X-Ray Photoelectron Studies on Some Oxides and Hydroxides of Cobalt, Nickel, and Copper

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X-Ray photoelectron spectra of some simple and mixed oxides and hydroxides of copper, nickel, and cobalt have been studied with a view to determining spectral characteristics to allow the identification of each species. Oxides and hydroxides studied were Cu_2O, CuO, $Cu(OH)_2$, $CuFe_2O_4$, NiO, $Ni(OH)_2$, $NiFe_2O_4$, CoO, Co_2O_3, $CoOOH$, $Cu(OH)_2$, $CoAl_2O_4$, and $CoFe_2O_4$. The divalent oxides of these metals can be distinguished from the analogous hydroxides by the distinctly larger chemical shift of the metal core lines for the latter, by the energies of the satellite lines, and by the different O(1s) line binding energies. Oxides of copper(I) and copper(II) are distinguishable because of the lack of multielectron excitation satellites in the diamagnetic copper(I) oxide, and cobalt(III) oxides are distinguished from cobalt(II) oxides by the absence of such satellites in the former. Mixed oxides are sometimes identifiable on the basis of their satellite structure as well as the O(1s) line energy. Some experiments are also described involving oxide species produced on a nickel metal surface by ion bombardment.

In this laboratory, X-ray photoelectron spectroscopy (XPS) is being applied to the identification of surface corrosion products on materials such as stainless steel and other nickel-rich alloys. Under some aqueous conditions, metal hydroxides can precipitate on these alloys to form the major surface corrosion species. Under other conditions of solution pH or oxygen concentration, the surface layer comprises simple or mixed oxides. Because of its sensitivity to chemical structure on surfaces, XPS is of great potential value in the characterization of corrosion films (1, 2) but, first, a thorough familiarity is necessary with the XPS spectra of the oxides and hydroxides of alloy constituents; typically chromium, iron nickel, copper, and cobalt. Although the spectra of some of the individual oxides of these transition metals have been reported, no complete and comparative study of their oxides and hydroxides has been undertaken.

In this paper we report a study of the oxides of cobalt, nickel and copper. It has been shown (3–11) that many of the compounds of these elements have spectra with satellite line structure in addition to the normal core photoelectron lines. These additional spectral lines have been related either to a coupling between unpaired electrons in the atom (multiplet splitting) (12, 13) or a multiple electron excitation (shake-up) (7, 8, 14). In either case, interaction with metal valence electrons results, and the observed satellite line positions sometimes can be used to yield chemical information about the metal ion which supplements that obtained from the core line chemical shifts (1, 3, 15). Thus,

particular attention has been paid to the satellite peak structure in the oxides studied.

XPS studies have been reported for a series of copper and cobalt compounds covering a variety of valence states and stereochemical configurations (6–8). The appearance of shake-up satellite lines near the M(2p) core lines was shown to depend on the paramagnetism or diamagnetism of the compound. Also, the number and energy of these satellite lines was found to be related to the covalency of the bonding in the compound. In another study of nickel compounds (3), similar behavior of the satellite lines was found.

Oxides of nickel (10, 11, 16–24) and copper (10, 11, 18, 19, 22, 25–28) have been the subject of a number of additional XPS studies. In the case of nickel, NiO is the only characterized oxide which has been positively identified by XPS. Distinctive XPS spectra have been identified for both Cu_2O and CuO (27, 28).

In this work, the X-ray photoelectron spectra of the following oxides and hydroxides are reported: Cu_2O, CuO, $Cu(OH)_2$, $CuFe_2O_4$, NiO, $Ni(OH)_2$, $NiFe_2O_4$, CoO, Co_2O_3, $CoOOH$, $Cu(OH)_2$, $CoAl_2O_4$, and $CoFe_2O_4$. Additionally, some studies are reported of some nickel oxide species formed on nickel metal surfaces during high energy ion bombardment.

EXPERIMENTAL

Analytical Technique. All spectra were obtained using a McPherson ESCA-36 photoelectron spectrometer. The sample chamber was differentially pumped to a pressure of (1.33 × 10⁻⁶ pa) using a cryogenic panel (T = 14–18 K) which covered about one half of the surface area of the chamber. Non-monochromatized Al Kα or Mg Kα exciting X-radiation was used with the X-ray power normally set at 320 W.

The spectrometer dispersion constant was set using the known (29) 1253.6-eV energy difference between the Mg(1s) and Mg(2p) lines for a sputtered magnesium metal sample. The spectrometer dispersion constant was regularly checked using copper metal as a secondary standard and measuring the energy difference between the $Cu(2p^{3/2})$ and $Cu(3p^{3/2})$ line. The spectrometer work function (4.2–4.4 eV) was then set so that the $Au(4f^{7/2})$ peak center for metallic gold was located at a binding energy of 84.0 eV. The binding energies reported here were corrected for the relativistic change in electron kinetic energy that becomes significant in spectrometers where photoelectrons are not energy retarded before analysis (30). Depending on the kinetic energy, a correction of −0.05 eV to +0.35 eV in binding energy must be made (31).

Preparation of Compounds. Several of the oxides studied were prepared by more than one method in an effort to produce clearer spectral features and to determine the extent of surface charging. Initially all compounds were prepared or obtained commercially in powder form and their composition was confirmed by X-ray diffraction. The effect of possible surface hydration on the spectra was investigated by heating CuO, NiO, CoO, and $CoAl_2O_4$ powders to 200 °C under vacuum and subsequently transferring the sample into the spectrometer in an argon-filled glove bag. Only in the case

Table I. Electron Binding Energies for Copper Oxides and Hydroxides, eV

	$Cu(2p^{3/2})$	$Cu(3p^{3/2})$	$Cu(3s^{1/2})$	$O(1s^{1/2})$
Cu metal	932.5 ± 0.15 (1.1 eV)[a]	75.1 ± 0.15	122.2 ± 0.2	...
Cu_2O	932.5 ± 0.2 (1.2 eV)	75.1 ± 0.15	122.2 ± 0.2	530.5 ± 0.2 (1.2 eV)
CuO	933.8 ± 0.2 (2.9 eV)	76.2 ± 0.2	123.5 ± 0.3	529.6 ± 0.15 (1.3 eV)
$Cu(OH)_2$	934.4 ● 0.2 (2.6 eV)	77.0 ± 0.25	124.1 ± 0.25	530.9 ± 0.2 (1.8 eV)
$CuFe_2O_4$	933.7 ± 0.3 (2.4 eV)	76.4 ± 0.3	...	529.7 ± 0.2

[a] The value in parentheses is the full width of the principal photoelectron line at half maximum.

of CuO were narrower line widths observed following such treatment. Powders were presented to the spectrometer on grooved copper plates which were found to contribute less to surface charging than any other mount investigated.

The oxides NiO, CoO, and Cu_2O were also grown as very thin films on the appropriate metal surface. The metal surface, after cleaning by argon ion bombardment, was placed in an inert gas glove bag and heated to 200 °C after admitting about 1% oxygen to the atmosphere. Thin films of the oxides CuO, Cu_2O, and $Cu(OH)_2$ were also produced on copper metal surfaces by electrodeposition from solution (32). Spectra from oxides grown on metal surfaces had slightly narrower line widths and, except for $Cu(OH)_2$, showed no evidence of charging.

Sample Charging. Sample charging was measured by the displacement of the surface carbon C(1s) line from 285.1 ± 0.2 eV and the displacement of the Au($4f^{7/2}$) line for a thin film of gold deposited on the surface. By using the mounting procedures previously described, surface charging could be reduced to the detection limit (0.2 eV) for all compounds except the divalent hydroxides. Corrections to the binding energy values for these latter compounds were made using both the carbon (30) and gold charging (33) shift methods which agreed to within 0.2 eV.

RESULTS

Copper. Binding energies for the $Cu(2p^{3/2})$, $Cu(3p^{3/2})$, $Cu(3s)$ and $O(1s)$ lines are given in Table I for the oxides studied and for Cu metal, and some detailed spectra of the lines are given in Figure 1. The copper $2p^{3/2}$ core line position for CuO is shifted 1.3 eV above that for copper metal and compares with the value of 1.4 eV observed by Robert and Offergeld (26). The Cu ($2p^{3/2}$) line for $Cu(OH)_2$ is shifted a further 0.6 eV to higher binding energy which is adequate to permit differentiation of copper(II) hydroxide from the oxide. Copper(II) ferrite, on the other hand, has binding energies so close to those for CuO and such a virtually identical satellite structure that it is not possible to distinguish the two compounds.

The oxygen O(1s) line position is considerably different in each oxide species. Relatively narrow lines (FWHM = 1.3 eV) are observed for CuO and Cu_2O at 529.6 eV and 530.5 eV, respectively. A broader (FWHM = 1.8 eV) oxygen singlet is found for $Cu(OH)_2$ at 530.9 eV.

Well defined satellite structure is associated with the $Cu(2p^{3/2})$ lines for all copper(II) compounds studied. The satellite band appears to consist in each case of two overlapping peaks (see arrows 1 and 2) separated by 2.0 eV. Weak but distinct satellite structure was seen above the 3p (not shown) and 3s lines of CuO and $Cu(OH)_2$ with maxima for both at 6.5 eV above the 3s lines (see Figure 1). The magnitude of the spin orbit splitting of the Cu(2p) and Cu(3p) lines in these compounds was changed less than 0.2 eV from that in the metal.

One major difference between copper(I) oxide and copper(II) oxide is the prominent satellite structure on the high binding energy side of the copper core lines in copper (II) oxide. This has also been observed by several other investigators (21, 27, 28) and is attributed to the filled 3d
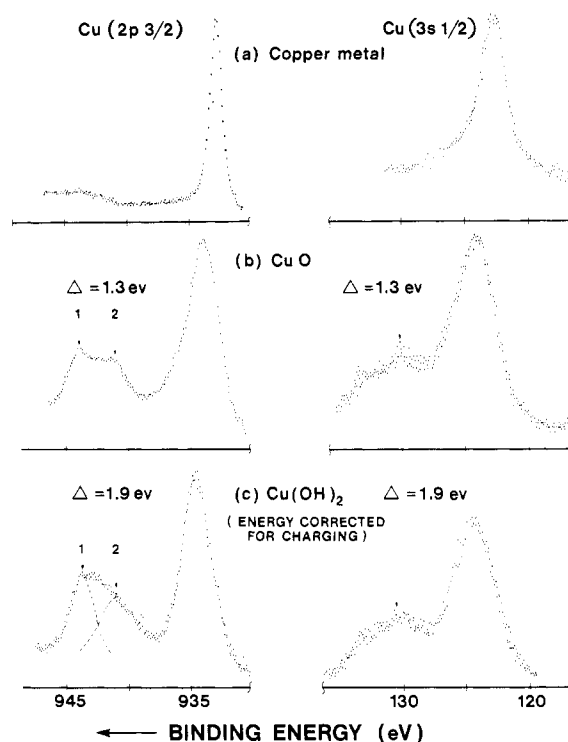
Figure 1. $Cu(2p^{3/2})$ and Cu(3s) spectra for (a) copper metal, (b) CuO, (c) $Cu(OH)_2$

shell of Cu^{1+} which prevents the ligand–metal charge transfer shake-up transition from occurring (34). No chemical shift (<0.1 eV) of the copper core lines in Cu_2O can be detected with respect to the binding energies for copper metal, nor is any change in core line width detected in the oxide compared with that in the metal. Although the metal core line positions are of little value in distinguishing copper(I) oxide from the metal, Schoen (35) has shown that a clear differentiation can be made using their Cu $L_3M_{4,5}M_{4,5}$ Auger spectra.

$Cu(OH)_2$ and $CuFe_2O_4$ appeared to partially decompose in the X-ray beam unless deposited in a very thin film on the metal. Similar decomposition of other copper(II) compounds was observed by Frost et al. (6). The major decomposition product of $Cu(OH)_2$ has a $Cu(2p^{3/2})$ binding energy around 932.5 eV and is likely a cuprous compound since the shake-up satellite intensities decrease as the decomposition principal line grows in. In practice, the cupric hydroxide spectra are often broadened or appear as two peaks because of the presence of the decomposition product.

Nickel. In Table II, $Ni(2p^{3/2})$, $Ni(3p^{3/2})$, $Ni(3s^{1/2})$ and O(1s) core line positions are given for Ni metal, NiO, $Ni(OH)_2$, and $NiFe_2O_4$. Figure 2 shows $Ni(2p^{3/2})$ and $Ni(3s^{1/2})$ spectra for these compounds.

The $Ni(2p^{3/2})$ spectrum of NiO has been discussed in

Table II. Electron Binding Energies for Nickel Oxides and Hydroxides, eV

	$Ni(2p^{3/2})$	$Ni(3p^{3/2})$	$Ni(3s^{1/2})$	$O(1s^{1/2})$
Ni metal	852.5 ± 0.1	66.3 ± 0.15	110.7 ± 0.2	...
NiO	854.0 ± 0.15	67.3 ± 0.2	111.8 ± 0.2	529.6 ± 0.15 (1.3 eV)
$Ni(OH)_2$	855.6 ± 0.3	68.0 ± 0.3	112.7 ± 0.2	531.2 ± 0.3 (1.8 eV)
$Ni Fe_2O_4$	855.4 ± 0.2	68.1 ± 0.2	113.0 ± 0.3	529.9 ± 0.15 (1.8 eV)
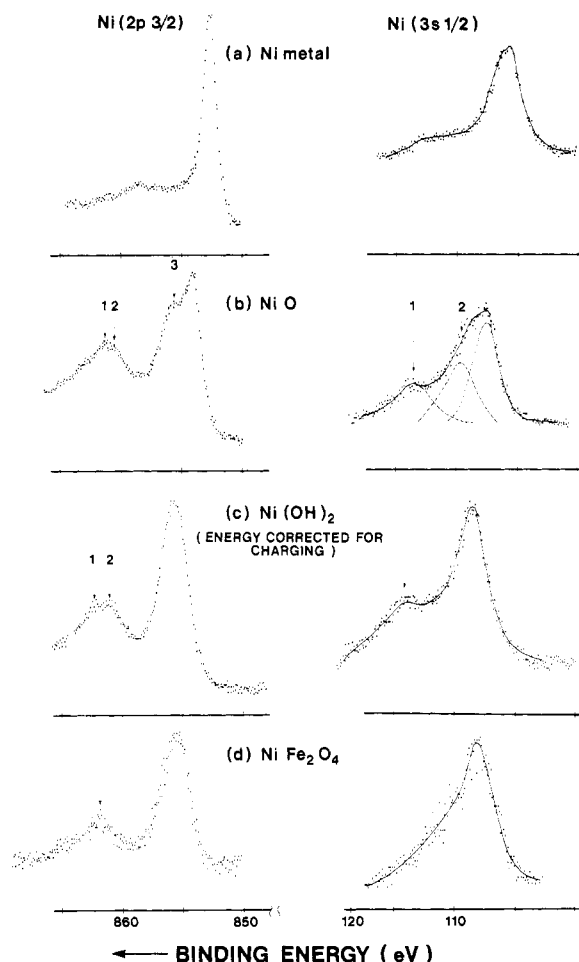
Figure 2. $Ni(2p^{3/2})$ and Ni(3s) spectra for (a) nickel metal, (b) NiO, (c) $Ni(OH)_2$, (d) $NiFe_2O_4$

Figure 3. $Ni(2p^{3/2})$ and O(1s) spectra for (a) nickel metal surface lightly oxidized; (b) surface in (a) following argon ion bombardment; (c) nickel metal surface following O_2 ion bombardment

other work (9, 17–19, 24, 26, 37), but some further details are presented here (see Figure 2b). The strong broad satellite band consistently has definable maxima at 6.6 eV (arrow No. 2) and 7.2 eV (arrow No. 1) above the principal line. Bands in this energy region for paramagnetic nickel compounds have been ascribed to a charge transfer multielectron transition (14). The prominent satellite shoulder 1.8 eV above the $Ni(2p^{3/2})$ principal line (arrow No. 3) is apparently unique to NiO. It has the same shape and width (FWHM = 1.8 eV) as the principal line.

In the Ni(3s) spectrum of NiO, prominent satellite structure is also observed. A reasonable deconvolution is obtained using two satellite peaks −2.1 eV and 6.0 eV above the Ni(3s) principal line (see Figure 2). Satellite structure associated with the Ni(3p) line of NiO (not shown) is by comparison rather weak and diffuse and the energy difference between the satellite band maximum and the principal line (∼6 eV) cannot be defined to better than ±0.5 eV.

In the Ni(2p) spectrum of $Ni(OH)_2$ (see Figure 2c), the principal line is not accompanied by a satellite shoulder as
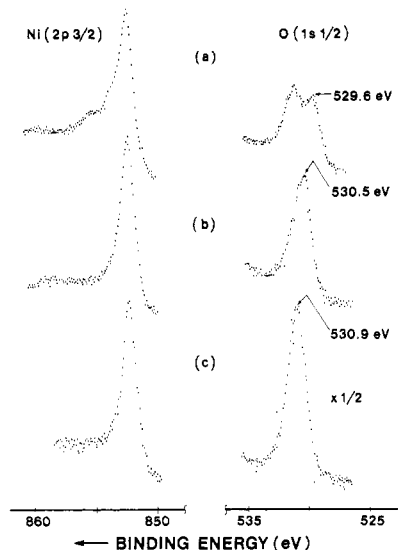
in the case of NiO. The higher binding energy satellite band, again ascribed to a multielectron excitation, is much narrower than the equivalent NiO band and is shifted to lower energy with band maxima at 5.4 and 6.7 eV. The Ni(3p) (not shown) and Ni(3s) lines for $Ni(OH)_2$ have stronger satellite bands than these same lines for NiO. The Ni(3s) spectrum exhibits a particularly clear satellite band 5.5 eV above the principal line.

In the Ni(2p) spectrum of $NiFe_2O_4$ (see Figure 2d) the binding energy of the principal $Ni(2p^{3/2})$ line is only slightly lower than that for $Ni(OH)_2$. However, the two can be distinguished by the different shape and energy of the $Ni(2p^{3/2})$ satellite band, by the prominent Ni(3s) satellite seen for $Ni(OH)_2$ but not for $NiFe_2O_4$, and finally by the fact that $Ni(OH)_2$ invariably exhibits 3–3.5 eV of surface charging while $NiFe_2O_4$ has not been found to exhibit any charging under our experimental conditions.

The O(1s) line positions of various nickel oxides (see Table II) provide another means for their identification. The O(1s) lines for NiO and $NiFe_2O_4$ are separated by 0.4 eV while that for $Ni(OH)_2$ is 1.6 eV above the NiO O(1s) line.

In the course of preparing and studying thin NiO films on a nickel surface, we found evidence from ion bombardment experiments of some other discrete nickel oxide species. One of these (Oxide(I)) was produced by the argon ion bombardment of monolayer quantities of NiO on a nickel metal substrate. This thickness of NiO could be produced by exposing an ion etched clean surface to ∼1.3 × 10^{-2} pa of oxygen for a few seconds. In Figure 3a, the high binding energy shoulder on the $Ni(2p^{3/2})$ peak and the O(1s) binding energy at 529.6 eV show that such a film has been formed. Bombardment of the thin film for 30 seconds with a flux of 200 $\mu A/m^2$ of the 10-keV argon ions resulted

Table III. Electron Binding Energies for Cobalt Oxides and Hydroxides, eV

	Co(2p$^{3/2}$)	Co(3p$^{3/2}$)	Co(3s$^{1/2}$)	O(1s$^{1/2}$)
Co metal	778.0 ± 0.1 (1.7 eV)	59.3 ± 0.15	101.0 ± 0.2 eV	...
CoO	780.0 ± 0.15 (2.7 eV)	60.2 ± 0.2	102.0 ± 0.2 eV	529.6 ± 0.15 (1.3 eV)
Co$_2$O$_3$	779.9 ± 0.2 (2.8 eV)	61.1 ± 0.25	102.7 ± 0.3 eV	529.9 ± 0.2 (1.6 eV)
CoOOH	780.0 ± 0.2 (1.8 eV)	61.1 ± 0.25	103.0 ± 0.2 eV	529.7 ± 0.3 531.2 ± 0.3
Co(OH)$_2$	781.0 ± 0.2 (3.2 eV)	61.1 ± 0.25	102.6 ± 0.2 eV	531.2 ± (1.8 eV)
CoAl$_2$O$_4$	780.6 ± 0.2 (3.4 eV)	61.2 ± 0.3	102.9 ± 0.2 eV	530.7 ± 0.2 (1.7 eV)
CoFe$_2$O$_4$	779.9 ± 0.2 (3.5 eV)	59.9 ± 0.3	...	529.9 ± 0.2 (1.7 eV)

in the complete disappearance of the oxide shoulder on the Ni(2p$^{3/2}$) metal peak. The O(1s) line, was practically unchanged in intensity, but shifted upward in binding energy to 530.5 eV (see Figure 3b). This binding energy is sufficiently close to the NiO O(1s) peak to suggest that a relatively strong nickel–oxygen bond has been formed (38), but the Ni(2p$^{3/2}$) binding energy for the species must be within 0.2 eV of the binding energy for the metal itself.

Oxide(II) was produced by the action of 10-keV O$_2^+$ ions (50 μA/m^2) on a clean nickel surface for 5 seconds. Following this treatment, a strong symmetrical O(1s) line was found at 530.9 eV, but the Ni(2p$^{3/2}$) line again showed no chemical shift that would indicate the formation of NiO (see Figure 3c). The attenuation of the Ni(2p) and Ni(3p) line intensities during the formation of oxide(II) suggests that, in this case, the oxygen is preferentially located on the nickel surface rather than within the crystal as is believed to be the case of Oxide(I).

Cobalt. Binding energies for the Co(2p$^{3/2}$), Co(3p$^{3/2}$), Co(3s$^{1/2}$) and O(1s) lines are given for cobalt metal and for the cobalt oxygen compounds CoO, Co$_2$O$_3$, CoOOH, Co(OH)$_2$, CoAl$_2$O$_4$, and CoFe$_2$O$_4$ in Table III. Figure 4 shows the Co(2p$^{3/2}$) and Co(3s) line shapes for several of these compounds.

As in the case of some nickel and copper oxides, the Co(2p) line position for some cobalt(II) species is sufficiently chemically shifted to allow ready identification. The Co(2p$^{3/2}$) line for Co(OH)$_2$, for example, is shifted 1.0 eV higher in binding energy with respect to CoO. This compares with a shift of 1.6 eV observed between Ni(OH)$_2$ and NiO. The Co(2p$^{3/2}$) line of the mixed oxide spinel CoFe$_2$O$_4$, however, is identical in binding energy to the monoxide CoO. This contrasts with the relatively large binding energy difference (1.4 eV) observed between NiO and NiFe$_2$O$_4$. The Co(2p) binding energies for the Co(III) oxides CoOOH (780.0 eV) and Co$_2$O$_3$ (779.9 eV) are also indistinguishable from that for CoO (780.0 eV).

The satellite structure associated with the Co(2p$^{3/2}$) line of CoO is as complex as that for NiO and CuO (see Figure 4). The strong band has two distinguishable components at 5.5 eV (arrow No. 2) and 6.5 eV (arrow No. 1) above the principal line. In addition, a deconvolution of the Co(2p$^{3/2}$) principal line suggests the presence of a satellite line at 2.1 eV above the principal line. This could be analogous to the stronger satellite line observed in the Ni(2p) spectrum 1.8 eV above the principal line. The 3s line of CoO has a lengthy high binding energy tail which can be deconvoluted into two components at 2.7 eV (arrow No. 1) and 5.8 eV (arrow No. 2) above the principal line.

Cobalt hydroxide has a Co(2p$^{3/2}$) spectrum with a broad satellite band centered at 5.6 eV and a Co(3s) line with a
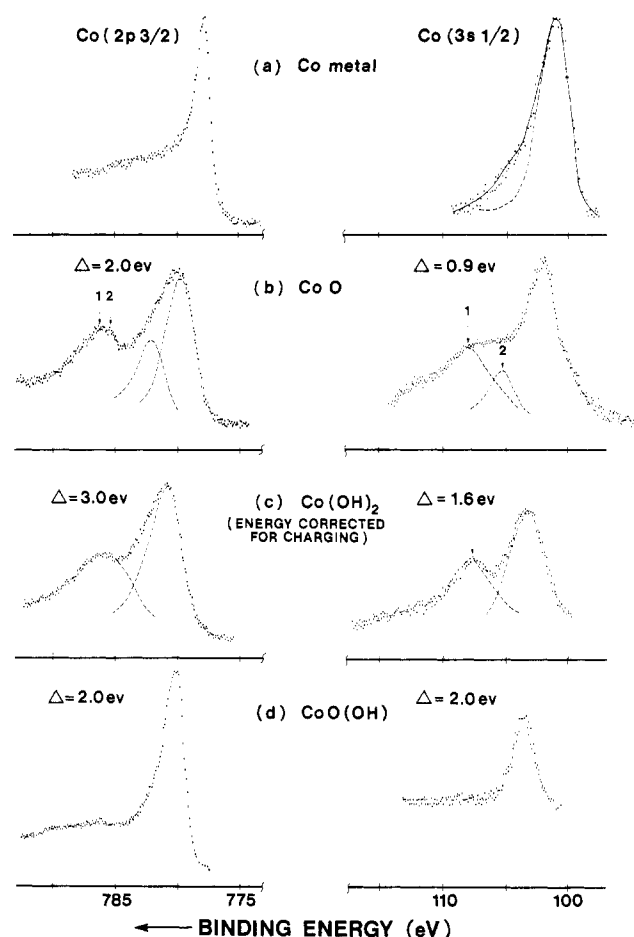

Figure 4. Co(2p$^{3/2}$) and Co(3s) spectra for (a) cobalt metal, (b) CoO, (c) Co(OH)$_2$, (d) CoOOH

clearly defined strong satellite line 4.5 eV (see arrow) above the principal line. A similar distinct satellite line appears in the M(3s) spectrum of the nickel analog.

Satellite lines which are seen in the Co(2p) spectra (not shown) for the spinels CoAl$_2$O$_4$ and CoFe$_2$O$_4$ are centered in each case about 5 to 6 eV above the principal line. These lines tend to be broad and are not particularly suitable for identification purposes.

Cobalt(III) oxides exhibit no satellites in their Co(3s) spectra and only very weak satellite bands appear in the Co(2p) spectra. Frost et al. (7, 8) have shown that high spin cobalt(II) compounds have intense satellite bands associated with both these lines, while satellite lines for the low spin cobalt(III) compounds are either weak or missing. The absence of any satellite structure in the Co(3s) spectra for

	$M(2p^{3/2})$, eV	$M(3p^{3/2})$, eV	$M(3s^{1/2})$, eV
Cu_2O	<0.1	<0.1	<0.1
CuO	1.3 ± 0.15	1.1 ± 0.2	1.3 ± 0.2
$Cu(OH)_2$	1.9 ± 0.2	1.9 ± 0.2	1.9 ± 0.25
NiO	1.5 ± 0.15	1.0 ± 0.2	1.1 ± 0.25
$Ni(OH)_2$	3.0 ± 0.25	1.7 ± 0.25	2.0 ± 0.35
CoO	2.0 ± 0.15	0.9 ± 0.25	1.0 ± 0.25
$Co(OH)_2$	3.0 ± 0.25	1.8 ± 0.3	1.6 ± 0.25
CoOOH	2.0 ± 0.15	1.8 ± 0.25	2.0 ± 0.2
Co_2O_3	1.9 ± 0.2	1.8 ± 0.25	1.7 ± 0.2

	$M(2p^{3/2})$, • 0.3 eV			$M(3s^{1/2})$, ± 0.3 eV	
CuO	...	7.8	10.2		
$Cu(OH)_2$	...	6.2	9.0		6.5
NiO	1.8	6.5	7.2	2.3	6.0
$Ni(OH)_2$	...	5.6	6.6		5.5
CoO	2.1	5.6	6.4	2.7	5.8
$Co(OH)_2$	...	~5.0			4.6

CoO(OH) and Co_2O_3 indicates that these oxides are diamagnetic (12) and are thus readily distinguishable from the high spin cobalt(II) oxides, all of which have prominent satellite structure. On this basis, the oxide layer on a cobalt metal surface which had been exposed to the atmosphere for several weeks was identified as a uniquely Co(III) oxide species since the Co(3s) line was a narrow singlet with no evidence of satellite structure.

Frost et al. (8) have shown that the Co(2p) spin-orbit splitting is affected by the net spin of the cobalt complex. This probably results from multiplet splitting of the Co(2p) lines for the high spin compounds which in turn, may be responsible for the broader Co(2p) line widths for these compounds. In this work, the Co(2p) line widths for the diamagnetic oxide CoO(OH) are indeed quite narrow, but, by contrast, all line widths for Co_2O_3 are as broad as the high spin oxides.

As in the case of copper and nickel, the O(1s) line positions are also useful for the structural identification of cobalt oxides. CoO and $Co(OH)_2$ have O(1s) binding energies which are experimentally identical to those of the nickel analogs. Of particular interest is the observation of two distinct oxygen peaks for the oxyhydroxide CoOOH—one at 531.1 eV corresponding to the hydroxyl oxygen and the second at 529.6 corresponding to an oxide oxygen.

DISCUSSION

Chemical Shifts. The chemical shifts of the metal 2p binding energies of the compounds studied are given in Table IV with respect to the binding energies of the metals. For the oxides CuO, NiO, and CoO, the M(2p) shift increases from copper to cobalt, perhaps reflecting increased crystal field stabilization of a complex with higher spin (5). The hydroxides of cobalt(II), nickel(II), and copper(II) are all shifted well above the binding energy for the analogous oxide and are thus readily distinguishable. The greater chemical shifts of the divalent hydroxides can be understood on the basis of the increased Pauling electronegativity differences between the metal and the surrounding oxygens. A chemical shift of 1.0 eV in the same direction has been found between ZnO and $Zn(OH)_2$ (39).

Another characteristic of the hydroxides, of possible practical use for determining their presence, is the strong surface charge effect displayed under all experimental conditions. Charging of 1–3 volts has even been observed for $Ni(OH)_2$ and $Cu(OH)_2$ deposited on metal in layers no thicker than 5 nm (39). It should be noted here that the extent of charging and the observed higher binding energies of the metal hydroxides may be partly connected if charging correction using gold or surface carbon is not perfect (40).

In the case of cobalt, the formal oxidation state appears to have little influence on the metal binding energy since virtually identical binding energies were found for Co_2O_3, CoOOH, and CoO. The absence of any obvious relationship between the formal oxidation state of nickel and the metal binding energies has been noted also by Matienzo et al. (3, 4).

The chemical shifts in Table IV for the M(3p) and M(3s) levels for nickel(II) and, particularly, cobalt(II) oxides are significantly smaller than those for the M(2p) levels. On the other hand, the chemical shifts for the cobalt(III) and copper(II) oxides are virtually identical for all the inner shell levels measured. The point charge model of an ion in a crystal developed by Citrin and Thomas (41), predicts that all electronic levels undergo equivalent chemical shifts compared with the free ion values. However, Siegbahn (42) has recently discussed some instances where second-order effects can cause nonequivalent chemical shifts in different core levels and has suggested that the life time for these states may affect the chemical shift. The lower chemical shifts found for the penultimate 3s and 3p shells of nickel-(II) and cobalt(II) oxides could also arise because multiplet interaction between the hole state in these shells and the unpaired 3d electrons results in a lowering of the binding energy of the measured major 3p or 3s component (12, 13). Multiplet splitting in the M(2p) level is expected to be considerably less because of lower electron overlap and the measured chemical shift in this level is thus much less affected. In the cobalt(III) oxides, the chemical shifts measured for each level are identical since all 3d electrons are paired in these diamagnetic compounds and no possibility of multiplet interaction is present. In the copper(II) oxides studied, chemical shifts in all levels were also equivalent, implying that little or no multiplet splitting occurs in these compounds.

The reasonably large variation of O(1s) binding energies for the various oxides examined, indicates the usefulness of this line for additional identification purposes. The most ionic oxygen occurs in the divalent oxides CuO, NiO, and CoO. A somewhat lower lattice energy and different crystal structure in CuO apparently does not affect the oxygen electronegativity to a noticeable extent. In general, oxides of related metals which are structurally analogous have very similar O(1s) binding energies. The hydroxides of cobalt and nickel, both with a brucite type structure, have the same O(1s) binding energies, within experimental error. Similarly Co_2O_3 and α-Fe_2O_3 (38), both with a corundum structure, have identical O(1s) binding energies, (within 0.1 eV). O(1s) binding energies for oxides such as $Fe(OH)_2$ and Ni_2O_3 would thus be expected to be close to the analogous structures above.

An additional peak appeared 1.6–1.9 eV to the high binding energy side of the main O(1s) peak for oxides of the structure MO, M_2O_3, and MFe_2O_4. This peak can be virtually eliminated by ion bombardment or in-situ heating of the oxide and thus does not arise from a multielectron

transition associated with the O(1s) line but probably results from a defect in the oxide lattice at the surface.

Satellite Structure. New or increased detail of the photoelectron satellite lines of the oxides has been obtained in the course of this work so that some similarities can be identified in the M(2p) satellite spectra of all the monoxides. In Table V, satellite band positions are given relative to the principal line for some oxides and hydroxides of cobalt, nickel, and copper. For each compound, two separate bands are observed whose energy above the principal line decreases from copper to cobalt. It is this group of bands in NiO which has been ascribed by Kim (19) as arising from an O(2p) $\rightarrow$ Ni(3d) charge transfer excitation. The band at 2.1 eV in CoO appears analogous to that seen at 1.8 eV in NiO, but it is not observed in CuO. This lower energy band in the $2p^{3/2}$ spectra of NiO and CoO could be due to multiplet splitting of the M(2p) core lines. Free ion calculations recently made by Gupta and Sen (43) on Ni^{2+} and Co^{2+} yield $M(2p^{3/2})$ splittings that are of comparable energies.

In the 3p spectra of these oxides, weak poorly-defined bands occur 5–6 eV above the principal line. In the 3s spectra of CoO and NiO however, the bands are considerably more intense relative to the principal line. The presence of multiplet interaction in this line has been suggested from the chemical shift data. Of the two bands deconvoluted from the M(3s) spectrum, the band near 6.0 eV likely arises from the multielectron process, since bands also occur at about the same energy in the 2p and 3p spectra of NiO and CoO. The band at 2.1 ± 0.2 eV in NiO could possibly arise from multiplet interaction. The Ni(3s) splitting in the highly ionic molecule NiF_2 has been found to be 3.1 eV (44), and splitting in more covalent nickel compounds is expected to be less than this value. In the Co(3s) spectrum of CoO, the deconvoluted band at 2.7 eV is likewise assigned to a multiplet splitting.

In the hydroxides of copper and nickel, the 2p shake-up bands again appear to consist of two components as was observed for the oxides (see Table V). The major difference is that the shake-up excitation energy has decreased by 1.0 eV in the case of copper and by somewhat less than a volt in the case of nickel and cobalt. These observations are consistent with the conclusion of Matienzo et al. (3, 4), that the shake-up excitation energy for a nickel ion decreases with increased ionicity and that the shape of the band is not strongly affected by the geometry of the ligand.

A characteristic feature of the spectra of all divalent hydroxides is the rather prominent satellite peak associated with the M(3s) line in these hydroxides. Although the appearance of these lines suggests multiplet splitting, the trend in the band energy (Co(OH)$_2$ 4.6 eV, Ni(OH)$_2$ 5.5 eV, and Cu(OH)$_2$ 6.5 eV) is opposite to that expected for multiplet interaction and thus these bands, like those in the 2p spectrum, likely arise from a multielectron excitation.

Oxides Produced by Ion Bombardment. Interaction of a high energy argon ion beam with an oxygen or a nickel surface results in the formation of a new oxide species. Although the O(1s) binding energy implies a bond strength greater than that resulting from chemisorption, no chemical shift is detected in any nickel line position. The interaction between O_2^+ ions and a nickel surface also produces a new surface species which is possibly preferentially oriented on the metal surface. Kim and Winograd (20), who have also carried out reactions between O_2^+ ions and a metal surface report different reaction products. However, in their case, reaction times were considerably longer so that a thicker oxide layer was formed.

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