Degradation of inter-atomic bonds during structural phase change in intermediate Ni-clusters (Ni$_{39}$–Ni$_{49}$)

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Results based on a symmetry- and spin-unrestricted tight-binding molecular-dynamics study are presented for the ground-state geometries of intermediate Ni$_n$, $n \in [39,49]$, clusters. A structural phase change is found to take place around $n = 43$ during which a structural transition from fcc/hcp structure to icosahedral one is observed. This is in good agreement with recent experimental findings. This structural transition is found to be associated with a degradation of the inter-atomic bond energy which indicates that the inter-atomic bond does not only depend on the coordination number of each atom but also on its point group symmetry. © 2004 American Institute of Physics. [DOI: 10.1063/1.1628676]

I. INTRODUCTION

The recent availability of experimental results on small and intermediate size transition metal clusters (mainly Ni$_n$, Fe$_n$, and Co$_n$, $n \leq 700$ atoms)$^{1-15}$ has posed a challenge to theoretical investigations to uncover the details of geometric and electronic properties of these systems. The experimental determinations of geometric properties of these clusters usually involve measuring their reactivity with light molecules (H$_2$O, NH$_3$, N$_2$, H$_2$, CO) by combining near threshold photo-ionization experiments with time-of-flight mass spectroscopy.$^{7,8}$

The initial results of these experiments have been conclusive only for Ni$_n$ clusters with number of atoms $n$ in the ranges $10 \leq n \leq 28$ and $49 \leq n \leq 200$ and have provided indications that icosahedral packing dominates in these sizes for Ni$_n$ clusters. By contrast, no conclusive answer was obtained for the cluster geometry of Ni$_n$ for $29 \leq n \leq 48$. Subsequent experiments, however, showed that Ni$_{38}$ departs from the icosahedral symmetry while Ni$_{39}$ has a structure based on global pentagonal symmetry. In particular, the Ni$_{38}$ cluster was found to exhibit a packing more consistent with a truncated fcc octahedron,$^{3,5}$ while Ni$_{39}$ was found to be more consistent with the cluster geometry proposed by Wetzel et al.$^{16}$ More recent experiments$^5$ on Ni clusters with number of atoms $n \in [46–49]$ have given evidence that Ni$_{46}$–Ni$_{49}$ clusters show either fcc or mixed fcc/hcp structure while Ni$_{40}$ is found to be more consistent with the icosahedral or decahedral packing, giving indication of a structural (phase) transition at $n = 49$.

Concurrent with experimental determination of structural properties, the Stern–Gerlach experiments$^{12-15}$ have further provided information on the average value of the magnetic moment per cluster-atom.$^{12-15}$ Other experimental information (no relevance to us in the present work) includes data for the ionization and affinity energies of the clusters, magnetic anisotropy measurements as well as vibrational and thermal properties.

The theoretical studies, in most cases, have favored icosahedral geometries for the ground states of Ni$_n \approx 200$ clusters.$^{16-26}$ Two recent theoretical works, however, have indicated a different trend for these clusters. While the work of Andriotis et al.$^{19}$ indicated a preference for the face centered cubic (fcc) geometry for clusters that cannot exhibit closed icosahedral geometry, the work of Wetzel et al.$^{16}$ demonstrated that the geometry of Ni$_n$ clusters with $24 \leq n \leq 55$ resemble neither the structures of rare-gas clusters nor the fragments of the bulk crystal lattice except where a stable icosahedral or bulk core is present. A possible packing sequence for Ni$_{33}$–Ni$_{37}$ clusters based on the icositetrahedron was recently suggested by Luo.$^{27}$ Furthermore, other theoretical calculations have provided a satisfactory description of the super-paramagnetic behavior of ferromagnetic Ni$_n$, Fe$_n$, and Co$_n$ clusters$^{28}$ and provided a quantitative description of the average magnetic moment per atom for these clusters.$^{22,25,26,29-33}$

The results of early calculations have shown evidence for the existence of a delicate interplay between the geometric and the magnetic properties of the clusters. In particular, it was established that the basic parameters which influence this inter-relation include the symmetry, the bond lengths, the coordination numbers and the size of the cluster. These observations have unequivocally demonstrated the necessity of performing spin and geometry unrestricted self-consistent calculations in order to correctly describe the ground-state geometry of the transition metal clusters. Such calculations, however, become computationally prohibitive for clusters with $n > 10$ due to excessive demands on computer re-
sources. As a result, most calculations for intermediate and large size clusters pertain either to constrained solutions (i.e., solutions that restrict one or more of the cluster degrees of freedom), or to approximate semiempirical models. The latter approach includes the tight-binding molecular-dynamics (TBMD) method that was proposed by us recently at different degrees of approximations (see, for example, Refs. 19 and 32 and references therein). The TBMD method was used to satisfactorily describe the existing experimental information concerning the ground state geometry and magnetization of the Ni$_n$, Fe$_n$, and Co$_n$ clusters; $n \approx 307$.

The recent availability of new experimental data for intermediate Ni$_n$ clusters with $n$ ranging from 39 to 49 coupled with the fact that currently no agreement exists on the ground-state structure of many of the Ni$_n$ clusters has provided the motivation for us to embark on a theoretical investigation of these clusters with a view to shed some light on the interesting problem of their ground-state geometry. In the following, we present our results for these clusters obtained using our TBMD method incorporating magnetic effects.\(^{32}\) The details of our method can be found elsewhere\(^{19,32}\) and will not be repeated here. However, for completeness a brief review of our method is included in the next section. It should be noted that we make use of Harrison’s universal tight-binding parameters\(^{34,35}\) suitably scaled with respect to the inter-atomic distance.

II. COMPUTATIONAL APPROACH

The details of our tight-binding molecular-dynamics (TBMD) scheme can be found in Ref. 32. Here we give a brief overview.

The total energy $U$ is written in its general form as a sum of several terms\(^{32}\)

$$U = U_{el} + U_{\text{rep}} + U_0,$$

where $U_{el}$ is the sum of the one-electron energies $E_n$ for the occupied states

$$U_{el} = \sum_n E_n,$$

In the tight-binding scheme $E_n$ is obtained by solving the characteristic equation

$$[H - E_n 1] C_n^0 = 0,$$

where $H$ is the Hamiltonian of the system.

The Hellmann–Feynman theorem for obtaining the electronic part of the force is given by\(^{32}\)

$$\frac{\partial E_n}{\partial x} = C_n^0 \frac{\partial}{\partial x} C_n^0.$$

The total energy expression also derives contributions from ion–ion repulsion interactions. This is approximated by a sum of pairwise repulsive terms and included in $U_{\text{rep}}$. This sum also contains the corrections arising from the double counting of electron–electron interactions in $U_{el}$.\(^{32}\) $U_0$ is a constant that merely shifts the zero of energy. The contribution to the total force from $U_{\text{rep}}$ is rather straightforward. One can then easily do molecular-dynamics simulations by numerically solving Newton’s equation

$$m \frac{d^2x}{dt^2} = F_x = -\frac{\partial U}{\partial x},$$

to obtain $x$ as a function of time.

Our TBMD scheme is based on a minimal set of five adjustable parameters. These are found to be sufficient for describing a wide range of properties and are determined by fitting to existing experimental data; the latter includes the bond length, the vibrational frequency and the binding energy of the dimer Ni$_2$, as well as the cohesive energy of the bulk and the lowest lying magnetic states of the trimer Ni$_3$ or/and the tetramer Ni$_4$. In the absence of experimental data, we fit to data for small clusters obtained using \textit{ab initio} methods. The set of parameters thus obtained ensures satisfactory transferability of the tight-binding calculational results and makes our method suitable for describing clusters and bulk systems on the same theoretical footing. The generalization of our approach to systems including more than one species is obvious. It is only required to determine the set of the five adjustable parameters for each species and for each different binary species-pair.

The fixed set of TB parameters\(^{35}\) are obtained from the universal scheme proposed by Harrison\(^{34}\) suitably scaled with respect to the interatomic distance.\(^{32}\)

Various levels of the TB-approximation are currently used in the literature. Most of them are restricted only to the treatment of $d$-orbital effects while completely ignoring $s$ and $p$ orbitals in the basis set used to expand the Hamiltonian.\(^{30}\) For smaller clusters, charge self-consistency may also be included although this is sometimes achieved in cluster geometries determined by simpler and less demanding computational methods (see, for example, discussion in Ref. 36).

There is a general agreement in the results among all these computational approaches, especially when data for the magnetic moment of the clusters are compared. Some differences, however, are found when comparing ground-state geometries obtained by the various computational schemes used. For example, we recall that contrary to previous investigations, our approach allowed us to predict structural changes in the Ni-clusters as their size is increased;\(^{19}\) a result that was justified experimentally by Parks and collaborators later on.\(^{5,6}\)

For Ni-clusters of intermediate and large sizes, the computational demands of the TB methods become prohibitive and it appears that simpler methods based on the classical potential description of the interatomic interactions must be employed. As we have shown in a recent report,\(^{37}\) such an approximation can be successful provided that the classical potential reproduces the small cluster features successfully. However, the majority of the classical potentials used fail to reproduce small cluster features and consequently produce results in disagreement with ours.\(^{37}\)

At the completion of the present work, we became aware of the work of Grigoryan and Springborg in which the embedded-atom method (EAM) is employed.\(^{38}\) Due to the
classical nature of this approach, a detailed exploration of the configuration space is possible and the reported results appear in partial agreement with both the TB-based results of Luo \(^{27}\) and the classical potential based results.\(^{39}\) Furthermore, the results of Ref. 38 support our previous findings\(^{19}\) with respect to the structural changes expected in Ni\(_n\) clusters as their size increases in the range of \(n \approx 40\). It is also worth noting that according to Ref. 38, our reported fcc-based structure for Ni\(_{13}\) (see, for example, Ref. 32) is found to be as likely a candidate as the icosahedral one (see Figs. 4(c) and 4(d) of Ref. 38).

### III. RESULTS AND DISCUSSION

In the present study of the Ni\(_n\) clusters with \(n \in [39–49]\) an extensive search of the configuration space was undertaken. In addition to the structures considered in our previous work,\(^{32}\) we also included the geometries proposed by Wetzel and DePristo\(^{40}\) (to be denoted by WD1, WD2, WD3, and WD4 structures, respectively) and a large number of structures exhibiting mixed fcc/hcp structure suggested by Parks.\(^{3}\) These structures have been extensively discussed in previous reports by Wetzel and DePristo\(^{16}\) and Parks and collaborators;\(^{3–5}\) they are consistent with the experimental data as obtained by applying the rules for molecular N\(_2\) binding.\(^{3,5,6}\) Our results are presented in Figs. 1 and 2.

In Fig. 1, we present the variation of the binding energy per atom in Ni\(_n\) clusters, as the number \(n\) of the cluster-atoms increases. In this graph only the lowest energy structure obtained in our calculations for each cluster-size (i.e., for each \(n\)) is considered. It is apparent that a structural change appears for \(n \approx 43\). In the inset we present the corresponding variation of the average magnetic moment (in Bohr magnetons) per cluster-atom.

In Fig. 2, we present the variation of the binding energy per atom in Ni\(_n\) clusters as a function of the average-number of bonds per cluster atom. The solid straight lines are least square fits to results obtained for clusters with \(n = 46–49\). The long dashed lines are least-square fits to results for \(n = 39–49\). The structural change can be predicted by the intersection of the solid lines. More accurate determination of the transition is obtained by the point of intersection of the long dashed lines.

The results presented here for the structural properties of Ni\(_n\) clusters complete our previous investigation\(^{32}\) and they are also in agreement with other works reported subsequent to Ref. 32. For example, the results reported here confirm the finding in Ref. 40 that the most stable geometry for the Ni\(_{39}\) cluster is the WD1 one [see Fig. 3(a)] among all the structures considered. (We, however, find the WD3 structure to be more stable than the WD2 structure, whereas the authors of Ref. 40 found the reverse to be the case. Furthermore, we find our fcc structure to be more stable than either WD2 or WD4 structure. This fcc structure was not considered by the authors of Ref. 40 in their investigations). Furthermore, it should be noted that our present results are in qualitative agreement with those of Ref. 38 according to which the fcc structure appears more pronounced around \(n \approx 38\) where the similarity index exhibits a pronounced peak. In the same reference we also see that in the range of transition (i.e., at

![Fig. 1. Variation of the binding energy per atom in Ni\(_n\) clusters, as the number \(n\) of the cluster-atoms increases.](image1)

![Fig. 2. Variation of the binding energy per atom in Ni\(_n\) clusters as a function of the average-number of bonds per cluster atom.](image2)

![Fig. 3. Ground state structures of relaxed Ni\(_n\) clusters: (a) Ni\(_{39}\) (in WD1 structure), (b) Ni\(_{15}\) (fcc), and (c) Ni\(_{17}\) (icos).](image3)
n \approx 43) both fcc and icosahedral structures appear possible while for n approaching 51 the icosahedral structure becomes more favorable.

The structural transition found in Ni\textsubscript{n} structures for n \approx 43 as their size increases is also in good agreement with the experimental findings showing this to take place for n = 49.\textsuperscript{3} The slight discrepancy in the exact value of n leads us to speculate that this discrepancy may be due either to some reconstruction effects upon N\textsubscript{2} adsorption or to an inadequacy of the theory to trace the possible low lying cluster states correctly. The structural change as a function of the cluster size is shown in Figs. 3(b) and 3(c). It can be also demonstrated from Fig. 2 as well.

More significantly, from Fig. 2 we get an additional and very valuable information. That is, we observe that the structural transition found in Ni\textsubscript{n} structures for n \approx 43 as their size increases is also in good agreement with the ground-state geometry and properties of Ni\textsubscript{n} towards an icosahedral ground state, which strengthens our earlier discussion that the determination of the ground-state geometry requires more elaborate calculations.

In conclusion, we have presented a systematic search for the ground-state geometry and properties of Ni\textsubscript{n}, n \in [39–49], clusters. Our results indicate that, in good agreement with recent experimental results, the Ni\textsubscript{n} clusters undergo a structural phase transition as their size increases. During this transition no appreciable change (<\approx 10\%) was found in the average value of the magnetic moment per cluster atom. However, a noticeable degradation of the bond strength has been found at the observed fcc/hcp to icosahedral transition. This observation demonstrates, for the first time, that the bond strength depends not only on the coordination number of the bonding atoms but also on the point group symmetry of the system.

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