Nature of Extra-Atomic Core-Hole Screening in Ferromagnetic Nickel

A. K. See and L. E. Klebanoff

Department of Chemistry and Zettlemoyer Center for Surface Studies, Lehigh University, Bethlehem, PA 18015

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Spin-resolved studies of Ni core-level photoemission are reported. The results indicate that the final-state Ni $3d$ electron configuration in *not* purely $3d^{10}$, in contradiction with early theories emphasizing complete $3d$-electron core-hole screening. A model is described in which extra-atomic screening involving unoccupied pure $3d$ states and unpolarized and hybridized $3d$-$4sp$ states leads qualitatively to a final-state $3d$ valence configuration of ~50% $3d^9$ and ~50% $3d^{10}$. The relationship of these results to more recent theory employing the Anderson impurity model is discussed.

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The manner in which an itinerant electron system responds to the creation of a core hole has been a central subject of solid-state photoemission studies for over twenty years. Shirley [1] emphasized the importance of core-hole screening by electrons on the photoexcited atom (atomic relaxation) as well as by electrons on neighboring atoms (extra-atomic relaxation). Extra-atomic relaxation in metallic Ni was critical to the theoretical developments that followed [2], since there is a strong variation in the metallic-to-atomic binding energy shift in going from Ni to Cu. This variation is attributed [2] to differences in valence configuration between atomic and metallic Ni (but not for Cu), and to efficient d-wave screening in Ni, contrasted with less efficient s, p-wave screening in Cu.

Extra-atomic screening in Ni is of great importance for theories of satellite structure in Ni x-ray photoelectron spectroscopy (XPS) spectra [3]. Many workers have attributed the main-line component of core-level XPS in Ni to a *local* final-state electron configuration of $c3d^{10}$ (c = core hole), whereas a 6-eV satellite is attributed to a $c3d^9$ configuration [3]. The $3d^{10}$ final state is theoretically achieved from the $(4sp)^1 3d^9$ initial state via d wave extra-atomic screening, in which a previously unoccupied $3d$ level is pulled below the Fermi level and occupied at the core-hole site [4,5]. On the basis of these studies, one would expect zero exchange splitting (or spin polarization) in the main-line component of Ni core-level spin-resolved XPS (SRXPS) spectra, since *the $3d^{10}$ valence configuration is intrinsically nonmagnetic*. Indeed, the original experimental evidence for the $c3d^{10}$ final state was an observed absence of exchange splitting in the spin-integrated main-line Ni $3s$ XPS component [6].

More recently, many-body $3d$ configuration interaction (CI) calculations [7–9] employing the Anderson impurity model have described the Ni ground state as a mixture of $3d^{10}$, $3d^9$, and $3d^8$ valence configurations with relative weights of ~32%, ~53%, and ~15%, respectively. The relative weights can vary when a core-level electron is photoemitted. The final-state configuration associated with the main core-level component has not been calculated, but a simple estimate suggests that ~10% $c3d^9$ and ~90% $c3d^{10}$ could be typical for this model [10].

We explore here the nature of extra-atomic core-hole screening in Ni metal with a SRXPS study. We concentrate on the main-line XPS components, and defer a comprehensive discussion of Ni core and valence XPS satellite structure to a future paper [11]. The SRXPS experiments were performed on a Ni (011) single crystal that was remanently magnetized in the surface plane along the $[1\bar{1}1]$ easy axis by a supporting iron yoke. The Ni (011) surface was cleaned by standard procedures and gave a sharp (1 × 1) LEED pattern. The SRXPS instrumentation has been described in detail elsewhere [12]. The photon source was an unmonochromatized MgK_α ($h\nu = 1253.6\,\mathrm{eV}$) x-ray source operating at 510 W. The instrumental energy resolution was 1.6 eV FWHM. SRXPS count rates (summed over both left and right detectors, peak plus background) for the Ni $2p_{3/2}$, $3p$, and $3s$ peaks were ~ 11 000, s^{-1}, ~920, s^{-1} and ~550 s^{-1}, respectively. During these studies the Sherman function S was 0.030 ± 0.003. The polarization data can be separated into individual $N\uparrow$ and $N\downarrow$ SRXPS spectra for the majority-spin (↑-spin) and minority-spin (↓-spin) photoelectrons, respectively, in a manner described previously [12]. The spin polarization of the Ni 30 eV secondary electrons was 0.048 ± 0.006, in agreement with previous work [13]. Checks of the experimental arrangement using Fe indicated negligible contribution from magnetic dichroism to our SRXPS data, due primarily to the use of a nominally unpolarized x-ray source and the rather high photoelectron kinetic energies.

In Fig. 1 we present SRXPS spectra for the main component of the Ni $3s$ level. A full analysis of the $3s$ level and its satellites will be presented elsewhere [11]. The solid lines through the data in Fig. 1 are simplex fits to each spin component using a single Doniach-Sunjic (DS) line shape [14] convoluted with a Gaussian of 1.6 eV FWHM. In contrast to expectations for a spin singlet (nonmagnetic) $3d^{10}$ final-state valence configuration, the Ni $3s$ main component is multiplet split, with the $N\uparrow$ DS component located 0.38 ± 0.06 eV to higher binding energy from the $N\downarrow$ DS component in a manner consistent with $3s$-$3d$ intra-atomic exchange. Detailed studies [11] indicate that the Ni $3s$ $N\uparrow$

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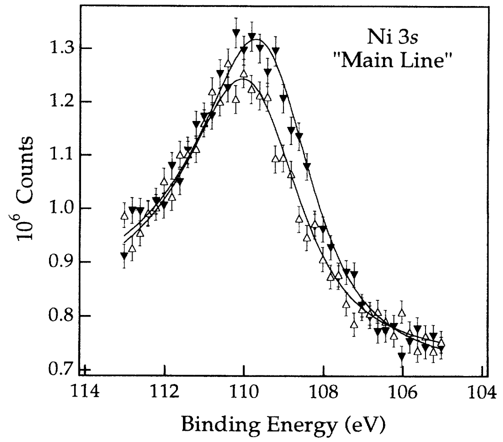

FIG. 1. $N\uparrow$ (△) and $N\downarrow$ (▼) SRXPS spectra for the main-line Ni 3s component. The solid lines are a single DS fit to each spin component.

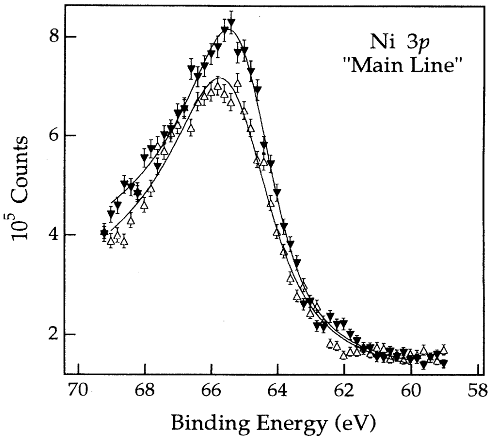

FIG. 2. $N\uparrow$ (△) and $N\downarrow$ (▼) SRXPS spectra for the main-line Ni 3p component. The solid lines are a single DS fit to each spin component.

and $N\downarrow$ components add together in such a way so as to create a single, though broad, peak in spin-integrated high-energy-resolution XPS.

Figure 2 displays SRXPS spectra for the main-line component of the Ni 3p level. Again, a net minority-spin polarization is observed, with a 0.30 ± 0.04 eV exchange splitting between the $N\uparrow$ and $N\downarrow$ 3p components. The Ni 3p data confirm the existence of multiplet effects in the main-line component of Ni core-level XPS and, with the Ni 3s SRXPS data, argue against a nonmagnetic $3d^{10}$ final-state valence configuration. Polarization effects have also been observed in previous ultraviolet-excited spin-resolved photoemission studies of the Ni 3p level [15].

Figure 3 shows SRXPS data concentrating on the main-line Ni $2p_{3/2}$ component. The intensity ratio $I\uparrow/I\downarrow$ is 0.93 ± 0.03, and the $N\uparrow$ component has the larger binding energy by 0.02 ± 0.02 eV (i.e., barely detectable). SRXPS studies of a Cu film (nonmagnetic) evaporated onto the Ni (011) surface and analyzed analogously to the Ni $2p_{3/2}$ data gave no Cu $2p_{3/2}$ spin splitting to within 5 meV, and an intensity ratio $I\uparrow/I\downarrow$ of 1.00 ± 0.01. This control experiment, and the net minority-spin polarization for the Ni $2p_{3/2}$ main component both indicate that the Ni $2p_{3/2}$ exchange splitting is nonzero, but clearly requires an improved spectroscopic energy resolution for quantitative characterization.

Although the Ni SRXPS data demonstrate conclusively that the main-line component is not *purely* $c3d^{10}$, as suggested previously [3], the main Ni core-level XPS components could have a mixed $c3d^9$, $c3d^{10}$ character. We construct an empirical argument to qualitatively evaluate this possibility. There is ample evidence [16,17] that the 3d electron count (and therefore the spin polarization) in metallic Fe and Co *does not* change upon the creation of a core hole. Using $2p_{3/2}$ and 3s exchange splittings for metallic Co [17] and Fe [18], and zero exchange splittings for nonmagnetic Cu, we can derive by interpolation the expected Ni 3s and $2p_{3/2}$ exchange splittings *were the Ni 3d spin polarization to remain the same as in the* $\sim 3d^9$ *initial state (0.56 electrons).* For Ni 3s and Ni $2p_{3/2}$ levels, these interpolated splittings are 1.18 and 0.065 eV, respectively. The measured Ni 3s and $2p_{3/2}$ exchange splittings are both ~30% of the expected values. If this decrease in core-valence exchange is completely attributed to a reduced valence spin polarization in the photoemission final state, then a final-state 3d spin of 0.18 electrons is inferred, corresponding to a 30% $c3d^9$ and 70% $c3d^{10}$ final-state mixture [19]. This estimate is probably a lower limit to the $c3d^9$ contribution, since the Ni 3p peak has a surprisingly large spin-dependent splitting and the magnitudes of the SRXPS spin polarizations for Ni are (when compared to Co [17] and Fe [18]) more consistent with a Ni final-state spin similar to that of the $(4sp)^1 3d^9$ initial state. Therefore, we believe that the true final-

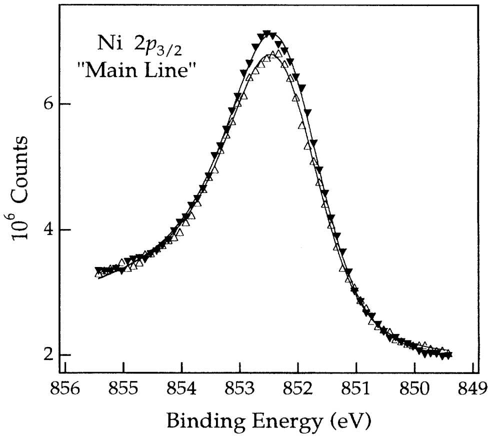

FIG. 3. Separate majority-spin ($N\uparrow$, △) and minority-spin ($N\downarrow$, ▼) SRXPS spectra for the main $2p_{3/2}$ component. The solid lines are a single DS fit to each spin component. The statistical error is smaller than the symbol size.

state Ni $3d$ valence composition following core electron ionization may be closer to $\sim 50\%$ $3d^9$, $\sim 50\%$ $3d^{10}$.

Figure 4 depicts a model of core-hole screening in Ni that is consistent with the SRXPS data, the inferred $3d$ final-state character, and electronic structure calculations of Ni [20]. *Prior* to photoelectric excitation, the valence configuration is $(4sp)^1 3d^9$ at the photoemitting Ni atom. For discussion purposes, we adopt a spin polarization of 0.5 electrons, so that below the Fermi level E_f, the $3d\uparrow$ and $3d\downarrow$ occupancies are 4.75 and 4.25 electrons, respectively. These electrons possess wave functions that, on average have a rather pure ($\sim 90\%$) $3d$ character [20]. Above E_f, there is a $3d$ level with a potential occupancy of one electron (i.e., one hole). However, there are also steeply dispersing unoccupied free-electron-like $4sp$ states that hybridize with this $3d$ level. As a result of this hybridization, approximately one half of the unoccupied $3d$ hole density (0.5 holes) exists in the form of heavily hybridized $3d$-$4sp$ states, while the other half (0.5 holes) retains a high $3d$ character [20]. Since the average radial extent ($\langle r \rangle$) of the $3d$ states is ~ 0.6 Å, whereas that for the free-electron states is (conservatively) more than twice as large [20], the unoccupied hybridized states are much more radially extended than the unoccupied $3d$ states that retain a high $3d$ character. As a result, the $3d$-$4sp$ unoccupied hybridized states are completely unpolarized, composed of 0.25 $\uparrow$-spin holes and 0.25 $\downarrow$-spin holes.

Upon core-hole creation, the $3d$ and $3d$-$4sp$ states depicted *above* E_f will be pulled partly (or wholly) below E_f at the core-hole site, as indicated by the short wavy arrows in Fig. 4. Since $3d$ and $4sp$ states are *both* shifted to lower energy by the core-hole potential, we expect the final-state hybridization and spin character of the $3d$ and $3d$-$4sp$ states to remain substantially, as depicted in Fig. 4. Extra-atomic screening, indicated by the long wavy arrows in Fig. 4, involves the transfer of charge from neighboring atoms to the $3d$ and $3d$-$4sp$ states at the photoexcited Ni atom. The core-hole screening charge will consist primarily of the $4sp$ electrons (with energy E_f) from nearest-neighbor Ni atoms, since the $4sp$ electrons are much more mobile than the $3d$ electrons. This screening requires not only that the process be energetically favored, but also that there be *significant orbital overlap* between nearest-neighbor $4sp$ electrons and the $3d$ and $3d$-$4sp$ states at the core-hole site. This required orbital overlap imposes spin conservation on the charge transfer. The large radial extent of the unoccupied $3d$-$4sp$ states should especially facilitate the transfer of both $\uparrow$-spin and $\downarrow$-spin $4sp$ nearest-neighbor screening charge to the $3d$-$4sp$ hybridized states. *Unpolarized* core-hole screening via the (initially unoccupied) hybridized and unpolarized $3d$-$4sp$ states (Fig. 4, right-hand side) will not significantly change the local spin polarization at the photoexcited atom in the XPS final state since the hybridized states are unpolarized, and will not significantly alter the $3d$ electron count from the initial-state value ($\sim 3d^9$). In contrast, the *polarized* transfer of exclusively $\downarrow$-spin $4sp$ electron density from neighboring atoms to (initially unoccupied) states of pure $3d\downarrow$ character (Fig. 4, left-hand side) would reduce the final-state valence spin polarization to zero (as in a $3d^{10}$ configuration). If the probability for core-hole-induced occupation is ~ 0.5 for both the $3d$-$4sp$ states and the pure $3d$ states, then the screening mechanism of Fig. 4 allows the initial-state spin polarization in the Ni valence band to survive at the $\sim 50\%$ level upon core-hole creation.

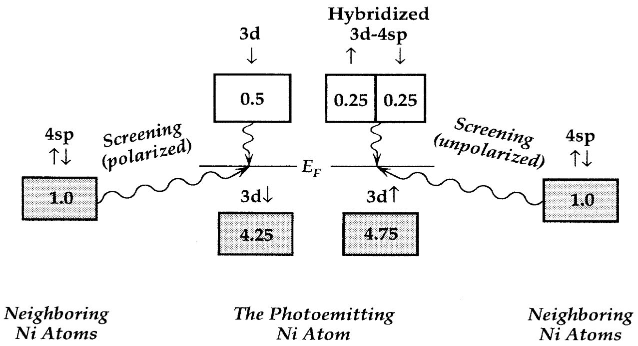

FIG. 4. A model of core-hole screening in Ni consistent with the SRXPS data. The ground-state electron (hole) occupancy below (above) E_f at the photoemitting Ni atom prior to photoelectric excitation is indicated numerically, based on Ref. [20]. A Ni $3d$ spin polarization of 0.5 electrons is assumed for the figure.

The spin polarization of the Ni main components may, alternatively, have an explanation in localized models employing Anderson impurity theory [7–9]. In these models, a main-component spin dependence could arise from the admixture of $3d^9$ and $3d^{10}$ atomiclike valence configurations in the final state associated with the Ni main component. The composition of this admixture in the final state for the main Ni core-level component has not been calculated, but a simple estimate suggests that it is primarily ($\sim 90\%$) $3d^{10}$ in character, with a small ($\sim 10\%$) $3d^9$ admixture [10]. The inerant-electron screening model of Fig. 4 suggests that the $c3d^9$ configuration survives at the $\sim 50\%$ level. Since the two models differ quantitatively, but not qualitatively, in their predictions for the main components, the main-component SRXPS data do not indicate a decisive preference for either model.

A preference may be indicated, however, by the spin polarization of the Ni core-level *satellites.* Based on the Anderson impurity work [7–9], one would predict that the spin-polarization of the Ni $3s$ 6-eV satellite would be consistent with expectations for a local $c3d^9$ configuration, with perhaps a small admixture from the $c3d^{10}$ configuration. In cases where LS coupling is valid (e.g., Ni $3s$ photoemission) the spin component along the magnetization direction is a conserved quantity [21], $M_s^{\text{in}} = M_s^{\text{fin}} + M_s^{\text{pe}}$. Adopting an initial-state (in) spin component $M_s^{\text{in}} = +\frac{1}{2}$, it is clear that the final-state (fin) spin components M_s^{fin} associated with the ^3D and ^1D atomic terms of the $3s^1 3d^9$ final-state configuration would generate exchange-split

↑-spin and ↓-spin photoelectron (pe) components ($M_s^{\mathrm{pe}} = +\frac{1}{2}, -\frac{1}{2}$, respectively) in the SRXPS spectra for the Ni $3s$ 6-eV satellite. A $3s^1 3d^{10}$ character would lead to zero satellite spin dependence. In contrast, the model of Fig. 4 indicates that extra-atomic screening is the basis for the *partial* reduction of the Ni $3d$ spin polarization in the final state. Both $3s^1 3d^9$ and $3s^1 3d^{10}$ final states should appear in the Ni $3s$ main component, due to the similar screening energies [22] associated with the pure $3d$ states and the unpolarized and hybridized $3d$-$4sp$ states. In the screening model (Fig. 4), the Ni $3s$ 6-eV satellite *should not* correspond to a local $3s^1 3d^{10}$ configuration, a local $3s^1 3d^9$ configuration, or an admixture of the two.

Figure 5 shows the spin polarization of the Ni $3s$ 6-eV satellite. The satellite is nearly 100% ↑-spin polarized *with no companion ↓-spin component.* This spin polarization is *inconsistent* with expectations based on a $3s^1 3d^9$ configuration, or a $3s^1 3d^9/3s^1 3d^{10}$ mixture. A comprehensive analysis [11] of the spin dependence of Ni core-level and valence-band satellites will show that the spin dependences can be understood in a manner consistent with the screening mechanism of Fig. 4.

The existence of substantial $3d$-$4sp$ screening in Ni indicates that the *difference* in extra-atomic screening for metallic Ni and Cu will not be nearly as large as that predicted from models assigning complete d-wave screening to Ni and s, p-wave screening to Cu [5]. This leaves the change in Ni configuration [2,22,23] from the gas-phase $4s^2 3d^8$ to the metallic $(4sp)^1 3d^9$ as the dominant contributor to the large metallic-to-gas-phase core-level shift of Ni relative to Cu. The appearance of a mixed $c3d^9/c3d^{10}$ character in the main Ni XPS components indicates that extra-atomic relaxation associated with $3d$ and $3d$-$4sp$ screening are similar, consistent with precedent theory [22].

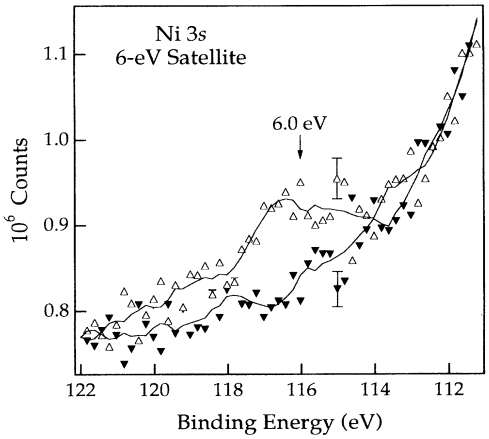

FIG. 5. Separate N↑ (△) and N↓ (▼) SRXPS spectra for the Ni $3s$ 6-eV satellite. The lines are 11-point second-order Savitsky-Golay smooths through the raw N↑ and N↓ data.

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