Available online at www.sciencedirect.com
ScienceDirect
Physics Letters A 360 (2007) 629–631
PHYSICS LETTERS A
www.elsevier.com/locate/pla

Structures and magnetic moments of Ni_n ($n = 10 \sim 60$) clusters

Y.H. Yao [a], X. Gu [a], M. Ji [a], X.G. Gong [a,*], Ding-sheng Wang [b]

[a] *Surface Physics Laboratory and Department of Physics, Fudan University, Shanghai 200433, China*
[b] *Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China*

Received 17 August 2006; accepted 22 August 2006

Available online 1 September 2006

Communicated by R. Wu

Abstract

We have studied the stable geometries of Ni_n clusters using the first principles method with ultrasoft pseudopotentials. It is found that the ground state structures of Ni_n ($n = 10 \sim 27$, $41 \sim 56$) are icosahedron-like, while Ni_{13} and Ni_{55} are perfect icosahedra, in agreement with experimental results. For Ni_n ($n = 28 \sim 40$), no simple growth mode can be found even though some of them display certain symmetry. The size dependence of magnetic moments calculated with these ground state structures nicely reproduces experimental trend. In general, we found two peaks around $n = 15 \sim 20$ and $n = 35 \sim 40$, and three dips at $n = 13$, 34, 55. The deviation between the calculated results and experimental data, assigned as the orbital magnetic moment, decreases monotonically as the cluster size increases.

PACS: 36.40.Mr; 36.40.Cg; 36.40.Qv; 31.15.Ew

Properties of nanoclusters are important for various fundamental and application researches. Due to the size effect and large ratio of surface to volume, nanoclusters usually adopt very complex structures and display unique features. One of the interesting topics in cluster science is the evolution of their geometries and physical properties toward the corresponding bulk asymptotes [1]. For example, peculiar oscillatory size dependence of magnetic moments has been reported for Fe, Co and Ni clusters and the bulk values are reached only when the number of atoms in cluster is larger than $500 \sim 700$ [2]. Various theoretical calculations have been performed to explain the experimental observations. Earlier calculations adopted bulk-like structures [3], and results were not reliable since magnetic moments typically depend on atomic structures. Wan et al. obtained atomic structures from empirical potential simulations [10] for Ni clusters with up to ~ 55 atoms. Using the tight-binding (TB) model, they found sizeable orbital magnetic moments and explained the usually large magnetic moments observed experimentally. Nonetheless, the agreement of the size dependence is less satisfactory, most likely due to the quality of structural optimization. Recently, it is feasible to search more reliably the ground state structures of small metal clusters by using the first principles methods. This enables us to study better their magnetic properties.

In this work, we first optimized the ground state geometries of Ni_N clusters ($N = 13 \sim 56$) through first principles calculations, starting from the structures produced by empirical potential simulations. Intriguingly, the experimental results of size dependence of magnetic moment are well reproduced in the whole range, indicating the importance of proper structural optimization for the determination of physical properties of nanoclusters.

Our calculations were based on the density functional theory, implemented in the VASP code [5], with the spin polarized Generalized Gradient Approximation (GGA) for the exchange correlation potentials [4]. The effect of core electrons was invoked through ultrasoft pseudopotentials. The wave functions were expanded in plane waves with an energy cutoff of 19.8 Ry. The calculated lattice constant and the magnetic moment for the fcc bulk Ni are 3.52 Å, and 0.61 μ_B, respectively. These results are in close agreement with the corresponding experimental values, 3.52 Å and 0.6 μ_B, indicating the validity of our

* Corresponding author.
E-mail address: xggong@fudan.edu.cn (X.G. Gong).

0375-9601/$ – see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.physleta.2006.08.059

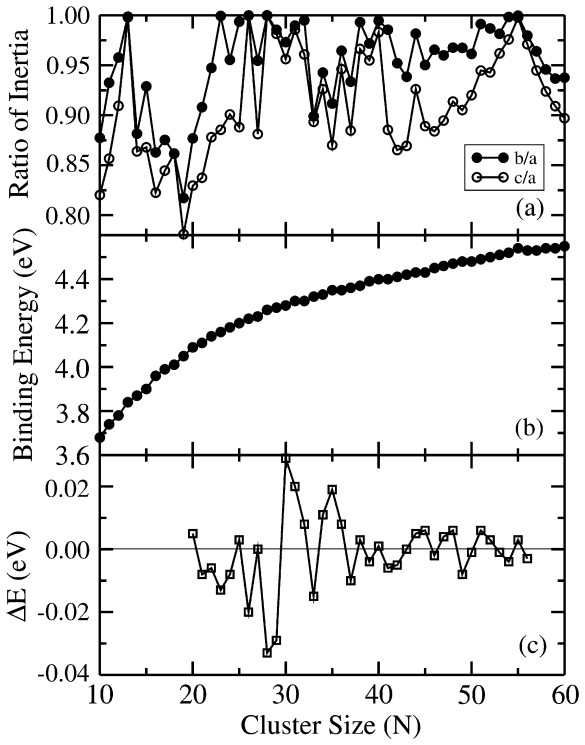

Fig. 1. (a) The ratios of the three principal inertias. (b) The binding energies per atom of Ni clusters. (c) The difference between binding energies of two structures, optimized with either the Sutton–Chen model potential or embedded potential.

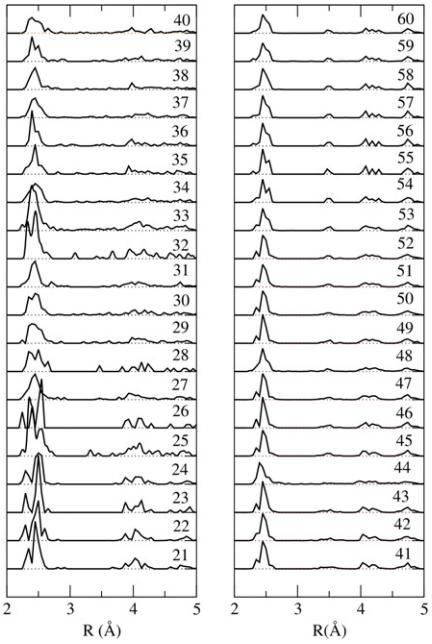

Fig. 2. The pair-correlation function of selected Ni clusters. The sudden changes near $n = 28$ and $n = 41$ indicate switches in growth mode.

computational treatments. For Ni clusters, we used a simple cubic supercell with a lattice size of 27 Å. Subsequently, we used only the Γ point to sample the Brillouin zone. The total energy was converged to 10^{-4} eV for the structural relaxation.

It is still very difficult to study the ground state structure of a cluster with a few tens of atoms by using the first principles molecular dynamics simulations. One of the authors optimized structures of Ni clusters using the generalized simulated annealing with Sutton–Chen version of Finnis–Sinclair (FS) model potential [6], one of the best for transition metals. The details of calculations and structural properties were published previously [7]. In this Letter, starting from the ground state structures and their first isomers obtained from the Sutton–Chen potential as well as those optimized through the embedded atom method [8], we further refine the atomic structures of Ni clusters through the first principles total energy minimization procedures.

Fig. 1 shows the binding energy differences resulted from two initial structures. The largest binding energy difference is only about 0.03 eV near $N \sim 30$, and it decreases as the size of clusters increases. None of the two model potentials has obvious advantage over the other. One can also conclude that none of the two model potentials can correctly predict all the ground state structures of Ni clusters, especially for the medium size clusters. Fig. 1 also shows the ratio of three rotational inertias of the ground state structures. Comparing to the corresponding results of their initial structures (Fig. 2 in Ref. [10]), the ground state structures obtained by the first principles method are closer to spherical, especially for clusters around $N \sim 30$ and $N \sim 40$.

We find that first principles structural relaxations do not change the general features obtained through model potential simulations. For clusters with $10 \sim 27$ atoms, Ni clusters adopt the icosahedron-like structures. Specially, Ni_{13} is a perfect icosahedron. Ni_{12}, Ni_{11} and Ni_{10} are formed by taking atoms away from Ni_{13}, whereas $Ni_{14} \sim Ni_{19}$ are constructed by successively adding atoms to Ni_{13} until a double icosahedron is completed in Ni_{19}. Subsequently, one can get structures of $Ni_{20} \sim Ni_{27}$ by capping atoms on the Ni_{19} cluster. All these structures are in good agreement with Parks' results [9].

Since Ni_{55} adopts the icosahedral-like structure, clusters near $N \sim 55$ are formed by adding or removing atoms to/from the icosahedron. For clusters with $N = 28 \sim 40$, the structures become very complex, since they are in the transition region from Ni_{13} icosahedron to Ni_{55} icosahedron. It is also the reason why the structures predicted from two model potentials are quite different in this regime. Although one still can identify the symmetry for some clusters, it is very difficult to assign a simple growth mode. The change of structural features can be seen in the pair-correlation functions as shown in Fig. 2, where amorphous-like profile is shown near $N \sim 32$.

With the well-optimized ground state structures, we calculated the magnetic moments for all Ni_n clusters using the spin polarized density functional theory and the results are displayed in Fig. 3 along with the experimental data [11]. The accordance is clear in the entire range, including the positions of three dips at $n = 13, \sim 34, 55$ as well as three apexes around $n = 15 \sim 20$ and $n = \sim 40$. The minima occurring at $n = 13$, and $n = 55$ can be attributed to the compact icosahedron structures. In these two clusters, the interatomic distances are short, and the average nearest neighbor numbers are high. The minimum around

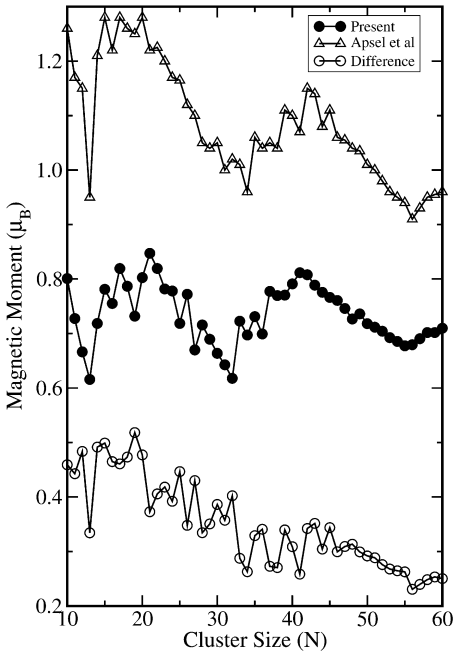

Fig. 3. The magnetic moments vs the size of clusters obtained from the present calculations (solid circles) and experiments (open triangles). The differences are given in circles.

$n \sim 34$ can also be attributed to short interatomic distances in the disordered structure.

Note that we did not include the effect of spin–orbit coupling, and hence our magnetic moments are smaller than the experimental values. If we assign the difference between the present theoretical and experiment data as the orbital magnetic moment, the size is quite large, e.g., $0.4 \sim 0.5\ \mu_B$ for Ni_{10} to Ni_{20}. This is not surprising since recent experiments found that the orbital moments can be as large as 10% to 30% of spin moment [12].

In summary, by combining model potential and first principles approaches, we have optimized the ground state structures of Ni_n clusters ($n = 10$ to 60). Neither Sutton–Chen potentials nor those optimized through the embedded atom method produce correctly atomic structures alone; ab initio optimization is essential for most clusters. The agreement between theory and experiment in the size dependence of magnetic moments is much improved with the new ground state geometries.

Acknowledgements

This work is supported by the National Science Foundation of China and the National Basic Research Program. X.G.G. is also supported by the Shanghai Science and Technology Foundation. The computation is performed in the Supercomputer Center of Shanghai, the Supercomputer Center of Fudan University and CCS, HFCAS.

References

[1] X.G. Gong, Q.Q. Zheng, Y.Z. He, Phys. Lett. A 181 (1993) 459.
[2] I.M.L. Billas, J.A. Becker, A. Châtelain, W.A. de Heer, Phys. Rev. Lett. 71 (1993) 4067;
I.M.L. Billas, J.A. Becker, A. Châtelain, W.A. de Heer, Science 265 (1994) 1682.
[3] J. Guevara, F. Parisi, A.M. Llois, M. Weissmann, Phys. Rev. B 55 (1997) 13283.
[4] J.P. Perdew, A. Zunger, Phys. Rev. B 23 (1981) 5048.
[5] G. Kresse, J. Hafner, Phys. Rev. B 47 (1993) 558;
G. Kresse, J. Furthmüller, Phys. Rev. B 54 (1996) 11169.
[6] A.P. Sutton, J. Chen, Philos. Mag. Lett. 61 (1990) 139.
[7] Y. Xiang, D.Y. Sun, X.G. Gong, J. Phys. Chem. A 104 (2000) 2746.
[8] J.M. Montejano-Carrizales, M.P. Iniguez, J.A. Alonso, M.J. Lopez, Phys. Rev. B 54 (1996) 5961.
[9] E.K. Parks, L. Zhu, J. Ho, S.J. Riley, J. Chem. Phys. 100 (1994) 7026.
[10] X.G. Wan, L. Zhou, J.M. Dong, T.K. Lee, D.-S. Wang, Phys. Rev. B 69 (2004) 174414.
[11] S.E. Apsel, J.W. Emmert, J. Deng, L.A. Bloomfield, Phys. Rev. Lett. 76 (1996) 1441.
[12] J.T. Lau, A. Föhlisch, M. Martins, R. Nietubyc, M. Reif, W. Wurth, New J. Phys. 4 (2002) 98.