

# 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  $\text{Ni}_n^-$  and  $\text{Cu}_n^-$  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  $\text{Ni}_n^-$  and  $\text{Cu}_n^-$  vanishes for  $n > 7$  corresponding to an increase in 3d delocalization. The data of  $\text{Pd}_n^-$  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  $\text{Pd}_7$  is a closed shell species (spin zero ground state).

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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 film [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  $\text{Ni}_n^-$ ,  $\text{Co}_n^-$ , and  $\text{Fe}_n^-$  clusters. Because of the improved energy resolution in our experiment [13] we are able to resolve fine structures in the photoelectron spectra of  $\text{Ni}_n^-$  and  $\text{Pd}_n^-$  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  $\text{Ni}_n^-$  clusters show a similarity with the spectra of  $\text{Cu}_n^-$  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-Gerlach 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  $\text{Pd}_7^-$  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  $\text{Ni}_n^-$  and  $\text{Cu}_n^-$  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

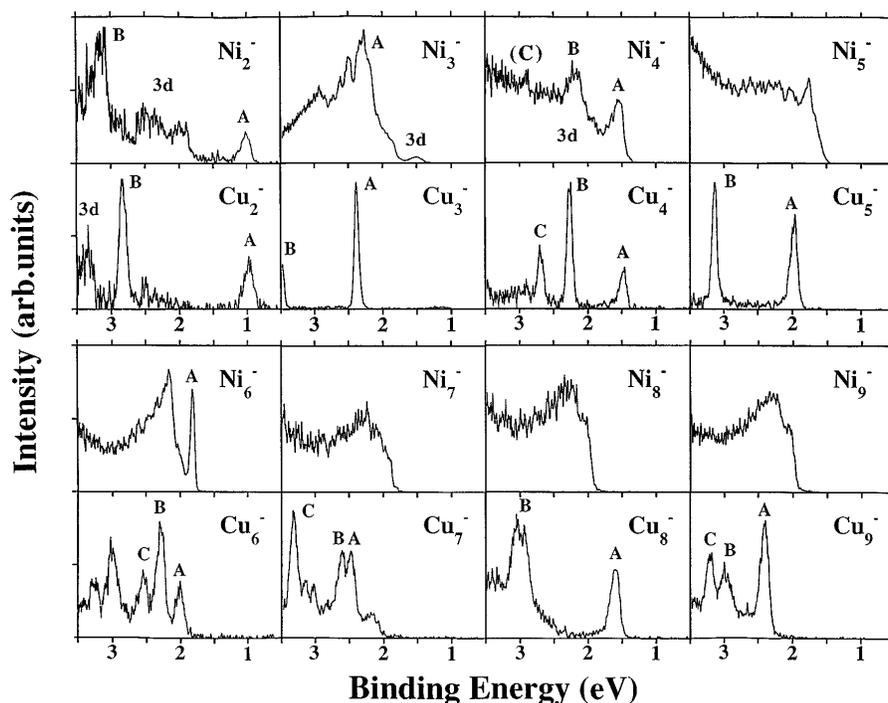


FIG. 1. Comparison of photoelectron spectra of  $\text{Ni}_n^-$  and  $\text{Cu}_n^-$  clusters in the binding energy range 0.5–3.5 eV. The photon energy is  $h\nu = 4.0$  eV. For a discussion of the marked features, see text.

size” effects and for each cluster the characteristic features can be assigned to emission from “electronic shells” [15]. Recent first principles calculations on  $\text{Cu}_n^-$  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.,  $\text{Cu}_9^-$ ).

The  $\text{Cu}_n^-$  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  $\text{Ni}_2^-$ ,  $\text{Ni}_4^-$ , and  $\text{Ni}_6^-$ . In the spectra of  $\text{Ni}_2^-$  and  $\text{Ni}_4^-$  there are even features at higher BE, which seem to correspond to the peaks observed in the spectra of  $\text{Cu}_2^-$  (A,B) and  $\text{Cu}_4^-$  (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  $\text{Cu}_2^-$  and  $\text{Ni}_2^-$  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  $\text{Ni}_n^-$  clusters should exhibit the same features due to  $s/p$  electron emission as the  $\text{Cu}_n^-$  spectra, but superimposed on the emission from the Ni  $3d^9$  states.

Indeed, exactly this kind of superimposition is seen in the spectra of  $\text{Ni}_2^-$  and  $\text{Ni}_4^-$ . In both dimer spectra two sharp peaks (A,B) are observed, which are assigned to emission from the bonding  $4s \sigma$  and the antibonding  $4s \sigma^*$  orbital (occupied by the additional electron). In the spectrum of  $\text{Ni}_2^-$  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  $\text{Ni}_2^-$  is slightly shifted towards higher BE with respect to  $\text{Cu}_2^-$ . 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  $4s \sigma^*$  orbital is occupied in  $\text{Ni}_2^-$ . 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  $\text{Ni}_2^-$ . 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  $3d^9 s$  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  $\text{Cu}_3^-$  exhibits a single peak at relatively high BE. The spectrum of  $\text{Ni}_3^-$  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  $\text{Ni}_3^-$  is stronger. The anion is probably linear [10] and according to calculations [19] in a linear  $\text{Ni}_3$  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  $\text{Ni}_2^-$ ,  $\text{Ni}_4^-$ , and  $\text{Ni}_6^-$  exhibit a separated peak A at low BE, which corresponds to the additional electron occupying a  $s/p$  orbital. In the spectrum of  $\text{Ni}_8^-$  no such peak is observed although a pronounced one is found for  $\text{Cu}_8^-$ . Starting from  $\text{Ni}_7^-$  all spectra look similar to the ones of  $\text{Ni}_7^-$ ,  $\text{Ni}_8^-$ , and  $\text{Ni}_9^-$ . 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. Presumably 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  $\text{Cu}_n^-$  clusters [17] the similarity of the photoelectron spectra of  $\text{Ni}_n^-$  and  $\text{Cu}_n^-$  clusters is very pronounced for the smallest clusters ( $\text{Ni}_2^-$ ,  $\text{Ni}_4^-$ ) 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  $\text{Ni}_n^-$  and  $\text{Cu}_n^-$  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  $\text{Ni}_5$  and  $\text{Ni}_9$  [21].

Figure 2 displays photoelectron spectra of  $\text{Pd}_n^-$  clusters with  $n = 3-8$ . The spectra of  $\text{Pd}_3^-$  and  $\text{Pd}_4^-$  show a limited similarity to the ones of  $\text{Ni}_3^-$  and  $\text{Ni}_4^-$ . Both trimer spectra exhibit a broad structured maximum around 2.5 eV BE. The spectrum of  $\text{Pd}_4^-$  exhibits the separated peak A at low BE similar to  $\text{Ni}_4^-$  indicating localized  $d$  orbitals. For  $\text{Pd}_5^-$  and  $\text{Pd}_6^-$  a similarity with the Ni data is not recognizable. Especially, the photoelectron spectrum of  $\text{Pd}_7^-$  exhibits a separated peak A at emission threshold. For  $\text{Ni}_n^-$ , 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  $\text{Pd}_7^-$  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

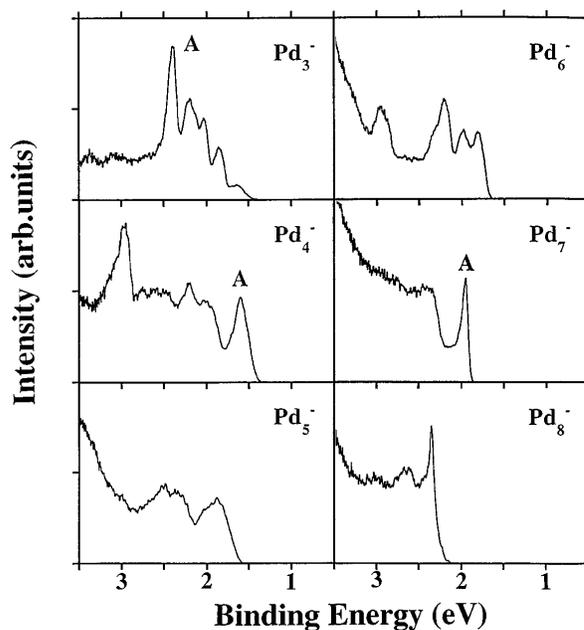


FIG. 2. Photoelectron spectra of  $\text{Pd}_n^-$  clusters obtained with a photon energy of  $h\nu = 4.0$  eV.

between the highest occupied molecular orbital (HOMO) and the LUMO. According to this interpretation  $\text{Pd}_7$  is a closed shell species with a HOMO-LUMO gap of approximately 0.3 eV and, therefore, nonmagnetic.

Figure 3 shows the vertical detachment energies (VDEs) of  $\text{Ni}_n^-$ ,  $\text{Pd}_n^-$ , and  $\text{Pt}_n^-$  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  $\text{Ni}_n$  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  $\text{Pd}_n^-$  clusters are similar to the ones of the  $\text{Ni}_n^-$  clusters up to  $n = 7$  (except for  $n = 1, 2$  [9]) and then show a steep increase approaching gradually the VDEs of the  $\text{Pt}_n^-$  clusters at  $n = 16$ . The Pd data suggest a transition from a localized “Ni-like” be-

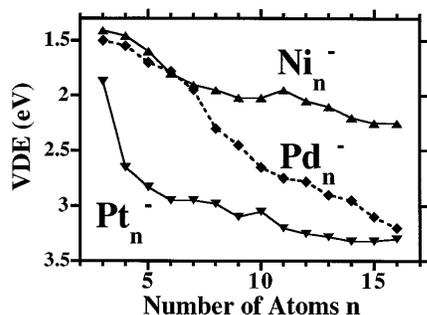


FIG. 3. Comparison of the vertical detachment energies (VDEs) of  $\text{Ni}_n^-$ ,  $\text{Pd}_n^-$ , and  $\text{Pt}_n^-$  clusters with  $n = 3-15$  atoms. The VDEs are extracted from the photoelectron spectra using the method described in Ref. [15].

havior to a delocalized “Pt-like” behavior. For  $\text{Pd}_7^-$ , the VDE is equal to that of  $\text{Ni}_7^-$ , 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  $\text{Pd}_3^-$ - $\text{Pd}_6^-$  might exhibit magnetic properties, while for the larger clusters starting from  $\text{Pd}_7^-$  a “transition” towards a Pt-like nonmagnetic behavior is found. Our photoemission spectra indicate that neutral  $\text{Pd}_7$  might have a zero spin ground state. For the larger  $\text{Pd}_n$  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 film 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  $\text{Ni}_n^-$  and  $\text{Pd}_n^-$  clusters, which are compared to the ones of  $\text{Cu}_n^-$  and  $\text{Pt}_n^-$  clusters. The data indicate an almost perfect localization on one of the Ni  $3d$  orbitals in very small clusters, which vanishes for larger clusters with  $n > 7$ . For small  $\text{Pd}_n^-$  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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