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X-ray Photoelectron Spectrum of Low-Spin Co(III) in $LiCoO_2$

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The X-ray photoelectron spectra for $LiCoO_2$ and the related oxides have been studied. The diamagnetic cobaltic ion in $LiCoO_2$ had the shake-up satellite peaks for cobalt subshells, and their relative intensities to the primary peaks for M subshells were larger than those for L_{II} and L_{III}. Valence band spectrum suggested that less than 75% of Co 3*d* electrons contributed to $2t_{2g}$ molecular orbital.

The trivalent cobalt ions in some oxides can have either the low-spin (t_{2g}^6) or the high-spin ($t_{2g}^4e_g^2$) configuration, and the configuration defines the electronic and magnetic properties. Several XPS studies on the oxides containing low-spin Co^{III} have been reported (*1–5*), and the oxides contained Co^{2+} or high-spin Co^{3+}, except $ZnCo_2O_4$ (*3*). It was reported that intense satellite peaks in Co 2*p*, 3*s*, and 3*p* spectra were not observed for the compounds containing Co^{III} (*6*). Then it was assumed that the XPS of Co^{III} coordinated by oxygen had no shake-up satellite peaks associated with core levels (*1*, *2*, *4*). The lack of the observation of the spectrum for only Co^{III} in oxides follows the insufficient discussions in XPS for the oxides containing cobalt ions. It is anticipated that the valence band spectrum for Co^{III} may have multiple excitation peak, as Co $2p_{1/2,3/2}$ and Co 3*p* peaks for $ZnCo_2O_4$ have the shake-up peaks (*3*). The location of the Zn 3*d* peak for $ZnCo_2O_4$ in the valence band prohibits us from a lengthy discussion of the valence band spectrum of Co^{III}. $LiCoO_2$ is convenient for studying the valence band because the Li 1*s* binding energy of Li^+ is about 57 eV from the Fermi level.

It was shown that in $LiCoO_2$ having NaCl-like structure the cobaltic ions are diamagnetic (*7*). Each Co^{III} or Li^+ ion in $LiCoO_2$ is surrounded by a distorted octahedron of oxygen (*8*). In the present work, XPS for $LiCoO_2$ and the related oxides were studied in order to clarify the spectrum of low-spin cobaltic ion. The cobalt oxides, Co_3O_4, $ZnCo_2O_4$, and $Li_xCo_{1-x}O$, have low-spin cobaltic ions octahedrally coordinated by oxygen as in $LiCoO_2$. The photoionization cross-section ratios of O 2*p* to O 2*s* shells for some oxides, having no 3*d* electrons, were measured in order to compare the photoionization cross sections of the average Co 3*d* shell in cobalt oxides. The XPS of the valence band spectrum in $LiCoO_2$ was explained by molecular orbital theory.

Experimental

The experiments were performed in an AEI ES 200 electron spectrometer using achromatic Al*Kα* radiation. The C 1*s* binding energy, 285.0 eV, of contamination carbon was used as calibration to compensate for the charging effects. The reproducibilities of the binding energy values were within ±0.2 eV.

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$Li_xCo_{1-x}O$ ($x = 0.13$, 0.20, and 0.50) were prepared by calcinating the mixtures of basic cobalt carbonate and lithium carbonate at 900–1000°C in air. This method yielded the same products as Johnston's method (*8*).

The other oxides and the pretreatment for measuring were described in a previous report (*3*).

Results

Figure 1 shows the O 1*s* spectra for oxides containing cobalt ions. Their spectra had different spectral patterns despite the similar preheating temperature in air.

The O 1*s* spectrum for Co_3O_4, reported by Chuang *et al.* (*5*), had two peaks, $BE = 530.8$ and 529.6 eV, the intensity ratio of which was 0.9, but the spectrum in Fig. 1b had a small tail on the high binding energy side of the 529.5-eV peak. The spectral pattern of CoO heated in the spectrometer at 800°C was similar to that of Co_3O_4.

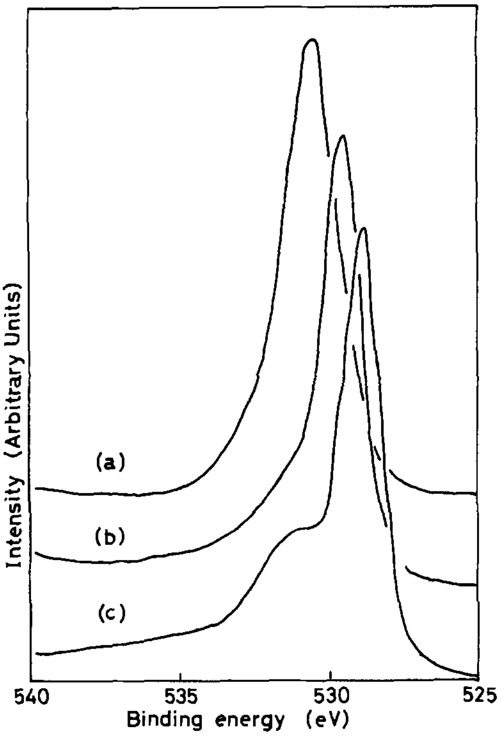

FIG. 1. XPS of O 1*s* for oxides containing cobalt ions heated in air: (a) $CoAl_2O_4$ at 1000°C, (b) Co_3O_4 at 800°C, (c) $LiCoO_2$ at 900–1000°C.

TABLE I

THE O 1*s* TO Co $2p_{3/2}$ INTENSITY RATIO OF THE OXIDES CONTAINING COBALT IONS[a]

	Experimental[b]	Theoretical[c]
CoO	0.5_0[d]	0.44
$CoAl_2O_4$	2.3_2[d]	1.76
Co_3O_4	0.6_7[d]	0.59
$ZnCo_2O_4$	1.2_4[e]	0.88
$LiCoO_2$	0.8_4[d]	0.88

[a] Co $2p_{3/2}$ intensity includes main and satellite peaks and O 1*s* intensity includes high and low *BE* components.

[b] Relative standard deviations are within 20%.

[c] From ionization cross-section ratio given in Ref. (*10*), assuming that mean free path of photoelectron is proportional to $E_K^{0.7}$ (*9*).

[d] Intensity ratios *C* 1*s*/O 1*s* are below 0.1.

[e] Intensity ratio *C* 1*s*/O 1*s* is below 0.3.

The O 1*s* spectrum for fresh $LiCoO_2$ quenched from 1000°C to room temperature in air had two distinct peaks, $BE = 530.8$ and 528.8 eV. The intensity ratio of the higher and lower binding energy peaks was about $\frac{1}{4}$. The ratio increased when the sample was exposed in air. The broad satellite peak was observed at $BE = 544$ eV.

The O 1*s* spectrum for $CoAl_2O_4$ coincided with that for Al_2O_3 in both binding energy and peak profile, and the FWHM of 2.2 eV was larger than that of 1.5 eV for Co_3O_4.

The experimental intensity ratio O 1*s*/Co $2p_{3/2}$ for oxides are given in Table I, where Co intensities include the main and satellite peaks, and the O 1*s* intensities include the higher and lower binding energy components. The ratios agree well with the theoretical ratios calculated on the assumption that the mean free path of a photoelectron depends only on $E_k^{0.7}$ (E_k: kinetic energy of photoelectron) (*9*), and that the photoionization cross-section ratio of these core levels equals the theoretical ratio (*10*). The theoretical intensity ratios were corrected by the spectrometer transition function.

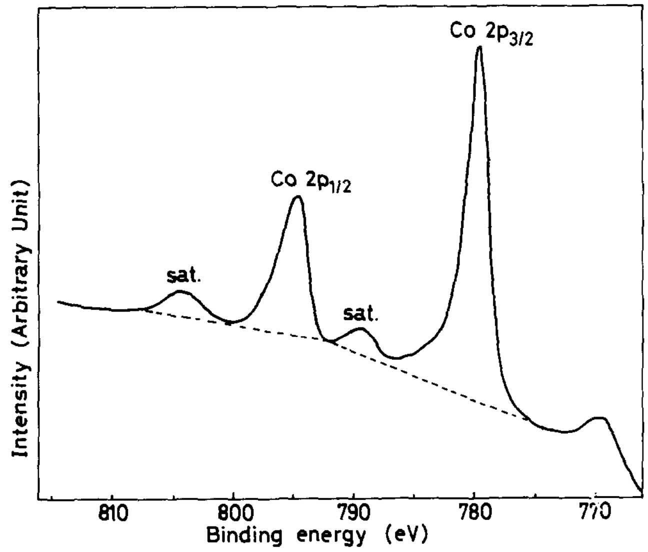

FIG. 2. XPS of Co 2*p* for $LiCoO_2$.

The spectra of cobalt core levels and valence band for $LiCoO_2$ are shown in Figs. 2–5. The sample heating at 200°C in the spectrometer yielded Co^{2+} spectra, which suggested decomposition of the sample. The spin–orbit splitting of Co 2*p* level was 15.1 eV, which is a typical value of low-spin Co^{III} compound (*6*). The binding energy of 779.5 eV of Co $2p_{3/2}$ for $LiCoO_2$ was smaller than that of 780.6 eV for $ZnCo_2O_4$. The satellite–

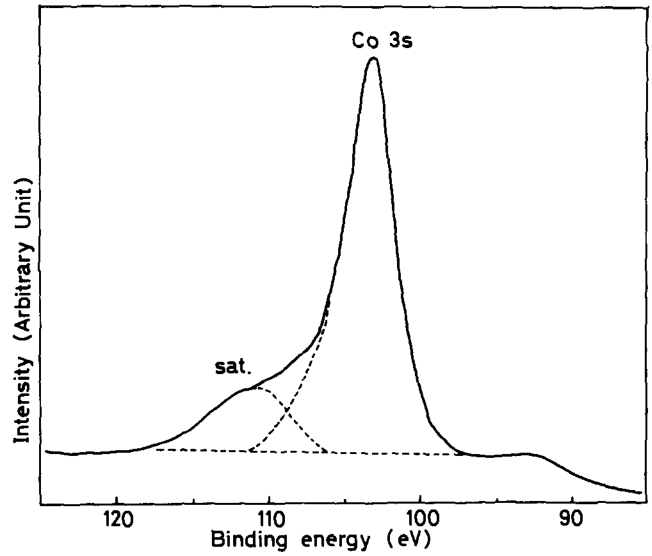

FIG. 3. XPS of Co 3*s* for $LiCoO_2$.

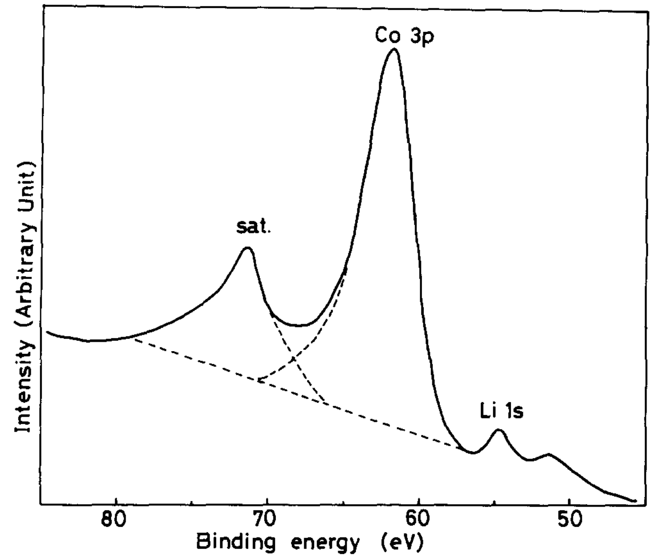

FIG. 4. XPS of Co 3*p* for $LiCoO_2$.

primary signal separation and the satellite–primary peak intensity ratio for each level are given in Table II, where the satellite peak is the difference of the total peak and the primary peak.

The powder samples of $Li_xCo_{1-x}O$ ($x \leq 0.2$) had particle sizes of about 15-μm diameter. The spectra for the sample were coincident with the spectrum of $LiCoO_2$. The Co 2*p* spectrum for ground powder $Li_{0.2}Co_{0.8}O$ sample of about 2-μm diameter is shown in Fig. 6. The Li 1*s* peak for the sample was not observed at $AlK\alpha_{3,4}$ radiation peak for Co 3*p*. After the ground sample was reheated at 900–1000°C in air for 1 hr, the spectra were entirely coincident with the spectrum for $LiCoO_2$.

$Li_xCo_{1-x}O$ has high-spin Co^{2+} and low-spin Co^{III} ions. If the surface composition of the

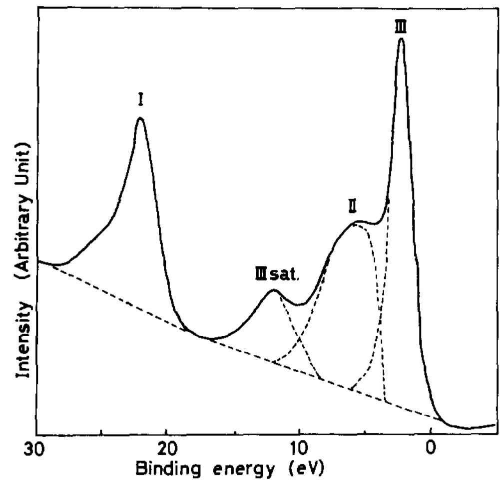

FIG. 5. XPS of valence band for $LiCoO_2$ (Roman numbers indicate the orbital group in Fig. 7).

TABLE II

THE SATELLITE–PRIMARY PEAK SEPARATION AND THE SATELLITE TO THE PRIMARY PEAK INTENSITY RATIO FOR COBALT LEVELS IN $LiCoO_2$

	Separation	Intensity ratio[a]
Co $2p_{1/2}$	9.5 eV	0.1_8
$2p_{3/2}$	10.6	0.1_0
$3s_{1/2}$	8.6	0.2_6
$3p_{1/2,\,3/2}$	9.5	0.3_8
III[b]	9.4	0.3_1

[a] Relative standard deviations are within 20%.

[b] See Fig. 5.

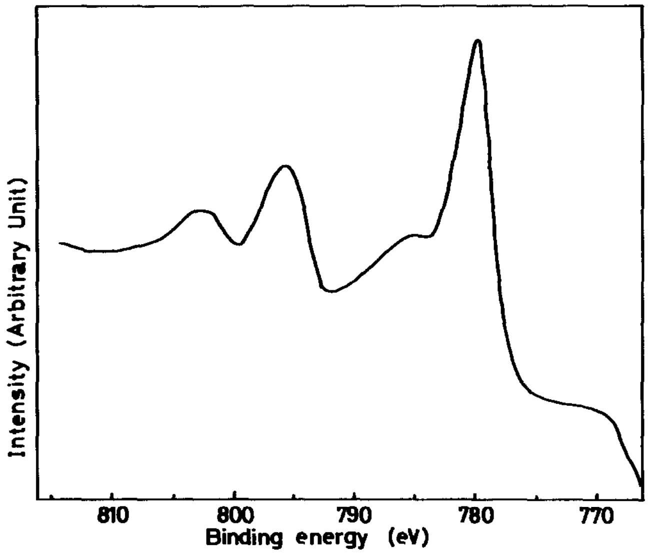

FIG. 6. XPS of Co 2*p* for ground sample of $Li_{0.2}Co_{0.8}O$.

sample was the same as the bulk composition, the ground and reheated samples should have the same spectra and the spectra should have an intermediate intensity ratio of Co 2*p* satellite peak to primary peak compared with those for CoO and $LiCoO_2$, because that Co^{2+} has high-intensity satellite peaks, and Co^{III} has low-intensity ones. If Li atoms were not present in the surface layer, the preparation conditions may give Co_3O_4 layer. These suggest that the enrichment of Li atoms on the surface layer gives $LiCoO_2$ layer on the surface of $Li_xCo_{1-x}O$.

Discussion

O 1s Spectra

The O 1*s* spectra for the cobalt–oxygen system have been summarized by Chuang *et al.* (*5*). They assigned lower binding energy O 1*s* peaks (529.4 to 530.0 eV) to stoichiometric oxygen in CoO and Co_3O_4, and higher binding energy O 1*s* peak to "nonstoichiometric oxygen" in the surface region where concentration varied with sample treatment procedure.

Cobaltous oxide is a *p*-type semiconductor with a deficit of metal (*11*). Nonstoichiometric cobaltous oxide $Co_{1-y}O$ has one crystallographically equivalent oxygen atom site. When the intensity ratio of higher binding energy O 1*s* peak to a lower one for a CoO single crystal exposed in air increased to 0.5, the Co 2*p* spectrum did not change. This may imply that higher binding energy O 1*s* is not nonstoichiometric oxygen in the surface region, but contaminant molecules containing oxygen atoms. The molecules, perhaps, may be H_2O and CO_2 (*12*) or O_2. As the amounts of the molecules on CoO and Co_3O_4 are low, the experimental ratios O 1*s*/Co $2p_{3/2}$ are coincident with the theoretical values.

It is interesting that FWHM of $CoAl_2O_4$, 2.2 eV, is larger than those of CoO and Co_3O_4, 1.5 eV.

The binding energy of O 1*s* for the molecules containing oxygen on the surface of some oxides falls in the range of 530 to 533 eV (*13–19*), and the $LiCoO_2$ has only one crystallographically equivalent oxygen site. Then it is thought that the lower and higher binding energy peaks originate from oxygen in the crystal and the molecules on the surface, respectively.

The ratio of total O 1*s* intensity to Co $2p_{3/2}$ for $LiCoO_2$ is in good agreement with the theoretical value. This means that Co $2p_{3/2}$ intensity is higher than the theoretical value. This may be due to the assumption that the escape depth of the photoelectron depends not on the material, but only on the kinetic energy of the phootelectron. As the inelastic-scattering cross section (the inverse of mean free path) of the Li atom for the Co 2*p* photoelectron is smaller than that of the Co atom (*9*), the Co 2*p* intensity may be larger than the theoretical value.

Satellites

The spectra of the low-spin cobaltic compounds have no satellites due to multiplet splittings. If the spectra of $LiCoO_2$ have only satellites arising from energy loss, O 1*s* spectrum may have similar satellite–primary signal separation of cobalt levels; however, it has only a satellite with separation of about 15 eV. The satellite is probably an energy loss peak.

It has been reported that $ZnCo_2O_4$ having low-spin Co^{III} had satellites with similar separations for each cobalt level, and no satellite for Zn 2*p* (*3*). These satellites were found in the spectra of Co_3O_4, where cobaltic ions are low-spin ions octahedrally coordinated by oxygen (*5*). These observations suggest that the satellites are associated with the Co^{III} atom or the CoO_6^{9-} cluster.

Brod'ko *et al.* explained the appearance of the satellites in cobalt compounds by the photoelectron-spin-exchange interaction with the electron of the transition element ions (*20*). The theory predicts that spin exchange between the photoelectron and paired electrons is forbidden, thus the paramagnetic Co^{2+} compounds have satellites, but the diamagnetic Co^{III} compounds have none. Then it is considered that the theory is insufficient for the satellites in $LiCoO_2$.

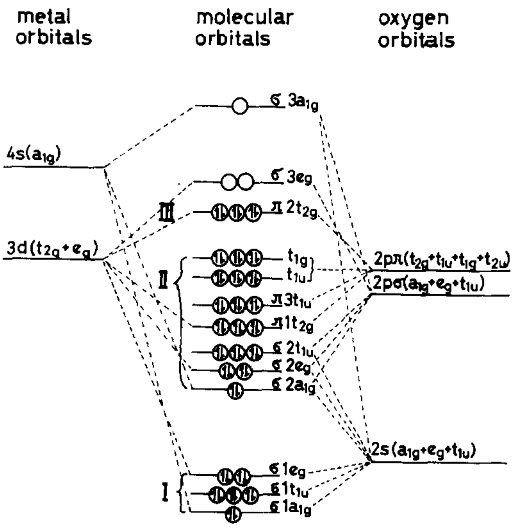

FIG. 7. Schematic atom–MO–atom energy level diagram for cobaltic ion in $LiCoO_2$ (not drawn to scale).

Many satellite lines in the transition-metal ions are usually explained as arising from multielectron excitation (electron shake up). The shake up in the transition-metal ions can be interpreted in terms of monopole charge-transfer processes (anion or ligand → metal 3*d*) using the sudden approximation (monopole selection rules) and molecular-orbital theory for the cluster model consisting of a metal and ligands (*21–23*). The sudden outer excitation is independent of the spin state of the transition-metal ions.

A schematic molecular-orbital energy diagram for low-spin cobaltic ions octahedrally coordinated by oxygen is shown in Fig. 7. As shake-up transition is a monopole transition and $2t_{2g}$ is filled, the possible transition is one from $2e_g$ to $3e_g$. The energy gap (Δ) between $3e_g$ and $2t_{2g}$ of Co^{III} in Co_3O_4 is estimated to be 2.7 eV (*24*), and the difference between peak III ($2t_{2g}$) and peak II is about 4 eV as shown in Fig. 5. Thus the energy difference of $2e_g$ and $3e_g$ for Co^{III} in $LiCoO_2$ is smaller than the satellite -primary peak separations of XPS. This may be due to the fact that Δ of the final state after photoemission is different from that of the initial state.

The low-spin complexes $[Co(en)_3]^{3+}$ and $[Co(NH_3)_6]^{3+}$ have nearly equal Δ (*25*) and satellite splittings (*26*) to those of $LiCoO_2$. On the other hand, $K_3[Co(CN)_6]$ has larger Δ, 4.3 eV (*25*), and satellite splitting, 13.3 eV (*3*). It may be considered that the larger Δ makes the complex have a larger satellite splitting and smaller satellite intensity in both cases of low-spin and high-spin complexes (MnX_2, X = F, Cl, and I) (*27*).

The XPS of low-spin cobaltic ions in $LiCoO_2$, $ZnCo_2O_4$, and Co_3O_4 had the shake-up satellite peaks, but the Co 3*s* spectrum of $YCoO_3$ has been well explained on the assumption that the low-spin cobaltic ion has no satellite peak (*4*). Then, it is thought that shake-up satellite intensity varies with the crystal field, even if the ions are coordinated by the same kind of element, oxygen, and in the same electron configurations.

In the high-spin cobalt complexes, the satellite of the Co 2*p* levels are shake-up peaks, whereas those of 3*s* and 3*p* levels are thought to arise largely from multiplet splittings of the levels (*6*). It means that the shake-up satellite intensities of 3*s* and 3*p* levels are relatively smaller than those of 2*p* levels. The calculations based on the overlap relativistic Hartree–Fock–Slater wave functions for Fe^{3+} ions indicate that the shake-up probability, as the result of photoionization in the 3*s* or 3*p* subshell, is only about $\frac{1}{3}$ of that for inner shells, 1*s* 2*s*, $2p_{1/2}$, and $2p_{3/2}$ (*28*). It is then interesting that the satellite intensities of Co *M* subshells in $LiCoO_2$ are larger than those of L_{II} and L_{III} as shown in Table II.

Valence Band

The valence spectrum for $LiCoO_2$ consists of four peaks as shown in Fig. 5.

The peak I of 22 eV may be assigned to the group I of orbitals in Fig. 7. The higher binding energy shoulder of peak I is considered to be the contaminant molecules containing oxygen on the surface layer, and its intensity is below $\frac{1}{3}$ of the major peak. As the photoelectron escape depth increases with increase of the kinetic energy of the photoelectron, it is reasonable that the intensity ratio of the molecules on the surface and crystal peaks of O 2*s* spectrum is smaller than that of O 1*s* spectrum.

Peak II is assigned to the group II of the orbitals in Fig. 7, or part of them (see later).

The lowest binding energy peak III, 2.4 eV from Fermi level, is assigned to the $2t_{2g}$ molecular orbital, because there is only one final state after the photoemission of $2t_{2g}$ electrons. The peaks corresponding to this state for $ZnCo_2O_4$ and Co_3O_4 are located at 1.9 and 1.4 eV, respectively.

$LiCoO_2$ and Co_3O_4 have the peaks at 11.8 and 10.9 eV, respectively. There are two possibilities for the origin of the peaks. One is a shake-up transition associated with $2t_{2g}$ photoemission. The peaks of Fe_3O_4 and $Fe_{1-x}O$ near BE = 11 eV had earlier been interpreted as multielectron satellites, but far-ultraviolet photoemission spectroscopy revealed that the peaks must be assigned to O 2*p* photoemission (*29*). The calculation for Fe_2O_3 using the SCF $X\alpha$ scattered wave cluster method indicated that σ orbitals of O

TABLE III

THE EXPERIMENTAL PHOTOIONIZATION CROSS-SECTION RATIO OF O 2*p* TO O 2*s* SUBSHELLS OXIDES

	Ratio[a]
MgO	0.2_6
Al_2O_3	0.4_5
SiO_2	0.5_0
TiO_2	0.5_4
V_2O_5	0.4_7
$LiCoO_2$	1.0_5[b]

[a] Relative standard deviations of the ratios are within 10%.

[b] II_1/I_1 (see text)

$2p$ were near 11 eV (*30*). An analogy follows that the other assignment of the peak is σ orbitals of O $2p$. In this interpretation, the energy difference between $2e_g$ and $3e_g$ orbitals is about 12.1 eV [$\Delta(\fallingdotseq 2.7$ eV) + 9.4 eV], which is larger than the satellite–primary peak separations in the core spectra. Then it is thought that the peak should be assigned to the shake-up peak.

We can discuss the composition of peak II because peak II is separated from peak III well enough to estimate the intensity.

Table III shows the photoionization cross-section ratio of 0 $2p$ to 0 $2s$ subshells for some oxides whose ions have no $3d$ electrons. The highest ionic oxide in Table III, MgO, has a low value, but the other oxides have similar values of averaged 0.5, so, it is assumed that the cross-section ratio of O $2p$ to O $2s$ subshells in $LiCoO_2$ is 0.5. If the $1t_{2g}$ level were entirely O $2p$, the intensity ratio peak II to peak I should be 0.5, which is 0.5 times the experimental value as shown in Table III. It suggests that $1t_{2g}$ must have quite a large Co $3d$ amplitude, and the photoionization cross section of Co $3d$ subshell is larger than that of O $2p$ subshell.

On the previous assumption of cross-section ratio of O $2p$ to O $2s$ subshells, relative Co $3d$ cross section in $LiCoO_2$ can be calculated in the following way:

$$(d + 2p)/2s = (II_i + III_i + III_{sat,i})/I_i,$$

where d, p, and s are cross-sections of Co $3d$, O $2p$, and O $2s$ subshells, and subscript "i" indicates the intensity of the peak. The Co $3d$ cross-sections of some oxides can be calculated by a similar method, where it is assumed that the overlap between Co $3d$ and O $2s$ orbitals can be negligible. The photoionization cross-sections of Co $3d$ subshell normalized to that of O $2s$ are tabulated in Table IV. The values may imply the average cross sections of free Co^{2+} and Co^{3+} ions. Although the number of $3d$ electrons decreases from 7 to 6, the value does not decrease. The theoretical calculation predicts that the photoionization cross sections of valence orbitals of some elements increase when the atoms ionize to the ions, for example, Mg to Mg^+ (*31*). It indicates that the photoionization cross-section depends not only on the number of electrons but on other factors.

TABLE IV

THE RELATIVE PHOTOIONIZATION CROSS SECTION OF AVERAGE Co $3d$ SUBSHELL NORMALIZED TO THAT OF O $2s$ SUBSHELL[a]

	Cross-section[b]
CoO	$2._9$
$CoAl_2O_4$	$3._0$
Co_3O_4	$2._8$
$LiCoO_2$	$3._9$

[a] Assuming that the photoionization cross-section ratio of O $2p$ to O $2s$ subshells is 0.5.

[b] Relative standard deviations are within 20%.

If O $2p$ did not contribute to $2t_{2g}$ and x% of Co $3d$ electrons contributed to the orbital group II in $LiCoO_2$, the values in Tables III and IV suggest that the intensity ratio $(III_i + III_{sat,i})/II_i$ was $3.9(1-x)/(1+3.9x)$, thus $x = 0.25$.

It is then concluded that less than 75% of Co $3d$ electrons contribute to $2t_{2g}$ molecular orbital. In other words, cobalt and oxygen atomic orbitals largely overlap in $LiCoO_2$. The XPS result for the low-spin cobaltic ion coincides with the NMR study of Co_3O_4, which indicates that the Co $3d$ wave function of the cobalt ion in Co_3O_4 is radially expanded relative to that of the free ion (*24*).

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