^4(t_{2g})^4(e_g)^4$ & 0.4 \\
\hline
\text{LiNiO$_2$} & $(2p_{1/2})^2(2p_{3/2})^2(t_{2g})^6(e_g)^4$ & 96.6 \\
 & $(2p_{1/2})^2(2p_{3/2})^4(t_{2g})^4(e_g)^2$ & 3.2 \\
\hline
\text{NiO} & $(2p_{1/2})^2(2p_{3/2})^4(t_{2g})^4(e_g)^0$ & 96.7 \\
 & $(2p_{1/2})^2(2p_{3/2})^2(t_{2g})^6(e_g)^4$ & 1.8 \\
 & $(2p_{1/2})^2(2p_{3/2})^4(t_{2g})^4(e_g)^4$ & 0.4 \\
\hline
\text{NiO$_2$} & $(2p_{1/2})^2(2p_{3/2})^2(t_{2g})^6(e_g)^4$ & 97.4 \\
 & $(2p_{1/2})^2(2p_{3/2})^4(t_{2g})^4(e_g)^2$ & 2.2 \\
 & $(2p_{1/2})^2(2p_{3/2})^4(t_{2g})^4(e_g)^2$ & 0.4 \\
\hline
\text{NiO$_2$} & $(2p_{1/2})^2(2p_{3/2})^2(t_{2g})^6(e_g)^4$ & 0.0 \\
 & $(2p_{1/2})^2(2p_{3/2})^2(t_{2g})^6(e_g)^4$ & 0.1 \\
 & $(2p_{1/2})^2(2p_{3/2})^4(t_{2g})^4(e_g)^2$ & 99.6 \\
\hline
\end{tabular}
state of NiO. Although we will take account of all configurations for the NEXAFS calculations to describe the initial state, the \((2p_{3/2})^3(2p_{3/2})^3(t_{2g})^6(e_g)^2\) configuration is found to be predominant, which agrees well with our intuition. Similar multielectron calculations were made for LiNiO\(_2\) and NiO\(_2\) imposing several spin configurations. It should be noted that more than 95\% of the initial states in all cases are composed of the dominant configuration.

**B. Multielectron eigenstates and theoretical NEXAFS**

1. NiO

Figure 1 schematically shows a one-electron view of eigenvalues of the NiO\(_{6}^{10-}\) cluster and the electronic transition from \(2p_{3/2}\) to \(e_g\) \((g_{3/2}\) in the relativistic expression). Since the \(t_{2g}\) orbitals also include \(g_{3/2}\) representation when translated into the relativistic expression, two kinds of transitions as shown in Fig. 1 need to be considered for \(L_3\) NEXAFS. Their final configurations are \((2p_{1/2})^3(2p_{3/2})^3(t_{2g})^6(e_g)^3\) and \((2p_{1/2})^3(2p_{3/2})^3(t_{2g})^6(e_g)^2\), respectively. A number of different ways to put a hole in the \(2p_{3/2}\) and seven electrons to the \(g_{3/2}\) orbitals is \(3 \times 3 = 9\), which include both of the two final configurations. Only the transition to \((2p_{1/2})^3(2p_{3/2})^3(t_{2g})^6(e_g)^3\) is allowed as an electric dipole transition. The allowed 16 transitions can be classified as \(A_{1g}+A_{2g}+E_u+2T_{1u}+2T_{2u}\), under \(O_h\) point group symmetry. The number of transitions and their irreducible representations for the four different types of transitions are summarized in Table II.

Figure 2(a) shows all 60 of the multielectron eigenvalues of the final states using vertical bars. They are classified by colors according to their final configurations. For example, red bars correspond to final configurations of \((2p_{1/2})^3(2p_{3/2})^3(t_{2g})^6(e_g)^2\). Figure 2(b) shows computed oscillator strength of the electric-dipole transition to each eigenstate with black bars. As explained in Table I, the initial states are predominantly composed of \((2p_{1/2})^3(2p_{3/2})^3(t_{2g})^6(e_g)^2\). Therefore, the transitions to final configurations \((2p_{1/2})^3(2p_{3/2})^3(t_{2g})^6(e_g)^3\) [red bars in Fig. 2(a)] and \((2p_{1/2})^3(2p_{3/2})^3(t_{2g})^6(e_g)^2\) [magenta bars in Fig. 2(a)] dominate to the oscillator strengths of Ni \(L_{2,3}\) NEXAFS because of the electric dipole selection rule. Figure 2(c) summarizes compositions of those two kinds of final configurations, i.e., \((2p_{1/2})^3(2p_{3/2})^3(t_{2g})^6(e_g)^3\) [red bars in Fig. 2(a)] and \((2p_{1/2})^3(2p_{3/2})^3(t_{2g})^6(e_g)^2\) [magenta bars in Fig. 2(a)].

Theoretical spectrum of the Ni \(L_{2,3}\) NEXAFS as shown in top panels was made by broadening the oscillator strengths using Gaussian functions with the dispersion \(\sigma=0.4\) eV [or full width at half maximum (FWHM)=0.94 eV]. The oscillator strengths are superposed on the theoretical spectrum with shortened black bars.

Using these diagrams, one can clearly interpret the origin of peaks in the theoretical spectrum. Peak \(a\) is composed of eigenstates that can be classified into \(A_{2g}, E_u, T_{1u}\), and \(T_{2u}\). Peak \(b\) can be ascribed predominantly to \(T_{1u}\). This shows higher transition energy of peak \(b\) than peak \(a\), because the eigenstate corresponding to peak \(b\) is a mixture of two configurations as shown in Fig. 1. As can be seen in Fig. 2(a), 24\% of the contribution is due to the \((2p_{1/2})^3(2p_{3/2})^3(t_{2g})^6(e_g)^4\) [green bars in Fig. 2(a)]. This configuration corresponds to the two electrons excitation shown in Fig. 1(b) and it is not allowed as an electric dipole transition. Although the component does not contribute to the oscillator strength, the mixing of the \(t_{2g} \rightarrow e_g\) excitation with the \(2p_{3/2} \rightarrow e_g\) excitation makes the transition energy higher than that without such mixing. The small peak \(c\) can be ascribed to \(T_{2u}\), which is energetically much more expensive because the major contribution to this eigenstate is the two electrons excitation. The origin of peaks \(d\) to \(f\) can be interpreted in a similar manner.

2. LiNiO\(_2\)

In the case of LiNiO\(_2\), the initial configuration is \((2p)^6(\phi_{3d})^2\). Two different spin configurations can be candidates for the initial configuration. One is low-spin configuration, which is mainly composed of \((2p_{1/2})^3(2p_{3/2})^3(t_{2g})^6(e_g)^4\) and the other is high-spin configuration, which is mainly composed of \((2p_{1/2})^3(2p_{3/2})^3(t_{2g})^6(e_g)^2\), as can be seen in Table I. Multielectron calculations were carried out, and 270 final states for Ni \(L_{2,3}\) NEXAFS were obtained as shown in Fig. 3(a). They are distinguished by colors according to their final configurations. Since the NiO\(_{6}^{10-}\) cluster in LiNiO\(_2\) shows \(D_{3d}\) symmetry, two irreducible representations, \(E_{1/2u}\) and \(E_{3/2u}\), appear in the final states. Depending on the choice of the initial configuration, the dipole transition probability is quite differ-
FIG. 2. (Color online) (a) Theoretical L_{2,3}-edge NEXAFS and ELNES for Ni(II) in NiO is shown in upper panel. Bars in upper panel shows the oscillator strengths for multielectron eigenstates. The following panels show the composition of final configurations for multielectron eigenstates in five symmetries. They are classified according to final configurations as distinguished by colors: red (2p_{1/2})^2(2p_{3/2})^4(t_{2g})^4(e_g)^4, green (2p_{1/2})^2(2p_{3/2})^4(t_{2g})^4(e_g)^4, magenta (2p_{1/2})^1(2p_{3/2})^4(t_{2g})^4(e_g)^3, and yellowish green (2p_{1/2})^1(2p_{3/2})^4(t_{2g})^4(e_g)^3. (b) Oscillator strengths for all final states in five symmetries. The lengths of bars were multiplied by 3 from that of the oscillator strengths superimposed on the theoretical spectrum (top panel) for easy visualization. (c) Compositions of final configurations for the dipole allowed transitions, i.e., (2p_{1/2})^2(2p_{3/2})^4(t_{2g})^4(e_g)^3 (red bars in a) and (2p_{1/2})^1(2p_{3/2})^4(t_{2g})^4(e_g)^3 (magenta bars in a).

When the initial configuration is low spin, i.e., (2p)^6(e_g)^1 configuration, only the transition to (2p)^5(t_{2g})^4(e_g)^2 is allowed. On the other hand, when the initial configuration is high spin, i.e., (2p_{1/2})^2(2p_{3/2})^4(t_{2g})^4(e_g)^2 configuration, transition can be allowed to either (2p)^5(t_{2g})^4(e_g)^2 or (2p)^5(t_{2g})^4(e_g)^3. The contributions from four final configurations are shown in Fig. 3(b). Theoretical spectrum of the Ni L_{2,3} NEXAFS was made in the same way as in Fig. 2 with dispersion of \( \sigma = 0.4 \) eV. As can be found from these figures, peaks a–c of the low-spin spectrum can be ascribed to the eigenstates that are predominantly composed of (2p_{1/2})^2(2p_{3/2})^4(t_{2g})^4(e_g)^2 [red bars in Fig. 3(a)]. Hence, peaks a–c can be translated as the 2p_{3/2} \rightarrow e_g excitation. Eigenstates that are responsible for the tiny peaks, d and e, at higher energies are predominantly composed of (2p_{1/2})^2(2p_{3/2})^4(t_{2g})^4(e_g)^3 [green bars in Fig. 3(a)], which is dipole forbidden. They are located much higher in transition energy than peaks a–c because of the mixture of the t_{2g} \rightarrow e_g and 2p_{3/2} \rightarrow e_g excitations. A similar analysis can be applied to L_{2,3}-edge. Peaks f–h are mainly due to the transition to (2p_{1/2})^2(2p_{3/2})^4(t_{2g})^4(e_g)^2 [magenta bars in Fig. 3(a)]. Peaks i and j are higher in energy because their major component is a dipole-forbidden two-electron excitation of 2p_{1/2} \rightarrow e_g with the t_{2g} \rightarrow e_g excitation.

When the initial configuration is high-spin, both of L_3 and L_2 peaks of the theoretical NEXAFS of NiO can be categorized into two groups originating from two different configurations. In the L_3-edge, peak a’ can be ascribed to 2p_{3/2} \rightarrow t_{2g} transition, and peaks b’–d’ to 2p_{3/2} \rightarrow e_g transition. Likewise in the L_2-edge, peaks e’ and f’ can be ascribed to 2p_{1/2} \rightarrow t_{2g} transition, and peaks g’ and h’ to 2p_{1/2} \rightarrow e_g transition.

3. NiO

Results for NiO, using a NiO\(_6^–\) cluster with D_{3d} symmetry are summarized in Fig. 4. Within the one-electron scheme, only two different spin configurations, i.e., high- and low-spin, are possible since the initial configuration is (2p)^6(\phi_{3d})^6. On the other hand within the multielectron scheme, some other spin configurations can be taken as initial configurations. An example is a middle-spin configuration, which is mainly composed of (2p_{1/2})^2(2p_{3/2})^4(t_{2g})^4(e_g)^1 configuration. Eigenvalues for the 720 final states for Ni L_{2,3} NEXAFS in the three irreducible
The composition of final configurations for multielectron eigenstates in $E_{1/2}$ and $E_{3/2}$ symmetries. They are classified according to final configurations as distinguished by colors; red $(2p_{1/2})^2(2p_{3/2})^1(t_{2g})^6(e_g)^3$, green $(2p_{1/2})^2(2p_{3/2})^2(t_{2g})^5(e_g)^2$, blue $(2p_{1/2})^2(2p_{3/2})^2(t_{2g})^4(e_g)^3$, magenta $(2p_{1/2})^1(2p_{3/2})^4(t_{2g})^6(e_g)^2$, yellowish green $(2p_{1/2})^1(2p_{3/2})^4(t_{2g})^5(e_g)^3$, and cyan $(2p_{1/2})^1(2p_{3/2})^4(t_{2g})^4(e_g)^4$. (b) Compositions of final configurations for the dipole-allowed transitions.

**4. Comparison to theoretical spectra**

In order to examine the adequacy of theoretical results obtained in the present study, we conducted ELNES experiments using transmission electron microscopy. Samples were commercial NiO powder, LiNiO$_2$ prepared by a solid-state method, and a NiO$_2$ sample obtained by electrochemical lithium extraction from LiNiO$_2$. ELNES was measured with energy resolution ranging from 0.8 to 1.0 eV FWHM of a zero-loss peak. More detail of the experimental procedure can be found elsewhere.

Figure 5 shows the experimental Ni $L_{2,3}$ ELNES of (a) NiO, (b) LiNiO$_2$, and (c) NiO$_2$. The experimental Ni $L_{2,3}$ NEXAFS of NiO with higher energy resolution is also shown below the ELNES for comparison. This spectrum was measured at BL25SU at SPring-8 (Hyogo, Japan), using the same sample as the ELNES measurement. As can be seen, not only the peak positions but also the spectral shapes of these three compounds are discernibly different. This clearly
First-principles multielectron calculations of Ni $L_{2,3}$ NEXAFS and ELNES of NiO, LiNiO$_2$, and NiO$_2$ have been made. Theoretical spectra not only satisfactorily reproduce the experimental spectra, but can also be used to interpret the experimental spectra. The present method is based on the robust multielectron quantum theory, which could be applied to the analysis and prediction of $L_{2,3}$-edge spectra of other transition-metal compounds. The major parts of the present study can be summarized as follows:

1. Relativistic four-component wave functions of molecular orbitals were obtained by solving Dirac equations within the local density approximation using model clusters of NiO$_m$, where $m$ is taken to be 10, 9, and 8 for NiO, LiNiO$_2$, and NiO$_2$, respectively.

2. Slater determinants composed of all Ni-2$p$ and 3$d$ orbitals in NiO$_m$ clusters were constructed using the relativistic molecular orbitals. Multielectron wave functions expressed by a linear combination of the Slater determinants were obtained by diagonalizing the multielectron Hamiltonian. The number of Slater determinants for the initial states was 45, 120, and 210 for NiO, LiNiO$_2$, and NiO$_2$, respectively. It was, respectively, 60, 270, and 720 for the final states. The eigenstates were analyzed in terms of symmetry and composition of electronic configurations.

3. The contributions of O-2$p$ orbitals through covalency can be automatically included without any other scheme, since the multielectron calculations were made using molecular orbitals instead of atomic orbitals. This is very important for transition-metal oxides with high formal charges, such as Ni(III) and Ni(IV).

4. Theoretical NEXAFS and ELNES within the electric dipole approximation were obtained by calculating oscillator strengths from several initial states to all of final states. Differences because of the initial states were discussed. The origin of satellite peaks in these spectra was also discussed.

5. Experimental ELNES for the three compounds were satisfactorily reproduced by the present calculations, which unambiguously show that Ni atoms are Ni(III) with a low-spin state in LiNiO$_2$, and Ni(IV) with a low-spin state in NiO$_2$. A remaining problem is a small overestimation of the chemical shift from NiO to NiO$_2$ by 0.7 eV. This may be ascribed to the use of small clusters in the present calculations, which needs to be clarified in the future. Currently, larger calculations are prohibitively expensive.

Ni $L_{2,3}$ NEXAFS of NiO and LiNiO$_2$ was reported by Montoro et al. in 1999.21 They found that the NEXAFS of LiNiO$_2$ was similar to that of NiO and concluded that the Ni ions in both of LiNiO$_2$ and NiO were Ni(II). In the present work, ELNES of LiNiO$_2$ is clearly different from that of NiO. The origin of the discrepancy has been discussed in Ref. 20. The spectra reported in Ref. 21 may reflect the electronic structure at the surface of the sample, but not the bulk.

### IV. SUMMARY AND CONCLUSIONS

First-principles multielectron calculations of Ni $L_{2,3}$ NEXAFS and ELNES of NiO, LiNiO$_2$, and NiO$_2$ have been made. Theoretical spectra not only satisfactorily reproduce the experimental spectra, but can also be used to interpret the experimental spectra. The present method is based on the robust multielectron quantum theory, which could be applied to the analysis and prediction of $L_{2,3}$-edge spectra of other transition-metal compounds. The major parts of the present study can be summarized as follows:

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