First-principles multielectron calculations of Ni $L_{2,3}$ NEXAFS and ELNES for LiNiO$_2$ and related compounds

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(Received 15 March 2005; revised manuscript received 24 June 2005; published 17 August 2005)

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 ($m=10, 9, 8$). 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.

DOI: 10.1103/PhysRevB.72.075123 PACS number(s): 78.70.Dm, 78.20.Bh, 71.15.Rf

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 ($n=4, 5, \ldots$) 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.

Multiplet 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 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\textsubscript{2}, and NiO\textsubscript{2} (Li-extracted LiNiO\textsubscript{2}). Then we show a method to investigate the origin of satellite peaks in the spectra in terms of symmetry and electronic configurations. LiNiO\textsubscript{2} and NiO\textsubscript{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\textsubscript{6} 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\textsubscript{2} [Ni(III)], and NiO\textsubscript{2} [Ni(IV)], respectively. The cluster model of NiO shows \( O_6 \) symmetry, while those of LiNiO\textsubscript{2} and NiO\textsubscript{2} show \( D_{3d} \) symmetry. The Ni-O bond lengths were 0.2090, 0.1967, and 0.1861 nm in NiO, LiNiO\textsubscript{2}, and NiO\textsubscript{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 due to lithium extraction. Changes in the electronic structure due to lithium extraction are 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

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

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

\[
h(r_i) = c\alpha \vec{p}_i + c^2 \vec{\beta} - \sum_{\nu} \frac{Z_{\nu}}{|r_i - R_{\nu}|} + V'(r_i),
\]

where \( \vec{\alpha}, \vec{\beta} \) are Dirac matrices, \( c \) is the velocity of light, \( \vec{p}_i \) is the momentum operator, \( Z_{\nu} \) 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,

\[
\Psi_i = \sum_{j=1}^{M} C_{ip} \Phi_p,
\]

where \( \Psi_i \) is the \( i \)th multielectron wave function, \( \Phi_p \) is the \( p \)th Slater determinant, and \( C_{ip} \) is the coefficient. Ni L_{2,3} NEXAFS of NiO is due to the transitions from \( (2p)^6(3d)^8 \) to \( (2p)^7(3d)^9 \), 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 (\( = C_6 \times 10C_5 \)) and that for \( (2p)^7(3d)^9 \) is 60 (\( = C_6 \times 10C_5 \)). Thus 105 Slater determinants were used as bases for multielectron wave functions. For LiNiO\textsubscript{2}
[Ni(III)], Ni $L_{2,3}$ NEXAFS corresponds to the transitions from $(2p)^6(3d)^7$ to $(2p)^5(3d)^8$. The number of Slater determinants for $(2p)^6(3d)^7$ is 120 ($\pi_c C_6 \times 10 C_7$) and that for $(2p)^7(3d)^8$ is 270 ($\pi_c C_5 \times 10 C_6$). 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 $(2p)^6(3d)^6$ to $(2p)^7(3d)^7$. The number of determinants is 210 ($\pi_c C_6 \times 10 C_6$) for $(2p)^6(3d)^6$ and 720 ($\pi_c C_5 \times 10 C_7$) for $(2p)^7(3d)^7$, thus, 930 in total.

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

$$I_o = \frac{2}{3} \langle E_i - E_f \rangle \left| \sum_{k=1}^{n} r_k \right|^2 \left| \Psi_i \right|^2 \left| \Psi_f \right|^2$$

(4)

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 $e_g(t_{2g})$ and $g_{3/2}t_{2g}$, should be employed. They are equivalent to $\gamma_g(t_{2g})$ and $\gamma_{8/3}(t_{2g})$ 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$\delta t_{2g}$. 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.
state of NiO. Although we will take account of all configurations for the NEXAFS calculations to describe the initial state, the \((2p_{3/2})^2(2p_{3/2})^1(t_{2g})^2(e_g)^2\) 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 \((2p_{1/2})^2(2p_{3/2})^1(t_{2g})^6(e_g)^3\) and \((2p_{1/2})^2(2p_{3/2})^1(t_{2g})^4(e_g)^4\), 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 \(C_1 \times g_c = 32\), which include both of the two final configurations. Only the transition to \((2p_{1/2})^2(2p_{3/2})^1(t_{2g})^6(e_g)^3\) is allowed as an electric dipole transition. The allowed 16 transitions can be classified as \(A_{1u} + A_{2u} + E_u + 2T_{1u} + 2T_{2u}\) 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 \((2p_{1/2})^2(2p_{3/2})^1(t_{2g})^6(e_g)^2\). 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 \((2p_{1/2})^2(2p_{3/2})^1(t_{2g})^6(e_g)^2\). Therefore, the transitions to final configurations \((2p_{1/2})^2(2p_{3/2})^1(t_{2g})^6(e_g)^3\) [red bars in Fig. 2(a)] and \((2p_{1/2})^2(2p_{3/2})^1(t_{2g})^4(e_g)^4\) [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., \((2p_{1/2})^2(2p_{3/2})^1(t_{2g})^6(e_g)^3\) [red bars in Fig. 2(a)] and \((2p_{1/2})^2(2p_{3/2})^1(t_{2g})^4(e_g)^4\) [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 \(A_{2u}, E_u, T_{1u}\), 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 \((2p_{1/2})^2(2p_{3/2})^2(t_{2g})^4(e_g)^2\) [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 \((2p_{1/2})^2(2p_{3/2})^2(t_{2g})^4(e_g)^2\) and the other is high-spin configuration, which is mainly composed of \((2p_{1/2})^2(2p_{3/2})^4(t_{2g})^2(e_g)^4\), 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, \(E_{1/2}\) and \(E_{3/2}\), appear in the final states. Depending on the choice of the initial configuration, the dipole transition probability is quite differ-
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...ent. When the initial configuration is low spin, i.e., 
\((2p)^6(t_{2g})^6(\epsilon_g)^1\) configuration, only the transition to 
\((2p)^5(t_{2g})^5(\epsilon_g)^2\) is allowed. On the other hand, when the 
initial configuration is high spin, i.e., 
\((2p)^7(t_{3g})^4(t_{2g})^5(\epsilon_g)^2\) configuration, transition can be allowed to either 
\((2p)^6(t_{2g})^6(\epsilon_g)^2\) or \((2p)^5(t_{2g})^5(\epsilon_g)^3\). 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 
\((2p)^6(t_{3g})^4(t_{2g})^5(\epsilon_g)^2\) [red bars in Fig. 3(a)]. 
Hence, peaks \(a\)–\(c\) can be translated as the \(2p_{3/2} \rightarrow \epsilon_g\) excitation. 
Eigenstates that are responsible for the tiny peaks, \(d\) and 
\(e\), at higher energies are predominantly composed of 
\((2p)^7(t_{3g})^4(t_{2g})^5(\epsilon_g)^3\) [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 \(t_{2g} \rightarrow \epsilon_g\) and \(2p_{3/2} \rightarrow \epsilon_g\) excitations. A similar analysis can be 
applied to \(L_{2-3}\)-edge. Peaks \(f\)–\(h\) are mainly due to the transition 
to \((2p)^6(t_{3g})^4(t_{2g})^5(\epsilon_g)^2\) [magenta bars in Fig. 3(a)]. 
Peaks \(i\) and \(j\) are higher in energy because their major com-
ponent is a dipole-forbidden two-electron excitation of 
\(2p_{1/2} \rightarrow \epsilon_g\) with the \(t_{2g} \rightarrow \epsilon_g\) excitation.

When the initial configuration is high-spin, both of \(L_3\) and 
\(L_2\) peaks of the theoretical NEXAFS of NiO can be categor-
ized into two groups originating from two different configu-
trations. In the \(L_2\)-edge, peak \(a\) can be ascribed to \(2p_{3/2} \rightarrow t_{2g}\) transition, and peaks \(b\)–\(d\) to \(2p_{3/2} \rightarrow \epsilon_g\) 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 \(2p_{1/2} \rightarrow \epsilon_g\) 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 ini-
tial configurations. An example is a middle-spin configu-
ration, which is mainly composed of \((2p)^7(t_{3g})^4(t_{2g})^5(\epsilon_g)^1\) configuration. Eigenvalues for the 
720 final states for Ni \(L_{2,3}\) NEXAFS in the three irreducible
FIG. 3. (Color online) (a) Theoretical $L_{2,3}$-edge NEXAFS and ELNES for a low and high-spin states for Ni(III) in LiNiO$_2$ are shown in the upper two panels. The following panels show the composition of final configurations for multielectron eigenstates in $E_{1/2u}$ and $E_{3/2u}$ symmetries. They are classified according to final configurations as distinguished by colors: red $(2p_{1/2})^2(2p_{3/2})^3(t_{2g})^4(e_g)^2$, green $(2p_{1/2})^2(2p_{3/2})^3(t_{2g})^3(e_g)^3$, blue $(2p_{1/2})^2(2p_{3/2})^3(t_{2g})^4(e_g)^2$, magenta $(2p_{1/2})^2(2p_{3/2})^4(t_{2g})^4(e_g)^2$, yellowish green $(2p_{1/2})^1(2p_{3/2})^1(t_{2g})^5(e_g)^3$, 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.

FIG. 4. (Color online) (a) Theoretical $L_{2,3}$-edge NEXAFS and ELNES for low and high-spin states for Ni(IV) in NiO$_2$ are shown in upper two panels. The following panels show the composition of final configurations for multielectron eigenstates in $A_{1g}$, $A_{2u}$, and $E_u$ symmetries. They are classified according to final configurations as distinguished by colors: red $(2p_{1/2})^2(2p_{3/2})^3(t_{2g})^4(e_g)^1$, green $(2p_{1/2})^2(2p_{3/2})^3(t_{2g})^3(e_g)^2$, blue $(2p_{1/2})^2(2p_{3/2})^3(t_{2g})^4(e_g)^1$, orange $(2p_{1/2})^2(2p_{3/2})^3(t_{2g})^3(e_g)^3$, magenta $(2p_{1/2})^2(2p_{3/2})^3(t_{2g})^4(e_g)^1$, yellowish green $(2p_{1/2})^1(2p_{3/2})^1(t_{2g})^5(e_g)^3$, cyan $(2p_{1/2})^1(2p_{3/2})^4(t_{2g})^4(e_g)^4$, and yellow $(2p_{1/2})^1(2p_{3/2})^4(t_{2g})^3(e_g)^4$. (b) Compositions of final configurations for the dipole-allowed transitions.

representations were obtained by the present multielectron calculation. They are distinguished according to their final configurations, as shown in Fig. 4(a). Similar to the other two systems, some mixtures among different configurations can be seen as the overlapping of colored areas. The contributions from the six final configurations are shown in Fig. 4(b). Despite the presence of many final states, theoretical Ni $L_{2,3}$ NEXAFS looks simple when the initial state is low spin. It is composed of two strong peaks, $b$ and $e$, with tiny satellite peaks. This is because only $(2p_{1/2})^2(2p_{3/2})^3(t_{2g})^4(e_g)^1$ [red bars in Fig. 4(a)] and $(2p_{1/2})^1(2p_{3/2})^3(t_{2g})^6(e_g)^1$ configurations [magenta bars in Fig. 4(a)] are allowed as an electric dipole transition. On the other hand, two other calculations with different initial states produce completely different theoretical NEXAFS. (Theoretical NEXAFS from the middle-spin state is not shown in Fig. 4.) This clearly implies that the $L_{2,3}$ NEXAFS can be used to identify initial electronic states of Ni if reliable theoretical spectra or referential spectra are available.

4. Comparison to experimental spectra

In order to examine the adequacy of theoretical results obtained in the present study, we conducted ELNES experi-
FIG. 5. Experimental Ni $L_{2,3}$-edge ELNES of (a) NiO, (b) LiNiO$_2$, and (c) NiO$_2$ as compared to theoretical spectra. For NiO, Ni $L_{2,3}$ NEXAFS with a higher energy resolution is also shown to see detailed structures. For theoretical spectra of LiNiO$_2$ and NiO$_2$, low-spin states are chosen as initial states. The absolute transition energy of the theoretical spectrum of NiO, LiNiO$_2$, and NiO$_2$ are shifted by 1.9, 1.6, and 1.2 eV, respectively, in order to see best matches with experimental spectra.

implies that electronic structures of Ni in the three compounds are quite different. Theoretical spectra of the three compounds showing best agreement to experimental spectra are displayed below the corresponding experimental spectra in Fig. 5. The energy scales of the theoretical spectra are translated in order to see the best matches with experimental spectra. Because the magnitude of chemical shift from NiO to NiO$_2$ is slightly overestimated, the magnitudes of translations are 1.9, 1.6, and 1.2 eV, for NiO, LiNiO$_2$ and NiO$_2$, respectively. In these theoretical spectra, low-spin states are chosen for LiNiO$_2$ and NiO$_2$ as initial states. Spectral shape of these two compounds cannot be explained with the other initial states. We can therefore conclude that the ground state of Ni atoms is Ni(II) in NiO as widely accepted, Ni(III) with low-spin state in LiNiO$_2$, and Ni(IV) with 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:

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$_m^{n-}$, 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$_m^{n-}$ 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$_2$. 

075123-7
ACKNOWLEDGMENTS

This work was supported by three programs from Ministry of Education, Science, Sports, and Culture of Japan, i.e., (i) Grant-in-aid for Scientific Research on Priority Areas (No. 751), (ii) Computational materials science unit in Kyoto University, and (iii) twenty-first century COE program. H.I., Y.K., and T. M. thank the Japan Society for the Promotion of Science (JSPS) for their research fellowship. NEXAFS measurement at SPring-8 was made under Proposal No. 2004A0402-NSc-np-Na.

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