RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 52, NUMBER 16 15 OCTOBER 1995-II

# Electronic structure and magnetic behavior of $Ni_{13}$ clusters

F. A. Reuse
*Institut de Physique Experimentale, Ecole Polytechnique Federale de Laussane, CH-1015 Lausanne, Switzerland*

S. N. Khanna
*Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284-2000*

S. Bernel
*Service Informatique Central, Ecole Polytechnique Federale de Lausanne, Ch-1015 Lausanne, Switzerland*

(Received 19 June 1995)

Electronic-structure studies on a $Ni_{13}$ cluster have been carried out using a linear-combination-of-atomic-orbitals–molecular-orbital approach within the density-functional formalism. The ground state is shown to be a distorted $D_{3d}$ icosahedron. The cluster has a magnetic moment per atom close to the bulk and is marked by a number of higher spin states close to the ground state. Their effect on the observed magnetic behavior is discussed.

Small atomic clusters[1] are now known to display geometrical arrangements and physical, chemical, electronic, and magnetic properties that are different from the bulk. The properties evolve with size and composition and this has provided hope of generating new materials with tailored properties using suitably designed clusters. The recent interest in clusters has been on transition-metal clusters, mainly due to their interesting magnetic behaviors. For example, Stern-Gerlach experiments[2,3] on small clusters of Fe, Co, and Ni, which are itinerant ferromagnets in bulk, show that the clusters exhibit a variety of behaviors depending on their temperature. At high temperatures, the clusters show behaviors reminiscent of superparamagnetism,[4] while at low rotational temperatures they show effects assigned to magnetic resonance.[5] What is surprising is that the magnetization of certain clusters increases with temperature.[2] There are also indications that the magnetic moment depends on the site and that the surface atoms have higher moments than the interior atoms.[6,7] Since the magnetic moment is determined by electronic structure, which in turn depends on the geometry, a detailed study of these quantities is crucial for an understanding of these clusters.

In this paper we present a detailed study of the ground-state geometry, its electronic structure, and the nature of low-lying spin states of an $Ni_{13}$ cluster. Recent experiments[8] using molecular absorption of $N_2$ on $Ni_n$ clusters as a way to determine their geometry indicate that $Ni_{13}$ has an icosahedral structure. Earlier theoretical studies[9] are also based on such a geometry. While our studies carried out on icosahedral and cuboctahedral clusters do find the icosahedral geometry to be more stable, in agreement with experiment, we show that the resulting electronic structure is not compatible with the icosahedral symmetry. The perfect icosahedron is shown to undergo distortion. Further, the ground state is marked by several low-lying high spin states. It is shown that this could lead to an abnormal temperature dependence of the magnetic moment. We finally discuss the local moments and study the variation in moment between the central and outer atoms. The nature of orbitals contributing to the moment is examined via a decomposition of the charge density into different angular-momentum states.

The theoretical studies were carried out using a linear-combination-of-atomic-orbitals–molecular-orbital (LCAO-MO) approach.[10] The molecular orbitals were made out of a linear combination of atomic orbitals taken as Gaussian functions centered at the atomic sites. The exchange correlation effects were included via a local-spin-density functional proposed by Ceperley and Adler.[11] The inner cores were replaced by norm-conserving nonlocal pseudopotentials proposed by Bachelet, Hammann, and Schluter.[12] To construct the basis sets, the atomic pseudoequation was solved numerically on a radial grid of points. The basis functions were then obtained via a nonlinear fit of the resulting numerical atomic orbitals. They were tested in several ways for their completeness and ability to reproduce the total energy, the one-electron levels, and the ionization potential based on the numerical integration of the atomic equation. The final basis set consisted of $4s$, $1p$, and $3d$ Gaussian functions. The central atom did not have any $p$ Gaussians because they will not couple due to symmetry. The Kohn-Sham equations[13] were solved by fitting the charge density and the exchange-correlation potential and energy by Gaussians centered at the atomic sites and in between the atoms. For details the reader is referred to our earlier papers.[14]

We first consider results on symmetric clusters. The clusters having icosahedral and cuboctahedral shapes were studied. In each case, the radial distance defining the structure was optimized. In addition to the geometry, various possible spin configurations were calculated. The highest occupied molecular levels for spin up and down often had degeneracies and a small temperature was introduced to facilitate the convergence. The various multiplets had nearly the same equilibrium bond length, and in Fig. 1 we show the relative energy of states with different total spins for the icosahedral ($I_h$) and octahedral ($O_h$) geometry. For $I_h$ geometry, our calculations yield a lowest-energy state for spin $S=4$ with a binding energy of 4.23 eV/atom and a bond length of 4.15 a.u. The bond length is comparable with that obtained in

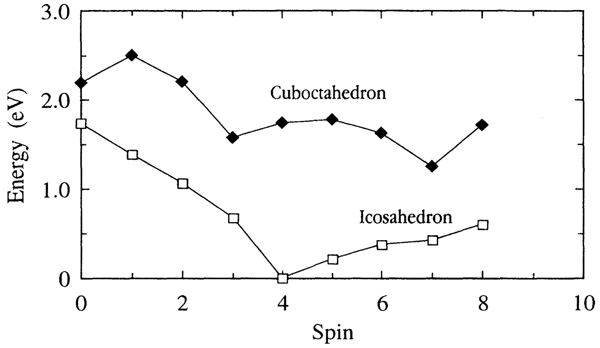

FIG. 1. Relative energy of various spin configurations in icosahedral and cuboctahedral clusters. All energies are referred to the $I_h$ state with $S=4$ as the zero of energy.

previous studies.[9] One notes several things. For all the spins, the icosahedral clusters are more stable than the cuboctahedral clusters. What is interesting is that the $S=4$ state is followed by states of $S=5-8$, the energies of which are 0.22–0.6 eV higher than the ground state. States with $S=0-3$ are 0.68–1.74 eV higher in energy. As we will discuss later, this can have consequences on the magnetic behavior.

While an icosahedral $S=4$ has the lowest energy, an analysis of the resulting molecular orbitals indicated that the highest occupied orbital had a degeneracy of 5 with only three electrons. The cluster could, therefore, undergo a Jahn-Teller distortion. Two possible distortions were tried and for each distortion all the spin states were calculated. In the first, the cluster was allowed a $D_{5d}$ distortion. Lowering the symmetry from $I_h$ to $D_{5d}$ did not change the energy. The cluster was then allowed a $D_{3d}$ distortion. This lowered the total energy and the ground state had $S=4$. The distortion also lifted the degeneracy of the highest occupied orbital for the $S=4$ state in $I_h$ symmetry, breaking it into a doubly degenerate and a singly degenerate orbital, followed by a doubly degenerate orbital. The different bond lengths in the distorted structure are shown in Fig. 2. Note that the distortion from the perfect $I_h$ is only minimal. The Ni atoms in the topmost and next lower triangle had radial distances of 4.08 and 4.17 a.u., respectively, compared to the original radial length of 4.15 a.u. The energy gain in the distortion was only 0.16 eV. To examine more closely the nature of bonding, we show in Fig. 3 the charge density in an ellipsoidal plot, which shows the electron density from the highest three occupied orbitals on a spherical surface of a radius equal to the mean distance

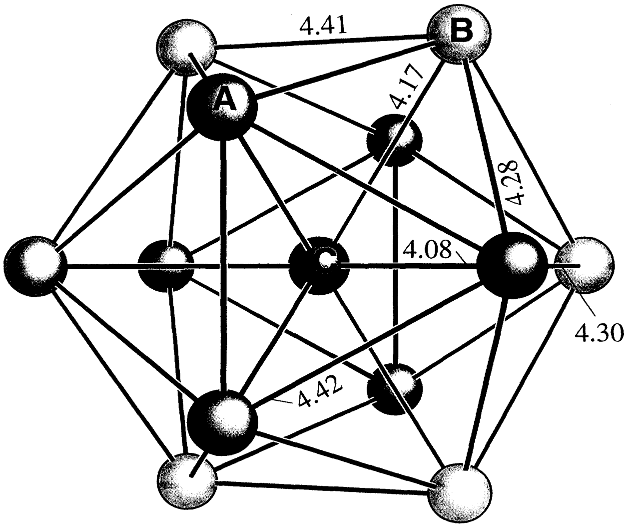

FIG. 2. Geometry of the ground-state $D_{3d}$ cluster. The distances are in atomic units.

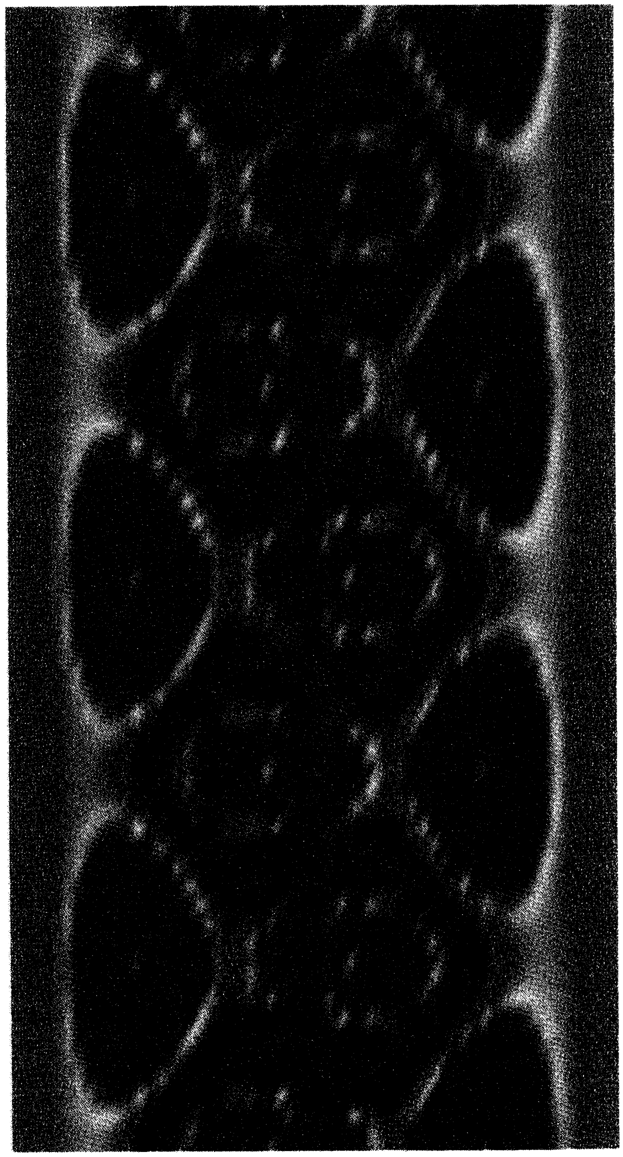

FIG. 3. Charge density on a spherical surface of radius equal to the mean radius of outer atoms in a $D_{3d}$ cluster projected onto a plane. The projection is done by taking spherical coordinates $\phi$ ($0\leq\phi\leq2\pi$) as $x$ axis and $\theta$ ($0\leq\theta\leq\pi$) as $y$ axis. The red regions indicate the highest density decreasing in the order red, yellow, green, blue, and mauve. Mauve corresponds to zero density.

of surface atoms from the central atom. The projection is carried out by using spherical coordinates $\phi$ and $\theta$ as the $x$ and $y$ coordinates. $\phi$ varies from 0 to $2\pi$ while $\theta$ goes from 0 to $\pi$. It is interesting to note that the cluster breaks into two regions. The maximum bonding is due to the atoms in the topmost triangle interacting with each other and with atoms in the second lowest triangle, and similarly for the atoms in the lowest triangle interacting with each other and with those in the second highest triangle. There are thus six vertical bonds between atoms belonging to different triangles. Both the $s$ and $d$ states contribute to the bonding. A global Mulliken population analysis shows that there are, on average, 0.89 $s$, 0.39 $p$, and 8.72 $d$ electrons per atom.

We now discuss the magnetic behavior of $Ni_{13}$. The ground state has a total spin of $S=4$. This corresponds to a moment of $0.61\mu_B$ per atom close to the bulk value of 0.6 $\mu_B$ per atom. This shows that the cluster is as magnetic as the bulk. Note that the experiments[16] on small clusters containing a few dozen to several hundred atoms indicate that they are almost 20% more magnetic than the bulk. We had earlier calculated[15] the ground states of smaller $Ni_n$ clusters containing 2–6 atoms and had shown that the magnetic moment changes considerably with size. In particular, $Ni_5$ was predicted to have a moment of about $1.6\mu_B$ per atom, almost 2.5 times the bulk value. The present results show that $Ni_{13}$ is far less magnetic than some of the smaller clusters as well as bigger clusters. The magnetic moment, thus, changes significantly with size. This also shows that the suggestion[17] that the most symmetric clusters (clusters with complete icosahedral shells) are the most magnetic is not true in this case.

A Mulliken spin population analysis indicates that the local magnetic moment varies with site. The analysis shows that the sites $A$, $B$, and $C$ marked in Fig. 1 have moments of 0.65, 0.60, and $0.52\mu_B$, respectively. An angular-momentum decomposition shows that the dominant contribution is due to $d$ electrons. That the central atom has lower moment than the surface atoms is in agreement with the previous suggestion[7,18] that the moment is governed by local coordination and atoms with higher coordination have lower moments. This is also in agreement with recent experiments[6] which confirm that the surface sites in clusters are more magnetic than interior sites. The present studies go beyond the local coordination and show that different surface sites have different local magnetic moments. This can be traced to the differences in their local environment. Whereas sites marked $A$ or $B$ have an identical number of nearest neighbors, $A$ sites have a larger nearest-neighbor separation than $B$ sites. This is consistent with the previous studies in bulk,[18] which indicate that a contraction in interparticle spacing reduces the local moment.

The present studies also provide insight into the abnormal temperature dependence of magnetization observed in some clusters and predict that $Ni_{13}$ may belong to this class. As mentioned before, Stern-Gerlach experiments[2] on small transition-metal clusters show that in certain clusters the magnetization increases with temperature. We believe that this could be due to the ordering of the various spin configurations in the cluster. As shown in Fig. 1, the state with $S=4$ is followed by close-lying states with $S=5$, 6, 7, and 8, whereas states with $S=0$, 1, or 2 have much higher energies. Although this energy structure was calculated for the $I_h$ symmetry, the minimal distortion in going to a $D_{3d}$ structure does not change this relative ordering. For example, the energy difference between $S=4$ and $S=5$ states changed from 0.23 eV in perfect $I_h$ to 0.19 eV in distorted structure. It is then clear that if $Ni_{13}$ in its ground state is heated, it will occupy states with higher spins first and hence would undergo an increase in the total intrinsic moment. This would lead to an increase of cluster magnetization, which is determined by the overall cluster moment, if the occupation of higher spin states overrides the decrease in magnetization due to increase in temperature.[4] This should be observable in experiments at different temperatures.

To conclude, we have provided a detailed investigation of the ground-state geometry, as well as the electronic state and its role in determining the ground state and the low-lying excited states in a $Ni_{13}$ cluster. We have shown that the true ground state is a distorted $D_{3d}$ structure. It will be interesting to examine a pseudorotation of this massive cluster where it passes from one $D_{3d}$ axis to the other. Since the cluster has several low-lying spin states, one can expect the rotational modes to provide means for spin relaxations. We are currently investigating these important effects. Our results also show that there are significant variations in moment with size and that the most symmetric icosahedral clusters are not necessarily the most magnetic. We hope that these results will stimulate further experiments in small Ni clusters to verify our predictions.

One of us (S.N.K.) is thankful to the Army Research Office (DAAL-03-89-K-0015) for financial support.

---

[1] *Small Particles and Inorganic Clusters*, Proceedings of the Sixth International Meeting on Small Particles and Inorganic Clusters, edited by R. S. Berry, J. Burdett, and A. W. Castleman, Jr. [Z. Phys. **26** (1993)]; V. Bonacic-Koutecky, P. Fantucci, and J. Koutecky, Chem. Rev. **91**, 1035 (1991); M. Castro and D. R. Salahub, Phys. Rev. B **47**, 10 955 (1993).

[2] W. A. de Heer, P. Milani, and A. Chatelain, Phys. Rev. Lett. **65**, 488 (1990).

[3] J. P. Bucher, D. C. Douglass, and L. Bloomfield, Phys. Rev. Lett. **66**, 3052 (1991).

[4] S. N. Khanna and S. Linderoth, Phys. Rev. Lett. **67**, 742 (1991).

[5] I. M. L. Billas, W. A. de Heer, and A. Chatelain, J. Non-Cryst. Solids **179**, 316 (1994).

[6] M. R. Press, F. Liu, S. N. Khanna, and P. Jena, Phys. Rev. B **40**, 399 (1989).

[7] I. M. L. Billas, A. Chatelain, and W. A. de Heer, Science **265**, 1682 (1994).

[8] E. K. Parks, L. Zhu, J. Ho, and S. J. Riley, J. Chem. Phys. **100**, 7206 (1994).

[9] M. S. Stave and A. E. Depristo, J. Chem. Phys. **97**, 3386 (1992).

[10] W. J. Hehre, L. Radom, P. von R. Schleyer, and J. A. Pople, *Ab*

*Initio Molecular Orbital Theory* (Wiley, New York, 1986).
[11] D. M. Ceperley and B. J. Adler, Phys. Rev. Lett. **45**, 566 (1980).
[12] G. B. Bachelet, D. R. Hammann, and M. Schluter, Phys. Rev. B **26**, 4199 (1982).
[13] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[14] F. Reuse, S. N. Khanna, V. de Coulon, and J. Buttet, Phys. Rev. B **41**, 11 743 (1990).
[15] F. A. Reuse and S. N. Khanna, Chem. Phys. Lett. **234**, 77 (1995).
[16] J. G. Louderback, A. J. Cox, L. J. Lising, D. C. Douglass, and L. A. Bloomfield, Z. Phys. D **26**, 301 (1993).
[17] B. I. Dunlap, Phys. Rev. A **41** 5691 (1990).
[18] F. Liu, S. N. Khanna, and P. Jena, Phys. Rev. B **43**, 8179 (1992).

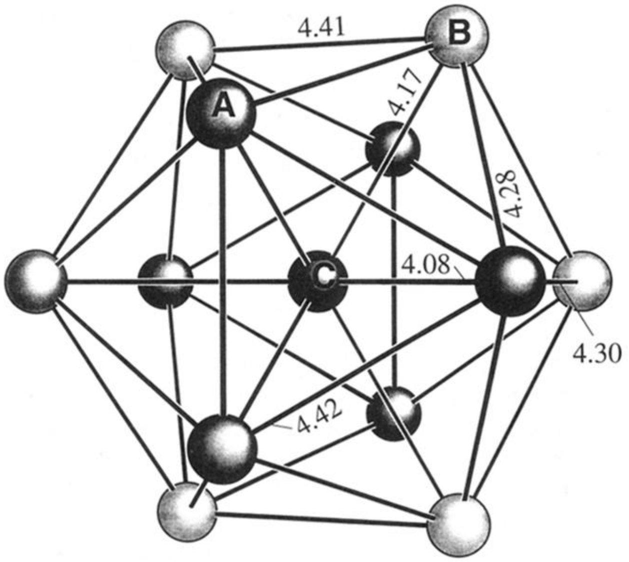

FIG. 2. Geometry of the ground-state $D_{3d}$ cluster. The distances are in atomic units.

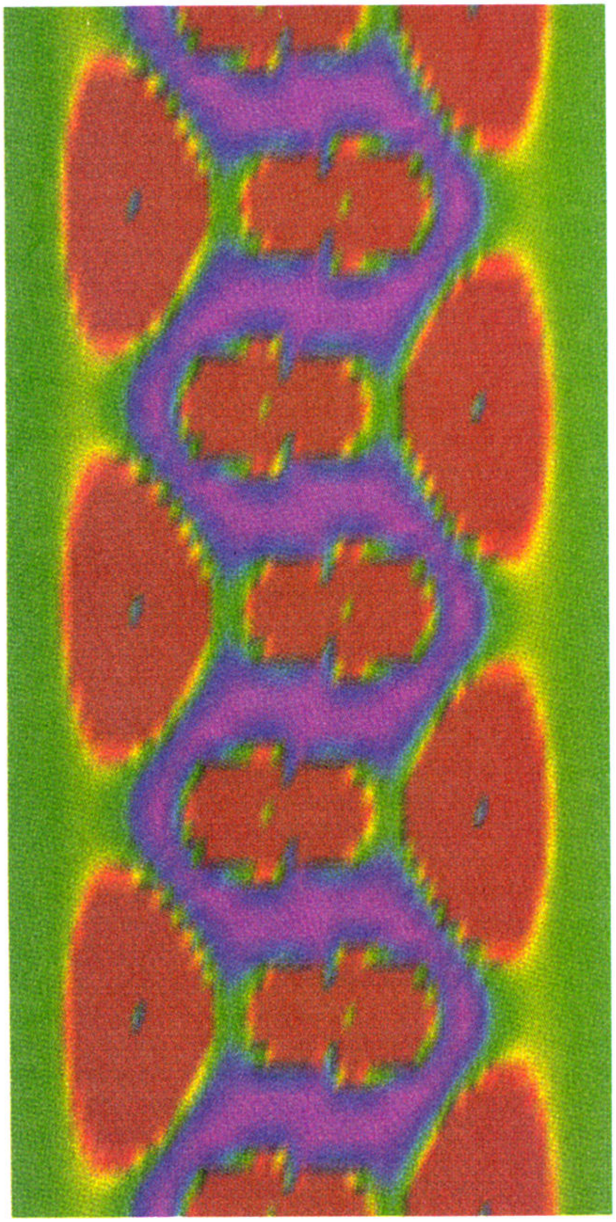

FIG. 3. Charge density on a spherical surface of radius equal to the mean radius of outer atoms in a $D_{3d}$ cluster projected onto a plane. The projection is done by taking spherical coordinates $\phi$ ($0 \leq \phi \leq 2\pi$) as $x$ axis and $\theta$ ($0 \leq \theta \leq \pi$) as $y$ axis. The red regions indicate the highest density decreasing in the order red, yellow, green, blue, and mauve. Mauve corresponds to zero density.