Configuration mixing in the 3s -hole state of transition-metal ions*

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Results of configuration-interaction calculations for transition-metal ions and for neutral Co and Ni atoms are used to interpret 3s -photoelectron spectra of transition-metal salts. Only internal configurations with electrons in the 3s, 3p, and 3d orbitals are included for the ions. For the neutral atoms the 4s orbitals are also considered in the internal set. An N -electron basis consisting of L S -projected determinants is used with a numerical Hartree-Fock orbital basis, obtained from a statistical self-consistent-field (SCF) potential including full exchange. Different sets of occupation numbers have been used to determine the SCF potentials, following ideas of Linderberg and Öhrn. Both observed 3s splittings and relative intensities, where available, are adequately estimated by the calculations. Comparisons are also made to much more ambitious calculations, which are available, in some cases, and good agreement is found.

INTRODUCTION

The splitting of the 3s -photoelectron line of ionic transition-metal salts was experimentally observed some years ago.[1-3] The first calculations done with a one-electron model on the exchange interaction between the 3s electron and the unpaired 3d electrons gave values which were roughly twice as large as the measured splitting,[3,4] thus indicating that the observed fine structure was not likely to be due to the spin exchange only.

One suggested explanation is that the ligand field in the salts is strong enough to cause a "delocalization" of the 3d electrons and decrease the splitting.[3,5] Spin-polarized calculations within the multiple scattering $X\alpha$ formalism gave results very close to the measured 3s splitting.[6] However, corresponding calculation for a free transition-metal ion gave a splitting very close to the value calculated for the complex.[6] This can be interpreted to mean that the agreement between the calculation for the complex and experiment was due to the fact that the $X\alpha$ exchange approximation underestimates exchange splitting compared to full Hartree-Fock nonlocal exchange, rather than due to the presence of the ligand atoms.

An alternative explanation for the small measured splitting has been given by Bagus *et al.*[7] on the basis of a configuration-interaction (CI) calculation on the Mn^{2+} ion. The configuration mixing together with the electron correlation in the final core-hole state was shown to be large enough to reduce the splitting and also to show the correct deviation of the relative intensities from the multiplicity ratios. Fine structure, predicted to appear in the 3s -photoelectron spectrum, was later found in the spectrum of MnF_2.[8]

In this paper we report on studies of the multiplet structure of the 3s hole states in a series of $3d^n$ transition-metal ions and of neutral Co and Ni

atoms. The details of the method used to calculate the configuration mixing are described in the next section, and in the following two sections we report the results for the ions and for the neutral systems, respectively.

METHOD

Photoelectron spectra of ionic transition-metal compounds can be studied by first considering the metal ion in the initial state

$$(\text{core } 3s^2 3p^6 3d^n)\, {}^{2S+1}L , \qquad (1)$$

where the core consists of doubly occupied 1s, 2s, and 2p orbitals. The emission of a 3s electron gives rise to two different final states,

$$[\text{core } 3s(^2S) 3p^6 3d^n(^{2S+1}L)]\, {}^{2(S+1)}L , $$
$$[\text{core } 3s(^2S) 3p^6 3d^n(^{2S+1}L)]\, {}^{2S}L . \qquad (2)$$

In the experiment the energy differences can be measured between the initial state (1) which is not split, and the two final states (2). The fine structure of the spectrum can thus be studied by considering the multiplet structure of the final states.

Different approaches to calculate the splitting between the two states, labeled by (2), have been described in Ref. 9, from where it is also evident that a simple one-electron model is insufficient to explain the fine structure in the measured spectra. States with symmetry designations ${}^{2(S+1)}L$ and ${}^{2S}L$ can arise not only from the configurations (2) but also from electron configurations with different distribution of electrons in the 3s hole state. Including such additional configurations will, of course, through configuration mixing, affect both the calculated splittings and intensities.

We have limited our calculations to configurations that can be formed by redistributing the $(n+7)$ M-shell electrons of a $3d^n$ ion in the 3s, 3p, and 3d subshells. Similarly, for a $3d^n 4s^2$ metal atom

TABLE I. Number of projected determinantal basis functions for the $3s$ hole states of the doubly positive transition-metal ions.

n	State symmetry	$3s\,3p^6\,3d^n$	$3s^2\,3p^4\,3d^{n+1}$	$3s\,3p^4\,3d^{n+2}$	$3s^2\,3p^6\,3d^{n-1}$	$3p^6\,3d^{n+1}$	Total
1	^3D	1	5	18	•••	•••	24
1	^1D	1	6	13	•••	1	21
2	^4F	1	8	25	•••	1	35
2	^2F	1	12	29	•••	1	43
3	^5F	1	6	18	•••	•••	25
3	^3F	2	10	36	1	2	51
4	^6D	1	3	9	•••	•••	13
4	^4D	2	14	23	•••	1	40
5	^7S	1	•••	1	•••	•••	2
5	^5S	1	3	3	•••	•••	7
6	^6D	1	2	2	•••	•••	5
6	^4D	2	8	7	•••	1	18
7	^5F	1	1	1	•••	•••	3
7	^3F	2	6	3	2	1	14
8	^4F	1	•••	1	1	•••	3
8	^2F	1	2	•••	1	•••	4

with a $3s$ hole, we consider only the configurations formed by different occupations of the $3s$, $3p$, $3d$, and $4s$ subshells by the $(n+9)$ electrons of interest. These configurations have been classified as internal.[10] We have imposed the additional constraint to consider only those internal configurations which differ at most by double replacements from the reference configurations (2).

This description of the electron correlation in the final hole states is thus necessarily incomplete, since we have excluded configurations involving the virtual part of the orbital space, or configurations classified as semi-internal and external.[10] There is evidence that this limitation is not serious. The mixing of configurations which are nearly degenerate with (2) are likely to be of essential importance for the physical processes we want to study. The inclusion of other configurations would certainly be expected to change the numerical results somewhat, but the internal configurations form a suitable basis for a proper "zeroth-order" wave function for the processes of interest. More objections could perhaps be raised against our further limiting the configurations to those differing by at most two electrons in the occupations of the $3s$, $3p$, and $3d$ subshells from the case of the configurations (2). Our results will show that this is not an unreasonable approximation in comparison to the accuracy sought.

The number of symmetry-adapted N-electron basis functions for different d^n ions are given in Table I along with the electron configurations from which they originate. We construct the LS eigenstates by employing computer programs implementing the projection operator technique of Löwdin.[11] The normal final-state configuration, $3s\,3p^6\,3d^n$, gives only one $^{2(S+1)}L$ state and one ^{2S}L

state except in the cases of three, four, six, and seven $3d$ electrons when it gives two ^{2S}L states for each distribution of the electrons in the M shell. As shown in Table I, the number of symmetry-projected N-electron basis functions that we consider is very modest compared to most CI calculations.

We use the same numerical orbitals to construct the determinantal basis for all configurations. Since optimization of the orbital basis for different states within the single-configuration approximation has been found to have only a small effect[9] on the multiple splittings, we decided to investigate the possibility for obtaining a reasonable multiplet structure with a fixed orbital basis when configuration mixing is included.

The orbitals used are numerical solutions of Hartree-Fock equations.[12] Comparisons are made between calculations performed with different sets of these numerical orbitals. The orbitals were obtained from different self-consistent-field (SCF) potentials with full exchange obtained from various statistical energy functionals.[1,13]

Such energy functionals can be formed as averages of the many-electron Hamiltonian with respect to single-particle ensembles.[14] We can think of these averages as formed, with certain weights, over multiplets from configurations with varying number of electrons in the different subshells [grand canonical average (GCA)].[13] This procedure conveniently allows for the consideration of fractional occupation numbers. However, unless the spin-orbital occupation numbers are zero or unity, the number operator for electrons will have nonzero width. We can project the density operator of the ensemble onto an eigenspace of the number operator for electrons corresponding to

the desired number of electrons of the system [canonical average (CA)].[13] The resulting average is, in the case of a single open subshell identical to the Slater average (SA)[15] which is the weighted average over all multiplets arising from a given configuration.

The intensity of a photoelectron peak is proportional to the square of the transition-moment matrix element between the initial and final state. In the frozen-orbital approximation this reduces to the product of two factors. One being the one-electron transition-moment integral with the initial-state core orbital from which the electron has been ejected and the final-state continuum orbital of the photoelectron; the other being a product of overlap integrals between spectator orbitals. The overlap integrals vanish unless the spectator orbitals in the final state couple to a state of the same symmetry as they do in the initial state. In the frozen-orbital approximation the spectator orbitals are identical in the initial and final state. Thus the relative intensities become roughly proportional to the total multiplicity of the final state when the single-configuration approximation is used. When allowing for configuration mixing it can be argued that the relative intensities become proportional to

$$I(LS)_i = C_i^2(2S+1)(2L+1), \qquad (3)$$

where the final state has the total multiplicity $(2S+1)(2L+1)$, and where we are considering the ith root of the secular problem and C_i is the coefficient of the dominant initial-state configuration (2) in the final-state wave function, i.e., the eigenvector corresponding to the ith energy eigenvalue. It is seen from Eq. (3) that higher roots steal intensity from the main transition. This loss of intensity is quite large and an essential feature of the spectra observed in x-ray photoemission spectroscopy (XPS).[8]

One can question how well founded the expression in Eq. (3) is for the relative intensities. The frozen-orbital approximation is quite reasonable, since relaxation effects should be small for the case of an electron removed from the M shell. Even if the effect of the orbital relaxations were included it will be nearly the same for both final-state couplings (2) and thus not contribute to relative intensities. The neglect of configuration mixing in the initial state, which leads to Eq. (3), is also quite reasonable, since the initial state always is coupled to the highest multiplicity, which ensures the absence of strongly intermixing, nearly degenerate configurations coupling to N-electron basis functions of the same symmetry. The possible exception is the case of the Co atom, for which there is likely to be strong configuration mixing in the initial state. This will be discussed

further in the last section.

The very approximate nature of Eq. (3) makes it suitable only for rough estimates of the deviation of the observed intensities from the multiplicity ratio $(S+1)/S$. It will be used to predict whether a transition to a particular calculated state can be associated with the observed fine structure in the spectrum.

The calculations reported in the next sections have been performed on the IBM 370/165 computer at the University of Florida. The radial one-electron functions were calculated with the numerical Hartree-Fock program, originally written by Froese-Fischer[12] and then modified to handle statistical SCF potentials.[13] The programs for projecting the LS eigenfunctions were written by N. H. F. Beebe in our laboratory.

RESULTS FOR TRANSITION-METAL IONS

We first report some sample calculations on the Mn^{2+} ion using different SCF orbital basis sets. These calculations and others were done to test the effect of a fixed orbital basis on the multiplet structure in the $3s$ hole state. The Mn^{2+} ion was chosen since comparisons could be made to the results of Bagus et $al.$,[7] obtained with an MCHF method (multiconfigurational Hartree-Fock), which includes simultaneous optimization of both one-electron functions and the CI mixing coefficients. In Tables II and III we list the results together with the MCHF results as well as experimental results for MnF_2.[8]

The occupation numbers defining the density operator, with respect to which averages are formed, were chosen as follows:

$$3s^1\, 3p^6\, 3d^5(4s^{0.0001}) , \qquad (4)$$

where the small fraction of an electron in the $4s$ orbital makes it possible to generate also this orbital from the atomic SCF program within the GCA formalism. The $4s$ orbital generated in this manner is of no consequence for the results reported here, since excitations were allowed only within the M shell.

Another choice was

$$3s^{1.3}\, 3p^{4.5}\, 3d^{6.2}\, (4s^{0.0001}) , \qquad (5)$$

where the fractional occupation numbers were obtained as averages over the integer subshell occupation numbers of configurations $3s\, 3p^6\, 3d^5$, $3s^2\, 3p^4\, 3d^6$, and $3s\, 3p^4\, 3d^7$ weighted with $\sum_i(2S_i+1)$, where i runs over the different ^5S and ^7S states which can be constructed from each configuration.

In addition we show, in Tables II and III the results from our calculations with the orbitals determined from the Slater average (SA),[15] over the configuration $3s\, 3p^6\, 3d^5$.

The changes of the energies of the different

states from one basis to the next are of the order of a few tenths of an eV. Compared to the splittings of several eV, which we are interested in, these changes can be considered insignificant. We have chosen in the following to employ the GCA SCF orbitals calculated from the potential determined with the density operator defined by the subshell occupations of configuration (2), with a small fraction of an electron in the $4s$ orbital.

We note that the differences between our relative term energies and those of the MCHF calculations of Ref. 7 are less than 1 eV for most of the states and at most 2 eV. Since our conclusions, on the basis of atomic internal CI calculations, concerning the photoelectron spectra of a transition-metal compound will be qualitative, we consider the agreement for the energies in Table II and for the relative intensities in Table III to be sufficient for the purpose of studying the splittings of the $3s$-photoelectron line of ionic transition-metal salts.

The results for the $3s$ splittings, or the energy differences between the lowest $^{2(S+1)}L$ and ^{2S}L states, arising principally from the configuration $3s\,3p^6\,3d^n$, are given in Table IV. In the same table we list the results of a multiplet-hole-theory (MHT) calculation, which is a ΔSCF result, i.e., it involves separate Hartree-Fock calculations for the two states. We compare these results with the measured splittings for the corresponding metal fluoride. Because of their ionicity, the fluorides should offer a suitable comparison with the results of a calculation on the metal ions.

The MHT results show a discrepancy of approximately a factor of 2 when compared to the experimental splittings. The mixing between the internal configurations in our calculations lead to smaller splitting in all cases. The difference between our results and those of the MHT calculation can be considered as a measure of the importance of con-

TABLE II. Multiplet structure in the $3s$ hole state of Mn^{2+}.

State symmetry[a]	GCA I[b]	GCA II[b]	Energies (eV) SA[c]	MCHF[d]	Experiment[e]
$^7S_1$	0.0	0.0	0.0	0.0	0.0
$^7S_2$	105.15	105.06	104.95	103.50	...
$^5S_1$	4.28	4.38	4.48	4.67	6.62±0.1
$^5S_2$	20.35	20.44	20.57	22.34	20.7±0.1
$^5S_3$	23.59	23.77	24.02	23.67	
$^5S_4$	42.67	42.70	43.42	42.96	37.8±0.7
$^5S_5$	102.84	102.72	102.59	101.40	
$^5S_6$	117.16	117.22	117.35	116.45	
$^5S_7$	133.74	133.81	134.09	132.14	

[a]The subscript orders the roots in the symmetry block.
[b]Occupation numbers determining the grand canonical average I: $3s^1\,3p^6\,3d^5\,4s^{0.0001}$ and II: $3s^{1.3}\,3p^{4.5}\,3d^{6.2}\,4s^{0.0001}$.
[c]Slater's average over the configuration $3s^1\,3p^6\,3d^5$.
[d]Multiconfigurational Hartree-Fock, Ref. 7.
[e]Results from Ref. 8.

TABLE III. Relative intensities for the XPS spectrum of Mn^{2+}.

State symmetry[a]	GCA I[a]	GCA II[b]	SA[c]	CMTH[d]	Experiment[e]
$^7S_1/^5S_1$	2.27	2.29	2.32	2.20	2.3±0.1
$^5S_1/(^5S_2+^5S_3)$	2.77	2.70	2.59	2.87	2.1±0.1
$(^5S_2+^5S_3)/^5S_4$	1.45	1.48	1.51	1.58	2.5±0.1

[a-c],[e]See footnotes of Table II.
[d]Correlated multiplet-hole-theory, Ref. 7.

figuration mixing. This is justified since the splittings, as calculated from the diagonal Hamiltonian matrix elements corresponding to configuration (2) in the CI calculations, agree within tenths of an eV with the optimized MHT values for each case. From the results of Table IV we note that the discrepancy between the optimized MHT values and the present CI results for the $3s$ splitting is largest in the middle of the transition-metal series and decreases with decreasing number of unpaired $3d$ electrons. In all cases we obtain a splitting that is less than the measured value. The covalency effects, although likely to be small for these compounds, would, if included, further decrease the calculated values. It has, however, been found for Mn^{2+}, that the inclusion of semi-internal configurations, with excitations of one of the electrons of the K, L, or M shell, increases the energy difference between the ^7S and the lowest ^5S state by 3.5 eV.[7] The relative intensities were essentially left unaffected by the inclusion of these configurations.[7]

The intensity ratio of the two main components of the $3s$ spectrum as calculated from the expression of Eq. (3) is listed in the last column of Table IV. As expected this value is always greater than the ratio of the multiplicities of these two states, which indicates that the configuration mixing is more pronounced in the state with lower spin.

In Table V we summarize the fine structure, which judged from our calculations can be expected to be seen in the experimental $3s$ XPS spectra. Intensities are reported only for states with estimated intensities of more than 1% of that of the main transition to a $^{2(S+1)}L$ state. It is observed that only states with the dominant configuration $3s^2\,3p^4\,3d^{n+1}$ mix with the ground-state configuration strongly enough to be expected to have an observable intensity.

One could argue that in order to obtain the energies for these states with the same relative accuracy as the energies for the states of configuration (2), it is necessary to include configurations $3s^2\,3p^2\,3d^{n+3}$. However, these double replacements from the dominant configuration for these states have energy matrix elements about 100 eV higher than those of $3s^2\,3p^4\,3d^{n+1}$ and will mix only slightly

TABLE IV. 3s-splittings and relative intensities in the XPS spectra of transition-metal ions.

No. of 3d electrons	Ion	MHT[a]	CI calc.	Exp.	Comp.	Rel. int. Exp.	Rel. int. Calc.	$(S+1)/S$
3	Cr^{3+}	9.5 (9.2)[e]	3.3	4.2	CrF_3[b]	⋯	2.0	1.67
5	Mn^{2+}	14.3 (14.4)[e]	4.3	6.6	MnF_2[d]	2.3	2.2	1.40
5	Fe^{3+}	(16.1)[e]	5.4	7.0	FeF_3[b]	⋯	2.1	1.40
6	Fe^{2+}	12.4	4.5	6.1	FeF_2[e]	2.0	2.2	1.50
6	Co^{3+}	13.6	5.4	6.0	CoF_3[b]	⋯	2.1	1.50
7	Co^{2+}	10.3	5.5	5.0	CoF_2[b]	⋯	3.2	1.67
8	Ni^{2+}	8.1	3.9	4.0	NiF_2[b]	⋯	2.4	2.0

[a]Results from Ref. 9.
[b]Reference 2.
[e]Diagonal energies from the present calculation.

[d]Reference 8.
[e]Reference 16.

with them, resulting in small corrections to the energy eigenvalues.

Experimental energies for the weaker components of the ^{2S}L multiplet are available from XPS spectra of MnF_2,[9] FeF_2,[16] several Co compounds,[5] and also for CoO and NiO.[17] They are listed in Table VI. As has already been mentioned our results agrees with those of Ref. 7 for Mn^{2+} and will not be further discussed here.

For the ions with six 3d electrons (Fe^{2+} and Co^{3+}), we calculate one ^6D and six ^4D states with large relative intensities. In a recent XPS study of FeF_2 Kowalczyk et al.[16] have measured a splitting of 6.1 eV, and a relative intensity of the two main peaks of about 2:1. They also report on two additional peaks at energies of approximately 22 and 39 eV. This agrees quite well our results. The two first ^4D states, calculated to lie at 4.5 and 5.6 eV, are together responsible for the single, rather broad peak at 6.1 eV in the experimental spectrum. The observed intensity ratio 2.0, which differs from the simple multiplicity ratio of 1.5, agrees well with our calculated value of 2.2, which is obtained after adding the intensities of the two close-lying peaks at 4.5 and 5.6 eV. The two groups of weak peaks, separated by about 20 eV, can also be identified with peaks found in the experimental spectrum at 22 and 39 eV.

The Co^{2+} ion with seven d electrons has one ^5F and two ^3F states from the ground-state configuration, and two additional ^3F states with very low estimated intensities from the $3s^2\,3p^4\,3d^8$ configuration. In the experimental spectrum of CoF_2 Frost et al.[5] report one strong peak at 5.0 eV with an intensity of about 63% of that of the principal one. In addition they see a peak at 10.2 eV with about 70% intensity. They follow these two peaks through a series of Co halides, finding an increasing relative intensity for both of them as the

halogen atoms become heavier. Their interpretation is that a shake-up transition connected with the ^5F principal peak overlaps the first ^3F state and the additional peak in the experimental spectrum is due to a corresponding shake-up from the

TABLE V. Calculated fine structure in the 3s XPS spectra of $3d^n$ transition-metal ions.

Ion	State	Dominant config. 3s	Dominant config. 3p	Dominant config. 3d	Rel. energy (eV)	Rel. intensity
Mn^{2+}	^7S	1	6	5	0.0	100
	^5S	1	6	5	4.3	47
	^5S	2	4	6	20.4 ⎫	14
	^5S	2	4	6	23.8 ⎭	
	^5S	2	4	6	42.7	10
Fe^{3+}	^7S	1	6	5	0.0	100
	^5S	1	6	5	5.4	48
	^5S	2	4	6	23.7 ⎫	13
	^5S	2	4	6	27.1 ⎭	
	^5S	2	4	6	47.9	10
Fe^{2+}	^6D	1	6	6	0.0	100
	^4D	1	6	6	4.5	41
	^4D	1	6	6	5.6	4
	^4D	2	4	7	18.9	2
	^4D	2	4	7	22.8 ⎫	8
	^4D	2	4	7	24.5 ⎭	
	^4D	2	4	7	33.6	3
	^4D	2	4	7	44.7	7
Co^{3+}	^6D	1	6	6	0.0	100
	^4D	1	6	6	5.4	40
	^4D	1	6	6	6.5	7
	^4D	2	4	7	21.8	2
	^4D	2	4	7	26.0	3
	^4D	2	4	7	27.8	
	^4D	2	4	7	37.9	2
	^4D	2	4	7	49.8	6
Co^{2+}	^5F	1	6	7	0.0	100
	^3F	1	6	7	5.6	31
	^3F	1	6	7	8.2	25
	^3F	2	4	8	26.2	1
	^3F	2	4	8	34.8	2
Ni^{2+}	^4F	1	6	8	0.0	100
	^2F	1	6	8	3.9	41
	^2F	2	4	9	30.4	5
	^2F	2	4	9	45.8	3

TABLE VI. Measured fine structure in the 3s-XPS spectra of transition-metal compounds.

Relative energies in eV.				
FeF_2 [a]	CoF_2 [b]		CoO [c]	NiO [c]
energy	Energy	Int.	energy	energy
0.0	0.0	100	0.0	0.0
6.1	5.0	63	5.9	5.5
22	10.2	7	11.1	10.5
39			25	25

[a]Reference 16.
[b]Reference 5.
[c]Reference 17.

^3F peak. On the basis of our calculations we cannot account for the peak at 10.2 eV, and it seems not to be due to configuration mixing. The large relative intensity of the first ^3F line could possibly be connected to the two close-lying ^3F states at 5.6 and 8.2 eV, the intensities of which should be added.

The intensity ratio between the ^4F and the first of the three ^2F states of Ni^{2+} is calculated to be 2.4 compared to the multiplicity ratio of 2. The only experimental results available to us are for NiO, which is a less suitable compound to compare with calculations of Ni^{2+}. There is, however, a recent calculation by Wahlgren and Bagus[18] on the NiO_6^{10-} complex, which shows that the ligand field does not essentially change the multiplet structure of the 3s hole state. Their results agree with those reported in Table V, and also indicate that configuration mixing does not explain the peak at 10.5 eV in the experimental spectrum. The similarity of the spectra of NiO and CoO supports the assumption that the structure around 10 eV has a common origin in the two compounds. Further studies are needed to determine whether this origin is a shake-up process,[5] a multielectron excitation,[19] a band structure effect, or due to surface states.

RESULTS FOR Co AND Ni ATOMS

The multiplet structure of the 3s hole state for neutral Co and Ni atoms is expected to be different from that of the ions. The $3d^n 4s^2$, $3d^{n+1} 4s$, and $3d^{n+2}$ configurations could show significant mixing and could also interact considerably with configurations formed from them by electron redistribution.

The neglect of configuration interaction in the initial state could here be questioned. For Ni this neglect, however, seems quite reasonable, since the ground-state coupling of these configurations $[3d^8 4s^2(^3F)$, $3d^9 4s(^3D)$, and $3d^{10}(^1S)]$ all have different symmetry and cannot mix. The corresponding couplings for Co $[3d^7 4s^2(^4F)$, $3d^8 4s(^4F)$, and $3d^9(^2D)]$ would allow mixing between the first two

configurations, and lead to an initial state with more than one dominant configuration. A two-by-two CI for the corresponding projected determinants yielded a mixing coefficient for $3d^7 4s^2(^4F)$ of only 0.0064 in the eigenvector of the lower root. This was considered so small that it would be safe to regard, also in the case of Co, the initial state of the photoelectron emission not to be split.

Configurations formed by at most double replacements from both $3s\, 3p^6\, 3d^n\, 4s^2$ and $3s\, 3p^6\, 3d^{n+1} 4s$ were included in the final-state CI for both Co and Ni. The calculations were performed with two sets of orbitals, one obtained from an SCF potential determined within the GCA formalism with a density operator given by the occupation numbers $3s\, 3p^6\, 3d^n\, 4s$ and the other obtained similarly from occupation numbers $3s\, 3p^6\, 3d^{n+1}\, 4s$. The results of these two CI calculations were qualitatively similar. They show two groups of projected determinants with relatively strong internal interaction but a negligible mutual mixing. One set derives from the configuration $3s\, 3p^6\, 3d^n\, 4s^2$ and its double replacements, the other set derives from the configuration $3s\, 3p^6\, 3d^{n+1}\, 4s$ and its double replacements.

In order to make predictions about photoelectron spectra from the same kind of limited CI calculations as was done for the transition-metal ions, we have to decide which of the valence-electron configurations, $3d^n\, 4s^2$, $3d^{n+1}$, or $3d^{n+2}$, would be the dominant final-state configuration. Using the GCA SCF energy we find the $3d^{n+1}\, 4s$ configuration favored over $3d^n\, 4s^2$ by 0.20 hartree in Co and 0.29 hartree in Ni. This is not surprising, since this procedure is known to favor maximum 3d occupation.[13] Comparing in the same manner the configurations $3s\, 3p^6\, 3d^n\, 4s^2$ and $3s\, 3p^6\, 3d^{n+1}\, 4s$ for the 3s hole state we find the latter one lower by 0.45 hartree for Co and by 0.56 hartree for Ni. The $3d^{n+2}$ configuration would be uninteresting in connection with the limited CI considered here, since for Ni it would couple as a ^1S and for Co the most important internal rearrangement, $3p^2$ to $3s\, 3d$, also would give a ^1S, and thus lead to no mixing.

The relative energies and intensities, calculated by assuming $3d^n\, 4s^2$ to be the dominant valence-electron configuration in the final 3s hole state, were essentially the same as those obtained for the doubly ionized Co and Ni. The 4s orbital is doubly occupied in all configurations that mix strongly with $3s\, 3p^6\, 3d^n\, 4s^2$, and thus adds only a constant term to the total energies of the different states of a given symmetry. The only way that the 4s electrons affect the multiplet structure in this case is indirectly through the M-shell orbitals, which now are calculated in a potential to which a doubly occupied 4s orbital contributes. The change

TABLE VII. Predicted $3s$ XPS spectra from the calculated multiplet structure of Co and Ni atoms with a $3s$-hole.

System	State	Dominant configuration				Relative energy	Relative intensity
		$3s$	$3p$	$3d$	$4s$		
Co	^5F	1	6	8	1	0.0	100
	^3F	1	6	8	1	1.0	23
	^3F	1	6	8	1	3.4	30
	^3F	2	4	9	1	26.9	4
	^3F	2	4	9	1	41.0	2
Ni	^4D	1	6	9	1	0.0	100
	^2D	1	6	9	1	0.8	17
	^2D	1	6	9	1	2.2	30
	^2D	2	4	10	1	34.9	4

in the M-shell orbitals, due to the presence of the $4s$ electrons, is small. The expectation value of the radial distance to the nucleus changes for an electron by about 1.5% for a $3d$ orbital and by about 1% for a $3s$ or $3p$ orbital when a filled $4s$ orbital is added to the ion. As we mentioned earlier, the $3s$ splitting is not very sensitive to small changes in the radial orbitals. A rough estimate for the $3s$ splitting can be obtained from the exchange integrals. The $G^2(3s, 3d)$ integral is only about 1.5% larger in the doubly positive ion than in the neutral atom. All these considerations taken together make the similarity of the calculated multiplet structures of the $3s$ hole doubly ionized and neutral atom quite understandable for the case of a doubly occupied $4s$ orbital in the atom.

When we assume $3d^{n+1}4s$ to be the dominant final-state configuration for the valence electrons, we obtain the results which are given in Table VII. In comparing the results of Table VII with those of Table V we find obvious differences. For Co the $3s$ splitting is only 1.0 eV, much smaller than for the ion. This can be understood if we look closer at the coupling in the two ^3F states from the configuration $3s\,3p^6\,3d^7\,4s^2$ on the one hand and at the coupling of the two ^3F states from the configuration $3s\,3p^6\,3d^8\,4s$, on the other. In the first case the seven $3d$ electron can couple to a ^4F and to a ^2F. The quartet when coupled with a $3s(^2S)$ gives either a ^5F or a ^3F. The second ^3F with the same electron configuration comes from the coupling of the $3s(^2S)$ to the $3d^7(^2F)$. The $3s$ splitting in the sense we have discussed it in the previous sections is the energy difference between the ^5F and the ^3F with the $d^7(^4F)$ parent. In the single-configuration approximation a rough qualitative estimate for this splitting is obtained from the $G^2(3s, 3d)$ exchange integral.

In the case of the configuration $3s\,3p^6\,3d^8\,4s$ we note that the ^5F is the result of the coupling $\{[3s\alpha(^2S)3d^8(^3F)](^4F)4s\alpha(^2S)\}(^5F)$, and the two different ^3F states are (a) $\{[3s\beta(^2S)3d^8(^3F)](^2F)4s\alpha \times(^2S)\}(^3F)$, and (b) $\{[3s\alpha(^2S)3d^8(^3F)](^4F)4s\beta\}(^3F)$.

The $3s$ splitting being the difference between the energies of ^5F and the ^3F(a) is roughly determined by the $(3s, 3d)$ and the $(3s, 4s)$ exchange interaction. The energy difference between the ^5F and the ^3F(b) is similarly determined by the $(3d, 4s)$ and the $(3s, 4s)$ exchanges. The $(3d, 4s)$ exchange is much smaller than the $(3s, 3d)$ interaction and consequently we identify the first ^3F state at 1.0 eV as ^3F(b). We also calculate another structure at 3.4 eV and two very weak lines at 26.9 and 41 eV, respectively, as reported in Table VII. The value of the $3s$ splitting to be compared with the results for the Co^{2+} ion is thus 3.4 eV; i.e., 2.2 eV smaller than the splitting in the $3d^7$ case. This obviously is due to the reduced $(3s, 3d)$ exchange since we now have one unpaired $4s$ electron instead of the unpaired $3d$ electron and the $(3s, 4s)$ exchange being much smaller than the $(3s, 3d)$ exchange.

Similar comments can be made about nickel. The $3d^8 4s^2$ configuration of Ni yields a $3s$ hole state spectrum very similar to what the $3d^8$ configuration does for the Ni^{2+} ion, as reported in Table VI. The configuration $3d^8 4s^2$ can couple to only one ^4F and one ^2F state.

In the case of the $3d^9 4s$ configuration for Ni, the doublet is split into two because of the different couplings with the $4s$ electron. The two cases (a) $\{[3s\beta(^2S)3d^9(^2D)](^1D)4s\alpha(^2S)\}(^2D)$ and (b) $\{[3s\alpha \times(^2S)3d^9(^2D)](^3D)4s\beta(^2S)\}(^2D)$ leads to doublets with a strong mutual interaction. Thus both of them will show a large estimated relative intensity. The sum of their intensities will be roughly the same as the relative intensity of the single ^2F term for Ni^{2+} ($3d^8$). The doublet at 0.8 eV has the dominant configuration (b) and thus the $3s$ splitting is 2.2 eV. This is again somewhat smaller than what is obtained for the $3d^8$ case.

It should be noted that these calculated spectra from the $3d^{n+1}4s$ configurations resemble closely the experimental $3s$ XPS spectra from Co and Ni metals. Instead of two resolved peaks indicating the splitting, the spectra have a strongly asymmetric main peak which agrees well with the calculations since the ^3F(b) and the ^2D(b) terms for Co and Ni, respectively, lie too close to the main peak to be resolved.

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