

Geometrical effects on the magnetism of small Ni clusters

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A self-consistent tight-binding method has been used to calculate the average magnetic moments $\bar{\mu}$ of Ni_N clusters between $N=5$ and 16. The geometrical structures were taken from the results of molecular-dynamics simulations with semiempirical potentials. The agreement with experiment (minima of $\bar{\mu}$ at $N=6$ and 13, and a maximum for $N=8$) is good, and the variations of the average magnetic moment are explained as a consequence of geometrical effects: low coordinated atoms have large magnetic moments. Furthermore, the deviation of the interatomic distances from a smooth behavior also influences the magnetic moments. The contribution of the sp electrons to the magnetism is found to be relevant for Ni clusters with less than ten atoms. [S0163-1829(97)06219-X]

Transition-metal clusters have been extensively investigated from both experimental and theoretical viewpoints. Besides the technological interest, mainly related to magnetic devices, the fundamental question of how the electronic properties, in particular the magnetism, evolve from the small cluster regime toward the macroscopic crystal has stimulated this effort. One of the most important characteristics intrinsically related to magnetic properties is the geometrical structure of the material. It is well known that the properties of itinerant $3d$ electrons are sensitive to changes in the position of the atoms within the system. Therefore, spatial symmetry effects and variations of the local coordination number are ingredients to be taken into account for a calculation of the magnetic properties.

One of the systems experimentally studied in most detail is nickel. The evolution of the average magnetic moment per atom $\bar{\mu}$ with cluster size has been measured by Billas *et al.*¹ and by Apsel *et al.*,² both groups using a Stern-Gerlach deflection technique. In these measurements, the average magnetic moment decreases, although nonmonotonically, as the cluster size increases, reaching the bulk value of $0.61\mu_B$ for a typical size of about 600 atoms. This decrease can be explained by the broadening of the d -band associated to the increase of the average coordination number.³ The experiments of Apsel *et al.*,² which were performed for size-selected clusters, display interesting features for cluster sizes smaller than 100 atoms. In this region, there are pronounced oscillations of the magnetic moment which give rise to a strong reduction of the magnetization for certain sizes (6, 13, 34, 56, ...) and a strong increase for other sizes (5, 8, 71, ..., and broad maxima around 20 and 42). Those magnetic magic numbers were suggested to occur as a consequence of the symmetry in the geometrical structure, and icosahedral growth appears as a candidate to explain the general trend.² Jensen and Bennemann⁴ developed a simple model for the average magnetic moment in transition-metal clusters in which the individual magnetic moments of the different atoms are determined by the atomic coordination around those atoms. By assuming bulklike structures (fcc, bcc) and different global cluster shapes (cubic, octahedral, cubo-octahedral) these authors demonstrated that $\bar{\mu}$ oscillates, and that this magnetic "shell structure" reflects the progressive formation

of atomic layers of the assumed cluster geometry. However, Fujima and Yamaguchi⁵ suggested a pure electronic-shell effect which completely neglects the geometrical structure. In that model, the delocalized sp electrons near the Fermi level indirectly control the number of holes in the minority-spin d band, and this number changes abruptly when the number of sp electrons is just enough to fill an electronic shell, in which case the whole shell becomes highly stabilized below the d bands.

It is our aim to shed some light on this complex problem by performing a self-consistent electronic calculation of the magnetic properties of Ni clusters as a function of cluster size. For the geometries we take those determined by molecular-dynamics simulations using a semiempirical many-body potential.⁶

The spin-polarized electronic structure has been determined by solving self-consistently a tight-binding (TB) Hamiltonian for the $3d$, $4s$, and $4p$ valence electrons in a mean-field approximation. Here we only give a brief account of the theory, and more details can be found in Ref. 7. In second quantization notation, this Hamiltonian has the expression:

$$H = \sum_{i\alpha\sigma} \varepsilon_{i\alpha\sigma} \hat{n}_{i\alpha\sigma} + \sum_{\substack{\alpha,\beta,\sigma \\ i \neq j}} t_{ij}^{\alpha\beta} \hat{c}_{i\alpha\sigma}^\dagger \hat{c}_{j\beta\sigma}, \quad (1)$$

where $\hat{c}_{i\alpha\sigma}^\dagger$ is the operator for the creation of an electron with spin σ and orbital state α at the atomic site i , $\hat{c}_{j\beta\sigma}$ is the annihilation operator, and $\hat{n}_{i\alpha\sigma}$ is the number operator. The hopping integrals $t_{ij}^{\alpha\beta}$ between orbitals α and β at atomic sites i and j are assumed to be spin independent, and have been fitted to reproduce the band structure of the metal at the observed bulk lattice constant.⁸ The variation of the hopping integrals with the interatomic distance r_{ij} is assumed to follow the usual power law $(r_0/r_{ij})^{l+l'+1}$, where r_0 is the bulk equilibrium distance and l and l' are the orbital angular momenta of the $(i\alpha\sigma)$ and $(j\beta\sigma)$ states involved in the hopping process. The spin-dependent diagonal terms account for the electron-electron interaction through a shift of the orbital energy levels

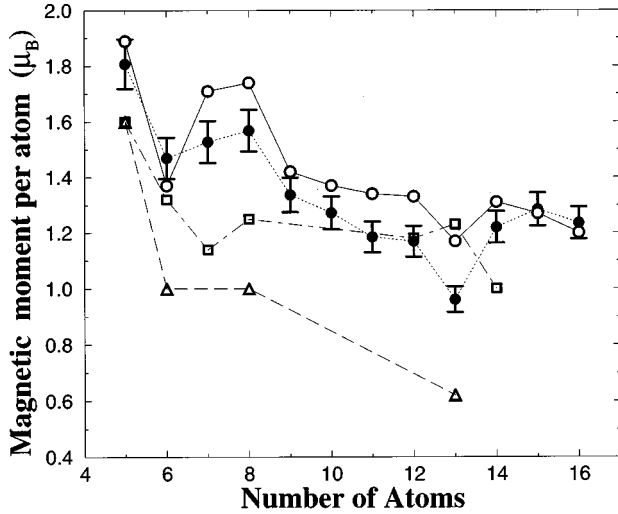


FIG. 1. Calculated (○) and experimental (Ref. 2) (●) average magnetic moments (per atom) of Ni clusters. Density-functional predictions (Ref. 12) (△) are given for $N=5, 6, 8,$ and $13,$ as well as the results of Ref. 13 (□), obtained with a Hubbard Hamiltonian combined with a TB molecular dynamics method, for $N=5-8,$ and $12-14.$

$$\varepsilon_{i\alpha\sigma} = \varepsilon_{i\alpha}^0 + z_{\sigma} \sum_{\beta} \frac{J_{\alpha\beta}}{2} \mu_{i\beta} + \Omega_{i\alpha}. \quad (2)$$

Here $\varepsilon_{i\alpha}^0$ are the bare orbital energies of paramagnetic bulk Ni. The second term is the shift due to the spin polarization of the electrons at site i ($\mu_{i\beta} = \langle \hat{n}_{i\beta\uparrow} \rangle - \langle \hat{n}_{i\beta\downarrow} \rangle$). In this term, $J_{\alpha\beta}$ are the exchange integrals and z_{σ} is the sign function ($z_{\uparrow}=1, z_{\downarrow}=-1$). All the exchange integrals involving s and p electrons are neglected, and J_{dd} is determined in order to reproduce the bulk magnetic moment. Finally, the self-consistent corrections $\Omega_{i\alpha}$ assure the local sp and d electronic occupations, fixed in our model by interpolating between the isolated atom (d^8, s^2, p^0) and the bulk ($d^{9.1}, sp^{0.9}$) according to the local number of neighbors. The spin-dependent local electronic occupations are self-consistently determined from the local densities of states:

$$\langle \hat{n}_{i\alpha\sigma} \rangle = \int_{-\infty}^{\varepsilon_F} \rho_{i\alpha\sigma}(\varepsilon) d\varepsilon, \quad (3)$$

which are calculated at each iteration by using the recursion method.⁹ In this way, the local magnetic moments ($\mu_i = \sum_{\alpha} \mu_{i\alpha}$) and the average magnetic moment [$\bar{\mu} = (1/N) \sum_i \mu_i$] of Ni_N clusters are obtained at the end of the self-consistent procedure.

The cluster geometries and interatomic distances used in the calculations have been taken from molecular dynamics simulations performed by López and Jellinek,⁶ who used a many-body potential¹⁰ whose form is based on tight-binding theory¹¹ and their parameters are fitted to properties of Ni_2 and bulk Ni.

The average magnetic moment per atom has been plotted in Fig. 1 for Ni clusters with $N=5-16$ atoms. We also include in the same figure the experimental results of Apsel *et al.*,² and the theoretical results of Reuse and Khana¹² and Andriotis, Lathiotakis, and Menon.¹³ Reuse and Khana used

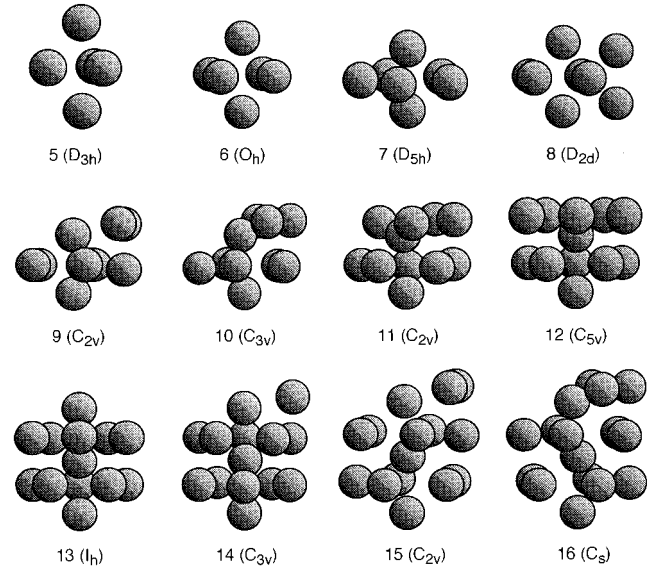


FIG. 2. Calculated most stable structures and their symmetries for $Ni_N, N=5-16.$

density-functional theory and certain specific geometries for $Ni_5, Ni_6, Ni_8,$ and Ni_{13} whereas Andriotis, Lathiotakis, and Menon combined a Hubbard Hamiltonian with a TB molecular-dynamics method. We obtain a perfect qualitative agreement with experiment: pronounced local minima of $\bar{\mu}$ at $N=6$ and $13,$ and a maximum at $N=8.$ In Fig. 2 we give the atomic structures for $N=5-16.$ Ni_{13} is an icosahedron with an atom inside. The coordination of the surface atoms in this cluster is $z=6.$ Either by removing or by adding one atom, the resulting clusters (Ni_{12} and $Ni_{14},$ respectively) contain some atoms with coordination lower than 6. Consequently, the minimum of $\bar{\mu}$ at Ni_{13} can be explained by the compact structure of this cluster. The local magnetic moments of $Ni_{12}, Ni_{13},$ and $Ni_{14},$ given in Table I, reflect the effect of coordination. Ni_{13} only has two types of inequivalent atoms (inner and surface atoms), and this number is larger for Ni_{12} and Ni_{14} (four and six types, respectively; these are explicitly indicated in Fig. 3). The low coordination of some atoms leads to large local magnetic moments, and consequently $\bar{\mu}$ increases. Ni_6 is an octahedron formed by atoms with coordination $z=4.$ In $Ni_7,$ which is a pentagonal bipyramid, the coordination of two atoms increases to $z=6,$ remaining $z=4$ for the rest. Ni_8 has four atoms with coordination $z=5$ and four atoms with coordination $z=4,$ which leads to a mean coordination slightly lower than in $Ni_7,$ and afterwards the coordination increases again for $Ni_9.$ This would lead us to expect a maximum of $\bar{\mu}$ for

TABLE I. Local magnetic moments at different types of inequivalent sites in the cluster, for $Ni_{12}, Ni_{13},$ and $Ni_{14}.$

Size	Type of site					
	1	2	3	4	5	6
$N=13$	0.84	1.20				
$N=12$	0.87	1.21	1.34	1.43		
$N=14$	0.79	1.22	1.39	1.35	1.33	1.68

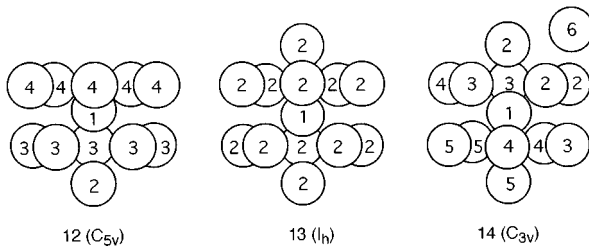


FIG. 3. Structure of Ni_{12} , Ni_{13} , and Ni_{14} , with the inequivalent sites indicated.

Ni_8 , which is indeed observed, and a minimum for Ni_7 . Instead, the observed and the calculated minima occur at Ni_6 , and the reason is that the average first-neighbor distance d has a local maximum at Ni_7 (d is larger at this cluster compared to Ni_6 and Ni_8). This anomalously large d works against the increase of the coordination number from Ni_6 to Ni_7 , and the larger separation between atoms in Ni_7 leads to the local minimum of $\bar{\mu}$ at Ni_6 . In summary, the oscillations in $\bar{\mu}$ between Ni_5 and Ni_{16} can be explained by purely geometrical effects: compact clusters have small $\bar{\mu}$, and clusters with low coordinated atoms and/or with large interatomic distances have large $\bar{\mu}$. The same ideas have been used to explain the behavior of the magnetic moment at planar surfaces or surfaces with defects.¹⁴

In Fig. 4 we compare the orbital-projected density of states of the clusters Ni_5 , Ni_6 , and Ni_7 . A common feature of the three sizes is the tendency toward magnetic saturation characteristic of the atomic limit. The occupied states of the majority-spin band have mainly d character with the exception of the peak closer to the Fermi level, that has sp character. d -holes are present in the minority-spin band, with a

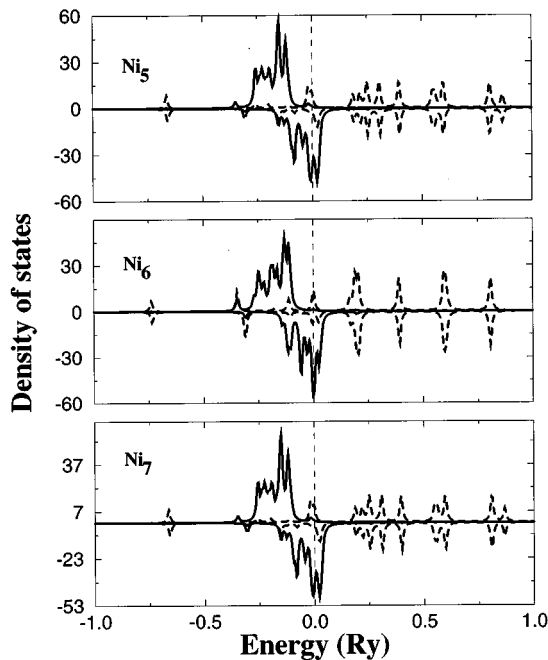


FIG. 4. Density of states, decomposed by orbital sp (dashed line) and d characters (thick line), for Ni_5 , Ni_6 , and Ni_7 . Positive (negative) values refer to up- (down-) spin. The vertical line indicates the position of the Fermi level.

large contribution of d states at the Fermi level. The integration of the density of states gives d magnetic moments of $1.6\mu_B$, $1.52\mu_B$, and $1.50\mu_B$ for Ni_5 , Ni_6 , and Ni_7 , respectively. The differences between the magnetic moments of the three clusters arise mainly from the sp states. For Ni_5 , the sp peak near the Fermi energy is split. The peak of the majority band lies in the occupied part of the spectrum, whereas the peak of the minority band lies in the unoccupied part. This sp splitting is also observed in Ni_7 , but not for Ni_6 . As a consequence, the sp magnetic moment for Ni_5 and Ni_7 ($0.29\mu_B$ and $0.21\mu_B$, respectively), points in the same direction of the d contribution, whereas for Ni_6 the sp contribution to the magnetic moment ($-0.15\mu_B$) points in the opposite direction. It is well known that for transition metals at the end of the series (Co, Ni, and Cu), the sp states contribute to the magnetism through $sp-d$ hybridization. Our cluster results give further support for this effect. The interplay between cluster symmetry and hybridization is accounted for in the self-consistent electronic structure calculation. The sp contribution to the magnetic moment appears to decay quickly with cluster size: already for sizes $N=12-14$, this sp contribution is negligible.

By comparing our results for 5, 6, 8, and 13 with those obtained by Reuse and Khanna¹² through *ab initio* linear combination of atomic orbital (LCAO) density-functional calculations, one notices the similar trend for 5-6-13 (although with a substantial difference in the values of $\bar{\mu}$), but a disagreement in the qualitative behavior for $N=8$. The strong increase of the magnetization experimentally measured between $N=6$ and 8 is not obtained by these authors. The geometries used in both theoretical calculations for $N=5$ and 6 and $N=13$ are similar, i.e., bipyramids for $N=5$ and 6 and an icosahedron for $N=13$, although with different interatomic distances (larger in our TB calculations), but for $N=8$ the geometry used by Reuse and Khanna is a regular cube, different from our structure given in Fig. 2. In order to clarify the source of the discrepancies between both theoretical calculations, we performed TB calculations for $N=5$, 6, and 8 using the geometries and interatomic distances of Reuse and Khanna, and obtained magnetic moments differing from our earlier ones by no more than $0.06\mu_B$. We then conclude that the discrepancies between the TB and LCAO density-functional theory calculations arise from the treatment of the electronic problem. Our calculations also reproduce the experimental trend better than those of Ref. 13. Those authors obtained a local maximum of $\bar{\mu}$ at Ni_{13} (instead of a minimum), and a spurious minimum at Ni_7 .

The icosahedral structure around Ni_{13} is consistent with reactivity experiments¹⁵ with N_2 and other molecules. Extending our calculations to larger clusters becomes increasingly difficult. The main reason is the determination of the geometrical structure of the cluster as a function of size. Reactivity experiments¹⁵⁻¹⁷ indicated the icosahedral structure near Ni_{55} , but the situation for sizes midway between Ni_{13} and Ni_{55} is less clear. Several calculations of the structures in this size range have been performed,^{13,18-20} although there are discrepancies between the results of the different methods. We performed preliminary calculations of the average magnetic moment for clusters near Ni_{55} using an icosahedral model, and we verified that $\bar{\mu}$ has a local minimum at

Ni₅₅ that can be explained by the same arguments used above to explain the local minimum at Ni₁₃. However, explaining the experimental magnetic moments of the whole sequence between Ni₁₃ and Ni₅₅ seems to be a much more demanding task which would require, no doubt, an accurate determination of the ground state geometries as a function of the cluster size.

Our calculations, although only covering a restricted range of cluster sizes, support the physical picture proposed by Jensen and Bennemann.⁴ In this picture surface and bulk-like atoms have different magnetic moments, and the oscillations of $\bar{\mu}$ originate from the progressive formation of shells of atoms, reflecting the atomic structure. Minima are predicted for $\bar{\mu}$ when the cluster has a compact atomic structure of closed atomic shells. Jensen and Bennemann studied the implications of an fcc cubo-octahedral (CO) growth as well as other growth models. Although they did not study the icosahedral (ICO) growth, perfect CO and ICO clusters have the same number of atoms: 13, 55, 147, . . . , so their model would predict minima of $\bar{\mu}$ for icosahedra with $N=13, 55, 147, \dots$. Our calculations confirm the ICO structure of Ni₁₃, and assuming the ICO structure around Ni₅₅ we obtain minima for $\bar{\mu}$ at $N=13$ and 55. Furthermore, this interpretation agrees with the location of the observed minima in Apsel *et al.*'s experiment.²

We are less certain about the interpretation of the experimental maxima of $\bar{\mu}$. The maximum at Ni₈ is reproduced in our calculations, again as a geometrical effect, and it is plausible that other maxima also arise from geometrical effects. However, maxima have been observed in the experiments² near $N=20, 40,$ and 70, which are well-known magic numbers of the spherical jellium model.²¹ The model of Fujima and Yamaguchi⁵ distinguishes between localized levels derived from atomic $3d$ electrons and delocalized levels derived from $4s$ electrons. The $4s$ -derived levels are described as electronic levels in a smooth harmonic potential, and lie

above the Fermi energy in small Ni clusters. But, as N grows, the binding energy of those highly degenerate levels increases, moving under the $3d$ band. Fujima and Yamaguchi's model assumes that this occurs suddenly when the number of electrons is just enough to fill a shell. Associated with this transfer there is a sudden increase in the number of holes in the minority d band, with an abrupt increase of $\bar{\mu}$. The mechanism of transfer of $4s$ -derived levels from above the Fermi level to below the d band is supported by earlier density-functional calculations by the same authors,²² and the maxima observed in the experiments near $N=20, 40,$ and 70 could be indicative of this effect. However in Fujima and Yamaguchi's model the minima and maxima are too close due to the drastic assumption of the global transfer of a whole electronic shell. The experiment reveals that the minima of $\bar{\mu}$ are well separated from the maxima, and the calculations²² also show that the transfer of electron levels is not as drastic. We conclude that Fujima and Yamaguchi's model fails in explaining the physical effect behind the minima of $\bar{\mu}$, but this model might have some relevance for explaining the maxima. More work is required to clarify the detailed behavior of $\bar{\mu}$ for N larger than 16.

In summary, we used molecular dynamics and the tight-binding method to calculate the average magnetic moment of Ni _{N} clusters between $N=5$ and 16. The agreement with the experimental results of Apsel *et al.*² in this size range is rather good, and the variation of $\bar{\mu}$ is explained as a consequence of geometrical effects: low coordinated atoms have large local magnetic moments. The deviation of interatomic distances from a smooth behavior also influences $\bar{\mu}$, sometimes strongly.

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