

Electronic structure and magnetic properties of Ni clusters

H. M. Duan,^{a)} X. G. Gong, and Q. Q. Zheng

Institute of Solid State Physics, Academia Sinica, 230031-Hefei, People's Republic of China

H. Q. Lin

Department of Physics, The Chinese University of Hong Kong, Shatin New Territory, Hong Kong

A systematic study on the ground state electronic structure and magnetic properties of Ni_n ($n = 2-39$ and 55) clusters are performed using the density functional calculation with the local spin-density approximation. The binding energy per atom increases monotonically. The occupation numbers do not change significantly for $n > 8$, which helps us to understand the experimental observation of the photoelectron spectroscopy. The obtained average magnetic moment per atom is larger than the bulk value, and the evolvement of these moments towards the bulk is in good agreement with the experimental trend. However, the average moments of "core" atoms are comparable to or even larger than that of surface atoms, which indicates that the usual conclusion of surface enhancement on magnetism in transition metal clusters may be improper for these Ni_n ($n = 14-39$) clusters. © 2001 American Institute of Physics. [DOI: 10.1063/1.1356036]

Due to the finite size effect, clusters can exhibit anomalous structural, electronic, and magnetic properties. The study of the cluster properties and its evolution as a function of the cluster size has been an important subject for both fundamental researches and technological applications. Theoretically, the first step of such a study is to determine the lowest energy structures of clusters, which is usually a very difficult task for clusters even containing a few tens of atoms due to the rapidly increased local minima as well as the number of structural parameters with increasing the cluster size. For transition metal clusters, this becomes even more complicated owing to the abundance of low-lying electron states and to the delocalization of d electrons. Experiments have shown that transition metal clusters have special and interesting properties. For example, for the small clusters, not only magnetic¹⁻³ but also nonmagnetic elements^{4,5} can have a net magnetic moment, and the average magnetic moment per atom is larger than the bulk value.

Because of the importance of their catalytic and magnetic properties, nickel clusters have been an interesting object of study for both experiments and theoretical calculations. Recently Apsel *et al.* measured the magnetic moments of Ni_n ($n = 5-740$) clusters.⁶ The intrinsic magnetic moment per atom was derived by using the superparamagnetic model.⁷ Their results showed that the average magnetic moment per atom of all these clusters is larger than the bulk value (about $0.60\mu_B$),⁸ and shows an oscillatory behavior, which is remarkable at a smaller cluster size range. There are also some first principles studies on the electronic structure and magnetic properties of nickel clusters,⁹⁻¹¹ but these studies deal only with clusters containing less than 20 atoms.

Considering the lack of first principles investigations of larger Ni clusters and the importance of the systematic investigations of the evolvement of the binding energy, $sp-d$ hybridization, magnetic moment, and density of states (DOS) as a function of cluster size, a systematic study of Ni_n ($n = 2-39$ and 55) clusters were give in this work.

Our study is based on the density functional theory (DFT) with the Barth-Hedin local spin density approximation (LSDA).¹² The numerical $3d$, $4s$, and $4p$ atomic wave functions of a Ni atom are used as the basis sets of valence orbitals and the core levels are treated by the frozen core approximation.

Started from the stable structure obtained by the generalized simulated annealing (GSA) algorithm,¹³ the structures

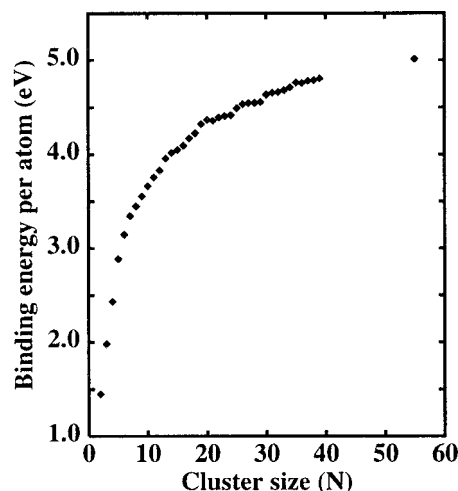


FIG. 1. Binding energy per atom of Ni_n ($n = 2-39$ and 55) clusters as a function of cluster size.

^{a)}Electronic mail: hmduan@theory.iissp.ac.cn

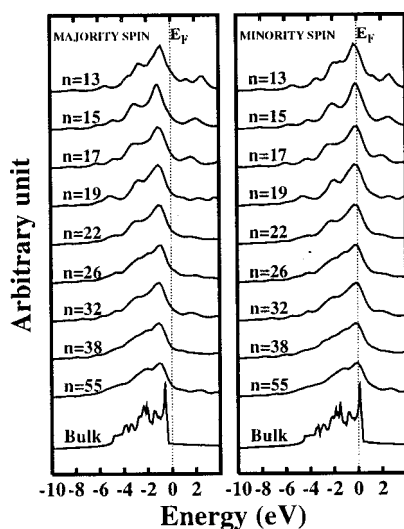


FIG. 2. The electronic density of states (DOS) per atom for both Ni_n ($n = 13, 15, 17, 19, 22, 26, 32, 38$, and 55) clusters and the fcc Ni crystal. The left represents majority spin and right is minority spin. E_F is shifted to the zero. With increasing the cluster size, DOS develops the bulk features.

of the calculated Ni_n ($n = 2-39$ and 55) clusters are further optimized by minimizing the LSDA total binding energy with respect to the interatomic distances within the symmetry constraint. For the Ni dimer, the obtained bond length of about 2.10 \AA and binding energy of 2.90 eV are in better agreement with experimental data¹⁴ (bond length of 2.155 \AA and binding energy of 2.068 eV) than previous LSDA results.⁹⁻¹¹

Figure 1 gives the binding energy per atom of these Ni clusters, this gives a generally monotonic increased trend which changes rapidly in a small cluster size range and tends to moderate for large ones. The binding energy per atom of Ni_{55} is about 5.01 eV , which is still much lower than the LSDA band result ($\sim 5.70 \text{ eV}$).¹⁵

The majority and minority DOS curves of some Ni_n ($n = 13, 15, 17, 19, 22, 26, 32, 38$, and 55) clusters are shown in Fig. 2. For comparison, the DOS curves of a band calculation by the linear muffin-tin orbital method on fcc Ni crystal are also shown in the same figure. For the similar binding in these clusters, there is a clear common feature among them that the majority spin $3d$ band is nearly completely filled, while the minority spin $3d$ band extends above the Fermi energy (E_F). With increasing the cluster size, a similarity between the general features of the DOS for the clusters and for the bulk crystal develops, but the complete bulk DOS behavior was still far from being reached for a cluster containing about 55 atoms.

Figure 3 shows the average number of electrons of $3d$, $4s$, and $4p$ orbitals for the nickel clusters obtained by the Mulliken population analysis. The number of $3d(4s+4p)$ electrons increase (decrease) rapidly and approach a maximum (minimum) at $n \sim 8$ and then change slowly as shown in Fig. 3, which indicates that the $sp-d$ hybridizations in Ni clusters evolve very quickly and tend to saturate at a small size ($n \sim 8$). The behavior of the variation of d electrons observed above may have an influence on physical properties of nickel clusters. For example, the recent experiments per-

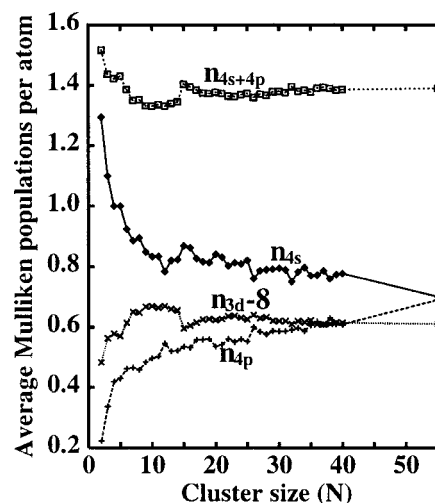


FIG. 3. The average Mulliken populations of $3d(\times)$, $4s(\diamond)$, $4p(+)$, and $4s+4p(\square)$ orbitals of Ni_n ($n = 2-39$) clusters. Values of $3d$ population are specially shown by subtracting a constant 8.

formed by Wang *et al.*^{16,17} on $3d$ transition metal clusters have shown that the discrete spectral features cannot be observed beyond a relatively small size of eight atoms for nickel clusters, and this is very different from that of Fe_n clusters in which the discrete spectral features can even be observed up to $n = 23$. The early emerging of large d electrons may be a possible reason explaining the experimental observations.

The recent experiment performed by Apsel *et al.*⁶ has given the effective magnetic moment of Ni_n ($n = 5-740$) clusters by utilizing the superparamagnetic model⁷ and the cluster temperature is in the range from 73 to 198 K . Their results indicated that the average magnetic moment per atom is larger than the bulk value ($0.6\mu_B$) and does not approach to this limit at $n = 740$, and the evolution towards the bulk is not monotonic. These authors attributed the magnetic mo-

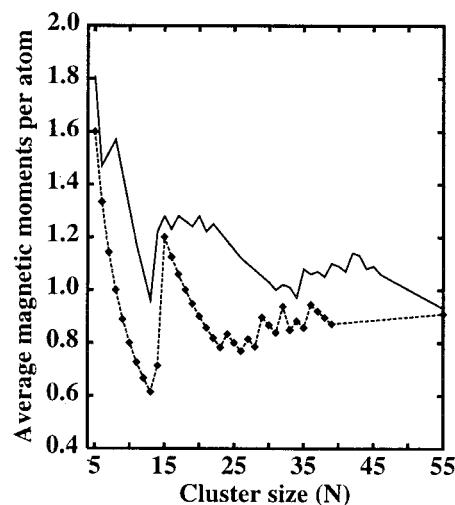


FIG. 4. Comparison between calculated (dashed line) and experimental (solid line) magnetic moments of Ni_n ($n = 5-39$) clusters. The experimental results are taken from Ref. 6. The theoretical results qualitatively reproduced the right trend of the experimental data.

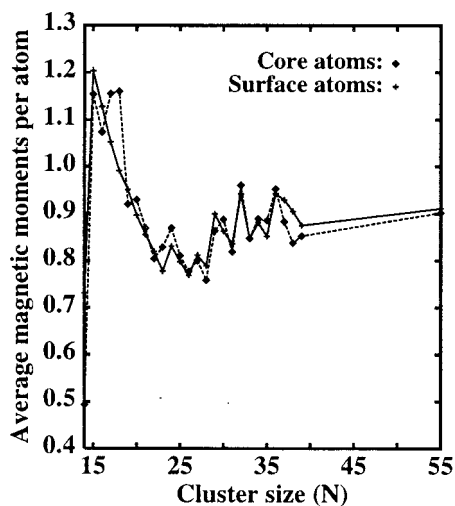


FIG. 5. Comparison of the average magnetic moments per atom of surface atoms (solid line) and “core” atoms (dashed line). Note that the moments of “core” atoms are comparable to or even larger than that of surface ones.

ment enhancement to the surface effects since surface atoms are low coordinated and can have larger moments than inner atoms. In Fig. 4 we compare our calculated average magnetic moments with the experimental results of Apsel *et al.*, our results are in agreement with the experimental trend. Both of them are larger than the bulk value and take on an oscillatory behavior.

In general, the magnetic moment of an atom of a cluster is sensitive to its environment (local condition) in the cluster. Surface atoms often have higher moments than that of the inner (core) ones, but for nickel clusters this would be more complex. Figure 5 shows the average magnetic moments of both core atoms and surface atoms of Ni_n ($n=14-39$ and 55) clusters as a function of cluster size. It is surprising that the average magnetic moments of core atoms are found to be very close to or even larger than that of the surface atoms which is in contrast to the common thought that surface atoms should be higher magnetic. The reason for the generally high moments of core atoms of Ni clusters can be partially explained by the charge transfer, in our opinion. Also contrary to the usual case, there are net charges (0–1 electron) transferred from core atoms to surface atoms in most cases, since generally the density of states near the Fermi level are mainly due to contributions from the minority spin, these charge transfer can enhance the moments of “core” atoms and reduce the moments of surface atoms. This anomalous behavior indicates that the usual conclusion of surface enhancement of magnetic moments in transition metal clusters⁶ may be improper in these Ni_n ($n=14-39$) clusters and suggests that it would be questionable to apply models such as

the effective coordinate one to describe the magnetic properties of Ni clusters.

In summary, we have performed systematic LSDA calculations for the Ni_n ($n=2-39$ and 55) clusters. The binding energy per atom of these clusters increases monotonically as a function of cluster size. The electron occupation numbers do not change significantly for clusters containing more than eight atoms but the complete bulk DOS behavior is still far from being for a cluster containing about 55 atoms, thus different cluster property evolves differently. The obtained average magnetic moments are larger than the bulk value, and the nonmonotonic development of these moments towards the bulk limit is in good agreement with the experimental trend. However, the average moments of “core” atoms can be comparable to or even larger than that of surface atoms, this can be attributed to the charge transfer from inner atoms to surface ones, and this indicates that the usual conclusion of surface enhancement of magnetic moments may be improper for these relatively small Ni_n ($n=14-39$) clusters.

One of the authors (H.M.D.) is greatly indebted to Professor Z. Zeng, Dr. Y. Xiang, Dr. S. Y. Wang, and Dr. J. L. Wang for their valuable help. This work was supported by the PanDeng Project 95-YU-41 and the NSF of China, the Nanoscale PanDeng project, and the CAS project.

- ¹J. G. Louderback, A. J. Cox, L. J. Lising, D. C. Douglass, and L. A. Bloomfield, *Z. Phys. D: At., Mol. Clusters* **26**, 301 (1993).
- ²I. M. L. Billas, J. A. Becker, A. Chatelain, and W. A. de Heer, *Phys. Rev. Lett.* **71**, 4067 (1993).
- ³I. M. L. Billas, A. Chatelain, and W. A. de Heer, *Science* **265**, 1682 (1994).
- ⁴B. V. Reddy, S. N. Khanna, and B. I. Dunlap, *Phys. Rev. Lett.* **70**, 3323 (1993).
- ⁵A. J. Cox, J. G. Louderback, and L. A. Bloomfield, *Phys. Rev. Lett.* **71**, 923 (1993).
- ⁶S. E. Apsel, J. W. Emmert, J. Deng, and L. A. Bloomfield, *Phys. Rev. Lett.* **76**, 1441 (1996).
- ⁷S. N. Khanna and S. Linderorth, *Phys. Rev. Lett.* **67**, 742 (1991).
- ⁸C. Kittel, *Introduction to Solid State Physics*, 5th ed. (Wiley, New York, 1976).
- ⁹M. Castro, C. Jamorski, and D. R. Salahub, *Chem. Phys. Lett.* **271**, 133 (1997).
- ¹⁰F. A. Reuse and S. N. Khanna, *Chem. Phys. Lett.* **234**, 77 (1995).
- ¹¹B. V. Reddy, S. K. Nayak, S. N. Khanna, R. K. Rao, and P. Jena, *J. Phys. Chem. A* **102**, 1748 (1998).
- ¹²U. von Barth and L. Hedin, *J. Phys. C* **5**, 1629 (1972).
- ¹³Y. Xiang, D. Y. Sun, and X. G. Gong, *J. Phys. Chem. A* **104**, 2746 (2000).
- ¹⁴M. D. Morse, G. P. Hansen, P. R. R. Langridge-Smith, L. S. Zheng, M. E. Geusic, D. L. Michalopoulos, and R. E. Smalley, *J. Chem. Phys.* **80**, 5400 (1984).
- ¹⁵V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).
- ¹⁶L. S. Wang and H. Wu, *Advances in Metal and Semiconductor clusters* (JAI, 1998), Vol. 4, pp. 299–343.
- ¹⁷L. S. Wang and H. Wu, *Z. Phys. Chem. (Munich)* **203**, 45 (1998).