s-d hybridization and evolution of the electronic and magnetic properties in small Co and Ni clusters

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Photoelectron spectra of cold Ni_n^- and Co_n^- clusters revealed discrete electronic features for $n<10$ for Ni and 20 for Co. These features, mainly due to detachment of $4s$ electrons, merge with $3d$-derived features at larger cluster sizes, indicating the onset of significant *s-d* hybridization. The current results clearly revealed how the electronic structure of Ni and Co clusters evolves from molecular to bulklike in the early stage of cluster growth. They also provide insight into the origin of the enhanced magnetism in small Ni and Co clusters, due to the localized nature of the $3d$ electrons.

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Atoms of the $3d$ transition-metal (TM) elements are characterized by their open *d* shell, which gives rise to magnetism and many other interesting physical and chemical properties.[1] However, as the atoms combine to form solids, *s-d* hybridization occurs and the $3d$ electrons participate in chemical bonding. Consequently, early transition metals completely lose their magnetism in bulk solids, and only Fe, Co, and Ni are known to be ferromagnetic among the $3d$ metals. It is expected that small clusters of the early transition metals should be magnetic and those of the late transition metals should possess enhanced magnetic moments. Extensive theoretical effort has been devoted to address the magnetism of TM clusters.[2–9] However, how the *s-d* hybridization evolves with cluster size, and the precise cluster size at which significant *s-d* hybridization occurs are still not known. At present no definitive experimental proofs of magnetism in clusters of the early transition metals have been obtained,[10] though enhanced magnetism has been observed in clusters of Fe, Co, and Ni in Stern-Gerlach-type experiments.[11,12] The magnetic moments of these clusters were shown to decrease rapidly with cluster size in the small-size regime and approach to the bulk value when the clusters reach a few hundred atoms.

Photoelectron spectroscopy (PES) of size-selected anion clusters has been a valuable technique to provide detailed electronic structures of a variety of atomic clusters and would be ideal to probe the *s-d* hybridization and its size evolution in TM clusters. However, limited quantitative electronic-structure information has been obtained from PES on the three magnetic $3d$ TM cluster systems[13–21] because their complicated electronic-level structures place stringent requirements on the experimental conditions in terms of instrumental resolution, cluster temperatures, cluster-size range, and available photon energies. In this paper, we address the issue of *s-d* hybridization in small Ni_n^- and Co_n^- clusters, using well-resolved PES data with cold cluster anions. Unprecedented sharp PES spectral features were observed for the Ni_n^- and Co_n^- clusters, allowing us to follow the *s-d* hybridization precisely. We show that significant *s-d* hybridization takes place precipitously at $n=10$ for Ni_n^- and at $n=20$ for Co_n^- clusters. These observations are consistent with the steep drop of magnetic moments in small clusters of both systems, and coincide with the onset of bulklike electronic structures for these clusters.

The experiment was performed using a magnetic-bottle PES apparatus with a laser-vaporization cluster source.[16,17] Briefly, a pure metal target (Ni or Co) was vaporized by a pulsed laser beam. The laser-generated plasma was mixed with an intense high-pressure helium carrier gas pulse, which induced cluster growth and provided cooling through a supersonic expansion. Negatively charged clusters were analyzed using a time-of-flight mass spectrometer. A cluster of interest was selected and decelerated before crossing with a detachment laser beam. The energy resolution of the apparatus was ~2.5% ($\Delta E_k/E_k$), i.e., ~25 meV for 1-eV electrons. Good instrumental resolution and cold clusters are both crucial to reveal the rich electronic states of the TM clusters. Hot clusters result in thermal broadening that smears out discrete electronic transitions even under high instrumental resolution. During previous experiment with Al_n^- clusters,[22] we found that cluster temperatures from the laser-vaporization source can span a wide range,[23] depending on the residence time of the clusters inside the nozzle and the firing timing of the vaporization laser relative to the carrier gas.[24] We had obtained PES spectra previously for both Ni_n^- and Co_n^-,[17,18] but not at cold experimental conditions. Our previous work on Al_n^- clusters indicated that cluster anions with ~250 K vibrational temperature can be achieved in our cluster source based on comparisons of experimental PES spectra with molecular-dynamic simulations.[23,24] In the current study, significantly improved PES data were obtained with carefully controlled cluster temperatures, allowing us to distinguish $4s$- from $3d$-derived features and follow precisely their size dependence.

The spectra of Ni_n^- and Co_n^- ($n=1-32$) at 355 nm are shown in Figs. 1 and 2, respectively. Sharp and intense features near the threshold were observed for small Ni_n^- clusters (Fig. 1). A single sharp peak was observed starting from Ni_6^- and it gradually merged with more congested higher binding-energy features. Starting at Ni_{10}^-, the sharp feature

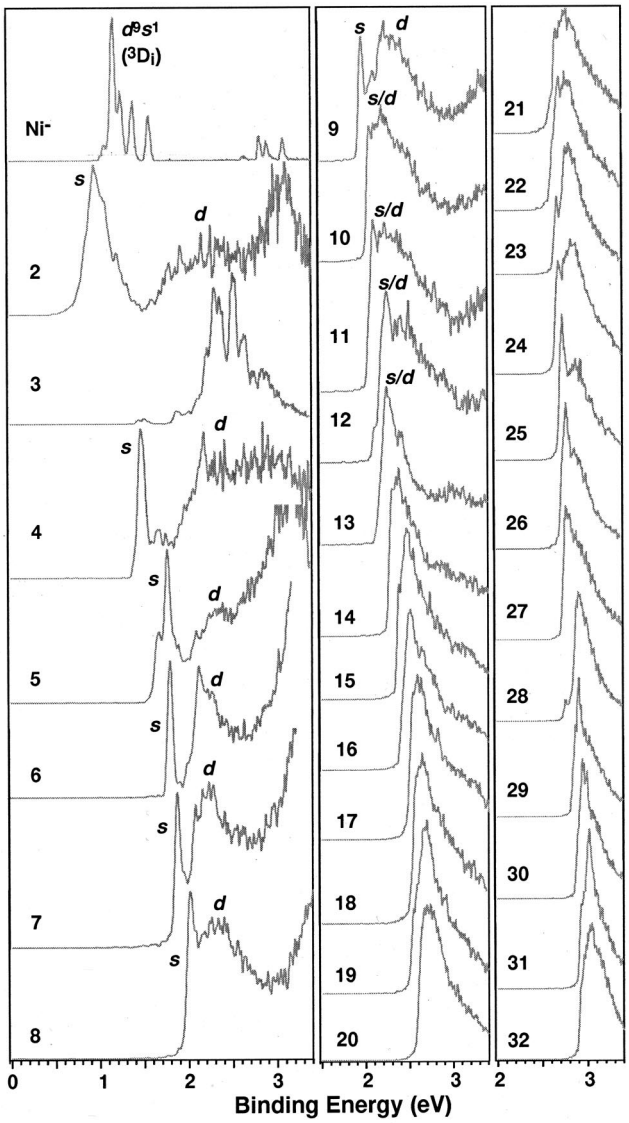

FIG. 1. Photoelectron spectra of Ni_n^- ($n=1-32$) at 355 nm (3.496 eV). *s* and *d* indicate detachment features predominantly from the 4*s* and 3*d* electrons, respectively. *s*/*d* indicates mixed 4*s* and 3*d* features.

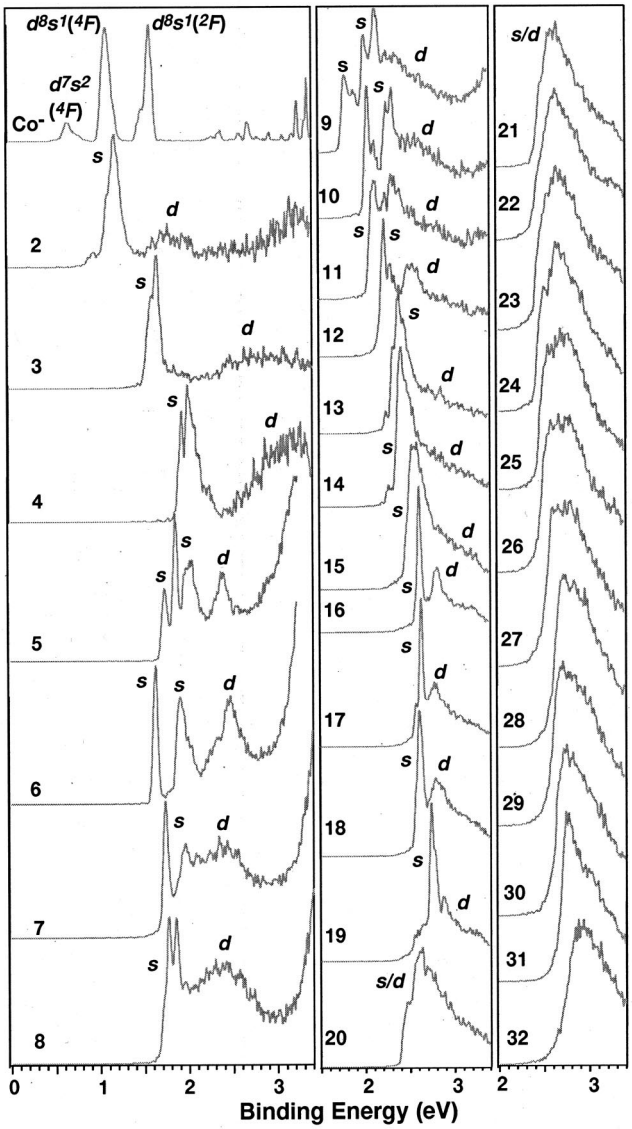

FIG. 2. Photoelectron spectra of Co_n^- ($n=1-32$) at 355 nm. See Fig. 1 caption.

completely merged with the dense high-binding-energy features and could no longer be resolved. Sharp threshold peaks were still observed in certain large clusters, notably from Ni_{23}^- to Ni_{26}^- (Fig. 1), likely due to highly symmetric polyicosahedral clusters, as suggested from chemisorption studies.[25] Similar and richer sharp features were observed in the spectra of small Co_n^- clusters (Fig. 2) and they persisted to a much larger cluster size of $n=19$, beyond which no sharp features could be resolved.

For late TM elements, the 3*d* orbitals are more localized due to the increased nuclear charges, and the chemical bonding in the small clusters is expected to be provided mainly by the 4*s* electrons. These bonding *s* electrons may be compared to Cu clusters, where the closed-shell 3*d* electrons are completely localized and have little participation in chemical bonding, which is provided exclusively by the 4*s* electrons. Well-resolved PES features due to the bonding 4*s* electrons have been observed for Cu_n^- clusters,[26] whereas the localized 3*d* electrons yielded narrow PES features at rather high electron binding energies. For the late 3*d* TM clusters, the open *d* shell, which is primarily responsible for the cluster magnetism, would give rise to very complicated PES features, in contrast to the simple Cu clusters with a closed 3*d* shell. Nevertheless, considerable similarity pertinent to the *s*-electron detachment was observed between the PES spectra of small Ni_n^- and Cu_n^- clusters[20] for $n=2-6$. It was then concluded that for $n<7$ in the Ni_n^- clusters the 3*d* orbitals are completely localized and the *s*-*d* hybridization starts with $n>7$, thus yielding the enhanced magnetic moments for the smaller clusters. The current spectra (Fig. 1) were better resolved and consistent with the previous data for $n=2-6$. However, a similar sharp threshold peak, which was resolved in the current data for $n=7-9$, was absent from the previous spectra,[20] due to either lower spectral resolution or not sufficiently cooled cluster anions.

The open *d* shell leads to complicated electronic spectra for TM clusters. Sharp and discrete peaks were not expected to be resolved for TM clusters beyond a few atoms. The central question is: what is the nature of the sharp threshold peaks in the PES spectra? In the previous PES work,[20] the sharp threshold peak in small Ni_n^- clusters ($n=2-6$) was identified compellingly as derived from 4*s* electrons by comparing with spectra of the corresponding Cu_n^- clusters. The highly congested features at high binding energies were assigned to be from 3*d* electrons. Since the sharp peak in Ni_7^- to Ni_9^- was not resolved in the previous work,[20] it was concluded, on the basis of the merging *s*-*d* features, that substantial *s*-*d* hybridization must take place starting from $n=7$. In the current study, we confirmed that the sharp and intense threshold features in both Ni_n^- and Co_n^- clusters were indeed due to detachment of 4*s* electrons by examining the spectra of the atoms and photon-energy-dependent studies. As seen from the spectra of Ni^- and Co^- in Figs. 1 and 2, at 355 nm the detachment cross sections of *s* electrons are much higher than those of *d* electrons. In fact, the detachment features from *d* electrons in Ni^- near the threshold were not even visible because they were completely overwhelmed by the features from detachment of the *s* electrons. This observation suggests that the sharp and intense features in the 355-nm PES spectra of the clusters should also be due to detachment of 4*s* electrons. The detachment cross sections for the *d* electrons were expected to increase with photon energies[27] and the relative intensities between the *s* and *d* features should decrease at higher photon energies. Indeed, we found that the intensities of all the sharp PES peaks in the Ni_n^- and Co_n^- clusters decreased at higher photon energies, as shown for Co_6^- and Ni_6^- in Fig. 3. This observation confirmed unequivocally that the sharp peaks near the threshold in the small Ni and Co clusters were due to detachment of *s* electrons. In fact, the congested 3*d* levels at higher binding energies give rise to two broad bands for the spectra of the hexamers (Fig. 3), already reminiscent of bulk valence photoemission spectra, which are dominated by emission features from *d* electrons.[28]

The above results confirmed the general validity of the approach to compare the electronic features of small Ni_n^- clusters with those of Cu_n^-.[20] Cu has a $3d^{10}4s^1$ electron configuration with a closed 3*d* shell. The 3*d* orbitals of Cu are completely localized and can be treated as part of the atomic core; the cohesion of bulk Cu is nearly exclusively provided by the 4*s* electrons, and the 3*d* band has very little dispersion. Although Ni has a $3d^84s^2$ ground-state configuration, the $3d^94s^1$ configuration is nearly degenerate and is only 0.025 eV higher. Thus, in bulk Ni, as well as in Ni clusters, it assumes the $3d^94s^1$ configuration, giving rise to a single 3*d* hole for each Ni atom. If the 3*d* electrons were completely localized in Ni, then bulk Ni would have a magnetic moment of $1\mu_b$/atom owing to the 3*d* hole. But *s*-*d* hybridization occurs and the *d* electrons contribute to the cohesion of bulk Ni, reducing its magnetic moment to $0.6\mu_b$/atom. Furthermore, the Fermi level of bulk transition metals is dominated by 3*d* levels due to the dispersions of the *s* and *d* bands, in contrast to Cu whose Fermi level consists purely of 4*s* levels because of the localized 3*d* band.

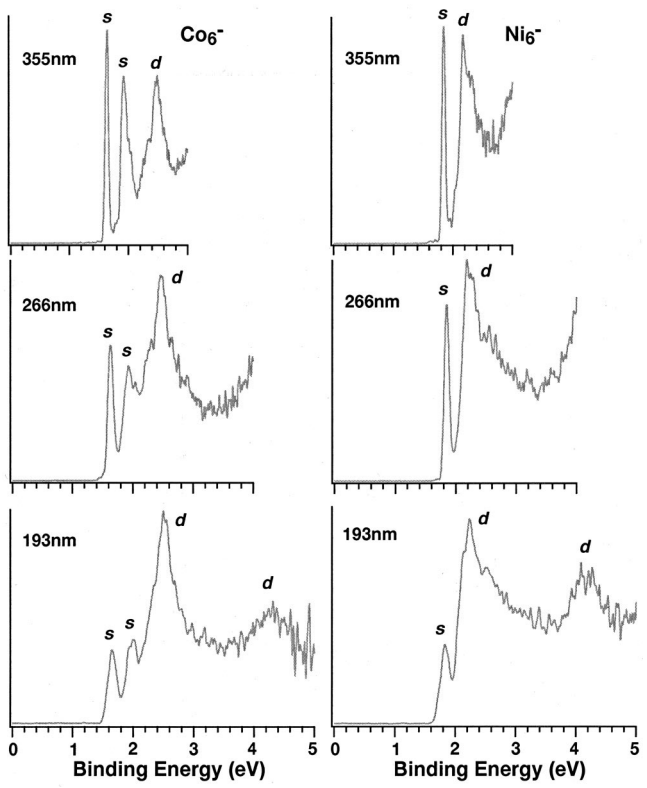

FIG. 3. Photon-energy-dependent spectra of Co_6^- and Ni_6^-, showing that at 355 nm the sharp and intense peaks near the threshold are due to detachment of *s* electrons and that the relative intensities between the *s* and *d* features decrease with increasing photon energies.

But for small Ni clusters, as is well known in Ni_2,[15] the chemical bonding is primarily provided by the *s* electrons, and the *d* electrons are largely localized giving rise to the similarity with the electronic structure of the corresponding Cu clusters, characterized by well-separated *s* and *d* levels. As cluster size increases, both the *s* and *d* bands broaden. At the onset of significant *s*-*d* hybridization, the *s* and *d* levels merge and the cluster Fermi level would now be dominated by the *d* levels, as is the case for the bulk. Our data show clearly that this occurs for Ni clusters at $n=10$, instead of 7, as concluded previously.[20]

Co is next to Ni in the periodic table and possesses an electron configuration of $3d^74s^2$. In clusters and bulk, Co assumes a configuration of $3d^84s^1$, with two *d* holes, which give rise to higher magnetic moments in the bulk ($1.7\mu_b$/atom) and clusters of Co, compared to that of Ni. But the electronic structure of the two systems was expected to be similar, and our PES data indeed indicate similarities between clusters of the two systems from $n=2-15$, except for $n=3$.[29] However, the fewer *d* electrons in Co clusters suggest that the 3*d*-derived levels should be slightly simpler, which was indeed born out from the better resolved *s*-derived features in the PES spectra of Co_n^- clusters (Figs. 2 and 3). More interestingly, *s*-derived PES features could be clearly identified up to $n=19$ for Co clusters and the onset for significant *s*-*d* hybridization only started from $n=20$. In fact, the critical sizes for the onsets of bulk electronic structures in

both Ni and Co clusters are also supported by the size evolution of their electron affinities (EA). Starting from $n=10$ for Ni and 20 for Co, the cluster EAs follow the predictions of the metallic droplet model (linearly dependent on the inverse of the cluster radius).[17,30] Interestingly, our observation is also consistent with the conclusion of a previous theoretical prediction of the nonmetal-metal transition in Ni clusters using Kubo's criterion.[31]

The commencement of significant *s-d* hybridization is expected to cause a dramatic reduction in the magnetic moments of the clusters. The magnetic moments of Ni clusters have been measured accurately from as small as $n=5$.[12] Indeed very large moments were observed for the small clusters and they were shown to decrease dramatically from $n=5$ to 10. More gradual size variations were observed above $n=10$, although local minima were displayed due to highly symmetric clusters, most notably at $n=13$ due to its I_h symmetry. The magnetic moments of Co clusters have also been measured more recently with higher precision from $n=15$ to 200.[32] Again, very large moments were observed for the small clusters and these moments underwent a significant drop from $n=15$ to 20, beyond which more gradual size variations were observed. The very high magnetic moments in the small Ni and Co clusters are consistent with the localized nature of the $3d$ electrons, and their more dramatic size dependence in the small-size regime parallels precisely the onset of significant *s-d* hybridization, as revealed from the PES data.

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