

Spin-resolved and high-energy-resolution XPS studies of the 3s and 2s levels of metallic cobalt

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Spin-resolved and high-energy-resolution x-ray photoelectron spectroscopy (XPS) measurements of the 3s and 2s levels of metallic cobalt are reported. The high-resolution 3s spectrum shows a multiplet splitting ΔE_{3s} of 3.3 ± 0.3 eV. The metallic value and literature ΔE_{3s} values for CoF_2 and CoF_3 display a linear variation with $(2S + 1)$ in accord with the Van Vleck model. This finding, combined with the absence of core-level XPS satellites in Co metal attributable to localized final-state 3d charge fluctuations, implies that intra-atomic exchange dominates the Co 3s spectrum, and indicates that the creation of a core hole does not alter the 3d electron population in metallic Co, CoF_2 , or CoF_3 . The large role played by intra-atomic exchange is explicitly revealed by spin-resolved XPS (SRXPS) investigation of the Co 3s level. The SRXPS data show a predominantly minority-spin character for the main (low-binding-energy) 3s component, and a strong majority-spin character for the smaller 3s component at higher binding energy. Although high-resolution Co 2s XPS measurements give no indication of multiplet structure, SRXPS Co 2s measurements reveal a 0.65 ± 0.3 eV exchange splitting between majority-spin and minority-spin components, as well as a significant spin dependence to the $L_1L_{2,3}M_{4,5}$ Coster-Kronig transition probability.

I. INTRODUCTION

The nature of core-level x-ray photoelectron spectroscopy (XPS) of atoms (or ions) with an unfilled 3d valence shell has been investigated experimentally¹⁻¹⁶ and theoretically¹⁵⁻²² for almost 25 years. A great deal of attention focused initially on the 3s level of Fe and Mn because these elements displayed large energy splittings in their 3s XPS spectra. The first interpretation of these splittings¹⁻⁵ assigned the 3s XPS spectral structure to "multiplet splitting." The intra-atomic exchange interaction is different for the two final-state configurations $3s^1 3p^6 3d^n (2S+2L)$ and $3s^1 3p^6 3d^n (2SL)$, for which the remaining 3s spin is coupled, respectively, parallel and antiparallel to the initial-state 3d spin S . The energy difference between these two final states is called the multiplet splitting.

In the Van Vleck formalism,²³ the multiplet splitting ΔE_{3s} produced by 3s level photoemission from an atom with an initial-state valence spin S in the 3d shell would be $\Delta E_{3s} = K(3s, 3d)(2S + 1)$, where $K(3s, 3d)$ is the intra-atomic exchange integral between the 3s and 3d levels. This model was generally supported by the observation that ΔE_{3s} for both iron¹³ and manganese^{13,14} varied linearly with $(2S + 1)$ for the metals and their fluorides. However, the splittings were found to be significantly reduced from those predicted by one-electron Hartree-Fock theory due to final-state configuration interaction.^{17,18}

Further studies examined the multiplet-splitting assignment more extensively. A great deal of work centered on core-level photoemission from ionic compounds.^{15,16,20,21} In these systems, it was proposed that a core hole can induce an interatomic electron transfer from the anions to the 3d metal ion in the XPS final state, thereby increasing the 3d valence-electron count (and therefore altering the net valence spin) from $3d^n$ to

$3d^{n+1}$. The existence of "locally screened" ($3d^{n+1}$) and "nonlocally screened" ($3d^n$) final states¹⁶ produces two sets of multiplet-split doublets. If the $3d^{n+1}$ configuration is lowest in energy, then the multiplet splitting will be based on a final-state valence-shell spin that is different than the initial-state spin S assumed in the Van Vleck model.

Recent theoretical and experimental efforts have examined in considerable detail the circumstances for which these extra-atomic influences become important. Hermsmeier *et al.*¹² have found that the 3s spectrum from gas-phase atomic Mn is essentially identical to that from MnF_2 , indicating that for MnF_2 (and to a lesser extent MnO), the Mn 3s spectrum is not significantly influenced by the solid-state environment, and therefore a variation in the final-state 3d population does not take place. Kinsinger *et al.*¹⁰ have argued that for a ground-state 3d electron count of six or less, final-state charge transfer does not significantly modify the 3s XPS spectrum and that the 3s multiplet splitting derives from a $3d^n$ final-state valence configuration. It is important to note that the arguments of Kinsinger *et al.* are based primarily on the highly ionic metal fluorides and oxides, for which final-state charge transfer from the ligand to the metal is theoretically less likely.¹⁵ These findings were generally supported by spin-resolved measurements of the metallic Fe 3s level,^{8,9} which displayed a strong spin dependence consistent with the multiplet-splitting view.

The linear dependence of ΔE_{3s} on $(2S + 1)$ for Fe and Mn metals and their fluorides^{13,14} is evidence against a final-state variation in the 3d electron count for these elements in highly ionic compounds. Such a variation is thought to occur for metallic Ni,²⁴⁻²⁶ for which core-level and valence-band XPS spectra display a main line and satellite assigned to $3d^{10} (3d^{n+1})$ and $3d^9 (3d^n)$ final-state configurations, respectively. However, there is

no experimental evidence for spectral structure caused by a variable final-state $3d$ electron count in XPS spectra from metallic Mn or Fe. The valence bands of Mn and Fe are much more delocalized than those of Ni. The absence of XPS satellite structure for Fe and Mn strongly suggests that a core hole in these metals *cannot* pull down a (previously unoccupied) localized $3d$ level below the Fermi level, and therefore *cannot* induce a local (atomic-like) increase in the final-state $3d$ electron count, contrary to the case for Ni. Thus the final-state $3d$ electron configuration for Mn and Fe is $3d^n$, the same as in the initial state.

If there could occur a final-state increase in the $3d$ electron population in the Mn and Fe fluorides, but not in the metals themselves, then a linear dependence of ΔE_{3s} on $(2S + 1)$ would be highly improbable. This is because the $3s$ - $3d$ exchange interaction in the fluorides would derive from the valence spin of a $3d^{n+1}$ configuration, *not* the initial-state $3d^n$ spin S used to construct the ΔE_{3s} vs $(2S + 1)$ plot. In contrast, the $3s$ - $3d$ intra-atomic exchange for the metal would be based on the valence spin of the $3d^n$ configuration. Recent theoretical work¹⁵ has supported these experimental findings, in that the final-state valence configuration for Fe and Mn fluorides is predicted to be $3d^n$. However, for less electronegative ligands, such as Cl^- and Br^- , the charge transfer theoretically increases, making the $3d^{n+1}$ configuration the lowest-energy final state. It is quite possible that the discrepancies discussed by Van Acker *et al.*⁷ between Fe magnetic moments measured by neutron diffraction and the Fe $3s$ splittings are attributable to an increased covalency in the metal-ligand bonding. Theoretical calculations¹⁵ of $3s$ XPS spectra have found that for highly ionic compounds in which the final-state $3d$ electron count is the same as that of the initial state (i.e., $3d^n$), a linear dependence of ΔE_{3s} on $(2S + 1)$ is approximately valid.

Although a purely atomic view has often been taken in the interpretation of multiplet splittings, in itinerant metals the delocalized nature of the valence band should in principle modify the spectrum. In particular, the $3s$ doublet intensity ratio would be 1:1 in a fully delocalized limit instead of the atomic limit of $(S + 1)/S$.²⁷ Recent spin-resolved XPS studies²⁸ have also shown that an atomic view is not applicable to the description of $n = 2$ photoemission from metallic Fe. The theoretical description of core-level photoemission from itinerant metals is a challenging problem and is still in early stages of development. An additional spectral complication is the recent observation⁶ that the Fe $3s$ photoemission spectrum displays a strong photon-energy dependence that significantly changes the relative intensities of the multiplet-split components.

Theoretically,^{20,21} the core-level XPS final-state configurations $3d^7$ and $3d^8$ are very nearly degenerate for CoF_2 , with the $3d^8$ configuration being slightly lower in energy. Compared to Fe and Mn, very little investigation of cobalt has been reported. Due to the reduced magnetic moment of ferromagnetic Co ($1.72\mu_B$) relative to Fe ($2.22\mu_B$) and Mn ($\sim 2.4\mu_B$), the metallic Co $3s$ splitting has been difficult to observe with the energy resolution previously available in XPS. Thus the linear dependence

of ΔE_{3s} with $(2S + 1)$ has not been evaluated for metallic Co. In addition, there has not yet been a spin-resolved XPS (SRXPS) study of the Co $3s$ level. We present here the first high-energy resolution [$\Delta E = 0.32$ eV full width at half maximum (FWHM)] and first SRXPS studies of the $3s$ level of metallic cobalt. We also present analogous spectra for the Co $2s$ level. The results demonstrate the dominance of intra-atomic exchange in these s -level XPS spectra of metallic Co, and indicate that for Co metal, CoF_2 and CoF_3 , the creation of a core hole does not cause an increase in the $3d$ population in the XPS final state.

II. EXPERIMENT

The high-energy-resolution XPS measurements employed Lehigh University's SCIENTA ESCA-300 x-ray photoelectron spectrometer. This instrument combines a rotating Al anode with monochromatization to provide an intense source of monochromatic photons. The energy analyzer is a very large (300-mm mean radius) 180° hemispherical sector electrostatic energy analyzer with multichannel detection at the exit plane. The overall spectroscopic energy resolution was 0.32 eV FWHM as judged from measurements of the width of the Fermi level of metallic Ni. The Co sample for the high-resolution measurements was a 99.996% pure polycrystalline foil that was argon-ion sputtered at 1.5 kV for 80 min. The pressure in the analysis chamber during measurement was 1.3×10^{-9} Torr.

SRXPS measurements were performed with an instrument described in detail elsewhere.²⁹ Briefly, the instrument consists of a V.G. MkII 150° hemispherical sector electrostatic energy analyzer coupled to a low-energy diffuse scattering electron spin detector.³⁰ During these studies the Sherman function was limited to 0.035. The photon source was an unmonochromatized Mg K_α (1253.6-eV) x-ray tube operating at 510 W. The overall energy resolution for the SRXPS measurements was 1.6 eV FWHM. The residual pressure in the SRXPS analysis chamber was 2×10^{-10} Torr during data acquisition.

The sample for SRXPS study was a polycrystalline Co metal film that was prepared by evaporating high-purity Co onto a cobalt-based magnetic glass of composition $\text{Co}_{66}\text{Fe}_4\text{Ni}_1\text{B}_{14}\text{Si}_{15}$.³¹ The magnetic glass was formed into a loop with its free ends clamped tightly together and magnetized by passing current through coils wrapped around the legs of the loop. The strong ferromagnetic exchange coupling between Co metal and the magnetic glass produced a Co film uniformly magnetized in the film plane (to be discussed) with negligible stray magnetic field. The thickness of the Co metal film was not explicitly measured but was sufficient to *completely* suppress the B $1s$ (1063 eV kinetic energy) and the Si $2s$ (1104 eV kinetic energy) photoelectrons emanating from the underlying cobalt glass. This ensures that the Co SRXPS spectra reflect metallic Co and not Co in the magnetic glass, and suggests that the Co metal film thickness was in excess of ~ 60 Å. Photoelectrons were collected normal to the film plane with an angular resolution of $\pm 11^\circ$.

III. RESULTS AND DISCUSSION

Figure 1 displays a high-energy-resolution XPS spectrum of the Co 3s level. In contrast to previous measurements,³ a distinct satellite appears on the high-binding-energy side of the main Co 3s component located at 100.7 eV. The apparent energy difference between the two components is 3.3 ± 0.3 eV. With this ΔE_{3s} value for the metal established, one can then address the question if the 3s multiplet splitting for Co scales with $(2S + 1)$, as predicted by the Van Vleck model, and as demonstrated previously for iron¹³ and manganese^{13,14} metals and their fluorides. Using the known magnetic moment of $1.72\mu_B$ for metallic cobalt,³² and adopting an electron g factor of 2.2 for Co,³³ one derives an S value of 0.78 for metallic cobalt. The 3s multiplet splittings for CoF₂ and CoF₃ have been measured previously² to be 5.0 and 6.0 eV, respectively. Figure 2 displays a plot of ΔE_{3s} vs $(2S + 1)$ for metallic Co, CoF₂, and CoF₃. The S values used for CoF₂ and CoF₃ ($\frac{3}{2}$ and 2, respectively) are derived from the Co valence configurations $3d^7$ and $3d^6$ appropriate for the Co²⁺ and Co³⁺ ions. The three data points fall quite well on a straight line, as observed for metallic Mn and Fe and their fluorides.^{13,14}

The linear correlation of Fig. 2 strongly suggests that the 3s-3d exchange interaction, as incorporated in the Van Vleck formalism, is the dominant contributor to the Co 3s lineshape, both for Co metal and for the cobalt fluorides. The Van Vleck formalism assumes that $K(3s, 3d)$ is constant for a given element from compound to compound. The linear dependence of ΔE_{3s} on $(2S + 1)$ for Mn,^{13,14} Fe,¹³ and now Co suggests that for the highly ionic compounds of these elements, $K(3s, 3d)$ is not very sensitive to variations in the solid-state environment. It has been argued previously^{14,34} that because the $K(3s, 3d)$ integral is spatially limited by the small radial extent (< 1 Å) of the 3s orbital, $K(3s, 3d)$ might be an essentially atomic parameter, unaffected by small

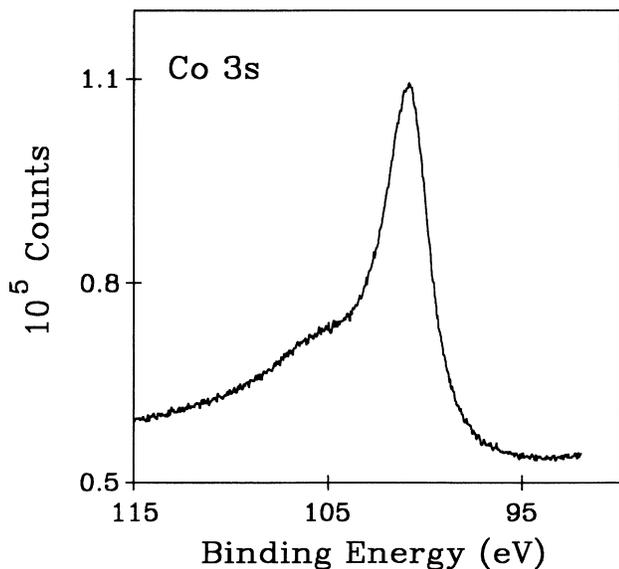


FIG. 1. High-energy-resolution XPS spectrum of the Co 3s level.

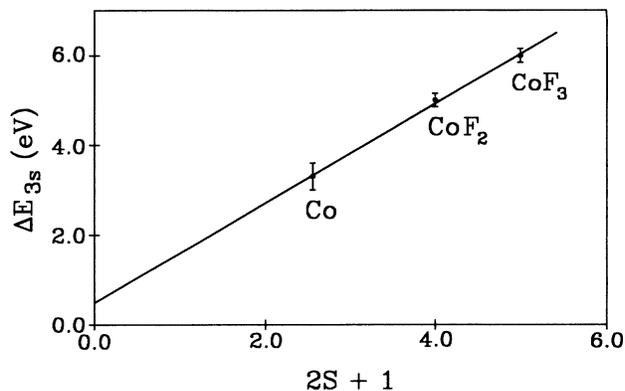


FIG. 2. Co 3s multiplet-splitting ΔE_{3s} plotted vs $2S + 1$ for metallic cobalt, CoF₂, and CoF₃. The ΔE_{3s} values for CoF₂ and CoF₃ are taken from Ref. 2. The solid line is a linear regression fit to the data points.

changes in the solid-state environment from compound to compound.

We find no experimental evidence of satellite structure in XPS from Co metal³⁵ caused by a variable final-state $3d$ electron count, such as that found in Ni.²⁴⁻²⁶ Evidently, the Co valence band, though more localized than that of Fe and Mn, is sufficiently delocalized to prevent a core hole from pulling down a $3d$ level below the Fermi energy, and therefore prevents a localized increase in the $3d$ electron count in the photoemission final state, such as that observed for Ni.

With this evidence for a $3d^n$ final-state configuration for Co metal, the fact that ΔE_{3s} for Co metal, CoF₂, and CoF₃ are all proportional to $(2S + 1)$ suggests that the final-state $3d$ electron configurations for CoF₂ and CoF₃ are also unchanged from those of the respective initial

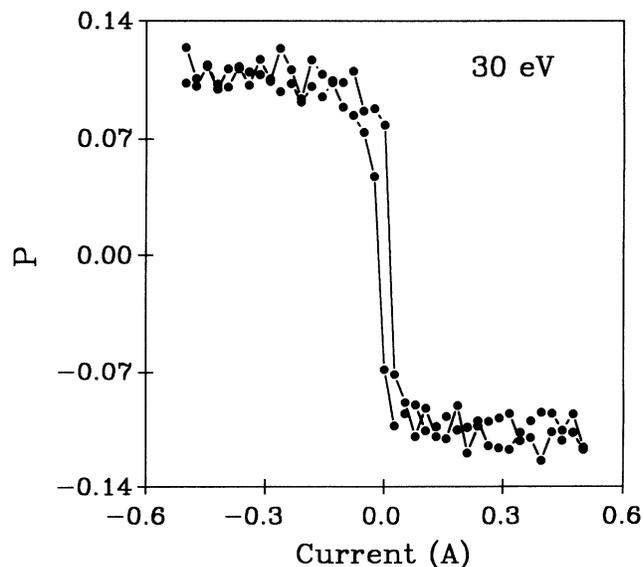


FIG. 3. A hysteresis curve of the evaporated Co film acquired with 30-eV kinetic energy spin-polarized secondary electrons. The current specifies the current passed through magnetizing coils wrapped around the legs of the magnetic glass substrate.

states. If there were a final-state increase in the 3*d* electron population in CoF₂ and CoF₃, but not in Co metal, then a linear dependence of ΔE_{3s} on $(2S+1)$ would be highly improbable, as discussed above for Mn and Fe. This is because the 3*s*-3*d* exchange interaction in CoF₂ and CoF₃ would be based on the valence spin of a 3*d*^{*n*+1} configuration (not the initial-state 3*d*^{*n*} spin *S* used to construct Fig. 3), whereas the intra-atomic exchange for Co metal would be based on 3*d*^{*n*}. Thus the energy separation between the two principal 3*s* spectral structures is determined by intra-atomic exchange associated with the initial-state 3*d*^{*n*} configuration. In this regard, Co metal and its fluorides are completely analogous to Mn and Fe metals and their fluorides.

Our conclusions regarding CoF₂ are in disagreement with theoretical calculations^{20,21} of the CoF₂ 3*s* XPS spectrum that predict the lowest-energy final-state valence configuration is 3*d*⁸, in which an electron from a ligand orbital is transferred to the 3*d* level of Co²⁺ upon core-hole creation. For this theory, the energy separation between the 3*s* XPS peaks would be determined by the net spin of the 3*d*⁸ configuration, thereby making the observed linear correlation in Fig. 2 highly improbable. It should be noted that the 3*d*⁸ configuration is only slightly lower in energy than the 3*d*⁷ configuration in the CoF₂ calculations.

If intra-atomic exchange is the dominant mechanism producing the spectral structure observed for 3*s* XPS from Co metal, there should exist a strong spin polarization to the spectral features. We have therefore investigated the spin polarization of the Co 3*s* level with SRXPS. Figure 3 displays a hysteresis curve acquired with spin-polarized 30-eV secondary electrons from Co. The sharp curve demonstrates a strong coupling of the Co film to the Co glass substrate, and also reveals a Co film that is magnetically saturated in the film plane. The 30-eV secondary electron spin polarization displayed in Fig. 3 is 0.115±0.01. The spin polarization of 13-eV Co metal secondary electrons was observed to be 0.15±0.01, in reasonable agreement with previous work.³⁶

Spin-resolved core-level data were collected into four channels $N_L^+, N_L^-, N_R^+, N_R^-$. Here, N_L^+ represents the number of electrons diffusely scattered to the left (*L*) from the Au target in the spin detector when the sample magnetization is positive (+). N_R^- is the number of electrons scattered to the right (*R*) from the Au target when the sample magnetization has been reversed to the negative (-) direction. The electron-beam polarization *P* can be expressed as³⁷

$$P = \frac{1}{S} \left[\frac{\sqrt{N_L^+ N_R^-} - \sqrt{N_L^- N_R^+}}{\sqrt{N_L^+ N_R^-} + \sqrt{N_L^- N_R^+}} \right], \quad (1)$$

where *S* is the analyzing power of the spin detector, known as the Sherman function. SRXPS measurements using both (+) and (-) magnetizations removes from the polarization data apparatus asymmetry effects unrelated to the spin of the electron beam. The polarization data can be separated into individual $N\uparrow$ and $N\downarrow$ SRXPS spectra for the majority-spin (\uparrow -spin) and minority-spin

(\downarrow -spin) photoelectrons, respectively, using the equations $N\uparrow = 2N_{\text{tot}}(1+P)$, $N\downarrow = 2N_{\text{tot}}(1-P)$, where $N_{\text{tot}} = (N_L^+ + N_L^- + N_R^+ + N_R^-)/4$. The statistical error bars ($\pm\delta N\uparrow\downarrow$) shown in the figures are calculated via the expression $\delta N\uparrow\downarrow = N\uparrow\downarrow(1/S\sqrt{4N_{\text{tot}}})$. The systematic uncertainty in the Sherman function *S* is estimated to be ±0.003. For all SRXPS measurements, the magnetizing current was switched from -0.5 to 0.5 A (see Fig. 3) in order to flip and saturate the magnetization of the Co film.

The $N\uparrow$ and $N\downarrow$ components for the Co 3*s* level are shown in Fig. 4, where the $N\uparrow$ spectrum has been shifted rigidly vertically by 2×10^5 counts to clarify the presentation. Count rates (summed over the *L* and *R* detectors) for the Co 3*s* level were approximately 160 s⁻¹, at 510 W x-ray power. The $N\downarrow$ component consists of a dominant peak at 100.6±0.1 eV binding energy, accompanied by a weak and broad \downarrow -spin background extending out to approximately 112-eV binding energy. The $N\uparrow$ component consists of a doublet. The higher-intensity $N\uparrow$ component is also located at ~100.6-eV binding energy, and is accompanied by a strong secondary component displaced ~3.5 eV to higher binding energy. The \uparrow -spin-to- \downarrow -spin intensity ratio ($I\uparrow/I\downarrow$) is 1.10. The spin-summed spectrum $N\uparrow + N\downarrow$ is identical to a Co 3*s* spectrum obtained with conventional XPS using the same energy resolution.

The strong spin dependence of the Co 3*s* SRXPS spectra displayed in Fig. 4 clearly indicates that the Co 3*s* spectral structure observed in Fig. 1 is multiplet in nature. One can qualitatively understand the 3*s* SRXPS spectrum by considering the emitting Co atom to reside in a ²H ground state with a valence-band spin of $\frac{1}{2}$ (the spin per atom in the metal is 0.78). Photoemission from the 3*s* level can produce ³H and ¹H final states corre-

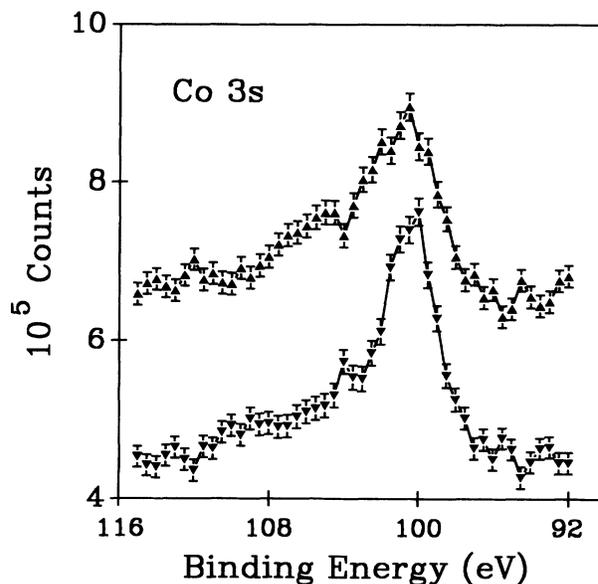


FIG. 4. Separate $N\uparrow$ and $N\downarrow$ SRXPS spectra for the Co 3*s* majority-spin (\blacktriangle) and minority-spin (\blacktriangledown) photoelectrons, respectively. The solid lines connect the experimental data points. The $N\uparrow$ spectrum has been shifted vertically by 2×10^5 counts to clarify the presentation.

sponding to parallel and antiparallel couplings, respectively, of the remaining $3s$ electron spin to the net spin in the valence shell. The 3H component would possess the lower binding energy due to the favorable $3s$ - $3d$ intra-atomic exchange interaction in the triplet final state. Thus the 3H final state would correspond to the lower binding energy feature at 100.6-eV binding energy, with the 1H state corresponding to the prominent satellite displaced about 3.5 eV to higher binding energy. By conservation of angular momentum,³⁸ one would expect the \downarrow -spin photoelectrons to produce only the 3H final state, while the \uparrow -spin photoelectrons would produce either the 3H or the 1H final states. Thus one would expect the 1H state to have an essentially 100% \uparrow -spin character, while the 3H would have a mixed spin polarization, but would be predominantly \downarrow -spin in character. These predictions are qualitatively observed in Fig. 4. We will refer to the 3H -like component for the metallic Co $3s$ spectrum as the high-spin ($|HS\rangle$) component, and the 1H -like component as the low-spin ($|LS\rangle$) component.

Although the \uparrow -spin and \downarrow -spin $|HS\rangle$ components have essentially the same binding energy, the \uparrow -spin $|HS\rangle$ component is significantly broader than the \downarrow -spin component. This reflects a shorter lifetime for the \uparrow -spin $3s$ hole due to a predominance of \uparrow -spin electrons in the Co valence band and spin conservation in the $3s$ hole-filling processes involving (directly or indirectly) the valence band. We have no explanation for the weak broad background observed in the Co $3s$ $N\downarrow$ SRXPS spectrum.

Note that since the $|HS\rangle$ \uparrow -spin and \downarrow -spin components have the same binding energy, the ΔE_{3s} value extracted from the spin-integrated high-resolution spectrum of Fig. 1 is a reasonable measurement for the energy difference between the $|LS\rangle$ and $|HS\rangle$ states. This fact, combined with the multiplet nature of the $3s$ components helps explain the correlation between ΔE_{3s} and $(2S+1)$ displayed in Fig. 2.

It is interesting to contrast the Co $3s$ SRXPS spectrum reported here with the spin-resolved Fe $3s$ photoemission measurements of Hillebrecht, Jungblut, and Kisker⁸ using 250-eV synchrotron radiation. Both $3s$ line shapes show a strong majority-spin polarization for the $|LS\rangle$ component of the $3s$ line shape. However, in Co there is also a strong majority-spin component at the $|HS\rangle$ position, whereas in Fe only a very weak shoulder is observed. Part of the difference may be due to the photon energies used in the two experiments. Qiu *et al.*⁶ have reported that the Fe $3s$ $|HS\rangle$ -to- $|LS\rangle$ intensity ratio increases threefold in increasing the photon energy from 200 to 1253 eV. It would be interesting to perform a SRXPS measurement of the Fe $3s$ level using the 1253.6-eV Mg $K\alpha$ radiation to see if significant majority-spin photoelectron intensity develops at the $|HS\rangle$ position. Both Fe and Co show an intense minority-spin component at the $|HS\rangle$ position. However, in Co the minority-spin spectrum displays a broad flat background extending out to 112-eV binding energy. There is a hint of an analogous background in the minority-spin Fe $3s$ data.⁸ However, the scatter in the Fe $3s$ data towards higher binding energy makes a definitive identification difficult.

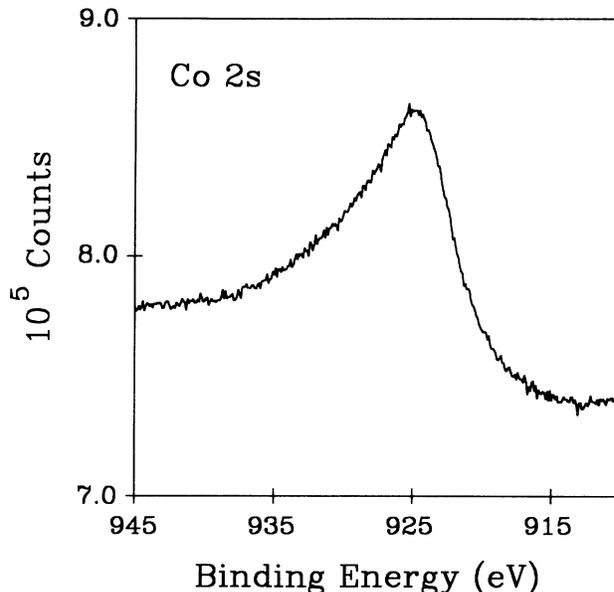


FIG. 5. High-energy-resolution XPS spectrum of the Co $2s$ level.

In comparison to the $3s$ level, relatively little attention has been paid to the $2s$ level of the $3d$ transition metals. This is because the $2s$ peak lies on a large spectral background and is significantly lifetime broadened by $L_1L_{2,3}X$ Coster-Kronig transitions,³⁹ making XPS measurement difficult. A high-energy-resolution XPS spectrum of the Co $2s$ level is shown in Fig. 5. In contrast to the high-resolution $3s$ XPS spectrum, the Co $2s$ spectrum shows essentially no evidence of multiplet structure.

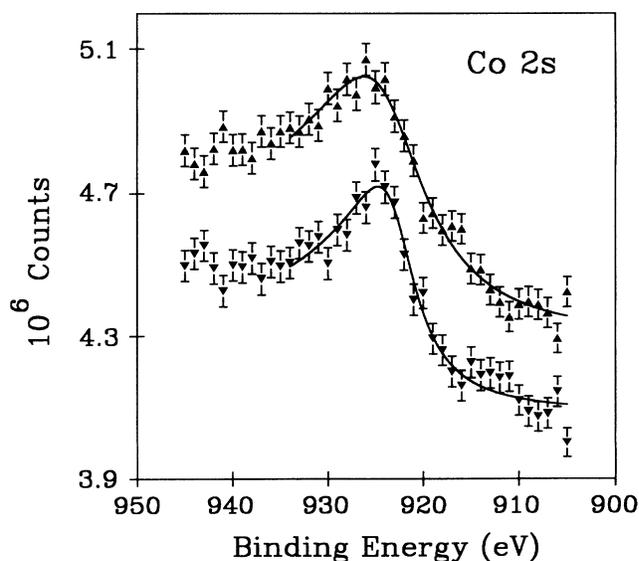


FIG. 6. Separate $N\uparrow$ and $N\downarrow$ SRXPS spectra for the Co $2s$ majority-spin (\blacktriangle) and minority-spin (\blacktriangledown) photoelectrons, respectively. The solid lines through the data are the result of a simplex fit to each spin component, over the binding energy range 905–934 eV, using a single Doniach-Sunjić line shape convoluted with a Gaussian of 1.6 eV FWHM.

To investigate this point further, we display in Fig. 6 SRXPS spectra for the Co 2s level. The solid lines in the figure are a simplex fit to each spin component, over the limited binding energy range 905–934 eV, using a single Doniach-Sunjic (DS) line shape⁴⁰ convoluted with a Gaussian of 1.6 eV FWHM representing the instrumental energy resolution. The DS line-shape analysis indicates that the $N\uparrow$ component lies 0.65 ± 0.3 eV to higher binding energy than the $N\downarrow$ component. The $N\uparrow$ 2s component has a much larger Lorentzian broadening (11.4 ± 0.5 eV FWHM) than the $N\downarrow$ component (6.3 ± 0.5 eV FWHM), suggesting that the $L_1L_{2,3}X$ Coster-Kronig transition probabilities have a large spin dependence. Most of the Coster-Kronig transition intensity lies in the $L_1L_{2,3}M_{4,5}$ channel.³⁹ It is plausible that the excess of majority-spin electrons in the valence band leads to a larger Coster-Kronig transition rate for the filling of the majority-spin 2s hole.

The singularity indices for the $N\uparrow$ and $N\downarrow$ components are very similar: 0.44 ± 0.04 and 0.50 ± 0.04 , respectively. The $I\uparrow/I\downarrow$ Co 2s intensity ratio is 1.2 ± 0.1 , in reasonable agreement with that obtained from the 3s level. Although the $|LS\rangle$ final state is not observed for the 2s level, the “exchange splitting” between the $N\uparrow$ and $N\downarrow$ components is qualitatively consistent with theoretical considerations of intra-atomic exchange.²⁷ One would expect a smaller exchange splitting for the 2s level than the 3s level due to the smaller radial overlap of the 2s and 3d orbitals.

In conclusion, SRXPS and high-energy-resolution XPS measurements of the 3s and 2s levels of metallic cobalt have been reported. The high-resolution spectrum of the 3s level gives a ΔE_{3s} value of 3.3 ± 0.3 eV. This metallic

ΔE_{3s} value and literature values for CoF_2 and CoF_3 display a linear variation with $(2S+1)$, in agreement with the Van Vleck model. This finding, combined with the absence of core-level XPS satellites in metallic Co attributable to localized final-state variations in the 3d electron count, implies that intra-atomic exchange dominates the Co 3s spectrum and furthermore suggests that the 3d valence configuration does not change upon core-electron removal (i.e., is the same in the initial and final states) for Co metal, CoF_2 , and CoF_3 . The large role played by intra-atomic exchange was explicitly demonstrated by SRXPS investigation of the Co 3s level, which revealed a predominantly minority-spin character for the $|HS\rangle$ component and a strong majority-spin character for the $|LS\rangle$ component. Although high-resolution Co 2s XPS measurements give no indication of multiplet structure, SRXPS Co 2s measurements detect a 0.65 ± 0.3 -eV exchange splitting between the spin components, and indicate a significant spin dependence to the $L_1L_{2,3}M_{4,5}$ Coster-Kronig transition probability.

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