Localization of 3d and 4d Electrons in Small Clusters: The "Roots" of Magnetism

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The photoelectron spectra of mass-selected negatively charged Ni_n^- and Cu_n^- clusters show similarities, which indicate an almost total localization of the Ni 3d orbitals corresponding to a maximum magnetic moment of $1\mu_B$ per Ni atom. The similarity between Ni_n^- and Cu_n^- vanishes for $n > 7$ corresponding to an increase in 3d delocalization. The data of Pd_n^- clusters suggest a Ni-like ("magnetic") electronic structure for $n = 3$–6 and a Pt-like ("nonmagnetic") one for $n > 15$. There are indications that neutral Pd_7 is a closed shell species (spin zero ground state). [S0031-9007(96)00482-6]

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According to Hund's rule all open shell atoms are magnetic in their ground state since the lowest energy corresponds to maximum alignment of the spins. Delocalization of the electronic states in solids quenches the magnetism such that only Fe, Co, and Ni remain as elemental solids displaying ferromagnetism. In systems with reduced dimensionality, e.g., thin films [1,2] or small particles [3–7], the magnetic moment per atom is expected to be larger than in the corresponding bulk metal. This effect is caused by the reduced coordination number, i.e., the lower number of nearest neighbors, which results in a higher degree of localization and a correspondingly reduced valence band width. Within the approximations of the Stoner model the enhanced density of states at the Fermi energy corresponds to an increased magnetic moment per atom (M/A). Localization additionally results in an enhanced exchange interaction of the d electrons and the moments of each atom are aligned by a (weak) interaction. The strength of this interaction determines the temperature dependence of the total magnetic moment and the Curie temperature. For total localization (separated atoms) M/A is maximized but the Curie temperature is zero. This general idea has been confirmed for small clusters of Fe, Co, and Ni in a Stern-Gerlach experiment [4], which shows an enhancement of M/A approximately up to the value of isolated atoms.

Spin and angle-integrated photoemission experiments [8–12] have been conducted to investigate the electronic structure of Ni_n^-, Co_n^-, and Fe_n^- clusters. Because of the improved energy resolution in our experiment [13] we are able to resolve fine structures in the photoelectron spectra of Ni_n^- and Pd_n^- clusters, which reflect sensitively upon the degree of localization of the d valence electrons.

First we focus on Ni as a typical example of a magnetic material to reveal the differences between a small Ni cluster ($M/A = 1\mu_B$ [4]) and bulk Ni ($M/A = 0.6\mu_B$). Surprisingly, our photoemission data of Ni_n^- clusters show a similarity with the spectra of Cu_n^- clusters. As bulk solids the two metals are quite different, because Ni is an open 3d-shell transition metal with a $\approx 3d^9 4s$ configuration, while Cu has a closed d shell and a single s electron with a $3d^{10}4s$ (alkalilike) configuration. However, in small clusters the degree of localization of the Ni $3d^9$ "cores" is so high [14] that the interaction of the neighboring $3d^9$ cores can be neglected as in the case of the Cu d^{10} cores [15] and the bonding is caused by the 4s electrons mainly.

The second topic is whether small clusters of 4d transition metals (Ru, Rh, Pd) might be ferromagnetic [3,6,7]. As a bulk metal Pd is "almost" ferromagnetic [16], and according to theory a slight enhancement of the 4d localization (e.g., by an increase of the interatomic distance by 6%) would give ferromagnetic Pd. Thus, the enhanced localization in small clusters is expected to result in a "magnetic" ground state (to be more exact a "superparamagnetic" ground state [4]). However, in the Stern-Garlach experiments [6] the Pd clusters (for $n > 12$; there are no data for $n < 10$) behave "nonmagnetic" in contrast to theoretical predictions [3]. In our photoemission experiment we find similarities to the Ni data for $n = 3 - 6$, which can be taken as a fingerprint of "magnetic" behavior. In contrast, the spectrum of Pd_7^- shows a feature which is typical for closed shell (nonmagnetic) species. For the larger Pd clusters we find a transition from a Ni-like ($n < 7$) to Pt-like (nonmagnetic) behavior ($n > 16$).

The experimental setup is described in detail elsewhere [13]. The cluster anions are produced in a laser vaporization source. The negatively charged clusters are accelerated in a pulsed electric field and depending on their time of flight the clusters separate into a chain of bunches of defined cluster size. The anion beam is directed into the source region of a "magnetic bottle" time-of-flight electron spectrometer, where a selected bunch is irradiated by a UV laser pulse (photon energy $h\nu = 4.0$ eV) and the kinetic energy of the detached electrons is measured.

Figure 1 shows a comparison of photoelectron spectra of Ni_n^- and Cu_n^- spectra with $n = 2$–9. The energy range corresponds to photoemission from the uppermost occupied orbitals, which are almost purely s/p derived for Cu. These delocalized s/p orbitals show strong "quantum

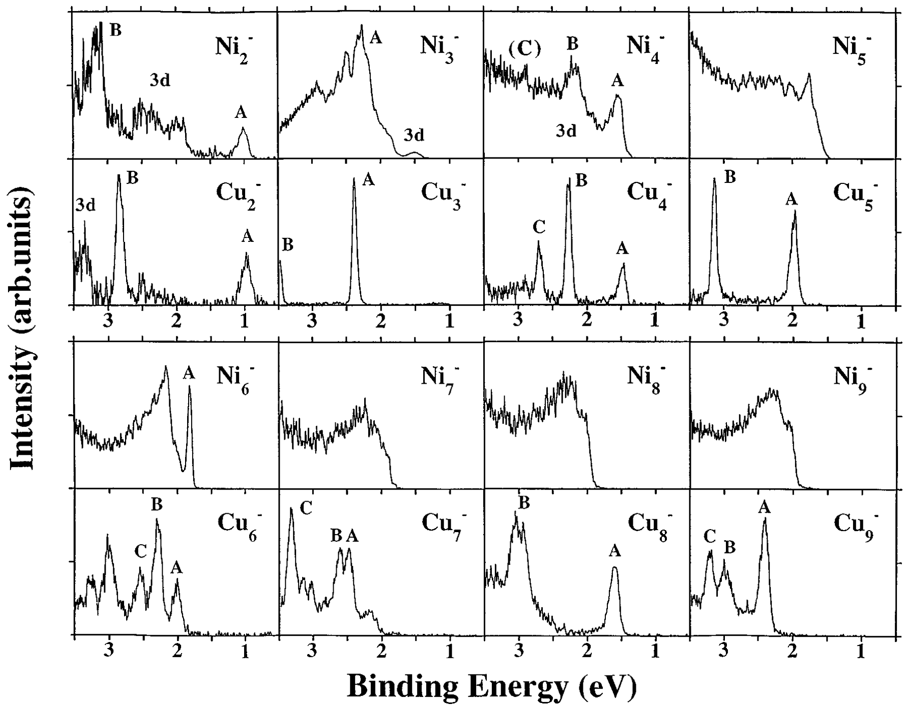

FIG. 1. Comparison of photoelectron spectra of Ni_n^- and Cu_n^- clusters in the binding energy range 0.5–3.5 eV. The photon energy is $h\nu = 4.0$ eV. For a discussion of the marked features, see text.

size" effects and for each cluster the characteristic features can be assigned to emission from "electronic shells" [15]. Recent first principles calculations on Cu_n^- clusters [17] give a quantitative analysis of the s/d hybridization. The calculations support the shell model assignments for the uppermost orbitals, but indicate a considerable s/d hybridization for the orbitals energetically closer to the Cu $3d$ band especially for the larger clusters (e.g., Cu_9^-).

The Cu_n^- clusters with $n = 2, 4, 6, 8$ have an odd number of electrons and the uppermost single electron is weakly bound. This corresponds to the appearance of a peak at low binding energy (BE) (marked A). Such an even/odd alternation is a property of clusters of simple metals (alkali metals, Cu, Ag, Au [18]). A similar peak "A" at almost the same BE appears also in the spectra of Ni_2^-, Ni_4^-, and Ni_6^-. In the spectra of Ni_2^- and Ni_4^- there are even features at higher BE, which seem to correspond to the peaks observed in the spectra of Cu_2^- (A,B) and Cu_4^- (A, B, C).

These similarities can be understood if for the Ni $3d^9$ cores a total localization is assumed. As a consequence, there is very little s/d hybridization and the clusters are bound by the $4s/p$ orbitals only. From that point of view the Ni $3d^9$ cores behave similar to the Cu $3d^{10}$ cores, which are located at higher BE and act almost like inner shells in small clusters [15]. The emission from the Cu $3d^{10}$ orbitals is at BEs >3.5 eV beyond the range shown in Fig. 1. The similarity of the spectra of Cu_2^- and Ni_2^- and the consequence of a very small contribution from the Ni $3d^9$ orbitals to the bond have already been discussed by Ho *et al.* [9]. If there is no contribution to the bonding from the $3d^9$ cores and also no s/d hybridization, the s/p electrons occupy similar orbitals for Ni and Cu clusters. Then the photoelectron spectra of the Ni_n^- clusters should exhibit the same features due to s/p electron emission as the Cu_n^- spectra, but superimposed on the emission from the Ni $3d^9$ states.

Indeed, exactly this kind of superimposition is seen in the spectra of Ni_2^- and Ni_4^-. In both dimer spectra two sharp peaks (A,B) are observed, which are assigned to emission from the bonding $4s$ σ and the antibonding $4s$ σ^* orbital (occupied by the additional electron). In the spectrum of Ni_2^- a broad emission signal (marked $3d$) in between the two peaks is assigned to emission from the Ni $3d$ orbitals. Feature B in the spectrum of Ni_2^- is slightly shifted towards higher BE with respect to Cu_2^-. The emission from the $3d^9$ cores is a broad structureless emission signal, because in the final state a $3d^8$ core is created, which gives rise to final state effects like multiplet splitting and shakeup processes [15].

It is interesting that the $4s$ σ^* orbital is occupied in Ni_2^-. In the single particle picture this orbital is less stable than the $3d$ orbitals. An additional electron is therefore expected to occupy a $3d$ orbital resulting in a $3d^{19}\sigma^2$ configuration of Ni_2^-. However, the configuration is $3d^{18}\sigma^2\sigma^*$ [9]. The reason is the strong Coulomb repulsion of the other 9 electrons occupying the $3d$ orbital. As a result, the d^{10} configuration of the Ni atom is about 1.7 eV less stable than the $3d^9s$ configuration [10]. Thus, as long as the $3d^9$ cores are highly localized, the additional electron will prefer a delocalized s/p orbital.

For the trimers the similarity is less well pronounced.

The spectrum of Cu_3^- exhibits a single peak at relatively high BE. The spectrum of Ni_3^- shows an intense maximum at about the same energy, but it is much broader with a considerable fine structure. We conclude that the s/d hybridization in Ni_3^- is stronger. The anion is probably linear [10] and according to calculations [19] in a linear Ni_3 the center atom has a $3d^8$ configuration to enhance the binding energy by an appropriate mixing with s/p orbitals; i.e., the trimer is special case.

The spectra of Ni_2^-, Ni_4^-, and Ni_6^- exhibit a separated peak A at low BE, which corresponds to the additional electron occupying a s/p orbital. In the spectrum of Ni_8^- no such peak is observed although a pronounced one is found for Cu_8^-. Starting from Ni_7^- all spectra look similar to the ones of Ni_7^-, Ni_8^-, and Ni_9^-. This is probably due to an increase in $3d$ delocalization, which is accompanied by an increased s/d hybridization. The sharp s/p features disappear due to mixing with d orbitals and broadening. Presumedly the additional electron now prefers to occupy one of the uppermost unoccupied d orbitals.

In agreement with the size dependence of the s/d hybridization in Cu_n^- clusters [17] the similarity of the photoelectron spectra of Ni_n^- and Cu_n^- clusters is very pronounced for the smallest clusters (Ni_2^-, Ni_4^-) even including features at higher BE. For the larger Cu clusters, only the uppermost orbitals exhibit a predominant s character [17], while in larger Ni clusters no such orbitals are expected to "survive," because of the $\approx$2 eV lower BE of the Ni $3d$ band. We conclude that the similarity of the Ni_n^- and Cu_n^- clusters with $n < 7$ can be explained by an extreme degree of localization and a weak s/d hybridization. For $n \geq 7$ the effect vanishes, because the $3d$ orbitals start to delocalize considerably. These findings are in qualitative agreement with the result of recent Stern-Gerlach experiments on small Ni clusters [20], which show a dramatic decrease of M/A between Ni_5 and Ni_9 [21].

Figure 2 displays photoelectron spectra of Pd_n^- clusters with $n = 3-8$. The spectra of Pd_3^- and Pd_4^- show a limited similarity to the ones of Ni_3^- and Ni_4^-. Both trimer spectra exhibit a broad structured maximum around 2.5 eV BE. The spectrum of Pd_4^- exhibits the separated peak A at low BE similar to Ni_4^- indicating localized d orbitals. For Pd_5^- and Pd_6^- a similarity with the Ni data is not recognizable. Especially, the photoelectron spectrum of Pd_7^- exhibits a separated peak A at emission threshold. For Ni_n^-, such a feature has been found for $n = 2, 4$, and 6, but it is not expected to appear for odd-numbered clusters. Therefore, the reason for the appearance of such a feature at $n = 7$ must be a different one. In clusters with small correlation effects a spectrum similar to the one of Pd_7^- indicates an electronic closed shell of the neutral cluster and the additional electron occupies the lowest unoccupied molecular orbital (LUMO) of the neutral (see, e.g., Ref. [15]). The gap between the first peak and the next emission feature is equal to the gap between the highest occupied molecular orbital (HOMO) and the LUMO. According to this interpretation Pd_7 is a closed shell species with a HOMO-LUMO gap of approximately 0.3 eV and, therefore, nonmagnetic.

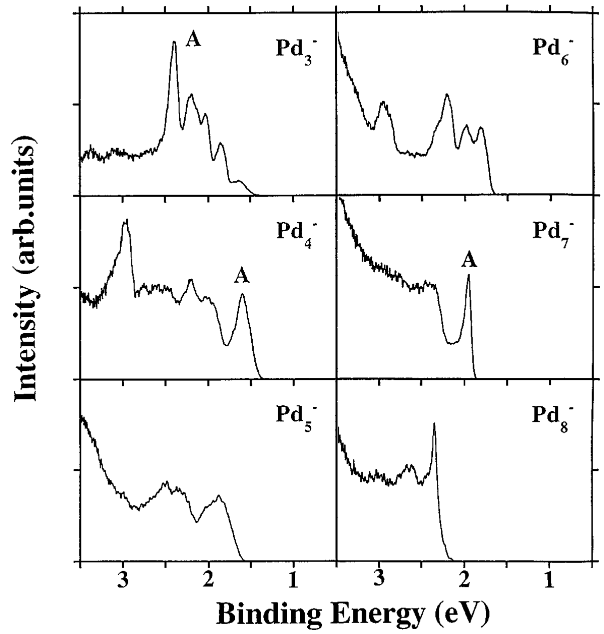

FIG. 2. Photoelectron spectra of Pd_n^- clusters obtained with a photon energy of $h\nu = 4.0$ eV.

Figure 3 shows the vertical detachment energies (VDEs) of Ni_n^-, Pd_n^-, and Pt_n^- clusters with $n = 3-16$. The VDEs correspond to the work functions of the negative particles and increase slowly with cluster size approaching the bulk work function. This size dependence is related to the "metallic" character of a cluster and can be described by an electrostatic model [22]. Interestingly, the size dependence of the VDEs cannot be described by this model for Ni_n clusters [8]. The Ni VDEs approach the bulk work function more slowly than the corresponding values of the Pt clusters (Fig. 3). The value of the VDE of the 15 atom cluster is closer to the corresponding bulk work function [23] by 0.5 eV for Pt compared to Ni. This is caused by the localization of the uppermost Ni valence electrons (predominantly $3d$). In totally localized orbitals the electrons do not "recognize" the size of the clusters and the VDEs are constant corresponding to the value of the isolated atom. In Pt clusters the $5d$ orbitals interact much stronger and contribute considerably to the bonding [9,10], which corresponds to an increased $5d$ delocalization. We consider the Pt clusters to be nonmagnetic because of the higher degree of delocalization, though there are yet no experimental data on the magnetic moments.

The VDEs of the Pd_n^- clusters are similar to the ones of the Ni_n^- clusters up to $n = 7$ (except for $n = 1, 2$ [9]) and then show a steep increase approaching gradually the VDEs of the Pt_n^- clusters at $n = 16$. The Pd data suggest a transition from a localized "Ni-like" be-

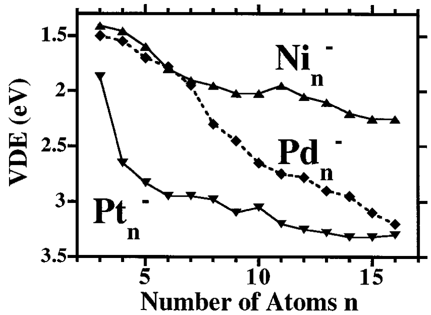

FIG. 3. Comparison of the vertical detachment energies (VDEs) of Ni_n^-, Pd_n^-, and Pt_n^- clusters with $n = 3-15$ atoms. The VDEs are extracted from the photoelectron spectra using the method described in Ref. [15].

havior to a delocalized "Pt-like" behavior. For Pd_7^-, the VDE is equal to that of Ni_7^-, but the electronic structure is completely different. This demonstrates that the VDEs (or the electron affinities) can be used only in comparison with other data to avoid misleading conclusions. However, from the similarity of the photoelectron spectra and the VDEs it can be deduced that Pd_3^--Pd_6^- might exhibit magnetic properties, while for the larger clusters starting from Pd_7^- a "transition" towards a Pt-like nonmagnetic behavior is found. Our photoemission spectra indicate that neutral Pd_7 might have a zero spin ground state. For the larger Pd_n clusters with $n = 8-11$ again a finite magnetic moment might exist, but is expected to gradually decrease to the value of Pt clusters (= 0) [6].

The question remains why the tendency to "magnetism" is weak in Pd. In Pd thin films and two-dimensional Pd clusters on surfaces a preference for a nonmagnetic d^{10} configuration is found [24]. This difference to Ni can be explained by the generally higher BEs of the $4d$ orbitals compared to the $3d$ ones.

In conclusion, we present photoelectron spectra of Ni_n^- and Pd_n^- clusters, which are compared to the ones of Cu_n^- and Pt_n^- clusters. The data indicate an almost perfect localization on of the Ni $3d$ orbitals in very small clusters, which vanishes for larger clusters with $n > 7$. For small Pd_n^- clusters we find a limited similarity to the Ni data indicating magnetic properties, but again around $n = 7$ a tendency towards nonmagnetic behavior is found. With our method effects of a strong localization can be detected, but the formation of a macroscopic magnetic moment corresponding to an alignment of the individual atomic magnets can only be determined in Stern-Gerlach experiments [4–7].

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