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# X-Ray Photoelectron Spectra of Inequivalent Atoms in Inorganic Compounds

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X-Ray photoelectron spectra of compounds containing inequivalent atoms were studied. The spectra of some compounds did not have separate peaks corresponding to inequivalent atoms, but their spectra were summations of the spectra of the compounds containing single kinds of atoms. In determining the chemical states of the atoms with XPS, the spectra of the compounds must be compared with the spectra of compounds having the same oxidation and coordination numbers, and the photoelectron spectral intensities are summations of the intensitites of the primary and satellite peaks.

Mixed valence compounds have characteristic physicochemical properties, which have been studied by many techniques. If the metal atoms are in crystallographically equivalent sites, there are possibilities of exchange of valence electrons between the atoms. If the relaxation time of the exchange is shorter than the time of the X-ray photoemission process ($10^{-18}$–$10^{-15}$ sec), the photoelectron spectrum must have a single peak for the metal atoms. On the other hand, if the exchange time is longer than the photoemission time, the spectrum must, in principle, have separate peaks corresponding to each atom, i.e., the atoms are inequivalent in the sense of X-ray photoelectron spectroscopy. The atoms on crystallographically different sites in single and mixed valence compounds are naturally inequivalent atoms. In this report, these two compound types will be called "the compounds containing inequivalent atoms in the X-ray photoelectron spectroscopic sense."

XPS has been thought of as a powerful technique to study compounds containing inequivalent atoms, and many studies have been made. It is not possible in all cases to determine the atomic ratio of the inequivalent atoms by only the spectra of the compounds without comparing them with the spectra of compounds containing single kinds of atoms. Some compounds have separate peaks corresponding to the inequivalent atoms but some compounds do not have separate peaks. It is desired that the spectral patterns of the compounds in the latter cases be explained for the purpose of obtaining a general determination method of oxidation or coordination numbers of the atoms. It is thought that the method is of benefit to interpreting the complex physicochemical properties of the compounds. For this purpose, the spectra of typical spinel structure iron and cobalt oxides were studied.

## Experimental

The experiments were performed in an AEI ES 200 electron spectrometer using

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achromatic AlK$\alpha$ radiation. The C 1*s* binding energy, 285.0 eV, of contamination carbon was used as calibration to compensate for charging effects. The reproducibilities of the binding energy values were within ±0.2 eV.

The samples, except for the following compounds, were previously described (*1*). Fayalite ($Fe_2SiO_4$) and ilmenite ($FeTiO_3$) single crystals were inserted into the spectrometer without exposure to air after crushing and mounting on aluminium metal plates in an argon atmosphere. The spectrum of wüstite ($Fe_{1-x}O$) was measured at the equilibrating temperature of 800°C, where the total pressure in the spectrometer was less than $2\times10^{-8}$ Torr (*2*). The surface of the sample did not contain $Fe_3O_4$ or $Fe_2O_3$.

## Results and Discussion

Many XPS studies concerning the compounds containing inequivalent atoms have been done. Some compounds have separate peaks corresponding to inequivalent atoms, but some compounds do not have separate peaks. Summarized in Table I are the combinations of properties of atoms in compounds that have particular spectral patterns.

In general, the higher the oxidation number of the metal atom and the higher the ionicity of the bond between metal and ligand, the higher the binding energy of the core level of the metal atoms (*3*, *4*). Paramagnetic ions have plural final states after photoionization of core electrons because of exchange interaction between core and valence electrons. On the other hand, diamagnetic ions have only one final state after photoionization. Thus the FWHM of core levels for paramagnetic ions are larger than those for diamagnetic ions. In first-row transition metal compounds, the intensity ratio of the shake-up satellite to primary peaks depends on the electron configuration of the metal atom. Thus the spectral patterns of the compounds containing inequivalent atoms were classified by the relationship between the oxidation number of the metal atom and its electronic configuration.

Chemical reactions, mainly the reduction of the higher oxidation number ion to the lower one, are induced by X-ray radiation in some compounds. In such cases, the spectra of the initial stages of measuring the XPS are discussed.

The compounds containing both low and high valence ions in diamagnetic states, Pt(2+) and Pt(4+) (*4*), and Sb(3+) and Sb(5+) (*6–8*), have separate peaks corresponding to inequivalent atoms. Tricker *et al.* report that the FWHM of Sb $3d_{5/2}$ for $Cs_3Sb(3+)_2Cl_9$ and $CsSb(5+)Cl_6$ were 2 eV, while the spectrum of $Cs_4Sb(3+)Sb(5+)Cl_{12}$ is deconvoluted into Gaussian peaks with FWHM of 1.5 eV (*6*). The peaks for Ag(1+) and Ag(3+) in AgO are not separated, and Ag 3*d* signals from AgO are broader than those from Ag and $Ag_2O$ (*9*). This means that the difference in chemical shift between Ag(1+) and Ag(3+) is smaller than the spectral width of the ions. The binding energy of Pt $4f_{7/2}$ in $K_2[Pt(CN)_4]Cl_{0.3}\cdot nH_2O$ is smaller than that in compounds having either Pt(2+) or Pt(4+), and the FWHM, 2.0 eV, of the mixed valence compound is larger than the FWHM. 1.85 eV of Pt(2+) and 1.9 eV of Pt(4+) (*5*). The mixed valence compound has high electric conductivity, so there is a possibility that the atoms are equivalent in the sense of XPS. Kim *et al.* (*10*) report that the Pb $4f_{7/2}$ peak for $Pb_3O_4$ can be deconvoluted into two peaks corresponding to Pb(2+) and Pb(4+), but the spectrum reported by Thomas and Tricker (*11*) has no evidence of a doublet structure or unusual broadening relative to the width of the Pb 4*f* signals from other lead oxides containing only one oxidation state of lead.

The spectra of typical compounds containing low valence ions in low-spin or diamagnetic states and high valence ions in

TABLE I

CLASSIFICATION OF X-RAY PHOTOELECTRON SPECTRAL PATTERNS FOR COMPOUNDS CONTAINING INEQUIVALENT ATOMS

| Combination of ions | Separation of peaks corresponding to inequivalent atoms | Typical | Exception |
|---|---|---|---|
| I<br>Low and high valence ions in diamagnetic states | Separation | Pt cpd (*5*), *Sb cpd (6–8)* | AgO (*9*)<br>Pt cpd (*5*) |
| II<br>Low valence ions in low-spin or diagmagnetic states and high valence ions in high-spin or paramagnetic states | Separation | Prussian-blue-type cpd (*12, 13*)<br>Fe cpd (*14*), Cu cpd (*15*)<br>Cu in $CuMn_2O_4$ (*1*),<br>Ru cpd (*16*)<br>Os cpd (*17*) | Ag cpd (*18*) |
| III<br>Same valence ions in low- and high-spin states | No separation | $K_2Mn[Mn(CN)_6]$<br>$Fe[Fe(CN)_5NO]$ | $YCoO_3$ at 293°K (*19*) |
| IV<br>Low valence ions in high-spin or paramagnetic states and high valence ions in low-spin or diamagnetic states | No separation | $Co_3[Co(CN)_6]_2$ (*12*)<br>$Co_3O_4$, $Li_xCo_{1-x}O$ (*20*) | $KCr_3O_8$ (*21*) |
| V<br>Low and high valence ions in high-spin or paramagnetic states | No Separation | $Mn_3O_4$ (*1*), $Fe_3O_4$, $Fe_{1-x}O$ (*2*)<br>V cpd (*22*), Mn in $CuMn_2O_4$ (*1*)<br>$Li_xNi_{1-x}O$ (*23*), Ir cpd (*24*),<br>U oxides (*25*) | $K_{0.5}FeF_3$ (*26*) |
| VI<br>Same valence ions in different crystallographic sites having same kinds of ligands | No separation | Al oxides (*27*), $\gamma$-$Mn_2O_3$ (*28*), $\gamma$-$Fe_2O_3$ (*29*), $Fe[CoFe]O_4$ | |

high-spin or paramagnetic states have separate peaks corresponding to the inequivalent atoms. The iron atoms in Prussian-blue-type compounds (*12*, *13*), and biferrocene Fe(2+, 3+) picrate (*14*) are inequivalent in the sense of Mössbauer spectroscopy and, of course, of XPS. On the other hand, charge-transfer spectra and vibration spectra having longer relaxation times than XPS show that Ru(2+, 3+) (*16*) and Os(2+, 3+) (*17*) compounds are valence-delocalized in the ground state, but the atoms are inequivalent in the sense of XPS. As the high coordination number of Ag(2+) in silver compounds decreases the binding energy of Ag(2+) and makes the difference of the binding energies between Ag(1+) and Ag(2+) small, peak separation is not observed (*18*).

The spectra of typical compounds containing the same valence ions in low- and high-spin states, low valence ions in high-spin or paramagnetic states and high valence ions in low-spin or diamagnetic states, and both low and high valence ions in high-spin or paramagnetic states do not have separate peaks corresponding to the inequivalent atoms. However, their spectral profiles are remarkably different from those of compounds having single kinds of atoms. Their spectra can be explained by summation spectra of inequivalent atoms. These will be discussed later. The Co 3*s* spectrum for $YCoO_3$ at 293°K is divided into high- and low-spin cobaltic ions, assuming that low-spin (diamagnetic) cobaltic ions have no shake-up satellite peaks (*19*). However, there remains an ambiguous point in the interpretation because it has been reported that the Co 3*s* spectrum of low-spin cobaltic ions in $LiCoO_2$ has a shake-up satellite peak (*20*). The spectrum for $KCr_3O_8$ has separate peaks corresponding to Cr(3+) and Cr(6+) (*21*). It is thought that the peak separation originates from the large difference of two oxidation numbers. Iron ions in $K_{0.5}FeF_3$ are high-spin ions, but the spectrum of $K_{0.5}FeF_3$ has separate peaks corresponding to Fe(2+) and Fe(3+) (*26*). It is considered that the peaks do not overlap each other because of a large chemical shift between Fe(2+) and Fe(3+) coordinated with $F^-$ ions, and because of weak shake-up satellite peaks due to the highly ionic bond between metal and ligand anions.

Compounds, for example, spinel oxides, containing ions of the same valence with different coordination numbers and coordinated by the same kinds of ligands do not exhibit separate peaks.

Spectra of mixed valence compounds not cited in Table I are summarized in the following.

DeAngelis and Schiavello report that the XPS spectrum of the W 4*f* level in $Na_xWO_3$ bronzes is explained by assuming presence of three oxidation states, W(4+, 5+, 6+) (*30*). However, Wertheim *et al.* report that the XPS spectra in vacuum-cleaved cubic $Na_xWO_3$ covering the entire composition range gave different binding energies from single valence W(4+) or W(6+) compounds, but no evidence for existence of multiple tungsten valence states in the bulk is obtained (*31*).

The binding energies of titanium core electron levels for $TiC_x$ (*32*) and $TiO_x$ (*33*) which have metallic properties linearly increase with the amount of nonmetallic elements. Since there is no interpretation as to whether or not the valence electrons in $TiC_x$ and $TiO_x$ are trapped during the photoemission process, the compounds are not included in Table I.

Typical compounds of groups (I) and (II) in Table I have separate peaks corresponding to the inequivalent atoms, but typical compounds of groups (III), (IV), (V), and (VI) do not have separate peaks. It is desirable that the spectral patterns of compounds of the latter groups be explained for the purpose of obtaining a general determination method of oxidation or coordination numbers of the ions. The spectral patterns of the typical spinel structure iron and cobalt oxides are discussed in the following.

Inverse-spinel structure oxide $Fe_3O_4$ has $Fe^{2+}$ and $Fe^{3+}$ on B sites in which iron atoms are octahedrally coordinated by oxygen. As the relaxation time of exchange of valence electrons between these atoms is $1.1 \times 10^{-9}$ sec at 300°K (*34*), the $Fe^{2+}$ and $Fe^{3+}$ are equivalent atoms in the Mössbauer spectroscopic sense but are inequivalent atoms in the sense of XPS. Thus the three inequivalent atoms are, in principle, distinguishable by their different chemical shifts, spectral patterns due to multiplet splittings, and shake-up processes. However, Fe 2*p* and Fe 3*p* spectra for $Fe_3O_4$ did not have three separate peaks as shown in Figs. 1 and 2. All ions in the compounds of group V in Table I except iridium ions have a broad primary peak due to the multiplet splitting and satellite peaks due to the multielectron excitations. As the binding energy differences between lower and higher oxidation number ions are smaller than the FWHM, the primary or satellite peaks corresponding to the inequivalent atoms overlap each other. Thus it is impossible to divide the spectra into the parts of the inequivalent atoms without comparing them with the spectra of compounds containing single kinds of atoms.

The spectra expected from $Fe^{3+}$ on *A* and *B* sites in $Fe_3O_4$ are discussed first. $\alpha$-$Fe_2O_3$ and $ZnFe_2O_4$ have the corundum and normal spinel structures, respectively, in which $Fe^{3+}$ are octahedrally coordinated by oxygen. The Fe 2*p* and Fe 3*p* spectra in these solids had near-equal binding energies of $710.3 \pm 0.2$ eV of Fe $2p_{3/2}$ and $56.0 \pm 0.3$ eV of Fe 3*p*, and satellite–primary peak energy separations of about 8.5 eV. McIntyre and Zetaruk have reported that the binding energies and multiplet splitting structures of Fe $2p_{3/2}$ and Fe 3*p* spectra for both $NiFe_2O_4$ and $CoFe_2O_4$ having inverse-spinel structures are the same (*35*). The Fe 2*p* spectrum for $CoFe_2O_4$ was different from that for $ZnFe_2O_4$ as shown in Fig. 4. These results mean that the binding energy, multiplet splitting, and shake-up satellite structures of the iron core level vary with coordination number, and suggest that there is no physical meaning in Asami's method in which the $Fe^{2+}$ spectrum in $Fe_3O_4$ was isolated by subtraction of Fe $2p_{3/2}$ of $Fe_2O_3$ from that for $Fe_3O_4$ (*36*).

The binding energies of electrons in ionic solids depend on Madelung potentials and relaxation energies (*37*). As iron, cobalt, and nickel have near-equal electron negativities (*38*), and $Fe_3O_4$, $CoFe_2O_4$, and $NiFe_2O_4$ have the same cation distribution in crystals and near-equal lattice constants (*35*), it is considered that binding energies of iron core levels for $Fe^{3+}$ in these solids are near equal. Thus it is considered that McIntyre and Zetaruk's assumption (*35*) in which the spectral patterns of iron core levels of $Fe^{3+}$ in $Fe_3O_4$ are the same as those in $NiFe_2O_4$ and $CoFe_2O_4$ is justifiable. They considered that the Fe $2p_{3/2}$ and Fe 3*p* spectra of $Fe^{2+}$ in $Fe_3O_4$ were the difference of the spectra of $Fe^{3+}$ in $NiFe_2O_4$ and those of $Fe^{2+}$ and $Fe^{3+}$ in $Fe_3O_4$.

The spectrum of the $Fe^{2+}$ on *B* sites is discussed next. The Fe 2*p* spectrum for fayalite is shown in Fig. 1d. Fayalite and ilmenite have $Fe^{2+}$ octahedrally coordinated by oxygen. They had nearly equal Fe $2p_{1/2,3/2}$ binding energies and shake-up satellite structures although their $Fe^{2+}$ have different next-nearest neighbor ions ($Si^{4+}$ or $Ti^{4+}$). Thus it is thought that the Fe 2*p* spectrum obtained from these solids is characteristic of $Fe^{2+}$ octahedrally coordinated by oxygen.

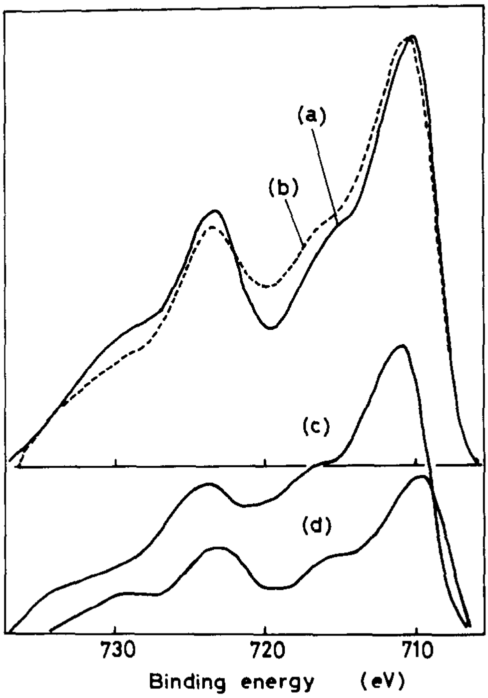

FIG. 1., Comparison of Fe 2*p* spectrum for $Fe_3O_4$ with the summation spectrum. The intensity ratio of $Fe^{3+}$ to $Fe^{2+}$ in the summation spectrum is 2/1, and the backgrounds of the spectra in Figs. 1, 3, and 4 are assumed to vary linearly. (a) $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$, (b) summation spectrum of (c) and (d), (c) $Fe^{3+}[CoFe^{3+}]O_4$, and (d) $Fe_2^{2+}SiO_4$.

It may be assumed from the above discussions that the spectra of $Fe^{3+}$ and $Fe^{2+}$ in $Fe_3O_4$ are nearly equal to those of $Fe[CoFe]O_4$ and $Fe_2SiO_4$, respectively.

The spectra of Fe 2*p* for (a) $Fe_3O_4$. (c) $Fe[CoFe]O_4$, (d) $Fe_2SiO_4$, and (b) the spectrum of summation of (c) and (d) are shown in Fig. 1. The intensity ratio of $Fe^{3+}$ and $Fe^{2+}$ in the summation spectrum is 2/1. The spectrum for $Fe_3O_4$ nearly coincided with the summation spectrum. The background of the spectra was assumed to vary linearly. The spectral intensity ratios of O 1*s* to metal 2*p* obtained by this method agreed well with the theoretical values in some oxides (*39*). The Fe $2p_{1/2}$ primary peak of $Fe^{3+}$ is superimposed on the shake-up satellite peak of Fe $2p_{3/2}$ (*39*), therefore the Fe $2p_{1/2}$ and Fe $2p_{3/2}$ levels are discussed together.

In this procedure, the shake-up satellite intensities were included in the intensities of iron core levels. On the other hand, McIntyre and Zetaruk calculate the $Fe^{3+}/Fe^{2+}$ intensity ratio of Fe $2p_{3/2}$ for $Fe_3O_4$ with only Fe $2p_{3/2}$ primary peak (*35*). They measured XPS using MgK$\alpha$ radiation, and then they wrongly assigned the shake-up satellite peak of Fe $2p_{3/2}$ for $Fe_2O_3$ to the multiplet splitting peak of Fe $2p_{1/2}$. (In MgK$\alpha$ radiation, the shake-up satellite peak of Fe $2p_{1/2}$ superimposes on the O KLL Auger peak.) Thus they do not discuss the satellite structures of $Fe^{2+}$ and $Fe^{3+}$. It has been shown that photoelectron spectral intensities of first-row transition elements are the summation of intensities of primary and satellite peaks (*12*, *39*). It is thought that the method of McIntyre and Zetaruk is convenient for rough estimation of inequivalent atoms, although it does not have any physical meaning.

The spectra of Fe 3*p* for $Fe_{1-x}O$, $Fe_3O_4$, and $\alpha$-$Fe_2O_3$ are shown in Fig. 2. The spectrum for $Fe_{1-x}O$ had a broad satellite peak with energy separation of primary and satellite peaks of about 20 eV. The spectrum for $\alpha$-$Fe_2O_3$ had a satellite with energy separation of 8.1 ± 0.4 eV. The FeK$\beta_{1,3}$ X-ray emission line results from a Fe 3*p*–1*s* transition, and in paramagenetic ions it has a satellite peak K$\beta'$ which is interpreted to be formed by the exchange interaction between the electrons of an open Fe 3*d* shell and those of the inner Fe 3*p* shell (*40*). The energy separations of K$\beta_{1,3}$ and K$\beta'$ for $Fe_{1-x}O$ and $Fe_2O_3$ are 13.4 and 14.3 eV (*40*). The comparison of XPS spectra with the X-ray emission spectra indicates that the satellite peaks of Fe 3*p* originate from the multiplet splitting of the Fe 3*p* level and electron energy loss for $Fe_{1-x}O$, and the shake-up peak associated with Fe 3*p* photoemission for $Fe_2O_3$, respectively. The spec-

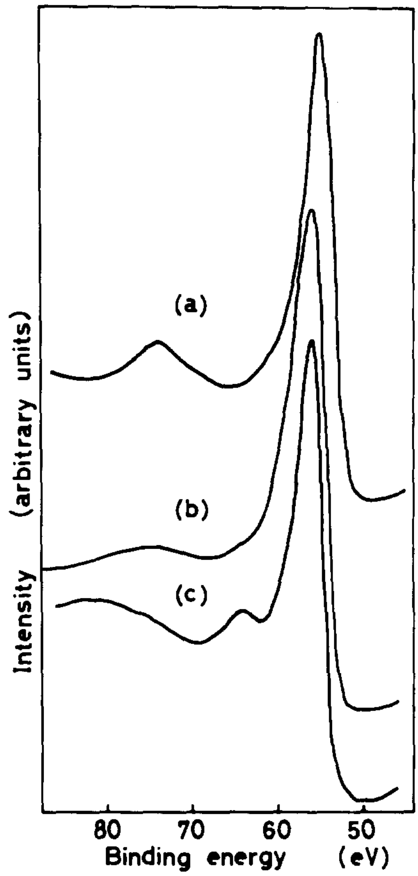

FIG. 2. Fe 3*p* spectra for iron oxides. (a) $Fe_{1-x}O$, (b) $Fe_3O_4$, and (c) $\alpha$–$Fe_2O_3$.

tral profile of $Fe_3O_4$ between 60 and 80 eV is nearly flat. This may indicate that the profile consists of a multiplet peak for $Fe^{2+}$ and a shake-up for $Fe^{3+}$. McIntyre and Zetaruk calculate the atomic ratio of $Fe^{2+}$ to $Fe^{3+}$ in $Fe_3O_4$ using only the primary Fe 3*p* peak, without considering the effect of the satellite peak on XPS spectral intensity. Thus their interpertation has little physical meaning as in the case of the Fe 2*p* level.

Normal spinel structure oxide $Co_3O_4$ has paramagnetic $Co^{2+}$ tetrahedrally coordinated and diamagnetic $Co^{III}$ octahedrally coordinated. It is assumed, as in the case of $Fe_3O_4$, that the Co 2*p* spectra of $Co^{2+}$ and $Co^{III}$ in $Co_3O_4$ are nearly equal to those of $CoAl_2O_4$ and $ZnCo_2O_4$ having normal spinel structures, respectively.

The spectra of Co 2*p* for (a) $Co_3O_4$, (c) $ZnCo_2O_4$, (d) $CoAl_2O_4$, and (b) the summation spectra of (c) and (d) are shown in Fig. 3, where the intensity ratio of $Co^{2+}$ to $Co^{III}$ in the summation spectrum is 1/2. The spectrum for $Co_3O_4$ nearly coincides with the summation spectrum.

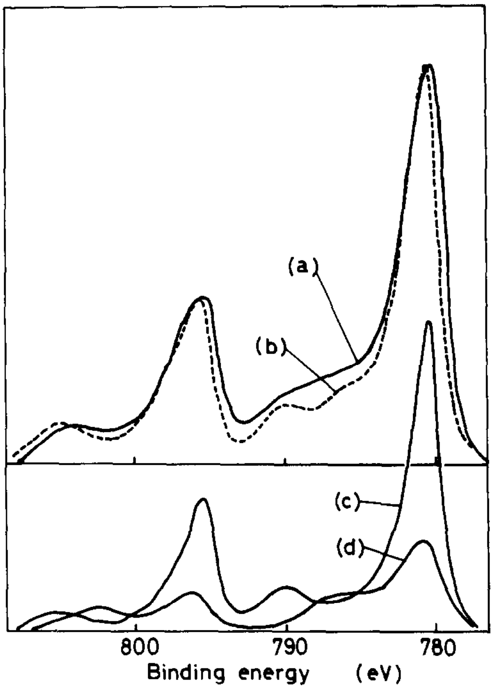

FIG. 3. Comparison of Co 2*p* spectrum of $C_3O_4$ with the summation spectrum. The intensity ratio of $Co^{III}$ to $Co^{2+}$ in the summation spectrum is 2/1. (a) $Co^{2+}[Co_2^{III}]O_4$, (b) summation spectrum of (c) and (d), (c) $Zn[Co_2^{III}]O_4$, and (d) $Co^{2+}[Al_2]O_4$.

Using a high-resolution spectrometer, Chuang *et al.* assigned the peaks at 780.7 and 796.0 eV of $Co_3O_4$ to Co $2p_{3/2}$ and Co $2p_{1/2}$ for $Co^{2+}$, respectively (*41*). The peaks were the higher binding energy shoulders of $Co^{III}$ peaks. The spin–orbit splitting of 15.3 eV for the Co 2*p* level for $Co^{2+}$ is abnormally smaller than about 16 eV for $Co^{2+}$ found for other spinel oxides (*1*). FWHM of $Co^{2+}$ is larger than that of diamagnetic $Co^{III}$ due to multiplet splittings. Thus it is thought that overlapping of the primary peaks of Co $2p_{1/2}$ or Co $2p_{3/2}$ of $Co^{2+}$ with those of $Co^{III}$ occurs to produce the spectral profile reported by Chuang *et al.*

The results of the $Fe_3O_4$ and $Co_3O_4$ investigations indicate that the atomic ratio of inequivalent atoms in the oxides cannot be determined by their spectra without comparing them with the spectra of single valence compounds, but their metal 2*p* spectra can be explained as summation of the spectra of single valence compounds. In other words, it may indicate that spectra can be divided into spectra corresponding to inequivalent atoms by use of spectra for compounds containing single kinds of atoms.

It is anticipated that the spectrum for tetrahedrally coordinated $Fe^{3+}$ can be obtained by subtraction of the spectrum for octahedrally coordinated $Fe^{3+}$ ($Fe^{3+}$ in normal spinel structure $ZnFe_2O_4$) from the spectrum for $Fe^{3+}$ tetrahedrally and octahedrally coordinated ($Fe^{3+}$ in inverse spinel structure oxide $Fe[CoFe]O_4$). The spectra of Fe 2*p* for (a) $Fe[CoFe]O_4$, (b) $ZnFe_2O_4$, and (c) spectrum (a) − spectrum (b) are shown in Fig. 4. The binding energy of Fe $2p_{3/2}$ in the difference spectrum is higher than that of $ZnFe_2O_4$. The direction of chemical shift with change of coordination number is parallel to that of the cobalt ion (*1*) but

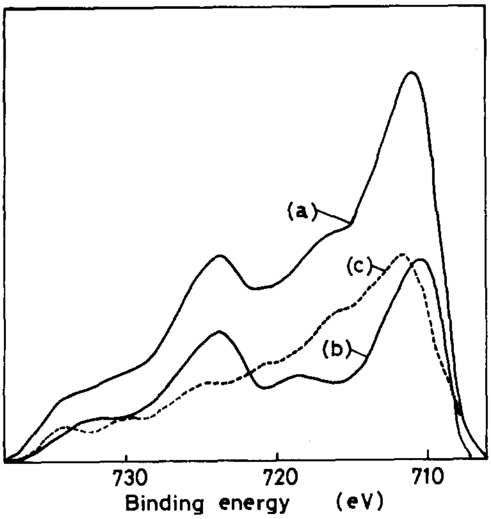

FIG. 4. Division of Fe $2p$ spectrum for $CoFe_2O_4$ into spectra for tetrahedrally and octahedrally coordinated $Fe^{3+}$. (a) $Fe[CoFe]O_4$, (b) $Zn[Fe_2]O_4$, and (c) spectrum (a) − spectrum (b).

opposite to those of aluminum (*42*) and nickel ion (*43*).

It is concluded that oxidation or coordination numbers of most ions in compounds containing inequivalent atoms can be determined by XPS spectra even if the spectra of the compounds do not have separate peaks corresponding to the inequivalent atoms. It is explained that the spectra are summations of spectra of the inequivalent atoms. The points of the determination method are as follows: The spectra of the compounds containing inequivalent atoms must be compared with the spectra of the compounds having similar chemical structure parameters such as oxidation and coordination numbers, and ligand field strength. In the first-row transition metal compounds, the photoelectron spectra intensitites are summations of the intensities of the primary and shake-up satellite peaks.

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