Structure and energetics of Ni clusters with up to 150 atoms

Valeri G. Grigoryan* and Michael Springborg†

Physical Chemistry, University of Saarland, 66123 Saarbrücken, Germany

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Abstract

We present a method (the Aufbau/Abbau method) for optimizing the structure of a whole series of clusters without making any assumptions on the structure. Subsequently, the method is combined with the embedded-atom method in determining the structure of the two energetically lowest isomers of Ni\textsubscript{N} clusters with \textit{N} up to 150. Finally, various analytical descriptors are introduced that are used in studying the overall shape of the clusters, their structure and stability, and possible growth and dissociation processes.

* Corresponding author. e-mail: vg.grigoryan@mx.uni-saarland.de; fax: +49 681 302 3857
† e-mail: m.springborg@mx.uni-saarland.de; fax: +49 681 302 3857
About two decades ago the experimental observation and theoretical description of so-called magic numbers in clusters of simple metals (see [1,2]) provided an excellent example of how experiment and theory could supplement each other in the development of the understanding of materials properties. The theoretical studies for any but the smallest clusters were based on the jellium model, i.e., the internal structure of the cluster was completely neglected and the core electrons and the nuclei were smeared out to a homogeneous jellium in whose field the valence electrons moved. Moreover, in the first studies the jellium was supposed to be spherical and to have sharp boundaries, although these assumptions in later studies have been relaxed partially (see [2]).

For theoretical studies of any other metal clusters $M_N$ than those of simple metals, one encounters the serious problem that when the valence electrons are anything but completely delocalized, the (spherical) jellium model may not provide a realistic approximation. This is, e.g., the case for transition-metal clusters where the nearest-neighbor interactions between the atoms are important, so that the precise structure of the cluster as well as the inhomogeneities of the electron density are to be included in any realistic description. Then, furthermore, the fact that the number of structural degrees of freedom $(3N - 6$ or $3N - 5)$ together with the fact that the number of metastable structures grows very fast with $N$ makes detailed systematic studies of how the properties depend on $N$ for any but the absolutely smallest clusters extremely demanding. On the other hand, the further development of this field requires a precise understanding of how the properties of interest depend on the structure, size, and composition of the clusters, which, unfortunately, is very difficult to achieve theoretically or experimentally.

Here we shall report results of a theoretical study of the structural and energetic properties of Ni$_N$ clusters for all $N$ up to 150. Our calculations have made no assumptions about the structure of the clusters whereby they differ from most other studies of these systems (see, e.g., [3,4,3,6,7] and references therein) of which the previously most detailed and unbiased study\(^3\) considered only up to $N = 80$. Since we have had to perform often several 1000 structure-relaxations for a given $N$ without making any assumption on structure or symmetry, parameter-free methods cannot be applied, and, therefore, we have employed the embedded-atom method (EAM) in the calculation of the total energy for a given structure. Moreover, we have developed an Aufbau/Abbau method for the structure optimization. This method is partly inspired by experimental conditions where clusters often are produced by
adding atoms individually to a seed, although the experiments often take place at conditions far from equilibrium and from \( T = 0 \) K. A preliminary description of our approach has been presented elsewhere\(^8,9\) but compared with that work the present one is much more accurate (through a much more detailed structure optimization that also includes more isomers), and, in addition, we shall here present various theoretical tools with which we can extract the fundamental structural and energetic properties of these clusters.

In our \textit{Aufbau/Abbau} method we consider clusters with \( L \) and \( L + P \) atoms with \( P \simeq 5 - 10 \). For each of those we study a set of randomly generated structures. Using a quasi-Newton method relaxed local-total-energy minima are identified and the structures of the lowest total energy selected. One by one atoms are added to the structure with \( L \) atoms (many hundred times for each size), and the structures are relaxed. Parallel, one by one atoms are removed from the structure with \( L + P \) atoms. From this two series of structures for \( L \leq N \leq L + P \) those structures of the lowest energies are chosen and these are used as seeds for a new set of calculations. First, when no lower total energies are found, it is assumed that the structures of the global-total-energy minima have been identified, and we proceed to larger clusters. In some few cases, extra high-symmetry structures were added as possible structures, which in one case (\( N = 75 \)) resulted in an otherwise unidentified lowest-energy structure. According to our experience, for a given \( N \) we have to consider about 500 randomly generated structures for the smallest values of \( N \) and about 1000 for the largest values. Moreover, about 3 \textit{Aufbau/Abbau} cycles are needed for the smaller \( N \) and up to 10 for the larger \( N \).

In comparison with our earlier study, the method has been extended so that by keeping track of more structures of the lowest total energies, we obtain the energetically lowest isomers for each size, and a much more detailed search has led to the identification of new structurals for several \( N \). Since our approach (as any other unbiased method for structure optimization of larger, low-symmetric systems) requires a large number of total-energy calculations for different, larger structures, it cannot be combined with accurate parameter-free electronic-structure methods, but has to be based on approximate schemes for calculating the total energy. Here, we combine the \textit{Aufbau/Abbau} method with the EAM method for the latter purpose.

The basic idea of the EAM\(^{10,11,12,13}\) is to consider every atom as an impurity embedded in a host provided by all other atoms. The tails of the electron densities of the host atoms
inside the guest atom lead to a modification in the energy of this atom, $F_i(\rho^h_i)$, where $i$ labels the atom, and $\rho^h_i$ is the electron density from the host atoms. Usually this is evaluated at the site of the nucleus of the $i$th atom. The remaining part of the binding energy of the system of interest is approximated through pair potentials, $\frac{1}{2} \sum_{j\neq i} \phi_{ij}(R_{ij})$ with $R_{ij}$ being the distance between atoms $i$ and $j$. The embedding energies $F_i$ and the pair potentials $\phi_{ij}$ have been obtained by fitting to theoretical and experimental information on different infinite systems. The EAM is conceptually simple, but it grasps the major parts of the interatomic interactions and gives accurate structural and energetic information on various extended and truncated systems.

Before discussing our results in detail we shall address the question of the accuracy of the EAM method. As such, it is constructed first of all for describing cohesion in extended metallic systems like crystals without or with defects and surfaces. Due to the complexity of the present study, it is not possible to apply a parameter-free method, and simpler methods like the EAM have to be used, but nevertheless it may be asked whether the EAM can be used for the, after all, relatively small systems of our present study. We shall therefore compare our calculated structural properties for nickel clusters with $N = 2, 3, 4, 5, 6, 7, 8$, and $13$ with those of accurate electronic-structure calculations using different density-functional methods. Table I list some of the key quantities in the structural characterization of the different clusters as obtained with the different methods, and in Fig. I our optimized structures are shown. It is seen in Table I that our results agree well with those of the other studies, both concerning the structure itself and concerning the interatomic distances. Most of the discrepancies are related to smaller distortions that may be due to electronic effects (e.g., Jahn-Teller distortions) that are not included in the EAM method. Thus, we conclude that our approach is accurate.

In Fig. 2 we show our calculated binding energy per atom for nickel clusters with $N$ ranging from 1 to 150. As is generally found, the binding energy for clusters is first of all a monotonously increasing function of $N$ with, however, some extra structure. In order to identify the latter more clearly, we show in the figure also the stability function $S(N) = E_{\text{tot}}(N + 1) + E_{\text{tot}}(N - 1) - 2E_{\text{tot}}(N)$ which has maxima for particularly stable structures. These are also marked in the figure. As we shall see, some of the particularly stable structures correspond to particularly symmetric ones. Particularly stable structures are found for $N = 13$ (the most pronounced one), 19, 23, 39, 55, and 147.
There exists some previous experimental and theoretical studies of the properties of Niₙ clusters, of which many focus on the inner structural aspects (including symmetry, see, e.g., [3,6,7,22,23,24]). The most detailed study of the energetics of Niₙ clusters is the theoretical one of Doye and Wales[3] who used the Sutton-Chen potential in calculating structural and energetic properties of Niₙ clusters with N up to 80. They find particular stability for N = 13, 38, 50, 55, 64, 71, 75, and 79, which is in partial agreement with our results. As discussed by Parks et al.[23,24] the structures given by Doye and Wales seem to deviate somewhat from experimental findings, suggesting that the Sutton-Chen potential is not sufficiently accurate for such studies. In a tight-binding molecular-dynamics study, Luo studied clusters with up to 55 atoms[4] He found most stable structures for N = 21, 31, 35, 38, 40, 47, 50, and 55, only partly in agreement with the results of Doye and Wales and of us. On the other hand, Montejano-Carrizales et al.[5] used the EAM in analysing the so-called umbrella growth models for icosahedral Ni clusters. Although they thereby make certain assumptions on the structure their N values for particularly stable structures are in general in good agreement with ours and with those of Doye and Wales. This leads support to the umbrella growth model. This conclusion is further supported below.

The special stability of the cluster sizes mentioned above is supported by comparing the energies of the two energetically lowest isomers. First for N = 6 and onwards we identify two different isomers, and their total-energy difference is shown in the lowest panel in Fig. 2. Here, the most significant features correlate closely with those of the stability function.

Besides the stability a number of other issues have attracted significant interest in cluster physics. These include the structure of the individual clusters, whether growth modes can be identified, and how the clusters will dissociate. We shall now address these issues.

For a given cluster Niₙ we calculate the eigenvalues \( I_{\alpha\alpha} \) of the matrix containing the moments of inertia \( \sum_{i=1}^{N} s_i t_i \) with s and t being the x, y, and z in a coordinate system with the origin at the center of mass of the cluster. For a spherical jellium \( I_{\alpha\alpha} \propto N^{5/3} \), and therefore we show (Fig. 3) \( I_{\alpha\alpha}/N^{5/3} \). If the three eigenvalues are identical the overall shape of the cluster is approximately spherical. Such clusters are marked with points in the lowest row in the uppermost part of the figure and are found for N = 1, 4, 6, 13, 26, 28, 38, and 55, which partially correspond to particularly stable clusters; cf. Fig. 2. When two of the eigenvalues are small and only one is large, the cluster is essentially prolate (cigar-shaped), whereas it with two large eigenvalues and one small one is oblate (lens-shaped). In the figure
we have marked which of the clusters have these two types of overall shapes. Except for the absolutely smallest clusters, we have that, if the cluster structures can be considered as obtained by adding atom by atom to a largely fixed core, the clusters will either be close to spherical (so that several changes between prolate and oblate structures are possible), or one or the other of the two structure types will dominate in large $N$-intervals. However, the results of Fig. 3 show that except for $N$ above about 137, the eigenvalues $I_{\alpha\alpha}$ are very different, so that the clusters have pronounced prolate or oblate shapes. Moreover, several changes between these two structure types occur in the range of $N$ we have considered.

A more detailed way of analysing whether the cluster with $N$ atoms can be considered as formed by adding a single atom to the cluster with $N - 1$ atoms is provided by defining similarity indices as follows. We calculate the $(N-1)(N-2)/2$ interatomic distances $d_{ij}^0$ (in a.u.) for the $(N-1)$-atom cluster and sort them. Subsequently, we consider all the possible $(N - 1)$-atomic parts of the $N$-atom cluster, and for those we also calculate and sort the interatomic distances $d_{ij}$. The smallest value of $q_1$ with $(N-1)(N-2)/2 q_1^2 = \sum_{i>j=1}^{N-1} (d_{ij}^0 - d_{ij})^2$ defines then the similarity index, $s_1 = (1 + q_1)^{-1}$, which is 1 for a cluster that is obtained by adding one atom to the previous one, and approaches 0 for very different structures. Another similarity index $s_2$ is obtained by instead of using the interatomic distances we use the distances of the individual atoms to the center of mass of the cluster. Denoting these so-called radial distances $r_i^0$ (in a.u.) for the $(N - 1)$-atom cluster and $r_i$ (in a.u.) for the $(N - 1)$-atom fragment of the $N$-atom cluster, we consider the smallest value of $q_2$ with $(N-1)q_2^2 = \sum_{i=1}^{N-1} (r_i^0 - r_i)^2$, and define $s_2 = (1 + q_2)^{-1}$.

These two functions are shown in Figs. 4(a) and (b). Up to $N$ around 40 both functions possess a number of peaks indicating that no simple growth mechanism can be identified. This is in accord with the experimental observations of Pellarin et al.\textsuperscript{25} who moreover suggest that above that the umbrella growth model agrees with their observations, in agreement with the results of Montejano-Carrizales et al.\textsuperscript{5} However, both of our similarity indices find for larger $N$ peaks at $N = 39, 51, 63, 73, 80, 87, 105,$ and 138, implying that also here size-dependent structural differences occur. Thus, in total we find an overall support for the umbrella growth model although for many values of $N$ this model does not give an exact description of the structure.

In order to obtain a quantitative estimate of the similarity of the structure for a given $N$ with that of a fragment of the crystal we proceed as follows. We consider a large, but finite
fragment of the fcc crystal structure and place a center (arbitrarily) at \((0,0,0), (\frac{1}{2}a,0,0)\), and \((\frac{1}{4}a,\frac{1}{4}a,0)\) (with \(a\) being the length of the unit cell). The set of distances from the atoms to any of these centers, \(\{r_i^{\text{fcc}}\}\), is sorted and compared with the radial distances for a given \(N\)-atom cluster, \(Nq_{\text{fcc}}^2 = \sum_{i=1}^{N}(r_i^{\text{fcc}} - r_i)^2\). This defines the fcc similarity index, \(s_{\text{fcc}} = (1 + q_{\text{fcc}})^{-1}\). A related icosahedral similarity index \(s_{\text{ico}}\) is defined by using the radial distances for the (relaxed) \(N = 309\) icosahedral cluster in comparing with the different clusters. The two functions are shown in Figs. 4(c) and (d). It is seen that in the range 73–79 the structure is related both to that of a fragment of the fcc crystal with, in addition, the center at \((0,0,0)\) and to the icosahedral structure. This indicates that in exactly this size range more different structural motifs are present. Two further peaks can be identified in Fig. 4(c): at \(N = 28\) which corresponds to the center at \((\frac{1}{2}a,0,0)\) and at \(N = 38\) which corresponds to the center at \((\frac{1}{4}a,\frac{1}{4}a,0)\). The lower panel shows that the icosahedral clusters are important around \(N = 13\), between \(N = 51\) and \(N = 55\), and above \(N = 138\). We finally notice that the structural characteristics often are not isolated to singular values of \(N\) but can be identified also around the peaks.

In order to get insight into possible fragmentation channels we analyse the calculated energies \(E_{\text{tot}}\) as a function of \(N\). Neglecting kinetic effects (this is a crude approximation and may have severe consequences for our conclusions), we seek for a given \(N\) that value of \(K\) for which the dissociation energy \(E_{\text{tot}}(N) - [E_{\text{tot}}(K) + E_{\text{tot}}(N-K)]\) is lowest. It turned out that, without exception, this value of \(K\) was always 0, indicating that any cluster is stabler than its dissociation products. This result is a consequence of the fact that \(E_{\text{tot}}(N)\) is upward curved, as indirectly can be seen in the upper part of Fig. 2.

Neglecting the \(K = 0\) solution we found the results shown in Fig. 5. Except for one case, \(K\) was found to be either 1 or 2, indicating that the clusters upon fragmentation will dissociate in a highly asymmetric way by splitting off a single or a pair of atoms. The exception is that of \(N = 16\) for which \(K = 3\) was found as a consequence of the particular stability of the \(N = 13\) cluster. The dissociation energies, also shown in Fig. 5, are seen to lie around 4 eV for \(K = 1\) and 2 and around 5 eV for \(K = 3\) for the larger clusters.

Concluding we have presented results of a theoretical study of structural and energetic properties of \(\text{Ni}_N\) clusters with all \(N\) up to \(N = 150\). We stress that this study is the first where a systematic study of energetics, growth, dissociation, and structure of not only the absolutely smallest clusters has been performed without more or less severe assumptions.
of the structure. Our structure optimization was performed using our own Aufbau/Abbau method, and due to the large number of total-energy calculations that was necessary we used the approximate EAM for this purpose. As the main result we obtained the structure and the total energy as functions of \( N \), and these results were then subsequently used in identifying particularly stable clusters, in classifying the overall shape of the clusters, in discussing whether a simple growth mechanism could be applied (this was found not to be the case), and in discussing possible fragmentation channels. In order to extract useful information from the obtained structural and energetic properties we introduced a number of quantitative measures and subsequently applied them on our results. For the first time it was shown that for \( 73 \leq N \leq 79 \) the clusters possess more different types of structural characteristics, and, moreover, our theoretical study is the first such to show that for \( N = 147 \) a magic number occurs for a multilayer icosahedron structure. This result is in perfect agreement with mass-spectroscopical experiments of Pellarin et al.\textsuperscript{25}. 

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| $N$ | This work | Ref. [15] | Ref. [16] | Ref. [17] | Ref. [18] | Ref. [19] |
|-----|-----------|-----------|-----------|-----------|-----------|-----------|
| 2   | $D_{\infty h}$ | $D_{\infty h}$ | $D_{\infty h}$ |            | $D_{\infty h}$ |           |
|     | 2.12 | 2.17 | 2.13 |            | 1.99 |           |
| 3   | $D_{3h}$ | $D_{3h}$ |            | $C_{2v}$ |           |           |
|     | 2.25 | 2.26 | 2.15 |           |           |           |
| 4   | $T_d$ | $D_{2d}$ ($\sim T_d$) | $D_{2d}$ | $D_{4h}$ |           |           |
|     | 2.32 | 2.33 | 2.17 | 2.10 |           |           |
| 5   | $D_{3h}$ | $D_{3h}$ |            | $D_{3h}$ |           |           |
|     | 2.35 | 2.36 | 2.25 |           |           |           |
| 6   | $O_h$ | $C_i$ ($\sim O_h$) | $D_{4h}$ |           |           |           |
|     | 2.36 | 2.40 | 2.33 |           |           |           |
| 7   | $D_{5h}$ |            | $C_{2v}$ ($\sim D_{5h}$) |           |           |           |
|     | 2.39 | 2.28 |           |           |           |           |
| 8   | $D_{2d}$ | $T_d$ | $D_2$ ($\sim D_{2d}$) | $D_{2d}$ | $O_h$ |           |
|     | 2.38 | 2.32 | 2.28 | 2.37 | 2.16 |           |
| 13  | $I_h$ | $\sim I_h$ | $\sim I_h$ |           |           |           |
|     | 2.36/2.48 | 2.41/2.53 |           |           | 2.23/2.34 |           |

**TABLE I:** Our optimized structures in comparison with those of *ab initio* density-functional calculations. In two cases ($N = 5$, Ref. [16] and $N = 7$, Ref. [17]) we compare with the second-lowest structure, and in another ($N = 4$, Ref. [19]) we give their results for the two energetically close minima. The second row gives averaged bond lengths in Å. With '$\sim$' we mark approximate symmetries. The experimental bond length for the dimer is $2.15-2.20$ Å (Refs. [20,21]).
FIG. 1: The optimized structure of the nickel clusters listed in Table I.
FIG. 2: The binding energy per atom for the energetically two lowest isomers (upper part), the stability function (middle part), and the total-energy difference for the two energetically lowest isomers (lowest part) for Ni\(_N\) clusters as functions of \(N\).
FIG. 3: The normalized eigenvalues of the matrix containing the moments of inertia as functions of $N$. The three solid curves gives the eigenvalues, and the dashed curve their average. In the upper part of the figure a simple estimate of the overall shape of the clusters is given: either being spherical (marked with points in the lowest row), cigar-shaped (points in the middle row), or lens-shaped (points in the uppermost row).
FIG. 4: The similarity indices (a) $s_1(N)$, (b) $s_2(N)$, (c) $s_{fcc}(N)$, and (d) $s_{ico}(N)$ for the Ni$_N$ clusters as a function of $N$. For details, see the text.
FIG. 5: The fragmentation channels for the Ni$_N$ clusters as functions of $N$. The upper panel shows the most probable size of the smallest split-off cluster, whereas the lower panel shows the dissociation energy for splitting off 1 (lowest curve), 2 (middle curve, shifted upwards by 2 eV), or 3 atoms (upper curve, shifted upwards by 4 eV).