Structure and Stability of Ni Clusters: a Tight-Binding Molecular-Dynamics Study.

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Abstract. – The tight-binding molecular-dynamics scheme incorporating d-electrons is used to
obtain a first systematic set of results for Ni clusters in the range 10 < n < 55 by full geometry
optimization. The relative stability of f.c.c. structures is compared with the two kinds of
icosahedral structures, open and full. Our results show the f.c.c. structure to be more stable than
the former, but less stable than the latter in this range. The general trends for Ni clusters of this
size are well described by our results. The method appears to provide a promising semi-empirical
method for studying interactions in both covalent and metallic systems.

Transition metal clusters (TMC) have recently been the subject of both experimental and
theoretical investigations. Unlike semiconductor clusters, the calculational difficulties
associated with TMCs pose severe challenge to theoretical efforts. As a result, it has not been
possible to form a satisfactory quantitative conclusion with regard to such important
properties as the binding energy per atom, bond lengths, ionization potentials and structural
stability. Calculations allowing for full geometry optimizations have been limited only up to
cruster size n = 5 [1-10]. On the experimental side, however, the usual preparation technique
of laser vaporization in a flow system for TMCs involves cluster growth far from
equilibrium [11, 12]. As a consequence, no magic numbers have been reported so far for bare
TMCs. At present the main success of both the theoretical and experimental efforts have
been in obtaining the various trends of the cluster properties either with respect to the
atomic number [13] of the constituent atoms or the cluster size [1-9].

Recently we introduced a tight-binding (TB) molecular-dynamics (MD) technique for
transition metal clusters [14] for a quantitative study of structural and electronic properties
of the TMCs following the successful application of the TB-MD method for semiconductor
systems [15,16]. The efficiency of the TB method derives from the fact that the Hamiltonian
matrix elements can be parameterized. The TB method also allows the extraction of electronic-
structure information. The TB scheme provides a useful semi-empirical method that bridges
the gap between the more accurate \textit{ab initio} methods with those employing completely
empirical \( n \)-body classical potentials. In the present letter we report our results for large \( \text{Ni}_n \)
clusters in the range \( 10 < n \leq 55 \).

Our calculational scheme for TMCs is similar in spirit to the one used for semiconductor
complexes [15-17] and is based on the calculation of the binding energy for fully optimized
structures. The details can be found in ref. [14]. Briefly, the binding energy, \( E_n \), for a cluster
consisting of \( n \) atoms is approximated by the following expression [14]:

\[
E_n (\mathbf{R}) = E_{\text{bs}} (\mathbf{R}) + E_{\text{rep}} (\mathbf{R}) + E_{\text{bond}} (\mathbf{R}),
\]

where \( \mathbf{R} \) specifies the geometric configuration of the cluster. The first term, \( E_{\text{bs}} \), is the band
structure contribution, obtained by summing the one-electron energies. The term, \( E_{\text{rep}} \), is
given by a repulsive pair potential and includes the effects of ion-ion interactions and
corrections to the double counting of the electron-electron interactions in the first term. The
last term, \( E_{\text{bond}} \), depends on the number of the bonds in the optimized system and is
necessary for a systematic calibration of binding energies for various cluster sizes.

Equation (1) is based on the following approximations and assumptions:

i) The band structure term, \( E_{\text{bs}} \), is obtained from a Hamiltonian whose parameters
have a scaling that is satisfactorily transferable. The present scheme utilizes the universal
Slater-Koster (SK) parameters of Harrison [18] with an exponential scaling with interatomic
distances. This scaling was tested and found to be more appropriate over larger ranges of
interatomic distances than the more popular power law, which is valid only over smaller
ranges [19]. A similar exponential scaling was reported to account better for atomic
relaxation near impurities and surfaces [20].

ii) The repulsive term, \( E_{\text{rep}} \), is written as a sum of pair potentials whose coefficient is
determined by requiring that correct experimental bond length for the dimer be
reproduced [14]. The scaling with interatomic distances for these functions is also taken to be
exponential.

iii) The \( E_{\text{bond}} \) term is a necessary addition to the first two terms in tight-binding theory
in order to accurately reproduce cohesive energies of dimers through bulk structures [14]. It
was introduced by Tomanek and Schluter [21] in the context of semiconductor clusters and
used in the tight-binding molecular-dynamics scheme to obtain agreement with \textit{ab initio}
results for small silicon clusters [17]. The presence of this term is necessary for distinguishing
the optimum geometrical configuration for a cluster of a given number of atoms. For the
TMCs, however, availability of only a limited experimental and \textit{ab initio} theoretical results
prevents an accurate determination of this term. In particular, the \textit{ab initio} theoretical
studies fail to agree among themselves and with experiment [1-8].

The present method, although semi-empirical in its present form, permits various
improvements that allow the proposed theory to take a firm \textit{ab-initio}–like character [22,23].
Implementation in the context of molecular-dynamics schemes will require further work.
Thus the present theory may be considered as a first step towards developing a computa-
tionally fast and efficient interaction model for commercially important semiconductor and metallic alloys capable of treating interactions in both covalent and metallic alloys. The success of the present scheme in its application to semiconductors and semiconductor compounds [15-17] and small Ni clusters [14] provided a motivation for the investigation of larger TMCs.

In the present work we address the question of structure and stability of Niₙ clusters with a number of atoms in the range 10 < n ≤ 55 using our orthogonal TB-MD method by performing a full geometry optimization with no symmetry constraints. Niₙ clusters with n ≤ 10 have already been studied in detail in our previous work [14] where geometries obtained for Niₙ, n ≤ 10 exhibited substantial differences from the corresponding Siₙ clusters.

For TMCs of larger sizes the limited experimental results for both bare and hydrogenated Coₙ and Niₙ clusters point to icosahedral geometry in the range 40 < n ≤ 161 [11]. This conclusion results from the interpretation of the free-energy changes ΔG°, during the H₂O absorption on both the bare and hydrogenated Coₙ and Niₙ clusters. Furthermore, similar studies [12] that involve reactions of bare Niₙ clusters with NH₃ support the icosahedral packing for clusters with n ≤ 29, 50 ≤ n ≤ 120 and with 140 ≤ n ≤ 170. No specific evidence for icosahedral structure was indicated for clusters with 29 ≤ n ≤ 49, while the evidence for icosahedral packing for n ≤ 29 was based on the geometries of Ni₁ (D₅h symmetry, also obtained in our work [14]), Ni₁₃ (icosahedral) and Ni₁₉ (polyicosahedral).

More recently, the analysis of mass distribution of large Ni and Co clusters with near-threshold photoionization experiments and standard time-of-flight mass spectroscopy has exhibited strong effects for cluster numbers n = 55, 147, 309 and 561 [24]. These features are consistent with closing of successive atomic shells in a cuboctahedral or icosahedral structure. Based on the observation that the filling sequence of cluster shells appears regular, Pellarin et al. [24] suggested the icosahedral structure to be more probable. For small Ni and Co clusters (n < 70), however, the exact structure is not well identified [24] and the icosahedral features are less evident for these clusters as many isomers can exist in this size domain. Finally, recent calculations on Cuₙ clusters [25], based on the effective medium theory, indicated that complete icosahedra are more stable than cubic structures for n ≤ 2500 atoms. For small Cuₙ clusters (n < 50) cubic structures of the type of the Wulff polyhedron were determined to be unstable because continuous heating was observed to transform them into icosahedral-type structures.

These results raise a significant and provocative question regarding the structural evolution of a TMC as a function of cluster size and eventual transformation into a fragment of bulk solid. The present work is intended to fill this gap in the relative-structural-stability information for small Niₙ clusters with n ≤ 55. Towards this end, we have applied our orthogonal TB-MD calculational scheme, described briefly above, and investigated the relative structural stabilities of Niₙ clusters in icosahedral and f.c.c. geometries by performing full optimizations at zero temperature. Our results are shown in table I. In fig. 1 we plot binding energies as a function of the number of atoms for the clusters considered in this work. Some of the various relaxed cluster geometries obtained using our molecular-dynamics scheme are shown in fig. 2 (f.c.c. type) and 3 (icosahedral).

For n = 13 two different structures are examined (see fig. 2 and 3): the first being a Mackay's icosahedron, and the other an f.c.c. cuboctahedron (one atom and its twelve first neighbors) [26]. The relaxed Mackay's icosahedron is found to be the more stable of the two (by 0.43 eV/atom). The f.c.c. structure, on the other hand, relaxed to an open structure with distortions. For Ni₁₉, however, the f.c.c.-type structure (adding second neighbors to the f.c.c. Ni₁₃) is found to be lower in energy than the open icosahedral geometry (built up by adding a six-atom cup over the Ni₁₃ icosahedron [12]) after optimization. The same result is
Table I.

<table>
<thead>
<tr>
<th>Number of atoms</th>
<th>Structure</th>
<th>Binding energy per atom (eV)</th>
<th>Average bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>icosahedral(*)</td>
<td>3.16</td>
<td>2.57</td>
</tr>
<tr>
<td>13</td>
<td>f.c.c.()(*)</td>
<td>2.73</td>
<td>2.48</td>
</tr>
<tr>
<td>14</td>
<td>f.c.c.(4)</td>
<td>3.01</td>
<td>2.49</td>
</tr>
<tr>
<td>15</td>
<td>b.c.c.()</td>
<td>3.04</td>
<td>2.52</td>
</tr>
<tr>
<td>19</td>
<td>icosahedral(5)</td>
<td>3.33</td>
<td>2.55</td>
</tr>
<tr>
<td>19</td>
<td>f.c.c.(5)</td>
<td>3.41</td>
<td>2.52</td>
</tr>
<tr>
<td>23</td>
<td>icosahedral(5)</td>
<td>3.38</td>
<td>2.59</td>
</tr>
<tr>
<td>23</td>
<td>f.c.c.(5)</td>
<td>3.43</td>
<td>2.55</td>
</tr>
<tr>
<td>38</td>
<td>f.c.c.(5)</td>
<td>3.94</td>
<td>2.55</td>
</tr>
<tr>
<td>39</td>
<td>icosahedral(5)</td>
<td>3.53</td>
<td>2.53</td>
</tr>
<tr>
<td>43</td>
<td>f.c.c.(5)</td>
<td>3.83</td>
<td>2.55</td>
</tr>
<tr>
<td>44</td>
<td>f.c.c.(5)</td>
<td>3.98</td>
<td>2.55</td>
</tr>
<tr>
<td>55</td>
<td>icosahedral(6)</td>
<td>4.27</td>
<td>2.59</td>
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<td>55</td>
<td>f.c.c.(6)</td>
<td>4.10</td>
<td>2.56</td>
</tr>
<tr>
<td>bulk</td>
<td>f.c.c.</td>
<td>4.44</td>
<td>2.50</td>
</tr>
</tbody>
</table>

(a) Full icosahedral geometry.
(b) Open icosahedral geometry (cf. ref.[12,24]).
(c) Central atom with first, second, third, and fourth neighbors, correspondingly.
(d) One, two etc. conventional cells with common face.
(e) Wulff polyhedron (cuboctahedron).
(f) Multi-octahedron.

found for Ni_{23} where the f.c.c. configuration (with two conventional f.c.c. cells with a common face) is found to be more stable than the corresponding icosahedron, the latter obtained by adding a square of 4-atoms to the Ni_{19} icosahedral cluster over a plane containing the axis of symmetry for Ni_{19}. For Ni_{55} we compare the stability of the second Mackay's icosahedron [12,26] with that of the f.c.c. cuboctahedron (one atom and all its neighbors up to the fourth shell). Here, the closed icosahedron is more stable with binding energy 0.17 eV/atom higher than the f.c.c. geometry, as can be seen in table I. The icosahedral Ni_{55} structure is the only one of the type of the closed icosahedron after Ni_{19}.

We have also considered the stability of Ni_{55} and Ni_{43} f.c.c.-type clusters, as well as the icosahedral Ni_{55}, the b.c.c. Ni_{19} and the dodekahedron Ni_{29} clusters. All our results are included in table I from which one can also see the trends for the binding energy per atom and the average bond length as the cluster size increases. As expected, there is an increase in the binding energy per atom on the average with the number of atoms, tending to an upper limit corresponding to the bulk value. Small variations from this trend may be understood in terms of the structural stability of these clusters. The average bond length is found to be
larger than that for the bulk. This is due to the relatively large ratio of surface atoms to bulk atoms that causes the average coordination for these clusters to be lower than in the bulk. The surface atoms are less tightly bound, causing an increase in the average bond length.

In conclusion, we have obtained a first systematic set of results for paramagnetic Ni clusters in the range $10 < n < 55$ by full geometry optimization using a consistent methodology. Our results for these clusters show the full icosahedral geometries to be more stable than f.c.c. types. There is a monotonic decrease in Jahn-Teller–type distortions with cluster size. Although magnetic effects are not included in the present study, our results are

Fig. 1. – Binding energy per atom vs. number of atoms for f.c.c. and icosahedral structures.

Fig. 2. – Relaxed geometries for f.c.c. structures.

Fig. 3. – Relaxed geometries for icosahedral structures.
in very good agreement with both theory [24] and experiment [11,12,24,25], for the cluster sizes examined. Earlier, similar agreement was obtained with theory and experiment for small Ni clusters [14]. The present method can be easily generalized to include magnetic effects provided that TB parameters are available for both spin directions [27]. On the other hand, the present method has already been applied successfully for semiconductor systems extensively [15-17], and therefore it appears to be a strong candidate for providing a useful semi-empirical method for studying interactions in both covalent and metallic systems. As the present method can take a firm ab initio character and avoid any fitting to experimental data [24], it appears to have much more general applicability than the recently proposed method of Cleri and Rosato [20].

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REFERENCES