Chemisorption of CO on Co(0001). II. Multielectron excitations

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The outer valence levels of CO chemisorbed on Co(0001) have been studied and discussed in a previous paper. In this paper we compare the photoionization of all core and valence levels for an adsorbate system [CO-Co(0001)] to those of a corresponding metal-molecule cluster [$Co_4(CO)_{12}$]. The observed multielectron excitations accompanying these molecular ionizations are discussed in detail. The observation of a resonance in the valence-band satellite of bulk cobalt will also be described.

I. INTRODUCTION

In a previous paper[1] the two-dimensional band structure of the outer valence levels (4σ, 5σ, and 1π) of CO molecules chemisorbed on Co(0001) was presented. Good agreement between experimental results and a simple tight-binding calculation was found. Such agreement demonstrated the adequacy of a one-electron picture in describing these outermost levels. This is the direct consequence of the delocalization of the hole created in these levels by the photoexcitation process. The hole delocalization is primarily due to the spatial extent of the valence levels and therefore an overlap of the wave functions of the levels on neighboring molecules.

Owing to the smaller spatial extent of the 1σ, 2σ, and 3σ CO molecular levels, it is much more likely that the one-electron picture will not be sufficient in describing photoemission out of these levels. In fact, a multitude of extra peaks which can be associated with these lower-lying levels are observed in photoemission spectra of CO coordinated on a cobalt surface or in a cobalt cluster (as in other CO-metal systems). These satellite features will be described and discussed in Sec. III. In Sec. IV we will discuss multielectron effects in an extended system and will present results on the satellite in the valence band of clean and CO-covered cobalt, which has a resonance in intensity as a function of photon energy.

II. EXPERIMENTAL

The experiments on the valence region of clean Co(0001) and CO-Co(0001) were performed at the University of Wisconsin Synchrotron Radiation Laboratory using techniques described previously in Greuter *et al.* (hereafter referred to as I).[1] These photoemission results were taken in an angle-resolved mode with *p*-polarized incident light and normal emission. The $Co_4(CO)_{12}$ data and CO-Co(0001) core-level spectra were recorded on a Leybold-Heraeus spectrometer LHS-100, using Mg and Al $K\alpha$ radiation. The satellite lines of the x-ray source were numerically subtracted. The carbonyl spectra were obtained from films condensed onto an Au substrate. Their thickness was controlled by monitoring the substrate signal. This served as energy calibration as well as a checkpoint against charging of the condensed layers. The work function of the carbonyl films was deduced from ultraviolet photoelectron spectroscopy (UPS) measurements (He I). All x-ray photoelectron spectroscopy (XPS) measurements were made with an angle-integrated analyzer. In addition, the CO-Co(0001) core-level spectra were independently reproduced in a Vacuum Generators Escalab 5.

III. MULTIELECTRON EXCITATIONS OF CO

The topic of multielectron excitations in small molecules has been addressed by various groups.[2] The analysis of these multielectron excitations accompanying the inner and outer core electron ionizations of adsorbed CO can lead to a detailed understanding of the screening processes and the chemical bond between the CO molecule and the substrate.[2(a)] A comparison between CO adsorbates and transition-metal carbonyl compounds has shown that only a few metal atoms are sufficient to provide the electron reservoir necessary to properly screen a core hole on the CO molecule.[3] Since multielectron excitations are a direct consequence of the screening of the hole, one expects carbonyl compounds and adsorbed CO to show similar core spectra. In this paper we present a comparison of all CO-induced ionizations from an adsorbate [CO-Co(0001)] with the complete set of corresponding ionizations from a carbonyl [$Co_4(CO)_{12}$]. Figure 1 compares the measured spectra of gas-phase CO,[4-6] the CO carbonyl, and CO adsorbed on Co(0001). All binding energies E_b are referenced to the vacuum level. The inner core-level spectra of free CO are arbitrarily shifted up towards the vacuum level, in order to line up with the corresponding main line of the carbonyl compound.

We start the discussion with the spectra for the deep-lying C 1*s* and O 1*s* core holes. Upon coordination to a transition-metal surface or cluster of transition-metal atoms, at least three general observations can be made in connection with these ionizations.

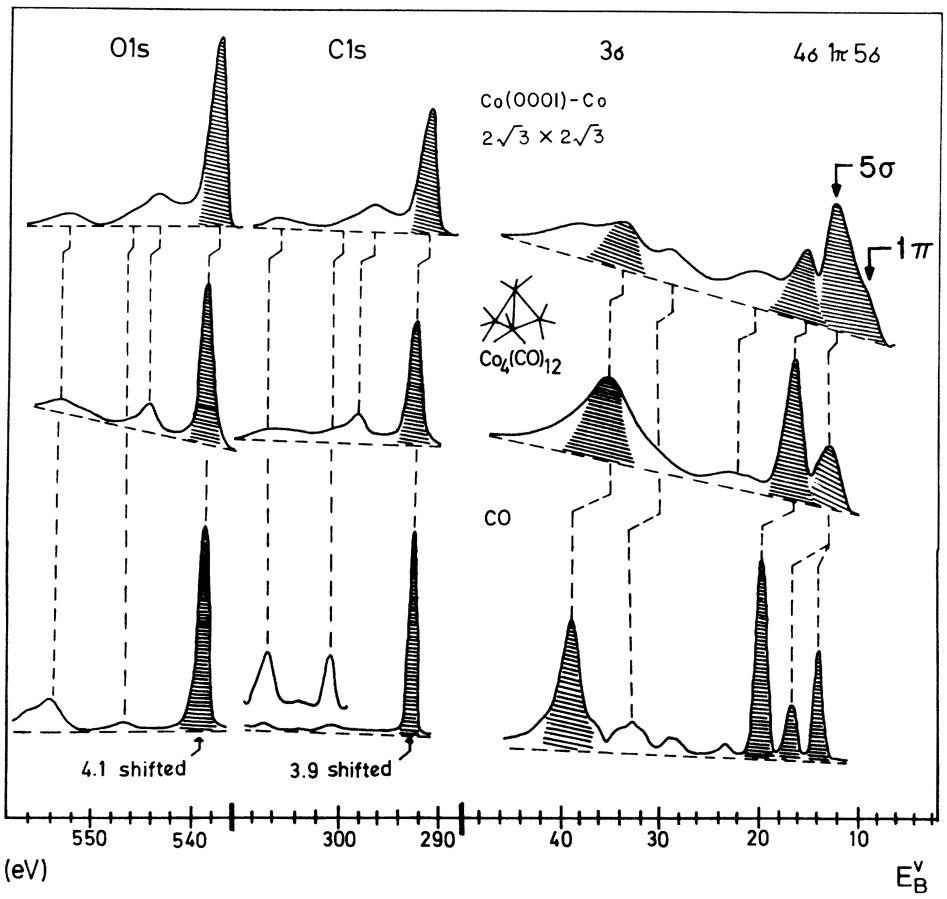

FIG. 1. Valence and core photoionization spectra of free CO, tetracobaltdodecacarbonyl [$Co_4(CO)_{12}$], and $(2\sqrt{3}\times 2\sqrt{3})R\,30°$ CO-Co(0001). The horizontal scale is binding energy in eV referenced to the vacuum level.

(i) The most intense lines, which we will refer to as the main lines, are shifted towards lower binding energies upon going from the gas phase to coordinated systems.

(ii) The satellites on the high-binding-energy side of the main lines, which are already present in the free molecule, shift in the same direction and approximately by the same amount as their main line.

(iii) Additional satellite peaks occur with sometimes considerably higher intensity than the CO-derived peaks known from the gas phase.

It has been shown[2(d),5] that all three observations can be understood on the basis of a simple theoretical model. The model involves the sudden removal of a core electron followed by the screening of the hole. The latter proceeds mainly through two electronic channels: One involves the electrons of the CO molecule and is already active in the free molecule. The second one involves the highly polarizable metal electrons.

In order to illustrate the underlying processes let us first consider a free CO molecule. The creation of a core hole leads in a primary *virtual* step to a change in the potential. This happens so rapidly that the valence electrons cannot follow immediately. This virtual hole state is therefore unscreened. In a second step the valence electrons rush in to screen the hole. They can only do this by simultaneously inducing valence excitations. The stabilization energy gained is about 13 eV for the C 1*s* hole and about 20 eV for the O 1*s* hole. The states that are populated via this screening mechanism basically follow the so called "monopole selection rule,"[7] provided the kinetic energy of the emitted electron is large. The intensity of the excited hole states and the main line is then given by

$$I \propto |\langle U_K | p | \phi_k \rangle \langle \psi_{ijk}^{\text{ion}} | \psi_k^R \rangle|^2 ,$$

where the nomenclature of Ref. 2(d) has been used. We have

$$\psi_f(ijk) = U_K \psi_{ijk}^{\text{ion}}(N-1) ,$$

the final-state wave function of the ion with U_K representing the emitted electron and $\psi_{ijk}^{\text{ion}}(N-1)$ the eigenstates of the ion with a hole in the kth core level and a valence electron excited from state j to i; $\psi_0^N = \phi_k^R \psi_k(N-1)$ is the neutral ground state with ϕ_k^R being the inner-shell orbital from which the initial photoionization occurs. This monopole selection rule says that the symmetry of an observable final hole state has to be the same as the symmetry of the primary (virtual) hole state. The energetically lowest excitations in a CO molecule that fulfill these symmetry requirements are the 1π-$2\pi^*$ excitations. They lead to the lowest lying satellites in the free molecule[8] and have intensities between 3% and 18% relative to the main line.[2(d)] Taking the electron spins into account we expect for each

1π-$2\pi^*$ excitation two doublets and one quartet state. Only the doublet states result from allowed transitions so that we expect two shakeup peaks originating from the 1π-$2\pi^*$ excitation. Both components are observed in the gas-phase core spectra for O 1*s* and C 1*s* ionization as can be seen in Fig. 1.

We can follow the energy shift of these shakeup peaks as the molecule is coordinated to transition-metal atoms in a cluster or on a surface. In particular, the higher lying satellite component at ~ 15 eV excitation energy is well resolved in the spectra of the coordinated systems (see Fig. 1). It is found at basically the same excitation energy relative to the main line as in the free molecule. The second component at ~ 8 eV can be observed as a shoulder on the new and more intense satellite peak at ~ 5 eV excitation energy. For both satellite components, the relative intensities have changed upon coordination. The overall shift of these 1π-$2\pi^*$ satellites as well as the main line is about 4 and 5 eV to lower binding energy for the carbonyl and the adsorbate, respectively. This shift, which is basically independent of whether a C 1*s* or O 1*s* electron is removed, is due to the screening by the metal electrons and is intimately connected with the appearance of the additional intense satellite at ~ 5 eV excitation energy.[5] To be precise, the shift is *not* caused by charge accumulation in the neutral ground state due to the bonding to a transition metal but instead is due to the new and additional screening of the hole state by the metal electrons. This extramolecular screening is small compared to the intramolecular screening (~ 4–5 eV compared to ~ 13 or ~ 20 eV). Therefore it is reasonable to assume that the relevant orbital structure of the ionized CO molecule has not changed dramatically upon coordination.

According to the above picture those satellites corresponding to 1π-$2\pi^*$ excitations in free CO persist in the coordinated systems. It must therefore be true that the 2π orbital is still at least partially unoccupied when CO is bound to a surface or in a complex. In other words, the 2π orbital is not pulled (completely) below the Fermi level, as frequently claimed.[2(c),9,10] It is true, however, that the 2π orbital is modified by coordination to a metal atom and by the presence of a core hole.[2(a)]

Figure 2 shows a schmematic view of the relevant single electron processes. On the left side is illustrated the well-known picture of the metal-2π interaction in a neutral system. With the creation of a core hole, the orbitals will be modified. Owing to the strong Coulomb forces introduced by the core hole the 2π, which initially is mainly localized

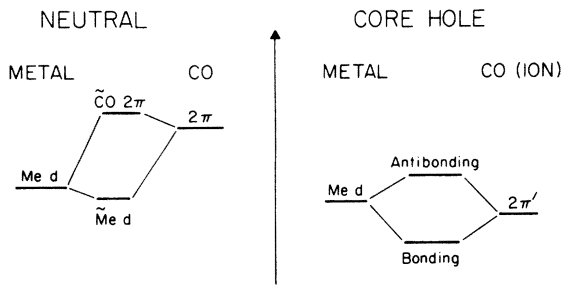

FIG. 2. Schematic picture for the interaction of metal *d* levels and CO 2π levels in the neutral system (left-hand side) and ion state (right-hand side).

on the CO molecules, becomes stabilized relative to the metal electrons. In the most simple-minded picture, the 2π orbital feels the presence of one excess charge in the CO molecule upon the ionization of a core electron. Consequently the 2π level will be pulled down in energy relative to the neutral molecule. Hence, the energy separation between the metal electron and the molecular 2π level decreases and the mixing between the metal and 2π wave functions increases. This process is indicated on the right-hand side of Fig. 2. Owing to the higher degree of mixing in the ion a new combination of bonding and antibonding levels is formed. Both levels now contain substantial metal as well as CO character. In other words, the amount of 2π-CO character of the bonding level has increased compared with the neutral system. (In the neutral system the bonding level has $\sim 10\%$ CO character at most.) Correspondingly the unoccupied level contains a larger metal component than in the neutral. As a result, we find that electrons have been transferred from the metal to the adsorbate upon the creation of the core hole.

The main features of the experimental spectra in Fig. 1 can be interpreted in terms of the simple picture in Fig. 2 if a basically unperturbed 1π orbital is added to this level scheme. (1) The main line (shaded area in Fig. 1) corresponds to a core hole with no additional valence excitations. There is an overall shift of ~ 4 eV to lower binding energy of the main line for the coordinated systems versus free CO. This shift is the result of extramolecular screening due primarily to the additional charge transferred from the metal to the 2π orbital. (2) The peaks about 6 and 14 eV below the main line in free CO (in either O 1*s* or C 1*s*) spectra persist as peaks or shoulders for CO bound in a cobalt cluster or on the cobalt surface. In the case of the free molecule, the peaks correspond to a core-hole excitation along with valence excitations from the 1π-$2\pi^*$. The situation is similar in the coordinated systems with the pure $2\pi^*$ in the free molecule replaced by the antibonding level formed from the metal *d*'s and the CO-2π. The intensity and energy of this transition will be slightly different due to the modified wave functions for the coordinated CO. The excitation energy depends on the energy position of the metal-2π antibonding orbital and is not expected to change much compared to the $2\pi^*$ orbital of the free-ionized CO molecule.[2(c)] (3) The new satellite observed only for coordinated CO at ~ 5 eV excitation energy (below the main line) corresponds to a shakeup transition between the bonding and antibonding metal-2π combinations and would therefore not be present in free CO. As an excitation is made from the bonding to antibonding orbital, charge will be transferred between the substrate and the adsorbate (or metal-atom cluster). The amount of charge which is transferred is determined by the relative degree to which the bonding and antibonding orbitals are localized on substrate or adsorbate. For a complete orbital mixing (metal *d*'s and CO 2π), this bonding-antibonding transition would not involve any charge transfer at all. In such a case both the lowest energy core-hole state as well as the bonding-antibonding excited state are "well-screened" states.[10] Their relative intensity depends very sensitively on the particular form of the many-body wave functions involved. The energy separation of the two states should be of the order of the energy gained by allowing for the metal electrons to screen

the hole. This energy ranges from 3—5 eV in carbonyl complexes[3] and depends on the metal-CO coupling. The energy gained for a carbonyl system is expected to be smaller than for a surface due to the fewer number of available metal electrons in the carbonyl and the differences in the geometrical arrangements.

Finally we would like to point out that the O 1*s* and C 1*s* core spectra in Fig. 1 show a remarkable similarity. Only small differences in the relative intensities of the relative peak positions are observed. This is not too surprising since in the model presented here basically the same excitation processes take place in response to the removal of a 1*s* electron from either the carbon or oxygen core. The observed differences depend on the detailed excited state interaction and they can only be discussed when more elaborate configuration interaction calculations on both core holes are available.[11]

Next we will discuss the outer and inner valence electron ionizations in free and coordinated CO, as shown on the right-hand side of Fig. 1. As mentioned in the experimental section, the carbonyl and free CO spectra have been taken in an angle integrated mode using x-ray excitation, while the adsorbate spectra were obtained using 110-eV photons and an angle-resolved spectrometer. Therefore the comparison can be made only under these restrictive conditions.

In contrast to the rather localized core holes we expect for the more delocalized valence holes a much stronger influence of the different environment in the carbonyl and surface systems. This is especially true for the uppermost 5σ, 1π, and 4σ ionizations due to the relatively large spatial extent of the associated molecular wave functions. As demonstrated in the previous paper (I) (Ref. 1) these orbitals in the adsorbed overlayer form bands with definite dispersion $[E(k)]$. In contrast, the electron momentum k is not a good quantum number for the cobalt carbonyl. As can be seen from the 5σ-1π region in Fig. 1, the influence of these effects on the ionization potential is of the order of ~ 1 eV. If we disregard these details, the spectra of adsorbate and compound again exhibit very similar features in the energy range beween 15 and 45 eV.

To assign the basic features of the adsorbate and carbonyl spectra we again compare them to the uncoordinated CO molecule. For the free molecule recent studies indicate[12,13] that the interpretation of shakeup peaks in core ionizations can be transferred to some extent to the valence ionizations. It is assumed that on each valence level a 1π-$2\pi^*$ transition occurs, namely on the 5σ and 4σ levels. This leads to four final states (a pair of states from each level), spaced in accordance with the energy separation. Since the two doublet states originating from the 1π-$2\pi^*$ excitation are split by about 7 eV (situated at 8 and 15 eV below the main line) and the 5σ-4σ separation in the free CO molecule is about 6 eV, we expect shakeup peaks to occur at about 3, 8, 9, and 15 eV below the 4σ emission. The 15 eV satellite would already interfere with the 3σ state which is situated 15—17 eV below the 4σ-ion state. In addition, a manifold of higher excited hole states due to π-π^* excitations on the 5σ and 4σ orbitals are situated in this energy range. Consequently the 3σ quasiparticle state lies within an energy region of high density of states. This leads to strong coupling and prohibits a simple interpretation in this energy range. Calculations[14,15] show that the intensity of the 3σ line is basically accumulated in two energy ranges, one is close to the quasiparticle energy and a second one is located about 7 eV lower in binding energy. This is close to the expected higher-binding-energy doublet state of the 1π-$2\pi^*$ excitation on the 4σ orbital.

When the molecule is bound to the surface, the 5σ orbital is shifted towards the 1π and 4σ orbitals, so that the energy separation between the 5σ and 4σ orbital is smaller by about a factor of 2. The 5σ orbital, which is primarily localized on the carbon atom in free CO, loses its localized character by interaction with the metal. For these reasons the simple model applicable to the free molecule can, at best, be used only to assign shakeup states originating from transitions on the 4σ orbital. Furthermore, it is expected that new satellite peaks might appear in the valence regions of coordinated CO's due to excitations analogous to the bonding-antibonding transitions discussed previously for core holes.[16] In principle, these excitations could occur on all CO valence levels. The intensities of the additional peaks depend on the degree of localization of the CO hole. If the hole is largely delocalized due to interactions with the metal or neighboring CO's, the additional Coulomb force felt by the unoccupied orbitals (i.e., $2\pi^*$) due to the ionization of an electron will not be particularly strong. Consequently the unoccupied level will not be pulled down in energy very much. The more the hole is localized, the stronger will be the Coulomb stabilization of the unoccupied orbitals. This increases the mixing between occupied metal and unoccupied CO levels and thereby increases the satellite intensities. As stated above the 5σ orbital becomes delocalized by the metal—CO bonding. Therefore the strongest satellite lines are expected for the 1π and 4σ levels. If we transfer the excitation energy for a bonding to antibonding transition from the core spectra to the valence ionizations we expect shakeup peaks just below the 4σ emission due to the 1π orbital and about 5 eV below the 4σ due to shakeup on the 4σ itself. In this energy region the shakeup structure is found for the adsorbate and for the compounds as can be seen in Fig. 1. In addition, He II spectra of $Co_4(CO)_{12}$ show that there are additional structure on the high-binding-energy side of the 4σ peak only 1.5 eV below the 4σ maximum. The intensity of this peak is rather small as in the case of the adsorbate. This is in contrast to similar studies of CO-Cu.[17] In the copper case, the peak just below the 4σ peak (on the higher-binding-energy side) is almost as intense as the main 4σ lines. This can easily be understood in the above model as a result of increased localization of the 4σ hole for CO-Cu vs CO-Cu(0001) due to the weaker bonding of CO to copper than to transition metals such as cobalt.

The region of the 3σ emission of adsorbate systems looks very similar to the 110 eV spectrum of condensed CO recently reported.[13] This similarity includes the peak at lower binding energy. This satellite peak may be due to coupling of the 3σ state to the component of the 1π-$2\pi^*$ excitation on the 4σ. This is consistent with the proposed model since we have assumed above that the excited states on the 4σ are not very strongly affected upon coordination. The peak on the high-binding-energy side of the 3σ emission is probably a satellite due to the bonding-antibonding excitation combined with the 3σ emission.

Summarizing, the satellite peaks accompanying the core- *and* valence-level photoionizations of coordinated CO can be interpreted in terms of a simple model[2(d)] that allows one to assign these peaks as electron excitations in an effectively screened ion potential.

IV. Co VALENCE-BAND SATELLITE

In this section we discuss the observation of a peak in the valence-band region of metallic Co. We assign this as being a satellite associated with the Co *d* bands, analogous to the 6-eV satellite reported for metallic Ni.[18,19] Similar satellite structures have been observed by photoemission in a number of other systems: nickel oxides and nickel compounds [NiO,[20,21] NiTe,[21] NiSb (Ref. 21)], copper and copper oxides [Cu,[19,22] CuO,[22] Cu_2O (Refs. 21 and 22)]; cobalt and cobalt compounds [Co,[18,23] $CeCo_2$,[24] CoTe,[24] and Y_4Co_3 (Ref. 24)], Ge and GeO_2,[25] Fe,[23] Cr,[31] etc. A significant number of theoretical papers have addressed the origin of these satellites,[26–29] primarily as multielectron excitations. These satellite peaks are particularly interesting since many exhibit resonances in intensity as the photon energy is swept through the 3*p* absorption threshold.

In Fig. 3 we have plotted photoemission spectra of clean Co(0001) recorded at several different photon energies. A small peak can be seen at about (4.5—5)-eV binding energy. The adsorption of CO did not have much effect upon the position or intensity of this peak, which indicates that its origin is in the bulk rather than at the surface. The observation of such a structure on clean Co(0001) has been reported before by Himpsel *et al.*[18] at about 5-eV binding energy, which agrees with our results. They attributed it

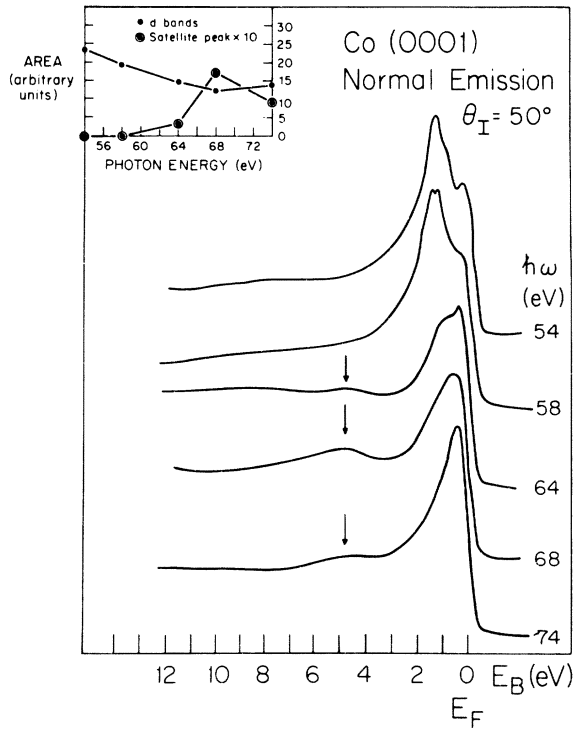

FIG. 3. Angle-resolved photoemission spectra of clean Co(0001) for normal emission and *p*-polarized light. Inset: normalized *d*-band and satellite intensities as a function of photon energy.

to a shakeup peak analogous to the satellite feature observed in bulk Ni at 6-eV binding energy. This assignment for Co is supported by the observation of Oh *et al.*[24] of similar satellite features, also at 4.5—5 eV below E_F, in $CeCo_2$, CoTe, and Y_4Co_3 compounds.[24] The existence of such a satellite in cobalt was predicted by Treglia *et al.*[28] They suggested that the satellite should be broader and weaker than in nickel, which is consistent with the results presented in Fig. 3. In particular, the maximum intensity of the satellite in Co is about 10% relative to the *d* bands, as shown in the inset in Fig. 3 and also noted in Ref. 18. In contrast, the Ni satellite reaches an intensity ~21% of the Ni *d* bands at resonance.[18]

In the inset in Fig. 3 we have plotted the normalized areas under satellite peaks and the *d* bands at several different photon energies. The incident photon flux was measured with a tungsten mesh electrode in the photon beam. As can be seen in the figure, the satellite goes through a maximum in intensity somewhere in the region of (65—68)-eV photon energy. The *d* bands show a corresponding dip in intensity in the same energy range. It is difficult to pinpoint the exact position or line shape of the resonance because the $M_{2,3}VV$ Auger peak sweeps through the valence band in this energy range. A similar enhancement of the satellite peak and corresponding decrease in the *d* bands is seen in bulk nickel.[21] In both cases (nickel and cobalt) the resonance occurs in the region of the 3*p* absorption threshold [~68 eV for Ni and ~62 for Co (Ref. 30)].

In the simplest picture, the satellite in cobalt (and other atoms and solids) is the result of photoionization of a 3*d* electron near the Fermi level combined with a simultaneous excitation of another *d* electron into an unoccupied 3*d* or 4*s* level above the Fermi level (but below the vacuum).

Following a treatment by Wendin *et al.*,[26] we let the atomic ground-state configuration of metallic cobalt be $3d^8 4s$. Then the main line corresponds to a $3d^7 4s$ configuration screened by the metallic electrons on the surrounding sites. The satellite is due to a 3*d*-4*s* (or 3*d*-3*d*) excitation coupled to a 3*d* hole, i.e., it corresponds to a screened $3d^6 4s^2$ (or $3d^7 4s^1$) state. Let us write the screened configuration as follows: $3\tilde{d}^8 4s$ for the main line and $3\tilde{d}^7 4s^2$ for the satellite, where the *d* hole has been subsequently filled in each case. The tilde indicates that the $3\tilde{d}^8$ and $3\tilde{d}^7$ configurations of the unscreened states are not necessarily the same as the ones in the initial state.

The lifetime of the screened two-hole, one-particle state ($3\tilde{d}^7 4s^2$) and its coupling to the screened $3\tilde{d}^8 4s$ depends on the localization of the *d* orbitals as well as on the number of empty *d* states. Ni has one more *d* electron than Co in the ground state. The extra plus charge associated with this electron will tend to spatially localize the 3*d* electrons in Ni more than in Co. Furthermore, Co has more empty 3*d* levels than Ni. The consequence of both of the above features is, according to Wendin *et al.*,[26] that the satellite in Co should be weaker than in Ni, as observed. Since the *d* electrons in Ni are more localized than in Co due to the extra plus charge in Ni, the 3*d* hole created in the shakeup transition will be more localized in Ni than in Co as well. This hole can therefore be more effectively screened in Ni. One consequence is that the satellite in Ni should be found at a greater binding energy with respect to the *d* bands than in Co, which is observed ($\langle E_{\rm sat} \rangle$

$-\langle E_{d\ \mathrm{band}}\rangle = 3.2$ and 3.5 eV for Co and Ni, respectively[18]). This trend is also observed in NiO.[20] In NiO, an insulator, the $3d$ electrons should be more localized than in metallic Ni. A satellite is observed at 9.2 eV below the main $3d$ line in NiO,[20] almost 6 eV higher in binding energy than in metallic Ni. The NiO satellite is also reported to be more intense than in Ni,[20] which is consistent with the above picture.

A resonance occurs in the satellite near the $3p$ absorption threshold because, at this photon energy, another channel for creating the same final satellite state is opened up. In particular, a $3p$ electron absorbs the photon and makes a transition into an unoccupied $3d$ or $4s$ level above E_F (both transitions are allowed by the $\Delta l = \pm 1$ selection rule for photons), leading to a $3p^5 3d^9 4s$ or $3p^5 3d^8 4s^2$ configuration, respectively.

The $3p$ hole will subsequently be filled in by an Auger-type decay process. (This is not a true Auger process as the $3p$ electron was initially excited into a unoccupied level above the Fermi level but *below* the vacuum.) As the hole is filled, either by the excited ($3p$) electron or by the valence electrons, one or more electrons will be ejected from the solid to conserve energy (so called autoionization or a super-Coster-Kronig transition).

A variety of final states are possible after the decay process is complete: one or more holes in the valence band, one or more electrons ejected, an electron left in or excited to a level above E_F. One such final state will be identical to the state created by directly photoemitting out of the Co $3d$ bands *and* simultaneously exciting another $3d$ electron into an unoccupied $3d$ or $4s$ level, i.e., a final state identical to the state giving rising to the 5-eV satellite in cobalt. The photoionization would in this case proceed as follows:

$$3p^6 3d^8 4s + h\nu \rightarrow 3p^5 3d^9 4s$$
$$\rightarrow e^- + 3p^6 3d^6 4s^2$$
$$\xrightarrow{\text{screening}} e^- + 3p^6 3\tilde{d}^7 4s^2$$

(satellite) or

$$3p^6 3d^8 4s + h\nu \rightarrow 3p^5 3d^8 4s^2$$
$$\rightarrow e^- + 3p^6 3d^6 4s^2$$
$$\xrightarrow{\text{screening}} e^- + 3p^6 3\tilde{d}^7 4s^2$$

(satellite). Since at the $3p$ threshold other channels have been opened up by which this final state can be reached, an enhancement in the intensity of the satellite peak is expected and observed, as shown in Fig. 3.

Another possible final state after the decay process described above is completed corresponds simply to removing an electron from a $3d$ level below E_F and ejecting it into the vacuum; in other words, a state identical to the "main line" in photoemission spectra. The photoionization would proceed as follows:

$$3p^6 3d^8 4s + h\nu \rightarrow 3p^5 3d^9 4s$$
$$\rightarrow e^- + 3p^6 3d^7 4s$$
$$\xrightarrow{\text{screening}} e^- + 3p^6 3\tilde{d}^8 4s$$

(main line) or

$$3p^6 3d^8 4s + h\nu \rightarrow 3p^5 3d^8 4s^2$$
$$\rightarrow e^- + 3p^6 3d^7 4s$$
$$\xrightarrow{\text{screening}} e^- + 3p^6 3\tilde{d}^8 4s$$

(main line). By the same argument given above for the Co satellite, one would also expect a resonant enhancement of the main line near the $3p$ threshold. Instead, a characteristic diminishing of intensity of the d bands is observed in both Ni and Co. This shows that the actual situation is more complicated than described above. The intensities of satellite and d bands near the threshold depend on the detailed dynamics of the screening process.[26] The result for Ni and Co is an enhancement of the satellite and an interference dip in the d bands near the $3p$ threshold.

In conclusion, we have observed a valence-band feature in metallic Co which undergoes a resonant enhancement at the $3p$ absorption threshold. We attribute this satellite feature to a shakeup off the Co d bands and have offered a qualitative description of the process leading to its enhancement.

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