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X-ray-photoelectron spectroscopic studies of the electronic structure of CoO[†]

K. S. Kim

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

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The x-ray-photoelectron valence-band and inner-shell spectra of CoO are presented and interpreted using the molecular-orbital theory for the CoO_6^{10-} cluster and the sudden approximation (monopole selection rules). The spectra are shown to exhibit the effects of monopole charge-transfer shake-up (O $2pe_g \rightarrow$ Co $3de_g$), multiplet splitting, and crystal-field splitting. The structure of Co $3d$ levels in CoO ($3d^7$) is broader than that of Ni $3d$ levels in NiO ($3d^8$), in agreement with the energy levels of the final hole state estimated from the Tanabe and Sugano diagrams for the d^6 and d^7 configurations. Shake-up satellite structures lying 5 to 10 eV below the main peaks in the Co inner-shell and valence-band levels suggest that the CoO optical-reflectance structure at 5.5 and 7.5 eV is associated with O $2p \rightarrow$ Co $3d$ transitions.

I. INTRODUCTION

X-ray-photoelectron spectroscopy (XPS or ESCA) has been used extensively to elucidate the electronic structure of the first-row transition-metal compounds. A number of studies have focused on satellite structures in both cation inner-shell and valence-band levels which arise from multielectron excitation (electron shakeup) and multiplet splitting,[1–13] since they provide information regarding the valence electronic structure of transition-metal compounds in addition to the x-ray photoionization processes in solids. However, the interpretations of satellite structure are in considerable disagreement. As discussed in detail in Refs. 6–8, part of the disagreement arose from contribution to XPS spectra from surface contaminants on the bulk species. For example, in earlier XPS studies of NiO the presence of a surface species, which is believed to be Ni_2O_3 (a gross surface-defect structure of NiO),[7,8,14,15] was not accounted for and all spectral data including those of Ni_2O_3 were characterized in terms of NiO. On the other hand, surface contaminants were erroneously reported to cause multielectron excitation in transition-metal compounds such as NiO, CuO, and Cu_2O.

Because of the surface sensitivity of XPS and the presence of surface contaminants on most of the samples exposed to air, the preparation and maintenance of clean surfaces or at least the careful evaluation of contributions to spectra from surface species is necessary to study the electronic structure of the bulk species using XPS data. One must be careful of surface contamination, particularly in XPS studies of oxides. According to a number of XPS studies on oxygen and air-exposed oxide surfaces which have been carried out because of their diverse catalytic and electrochemical properties, surface species exhibiting a regular crystal structure in higher-oxidation states,[16] gross defect structure[7,8,14] and polymorphism,[17] hydroxides or hydrates,[17] and carbonates[18] are usually present. Recently Hüfner and Wertheim[4] reported the XPS valence-band spectra of a number of transition-metal compounds including CoO. As will be discussed later, their CoO spectrum is similar to that of CoO covered with Co_3O_4. In this paper the CoO XPS spectra are presented and interpreted using the molecular-orbital theory for the CoO_6^{10-} cluster and monopole selection rules, in accordance with the interpretations of XPS spectra of other transition-metal compounds such as NiO and CuO.[6–8] Satellite structures lying 5–10 eV below the main peaks in the Co inner-shell and valence-band levels are attributed to monopole charge-transfer transitions (O $2pe_g \rightarrow$ Co $3de_g$) accompanying the primary photoionization process.

II. X-RAY-PHOTOELECTRON SPECTRA OF CoO

Spectra were recorded on a Hewlett-Packard 5950A ESCA spectrometer using monochromatic Al $K\alpha_{1,2}$ x rays. A detailed description of the spectrometer including accessories has been reported elsewhere.[14] The base pressure in the vacuum system has been improved by a titanium sublimation pump and a controlled-atmosphere box (Vacuum Atmosphere Co.) placed around the probe. The box was filled with N_2 (O_2 and $H_2O < 4$ ppm). The base pressure in the spectrometer was (2–5) $\times 10^{-9}$ Torr, and according to the residual-gas analysis the partial pressures of H_2O and O_2 were in the high 10^{-10}-Torr range. The full width at half-maximum band (FWHM) for the Au $4f_{7/2}$ peak obtained from clean Au foil was 0.8 eV under the experimental conditions in this work. Binding energies were referenced to the Au $4f_{7/2}$ peak at 83.8 eV or the Fermi level of Au evaporated onto the sample *in situ*. The thickness of the evaporated Au was equivalent to about 10 Å as determined from its XPS intensity. Such a Au phase is in discontinuous islands or particles and still exhibits the bulk XPS characteristics (i.e., its Au $4f_{7/2}$ binding energy is 83.8 eV) and experiences the same charging as the substrate.[19]

CoO (packed under Ar) and Co_3O_4 in powder form were obtained from Alfa and RIC/ROC. They were burnished on a gold plate with a sapphire bead in the atmosphere-controlled box filled with N_2 without exposing to air. A sample transfer device was used to permit evacuation before the sample was introduced into the atmosphere-controlled box. Co_3O_4 was also prepared by heating Co foil in air at (600–1200) °C. (The heated Co foil was placed in the sample transfer device, which was evacuated immediately.) Although Co is oxidized in air to a mixture of CoO and Co_3O_4 at (400–885) °C and to CoO at (900–1350) °C according to Paidassi *et al.*,[20] the XPS spectra of Co foils oxidized at (600–1200)°C were identical to those of the authentic Co_3O_4. This indicates that Co foils oxidized in the temperature range (600–1200) °C are covered with Co_3O_4 layers of at least 50 Å.

The XPS valence-band, Co inner-shell (2*s*, 2*p*, 3*s*, and 3*p*), and O 1*s* and 2*s* spectra of CoO are shown in Fig. 1, and the CoO XPS spectral features are summarized in Table I. The contribution to the XPS spectra from a surface species whose presence on the sample is indicated by a minor O 1*s* peak at 531.3 eV (peak 14) should be minimal. Since the intensity of peak 14 increased as the sample was exposed to oxygen *in situ*, the surface species is formed by interaction of CoO with oxygen; however, its identity is uncertain at this time. Very little carbon was detected: The (C 1*s*)/(O 1*s*) intensity ratio was less than 0.02. The XPS spectra of CoO shown in Fig. 1 agree well with those obtained from a cleaved single crystal by Pollak,[15] except the Co 2*s* spectrum, where he observed a single broad peak but not a shoulder (peak 21), probably because of low signal-to-noise ratio.

The XPS valence-band spectrum of Co_3O_4 shown in Fig. 2 similar to that of CoO reported by Hüfner and Wertheim,[4] except that the broad structure centered at 11.3 eV is not as clearly seen in their spectrum, probably because of lower signal-to-noise ratio. It is to be noted that they prepared CoO by heating Co in air and that, as mentioned above, in such preparations the surface layers sensitive to XPS measurement consist of Co_3O_4.

III. RESULTS AND DISCUSSION

The cluster or molecular-orbital model has provided a useful basis to describe electronically excited states of photoionized transition-metal compounds because shakeup satellite structures in the cation core and valence shells are attributable to monopole charge-transfer transitions (anion or ligand→ metal 3*d*).[6–8] The author[7] has shown that the XPS 3*d* valence electronic structure in NiO ($3d^8$) also can be explained within the framework of the ligand field and therefore molecular-orbital theory. The relative energy levels of the cluster photoionized in the 3*d* shell were estimated semiempirically from Tanabe and Sugano's diagram[21] for the d^7 confirguration. The XPS data of CoO will be interpreted similarly. Hüfner and Wertheim[4] have shown that the XPS 3*d* structure in insulating $3d^n$ compounds can be identified with the crystal-field states of the $3d^{n-1}$ final state.

Since the ground state[22] of CoO is $^4T_{1g}\,(t_{2g})^5\,(e_g)^2$, the configurations of the final hole states due to the Co 3*d* photoemission are $(t_{2g})^4(e_g)^2$ and $(t_{2g})^5e_g$. The allowed final states and their expected relative intensities are listed in Table II. Their relative energy levels can be determined using Tanabe and

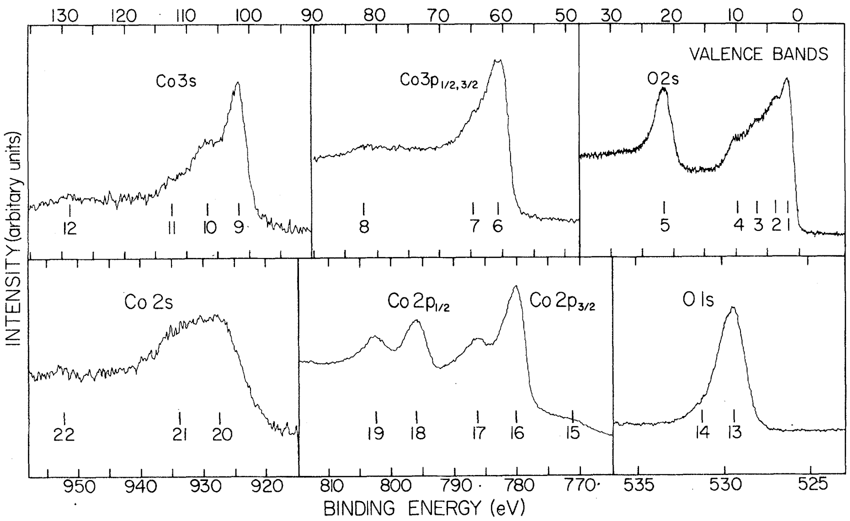

FIG. 1. X-ray-photoelectron inner-shell and valence-band spectra of CoO.

TABLE I. Assignments of the x-ray-photoelectron spectra of CoO.[a]

Peak number	Binding energy (eV)	Assignments	
		This work	Ref. 5.
Valence bands			
1	1.8	Co $3d$ ($e_g\alpha, t_{2g}\beta$)	Co $3d$ ($e_g\alpha, t_{2g}\beta$)
2	3.8	Co $3d$ ($t_{2g}\alpha, \beta$)	Co $3d$ ($t_{2g}\alpha$)
3	6.8	O $2p$	O $2p$, ME and EL
4	9.8	ME (O $2p \rightarrow$ Co $3d$)	O $2p$, ME and EL
O $2s$			
5	21.5		
Co $3p_{3/2,1/2}$			
6	60.4	MS	
7	64.4–69.5	MS[b], ME (O $2p \rightarrow$ Co $3d$)[c]	
8	81.4	EL	
Co $3s$			
9	101.8 (1.0, 3.2)[d]	MS	
10	106.5 (0.9, 6.2)[d]	MS[b], ME (O $2p \rightarrow$ Co $3d$)[c]	
11	112.5 (0.2, 6.2)[d]	MS or ME (O $2p \rightarrow$ Co $3d$)[c]	
12	126.4	EL	
O $1s$			
13	529.5 (1.0, 1.5)[d]	CoO	
14	531.3 (0.08, 1.5)[d]	Surface contaminant	
[e]	552.0	EL	
$L_3M_{2,3}M_{4,5}$			
15	771.3	Auger structure	
Co $2p_{3/2}$			
16	780.0		
17	786.3	ME (O $2p \rightarrow$ Co $3d$)	
Co $2p_{1/2}$			
18	800.8		
19	807.5	ME (O $2p \rightarrow$ Co $3d$)	
[e]	828.5	EL	
Co $2s$			
20	927.9 (1.0, 7.4)[d]		
21	933.5 (0.8, 7.2)[d]	ME (O $2p \rightarrow$ Co $3d$)	
22	962.5	EL	

[a] ME: multielectron excitation (electron shakeup); MS: multiplet splitting; EL: energy loss.

[b] Main contribution.

[c] See text.

[d] The relative intensity and FWHM are given in parentheses. The binding energy, intensity, and FWHM were determined by curve deconvolution with Gaussian peak shapes using a Du Pont 310 curve resolver.

[e] Not shown in Fig. 1.

Sugano's diagram for the d^6 configuration. Using a Dq value of 0.19 eV and a B value of 0.106 eV, the energy levels listed in Table II have been determined. [According to Cherkashin and Vilesov,[24] Dq for Co^{3+} in an octahedral coordination of the O^{2-} ions is 0.19 eV. Since B for CoO is 20% smaller than that of the free Co^{2+} (see Ref. 25) and B for free Co^{3+} is 0.132 eV, B for Co^{3+} in CoO is estimated to be 0.106 eV.] Then, as shown in Tables I and II, peak 1 may be attributed to $t_{2g}\beta$ and $e_g\alpha$, and peak 2 to $t_{2g}\alpha$ and β (see below). It is to be noted that peak 2 is lower but broader than peak 1 and therefore peaks 1 and 2 are almost equally intense, as expected from the results given in Table II.

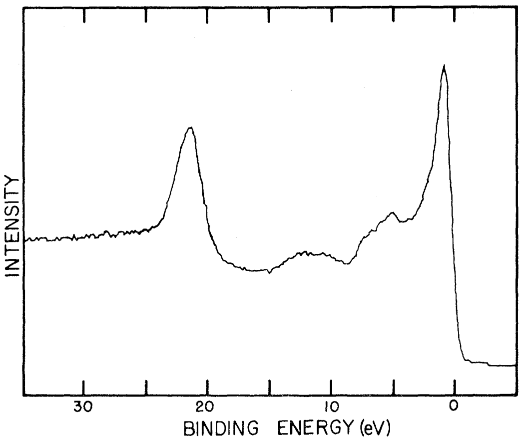

FIG. 2. X-ray-photoelectron valence-band spectrum of Co_3O_4 prepared by heating Co foil in air at 1100 °C.

Peak 3 centered at 6.8 eV is attributed to the O $2p$ photoemission because in the uv photoemission spectrum[26] the corresponding peak is much stronger than the Co $3d$ structure, whereas in the XPS spectrum peak 3 is weaker than the Co $3d$ structure. It is to be noted that the intensity of O $2p$ levels will increase with decreasing $h\nu$ relative to that of Co $3d$ levels.[27] The location of the O $2p$ structure in the XPS valence-band spectrum of NiO (peak 4 in Fig. 3) was also determined[7] based on the uv photoemission data. As discussed below, a broad structure at 9.8 eV (peak 4) is attributable to electron shakeup accompanying the Co $3d$ photoemission.

Satellite lines in transition-metal ions usually arise from either multielectron excitation (electron shakeup) or multiplet splitting. Assignment of shakeup satellite structure in transition-metal compounds has generated some controversy. However, the author believes that shakeup in transition-metal ions can be adequately interpreted in terms of monopole charge-transfer processes (anion or ligand→ metal $3d$) using the sudden approximation (monopole selection rules) and the molecular-orbital theory for the cluster model. The charge-transfer interpretation is based on the study of

TABLE II. Energy levels of the final states due to the 3d photoemission in CoO and NiO which are estimated from Tanabe and Sugano's diagrams.

	Configuration	Term[c]	Energy (eV)	Intensity ratio[d]	Peak number
CoO[a]					Fig. 1
Initial state	$(t_{2g})^5(e_g)^2$	$(^2T_{2g}\times{}^3A_{2g})\,{}^4T_{1g}$			
Final states	$(t_{2g})^4(e_g)^2$	$(^3T_{1g}\times{}^3A_{2g})\,{}^5T_{2g}$	0.0	$1.25(2\times\frac{5}{8})$	1
		$(^1A_{1g}\times{}^3A_{2g})\,{}^3A_{2g}$	4.3	$\frac{1}{3}$	2
		$(^1E_g\times{}^3A_{2g})\,{}^3E_g$	3.5	$\frac{2}{3}$	2
		$(^3T_{1g}\times{}^3A_{2g})\,{}^3T_{2g}$	2.8	$0.75(2\times\frac{3}{8})$	2
		$(^1T_{2g}\times{}^3A_{2g})\,{}^3T_{1g}$	2.6	2	2
	$(t_{2g})^5e_g$	$(^2T_{2g}\times{}^2E_g)\,{}^3T_{2g}$	1.6	1	1
		$(^2T_{2g}\times{}^2E_g)\,{}^3T_{1g}$	1.0	1	1
NiO[b]					Fig. 3
Initial state	$(t_{2g})^6(e_g)^2$	$^3A_{2g}$			
Final states	$(t_{2g})^5(e_g)^2$	$(^2T_{2g}\times{}^3A_{2g})\,{}^4T_{1g}$	0.0	3	1
		$(^2T_{2g}\times{}^3A_{2g})\,{}^2T_{1g}$	2.1	3	3
	$(t_{2g})^6e_g$	^2E_g	0.6	2	2

[a] $Dq=0.19$ eV and $B=0.106$ eV. See text.

[b] $Dq=0.18$ eV and $B=0.11$ eV. See Ref. 7.

[c] The allowed final states are chosen from the terms of the $t_{2g}^{m-1}\,e_g^n$ and $t_{2g}^m\,e_g^{n-1}$ configurations for the t_{2g} and e_g ionizations, respectively, considering that the initial term for the un-ionized shell is conserved. It is convenient to use the tables in the appendices of Ref. 23.

[d] It is assumed that the x-ray photoionization cross sections for t_{2g} and e_g are nearly the same. Then the intensity ratio of the final states is determined by the following steps: (a) The total intensities of the final states arising from the t_{2g} and e_g ionizations are proportional to the number of electrons present initially in each shell. (b) The total intensity of the $t_{2g}\alpha$ final states is proportional to the initial number of $t_{2g}\alpha$ electrons. The same applies to the $t_{2g}\beta$ and $e_g\alpha$ and β final states. (c) If more than one final state arises from one electron ionization, their intensity is proportional to their degenercy arising from spin and orbital. For example, the intensities of the $^5T_{2g}$ and $^3T_{2g}(t_{2g})^4(e_g)^2$ states of CoO are $2\times\frac{5}{8}$ and $2\times\frac{3}{8}$, respectively.

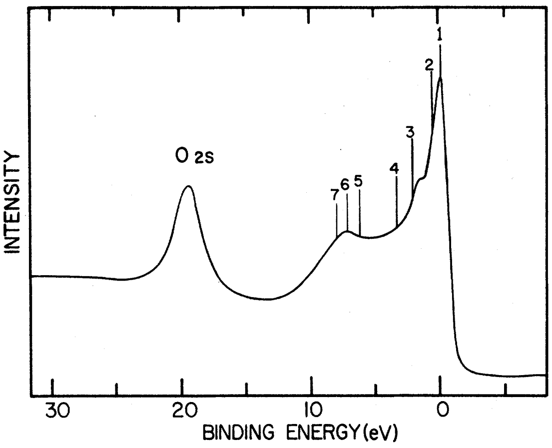

FIG. 3. X-ray-photoelectron valence-band spectrum of NiO (from Ref. 7). The energy is referenced to peak 1, which is 1.7 eV below the Fermi level of Au. The locations of peaks 2–7 and the O 2*s* peak are 0.6, 2.1, 3.3, 6.4, 7.2, 7.9, and 19.5 eV, respectively. Peaks 1–3 are attributable to the Ni 3*d* photoemission (see Table II), peak 4 to the O 2*p* photoemission, and the structure representing peaks 5–7 to charge transfer shakeup (O $2p \rightarrow$ Ni $3d$).

many different transition-metal compounds. A list of reasons has been discussed in detail elsewhere.[6–8] Additional evidence has been reported recently: the presence of satellites in transition-metal compounds with a $3d^0$ configuration such as Sc_2O_3, TiO_2, $SrTiO_3$, etc.[28–31] From the energetic viewpoint in these cases the observed satellites are attributable only to charge-transfer shakeup (anion → metal 3*d*). The fact that these compounds show shakeup satellites in the spectra of an anion as well as a cation indicates strong anion-cation orbital interaction, in agreement with the L_{III} x-ray emission results,[32] and therefore their charge-transfer origin.[31] (Note that heavier transition-metal compounds such as NiO and CuO show distinct shakeup satellites only in their cations.)

Photoemission of an electron with quantum numbers h from the N-electron system Ψ_0 can be written as

$$\Psi_0(N) + \text{photon} \rightarrow [\Psi_n^h(N-1)]^0 + e$$

where the superscript zero denotes the relaxed state corresponding to Hartree-Fock solutions of the remaining $(N-1)$-electron system. Simultaneous excitation of a valence electron from ψ_i to ψ_j^0 (shakeup) causes a satellite (Ψ_n^{h0}) below the main peak (Ψ_0^{h0}). Although the over-all process is governed by dipole selection rules, the main shakeup satellite structure in transition-metal compounds can be explained by monopole selection rules [i.e., for an atomic model $\Delta J = \Delta M_J = 0$ between Ψ_0^{h0} and Ψ_n^{h0} and $\Delta j = \Delta l = \Delta m_l = \Delta m_s = 0$ between ψ_i and ψ_j^0], according to the sudden and Hartree-Fock approximations.[33,34] These approximations and therefore monopole selection rules are less valid when the photon energy is relatively low or when electron correlation is strong. Shakeup satellite structures in He 1*s* and Ne 2*p* levels have been studied as a function of the photon energy.[35] These studies show that monopole shakeup structures are predominant even near the threshold, although dipole shakeup, in which the outgoing electron retains the angular momentum and the excited electron experiences the angular momentum change $\Delta l = \pm 1$, becomes important with decreasing photon energy. When correlation is strong between the outgoing electron and valence electrons, shakeup which involves a two-electron excitation to a configuration interaction state (i.e., $\Delta J = \Delta M_J = 0$, but without the angular-momentum conservation for the excited electrons) can occur. Such configuration interaction satellites have been observed in alkali ions[36] and noble gases,[37] but not in transition-metal ions. Therefore, shakeup satellite structure in the XPS spectra of transition-metal compounds can be interpreted in terms of monopole selection rules.

In CoO, as shown in Fig. 4, the allowed shakeup transitions are of the charge-transfer type such as

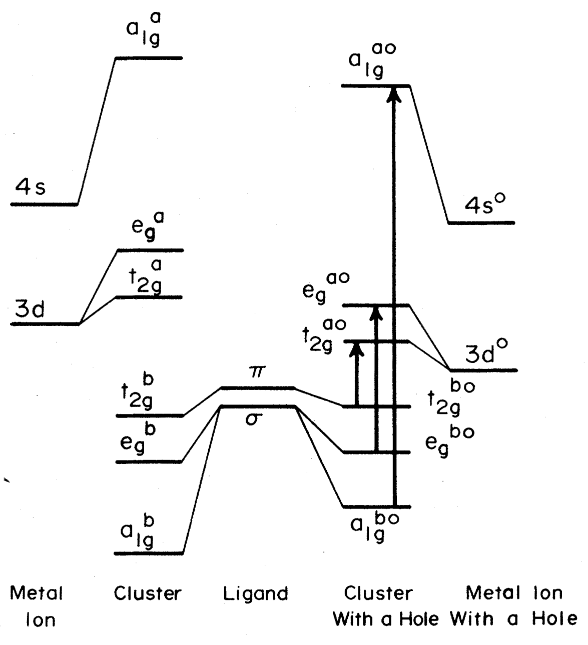

FIG. 4. Schematic energy separation between the main peak and possible monopole satellites in an octahedral cluster CoO_6^{10-}, $^4T_{1g}$ $(3dt_{2g})^5(3de_g)^2$. Only orbitals involved in shakeup are shown. The effects of orbital relaxation (Ref. 6) due to a photoionized vacancy are schematically shown in the right-hand side. The effects of exchange splitting are not shown.

O $2pt_{2g} \rightarrow$ Co $3d^0t^0_{2g}$, O $2pe_g \rightarrow$ Co $3d^0e^0_g$, O $2pa_{1g} \rightarrow$ Co $4s^0a^0_{1g}$, etc. The satellite due to O $2pe_g \rightarrow$ Co $3d^0e^0_g$, for example, is separated from the main line by the O $2p^0e^0_g \rightarrow$ Co $3d^0e^0_g$ transition energy (see below). Hereafter the superscript zero will be omitted, unless otherwise noted. Since Cu^+ and Zn^{2+} ions with a $3d^{10}$ configuration do not show any satellite lines, O $2pa_{1g} \rightarrow$ Co $4sa_{1g}$ shakeup is not expected to be important.[6] On the other hand, since O $2p$ - Co $3d$ mixing is stronger in e_g orbitals than in t_{2g} orbitals, the shakeup probability of O $2pe_g \rightarrow$ Co $3de_g$ will be greater than that of O $2pt_{2g} \rightarrow$ Co $3dt_{2g}$,[31] and therefore shakeup satellite structure in CoO is primarily attributable to the former shakeup. Even in $3d^0$ compounds M_xL_y where more $L\ \pi t_{2g} \rightarrow M\ 3dt_{2g}$ transitions are allowed than in CoO, only shakeup satellite structure arising from $L\ \sigma e_g \rightarrow M\ 3de_g$ transitions is clearly observable.[31]

Multiplet splitting in $3s$ and $2s$ shells of the first-row transition-metal ions in solids has been studied both theoretically and experimentally by several groups.[9-13] However, since satellites arising from both shakeup and multiplet splitting in transition-metal ions, except Ni^{2+} ($3d^8$) and Cu^{2+} ($3d^9$) ions, can appear in the same energy region of 4–10 eV below the main peaks in the core levels, their contribution must be determined through careful analysis in each core level. In the core levels of Ni^{2+} and Cu^{2+} ions, multiplet splitting is less than 4 eV, whereas shakeup excitation energies are 5–10 eV.[6] The following points are useful in the analysis of satellite structure in transition-metal ions.

(i) Shakeup satellite structures in the $1s$, $2s$, and $2p$ shells will be similar both in intensity and location. Smaller shakeup structure will be seen in the $3s$ and $3p$ than in the deeper shells because of the smaller change in the effective nuclear charge of the valence electrons when a $3s$ or $3p$ rather than a deeper electron is removed. Shakeup structure in the $3d$ valence shell can be as strong as those in the $2s$ and $2p$ shells because of strong correlation effects. These have been observed in Ni^{2+} ($3d^8$) and Cu^{2+} ($3d^9$) compounds such as NiO and CuO.[6,7]

(ii) To explain multiplet structure, it is important to take into account electron correlation effects (by means of the configuration interaction method) when a vacancy occurs in the same shell (i.e., $3s$) as the open shell.[9,10] Correlation effects are much less important when a vacancy occurs in another shell (i.e., $2s$). When a vacancy occurs in the $3s$ shell, configurations arising from the $3p^2 \rightarrow 3s3d$ excitations will mix strongly with the Hartree-Fock configuration because of their near degeneracy. The main multiplet splitting in $2s$ and $3s$ shells is roughly proportional to the number of unpaired $3d$ electrons.[11,12] For example, since MnF_2 shows weak shakeup structure 6.5 eV below the main Mn $2p_{3/2}$ peak[3,6,30] [the satellite/(main peak) intensity ratio is about 0.1], the strong satellite structures centered at 5.9 and 6.5 eV below the main peaks in the Mn $2s$ and $3s$ shells are attributable mostly (but not totally) to multiplet splitting.

Since multiplet splitting in the $2s$ shell of Mn^{2+} ions ($s=\frac{5}{2}$) is about 6 eV (MnO, 5.6 eV; MnF_2, 5.9 eV),[9-11] a 5.6-eV separation between peaks 20 and 21 in the Co $2s$ shell of CoO ($s=\frac{3}{2}$) is too large to be attributed to multiplet splitting. Therefore, peak 21 is attributed to O $2pe_g \rightarrow$ Co $3de_g$ shakeup. Satellite structures (peaks 17 and 19) in the Co $2p_{1/2,3/2}$ regions are also assigned to the same shakeup because they are similar to peak 21 in the Co $2s$ region in both intensity and location. Similar results have been obtained from NiO and CuO.[6-8] The unusually broad widths of peaks 20 and 21 are believed to be caused by multiplet splitting in addition to Coster-Kronig processes.

Let us consider photoemission in the Co $3s$ shell of CoO ($^4T_{1g}$) without inclusion of configuration interaction in multiplet splitting. Then, the final states are $^{5,3}T_{1g}$. Since the peak-10/peak-9 intensity ratio (0.9) is much stronger than $2S/(2S+2) = 0.6$ and since peak 10 is much broader than peak 9 (6.2 vs 3.2 eV), peak 10 is not attributable totally to the multiplet $^3T_{1g}$, although peak 9 is attributable to $^5T_{1g}$. The presence of strong shakeup satellite structures centered at 6–6.5 eV below the main peaks in the Co $2p_{3/2,1/2}$ and $2s$ regions suggests that peak 10 arises from both multiplet splitting and shakeup. Thus its low-binding-energy side is contributed from the former and its high-binding-energy side from shakeup. Then peak 11 is attributable to shakeup associated with the multiplet part of peak 10. If correlation effects are taken into consideration, the interpretation of the Co $3s$ spectrum is difficult. For example, using a free-ion model (the ground state of Co^{2+} is ^4F), the Co $3s$-hole final states are two ^5F and five ^3F multiplets, even if configurations due only to $3p^2 \rightarrow 3s3d$ excitations are included. A detailed theoretical calculation is required to understand the Co $3s$ spectrum. The main cause of the Co $3s$ multicomponent structure seems to be multiplet splitting. Although strong shakeup satellite structures are present in the Co $2s$ and $2p$ shells, contribution to the Co $3s$ spectrum from shakeup may be concluded to be small based on the presence of only weak 6-eV structure in the Co $3p$ spectrum. In the Co $3p$ region satellite structure is not clearly defined as in the Co $3s$ region. The main part of peak 7 is believed to arise from multiplet splitting and its high-binding-energy side from shakeup.

Weak satellite structures lying about 20 eV below the main peaks in the Co $2s$, $2p$, $3s$, and $3p$ and O $1s$ regions are assigned to characteristic energy loss. The 20-eV structure will not be seen in the O $1s$ region if it arises from shakeup, because the O $1s$ spectrum does not even show satellite structure due to O $2pe_g \to$ Co $3de_g$ shakeup. Energy-loss peaks will be seen at the same separation below each peak of both cation and anion. Therefore, the assignment of peaks 3 and 4 partly to energy loss[5] is somewhat questionable because the corresponding structure is not observed in the O $1s$ region. As discussed elsewhere,[31] it is important to study the spectra of both cation and anion for identification of satellite lines.

The assignments given above are summarized in Table I. Let us consider why shakeup satellite structure (peak 4) in the valence-band region lies below the O $2p$ structure (peak 3). It is convenient to use a one-electron model. Since the exchange splitting is approximately equal to the crystal-field splitting (~ 2 eV), the order of orbitals will be $2p\sigma < 2p\pi < 3dt_{2g}\alpha < 3dt_{2g}\beta \sim 3de_g\alpha < 3de_g\beta$ (unoccupied). Note that peaks 1 and 2, whose separation is 2 eV, are primarily associated with $3dt_{2g}\beta$ and $3de_g\alpha$, and $3dt_{2g}\alpha$, respectively (see Tables I and II). Therefore, the separation between the O $2p$ structure (peak 3) and the shakeup structure due to $2p\sigma(e_g)\beta$(or α) $\to 3de_g\beta$(or α) accompanying the Co $3d$ photoemission will be larger than at least the exchange splitting (~ 2 eV), in agreement wit the XPS data. The interpretation of peak 4 in terms of charge-transfer shakeup is also consistent with those of similar satellite structures in the valence-band spectra of NiO and CuO.[6,7] It is difficult to assign peak 4 (in addition to peak 3) to the O $2p$ levels because similar satellite structure is not seen in transition-metal compounds with a completely filled $3d$ shell (i.e., Cu_2O)[6,8] and because the intensity ratio (~ 1.4) of peaks 3 and 4 to the O $2s$ structure (peak 5) is too large. The XPS (O $2p$)/(O $2s$) peak-intensity ratio for a free oxygen atom[38,39] is less than 0.35 and the observed ratios for Sc_2O_3 and TiO_2,[40] with a $3d^0$ configuration, are about 0.5. It is to be noted that Sc_2O_3 and TiO_2 are more covalent than CoO and the covalency will increase the XPS O $2p$ cross section and therefore the (O $2p$)/(O $2s$) intensity ratio.

Direct comparison between photoemission and optical data is impossible, in principle, because photoemission spectra reflect the energy of the ionized state, whereas optical spectra reflect the energy of the nonionized state. The CoO optical data may therefore be compared with the XPS valence-electronic data of NiO if the effects of the larger nuclear charge on Ni^{2+} are taken into consideration. Since the increase of the nuclear charge by unity decreases O $2p \to M$ $3d$ transition energies only by 1–2 eV,[6] structure at 5.5 and 7.5 eV in the CoO reflectance spectrum[26] may be attributed to O $2p$ $\to$ Co $3d$ transitions based on shakeup satellite data in the XPS valence-band spectrum of NiO, shown in Fig. 3. The same conclusion can be obtained based on shakeup satellite data in the Co core shells of CoO, since a core vacancy decreases O $2p \to$ Co $3d$ transition energies only by 1–2 eV.[6] For example, since the separation between the main peak and shakeup satellite in the Co $2s$ region is 5.6 eV (this will be the average value for $2p^0e_g^0\alpha \to 3d^0e_g\alpha$ and $2p^0e_g^0\beta \to 3d^0e_g^0\beta$), the corresponding optical transitions ($2pe_g\alpha \to 3de_g\alpha$ and $2pe_g\beta \to 3de_g\beta$) will appear at 6.6–6.7 eV.

It should be emphasized that the use of CoO_6^{10-} cluster in this paper is confined to the description of photoionization, including shakeup, and optical transitions from O $2p$ to Co $3d$. There are delocalized features of the crystal electronic structure and related electrical, magnetic, and optical properties which are better described in terms of the band theory. Mattheiss,[25] who uses the augmented-plane-wave (APW) method, predicts a set of $3d$ bands of 3-eV width, separated by a 4.8-eV gap from O $2p$ bands which have a width of 2 eV. The APW Co $3d$–O $2p$ width is 9.8 eV. Although it is difficult to determine these values accurately from the XPS data because of the XPS resolution (0.5 eV) and the presence of shakeup satellite structure, these values do not seem to be consistent with the XPS results. The calculated $3d$-$2p$ band gap and $3d$-$2p$ width are larger and the calculated $3d$ bandwidth is narrower than the values estimated from the XPS data. In fact, Mattheiss pointed out that his APW calculations underestimate the $3d$ bandwidth, since the calculated $10Dq$ is about 30% smaller than the experimental value and $10Dq$ is approximately proportional to the $3d$ bandwidth, and that the actual $3d$ bandwidth is greater than his APW value and is about 4 eV. He also pointed out that the $3d$-$2p$ band gap and therefore the $3d$-$2p$ width are probably overestimated. However, the APW values cannot be compared directly with photoemission data because the APW energies represent the energy differences between the initial state and hypothetical unrelaxed or frozen final hole states, whereas relaxation effects enter into photoemission experiments. If the values for the $3d$-$2p$ gap and the $3d$-$2p$ width determined from the XPS data are corrected to remove the effects of relaxation and then to compare with the APW values, they will probably decrease becasue the relaxation energy due to the Co $3d$ photoemission is greater than that due to the O $2p$ photoemission,[7] disagreeing more with the APW values obtained by Mattheiss. Although the features of the APW band structure may be modified if the calculations are taken to self-consistency or if a different exchange approximation is used to construct the crystal potential,[25] the author feels that a molecular-orbital model and the final-state description more satisfactorily account for the XPS data of CoO near the Fermi level, as in the case of NiO. Since their optical-absorption structure arising from $3d \rightarrow 3d$ transitions can be explained in terms of multiplet and crystal-field splitting effects,[22,41] it is quite reasonable that their main $3d$ XPS structures or the ionized final states can be explained in terms of the same effects. In a one-electron band model, the $3d$ XPS structure may be explained by the initially occupied density of states. However, the presence of shakeup satellites which are closely related to hole-electron and electron-electron interactions and simultaneous orbital relaxation is not in favor of the initial-state description and a one-electron band model. In addition, the $3d$ orbitals in these oxides have been proposed to be rather localized, even though their description is in considerable disagreement.[25,42,43] It is to be noted that the x-ray absorption and emission spectra of transition-metal oxides have also been successfully explained in terms of a molecular cluster.[44] These spectra like XPS reflect the energy of the relaxed ionized final states.

The broad satellite structure centered at 11.4 eV in the XPS valence-band spectrum of Co_3O_4 (Fig. 2) is tentatively assigned to charge-transfer shakeup (O $2p \rightarrow$ Co $3d$), because similar structures are seen in the Co core shells. Shakeup satellite structures in both Co core and valence shells of Co_3O_4 are weaker than those of CoO. Further analysis of the Co_3O_4 XPS data is in progress.

IV. SUMMARY AND CONCLUSIONS

The XPS valence-band and inner-shell spectra of CoO exhibit the effects of crystal-field splitting, multiplet splitting, and electron shakeup.

(i) The XPS valence-band spectrum of CoO is composed of 4–5-eV-wide Co $3d$ levels with structure at 1.8 and 3.8 eV, a 4-eV-wide O $2p$ structure centered at 6.8 eV, and a 6-eV-wide structure centered at 9.8 eV which arises from monopole charge-transfer transitions (O $2pe_g \rightarrow$ Co $3de_g$) accompanying photoemission in the Co $3d$ shell. The XPS Co $3d$ structure in CoO is broader than the Ni $3d$ structure in NiO (4–5 vs 3 eV), in agreement with the energy levels of the final states estimated from Tanabe and Sugano's diagrams for the d^6 and d^7 configurations.

(ii) Satellite structures centered at about 6 eV below the main peaks in the Co $2s$, $2p$, $3d$, and possibly $3s$ and $3p$ shells arise from O $2pe_g \rightarrow$ Co $3de_g$ shakeup transitions. These results suggest that the CoO reflectance structure at 5.5 and 7.5 eV is associated with O $2p \rightarrow$ Co $3d$ transitions.

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