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STRUCTURAL FORMS AND ENERGIES OF Ni_n, n=12-14, CLUSTERS

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Abstract

Equilibrium structural forms of the Ni_n, n=12-14, clusters, as defined by an embedded-atom potential, are obtained using molecular dynamics and thermal quenching simulations. The isomers (locally stable geometric forms) are distinguished from those stationary structures that correspond to saddle points of the potential energy surface. Isomer statistics are obtained using a large number of initial quenching configurations generated along high-energy trajectories (the energies are high enough to "melt" the clusters). Probabilities of sampling the basins of attraction of the different isomers are computed and the spectra of their energies are analyzed.

1. INTRODUCTION

Clusters are finite aggregates which exhibit unique [1-5] physical and chemical properties. A systematic study of evolution of these properties with size allows elucidation of the transition from the molecular structure to condensed matter phase (clusters are larger than ordinary molecules, but too small compared to bulk materials). Therefore, interest in atomic and molecular clusters has been grown steadily in the last decade. These efforts today have established itself as a new scientific field so-called "nano-science". Investigations have become possible in these areas due to the development of methods and characterization of clusters of various elemental materials. The novelty in clusters largely due to the fact that their geometrical structures and properties are unique and both of them are size dependent.

The preferred methods of investigation for structural studies are electron diffraction, has been applied with significant success in mainly of gas phase clusters of rare gases [6,7] and molecular [8], and high-resolution electron microscopy [9,10]. In addition, a scanning tunnelling microscope probe has been used to examine silver and gold clusters supported on a graphite surface [11] and probing the structure of clusters via chemical methods [12]. The chemical method uses weakly interacting gas such as N_2 and some number of adsorbed molecules as functions of temperature and pressure. The number of adsorbed molecules can give an indication of a geometrical structure [12].

On the theoretical side, the structure and energetics of clusters as well as phase changes, isomerization and chemical reactivity [13-15] have been the focus of investigations. For the transition metals, there are number of approaches that are currently being pursued. One of these methods is based on embedded atom model (EAM) [13-17], analytic two- and three-body potentials [18] and potentials based on the tight-binding model [19,20]. In addition theoretical studies have been carried out for van der Waals, [2,20] ionic and covalent clusters [2] using molecular dynamics (MD). In this study we

have employed the EAM model potential energy surface parameterized by Voter and Chen [16] and studied phases of small nickel clusters Ni_n, n=12-14.

The details of the potential and computational procedure are discussed in the next Section. The numerical results and their analyses are given in Sec. 3.

2. INTERACTION POTENTIAL AND COMPUTATIONAL PROCEDURE

Pair potentials are generally not adequate for description of the energetics of metals due to the many-body character of the interatomic interactions. We represent the configurational energy of the nickel clusters by an embedded-atom potential [16], which has been used earlier to study structural and dynamical properties of nickel clusters [13,14]. Considerable part of the energy as described by this potential, is attributed to the so-called embedding term, which depends on the total local electronic density. The configurational energy E_i of each atom i is represented as

$$E_i = F_i(\bar{\rho}_i) + \frac{1}{2}\sum_{j \neq i} \Phi_{ij}(r_{ij}), \tag{1}$$

where F_i is the embedding term, Φ_{ij} is the pairwise-addition part of the interaction between atoms i and j, r_{ij} is the distance between atoms i and j, and $\bar{\rho}_i$ is the total "host" electron density at the position of atom i :

$$\bar{\rho}_i = \sum_{j \neq i} \rho_j(r_{ij}). \tag{2}$$

In Eq. (2), $\rho_j(r_{ij})$ is the electron density contributed by atom j at the position of atom i. The parameters of the potential are obtained by fitting simultaneously to properties of bulk nickel and those of Ni_2 (for details see Ref. [16]). As a consequence, this potential may have a broader range of validity, which includes clusters.

The equilibrium structural forms of Ni_n, n=12-14, clusters are obtained using MD and thermal quenching simulations. Hamilton's equations of motion were solved for all the atoms in a cluster using Hamming's modified 4th order predictor-corrector propagator with a step-size of 1×10^{-15} s. In order to obtain isomer statistics large number of independent initial quenching configurations, sample sizes of Ni_{12}, Ni_{13}, and Ni_{14} are 1049, 2469, and 1905, respectively, were recorded at every 500 simulation steps along high-energy trajectories. The internal energies (about T=2600 K) were high enough to "melt" the clusters. The thermal quenching of a cluster is completed in two phases. In the first phase each of independent initial configurations was quenched at every 5 simulation steps during a 10000-step run in order to trap the cluster at as many different basins of attraction as possible (this fast quenching does not allow the cluster by pass easily the high lying local minima). In the second stage the internal kinetic energy of the clusters is set to zero at every 50 or 100 simulation steps, and the runs are continued until the internal kinetic energies are completely removed (tolerance was set to zero). The second stage separated the locally stable isomers from those metastable ones (saddle points of the potential energy surface). We have obtained 100, 186, and 167 different stable isomers of Ni_{12}, Ni_{13}, and Ni_{14} clusters, respectively. The structures, energetics, and the probability of sampling are discussed in the next Section.

3. RESULTS AND DISCUSSIONS

The energetics and geometries of the first four lowest energy isomers of a Ni_{12} cluster are presented in Fig. 1. Pentagonal bipyramid structure is the "back bone" of the minimum energy geometry of the Ni_{12}. Its configuration is formed by two pentagonal bipyramids on top of each other, but one atom is missing from one of the pentagonal rings. The second lowest energy isomer has only one pentagonal bipyramid, and the remaining atoms, except one of them, form a tetrahedral bipyramid structure on its surface. Practically all the isomers are formed by aggregation of pentagonal, tetrahedral and triangular bipyramid structures. These are the building blocks of the cluster. As the energy of isomer increases, the structure becomes less symmetric, however, some of these building blocks still do exist.

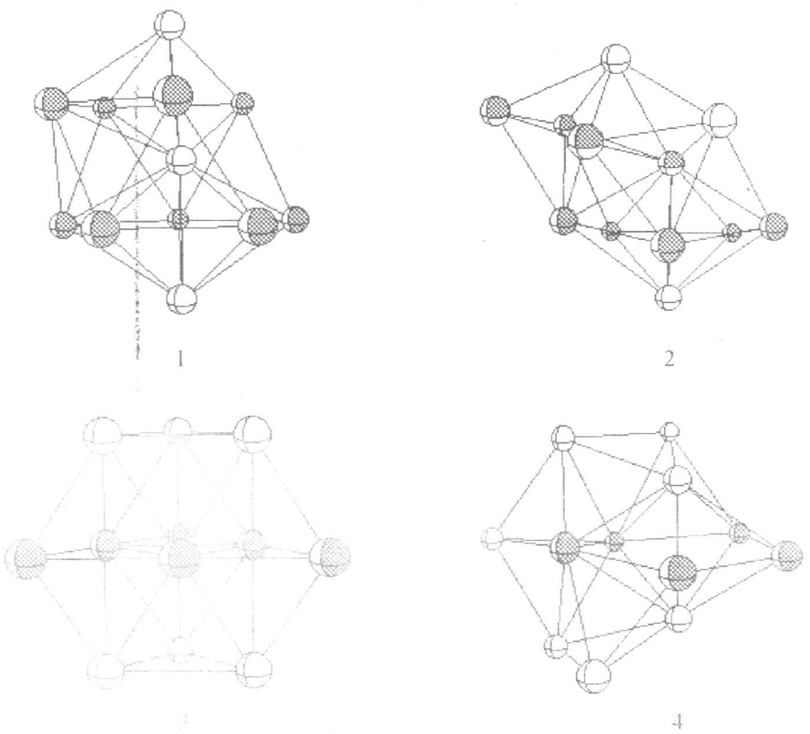

Fig. 1 The minimum energy geometries of the isomers of a Ni_{12} cluster. The energetics are -36.48 eV, -35.65 eV, -35.59 eV, and -35.58 eV, respectively.

We have obtained 100 different stable isomers of the Ni_{12}. Probability distribution of these isomers as a function of the isomer's energy is displayed in Fig. 2. These probabilities are calculated from the frequencies of sampling the basins of attraction of the different isomers. The number of independent initial conditions (sample size) is 1049. As seen, the lowest energy structure of the Ni_{12} (isomer 1 in Fig. 1) has the highest probability to be sampled. Further, this isomer is quite separated from the other energetically higher isomers. The energy gab between the first isomer and the next one is almost 1eV, however, the energy spacing between the other isomers is decreasing further as the internal energy increases. The isomers practically form 5 groups with respect to the internal energy. The first group contains only the first isomer (-36.48 eV), the second grouping is about -35.50 eV energy, the third group is formed near -35.00 eV, and the next one is at -34.50 eV. Energetically the highest last two isomers are also separated from the earlier groups, and

they form the 5th group. The full width of this energy spectrum is 3.48 eV, and contains 100 different isomers. The probability of the sampling of these isomers is "falling" exponentially as the energy of the isomers increases, and has the form of

$$P(E) = a e^{\left\{\frac{b}{E+c}\right\}}, \tag{3}$$

here, a, b and c are constants with a > 0 and b > 0 conditions, and E is the internal energy

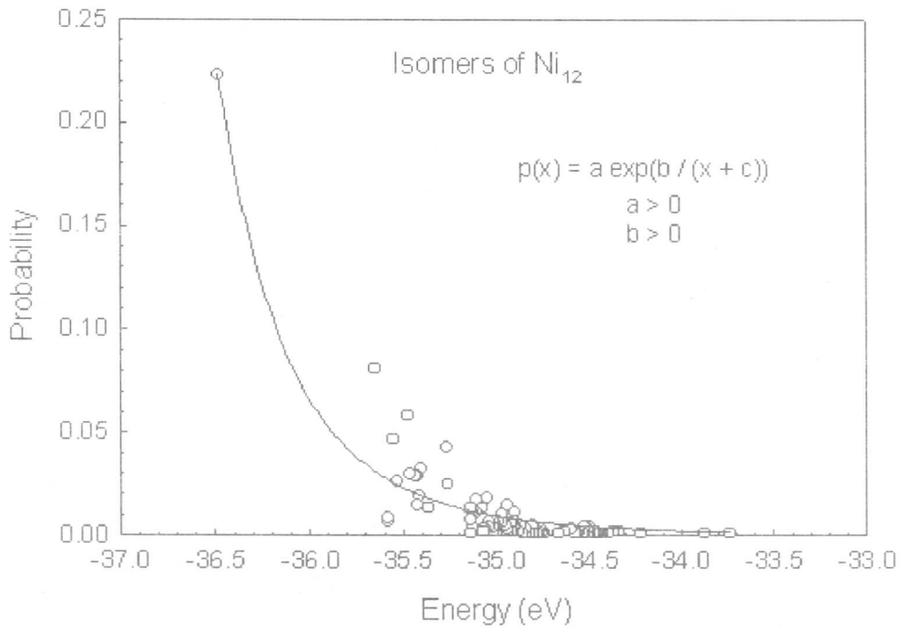

Fig. 2. The probability distribution of the isomers of a Ni_{12} cluster as a function of the internal energies of the quenched isomers.

of a quenched isomer (E < 0).

The minimum energy geometries and energetics of a Ni_{13} cluster are given in Fig. 3. The lowest energy isomer, 1, has a unique structure (icosahedral geometry); there is a nickel atom at the center and the remaining twelve atoms are forming a spherical shell around. Its energy is 1.63 eV less than the energy of the second isomer. This structure may also be viewed as double pentagonal bipyramids, such that one cap atom of a pentagonal bipyramid is shared. The second isomer is formed by removing one atom from a pentagonal ring on to the surface of the shell (over a polar cap), and this surface atom stays over a triangular face. The third isomer has a surface atom which was brought from the cap of the lower pentagonal bipyramid, and this atom is over a triangular face in the lower part of the equatorial region of an the icosahedral structure. The 4th isomer geometrically similar to the second one. The surface atom is over a triangular face just above the equatorial region. The isomers, except the first one, energetically very close to each other. A pentagonal bipyramid is a "back-bone" of these structures as well. The

total number of the isomers of a Ni_{13} obtained is 186, and the width of the energy spectrum of the isomers is about 2.00 eV.

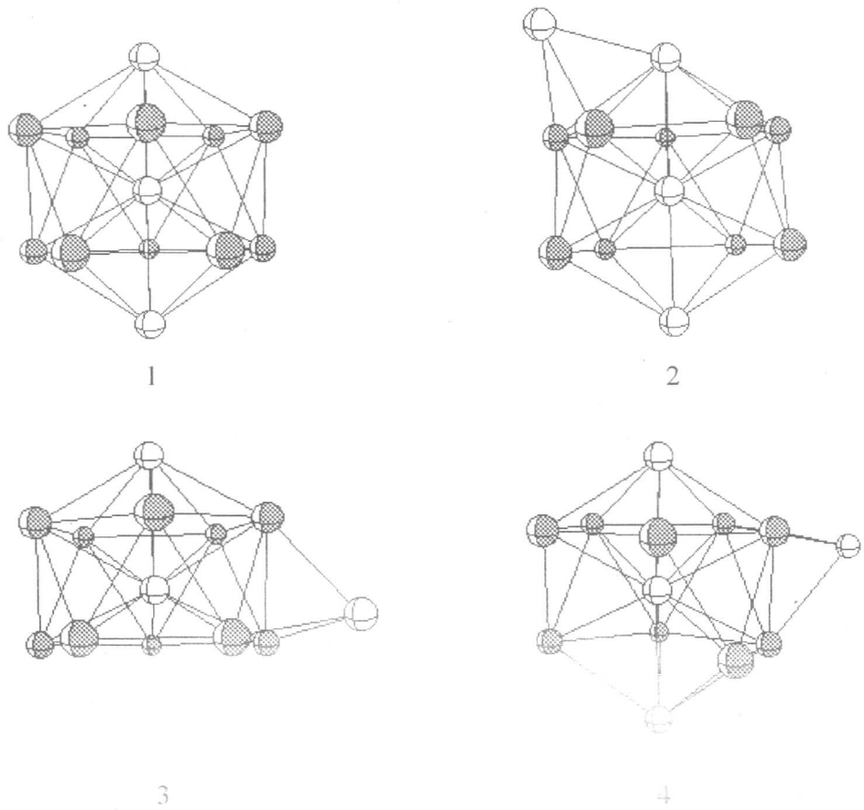

Fig. 3. The minimum energy geometries of the first four isomers of a Ni_{13} cluster. The energetics are -41.12 eV, -39.49 eV, -39.48 eV, and -39.44 eV, respectively.

In Fig. 4, the minimum energy structures of the first four isomers of a Ni_{14} cluster are displayed. The lowest energy structure of a Ni_{14} is formed by a Ni_{13} icosahedral geometry plus an atom over a triangular face. The second isomer is formed by moving the surface atom from a face to over one of the bridges of the pentagonal ring. The energy gap between the first (the lowest energy isomer) and the second isomers is relatively small (0.19 eV) compared to that of the other sizes (Ni_{12} and Ni_{13}). The first and second isomers are energetically separated from the other isomers (about 0.80 eV). The third isomer can be formed from the first isomer by moving one of the pentagonal ring atoms over a triangular face, as a result, there are two surface atoms on the polar region. On the other hand, the fourth isomer is obtained by removing the capping atom from the lower pentagonal bipyramid over a triangular face in the upper part of the equatorial region, and this surface atom forms a triangular bipyramid with the other surface atom over the upper polar region. In these isomers the building blocks of the structures are also clearly visible. The total number of the isomers of the Ni_{14} obtained is 167 and the width of the energy spectrum of the isomers is about 3.03 eV. A Ni_{12} cluster has the largest width of the energy spectrum, on the other hand, it has the smallest number of the stable isomers as seen in Table. 1.

Table 1.

Size	Number of Isomers	The width of the energy spectrum (eV)
Ni_{12}	100	3.48
Ni_{14}	167	3.03
Ni_{13}	186	2.00

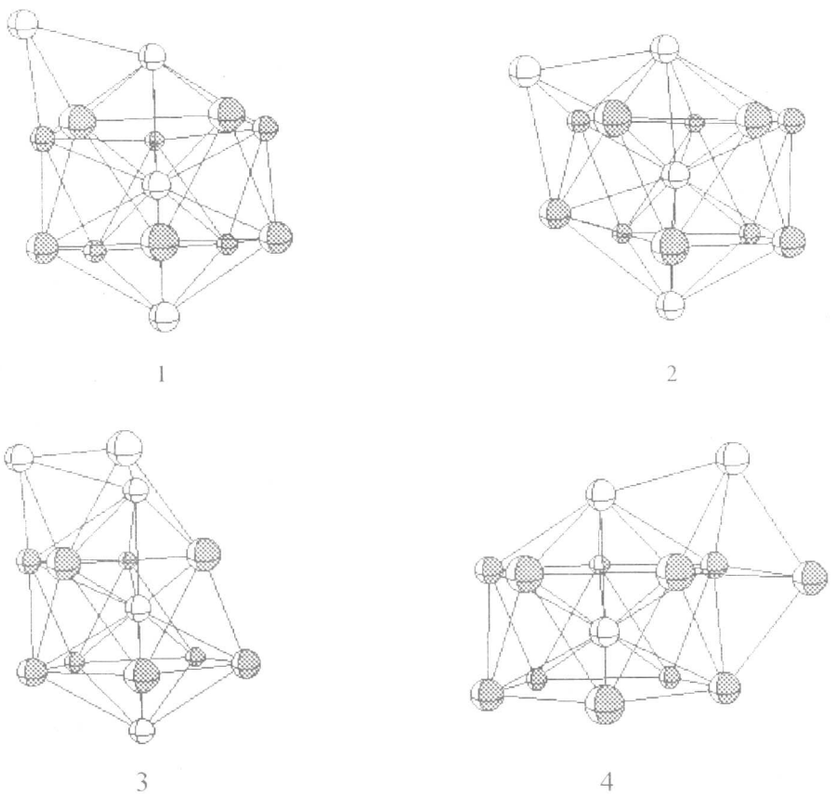

Fig. 4. The minimum energy geometries of the first four isomers of a Ni_{14} cluster. The energetics are -44.09 eV, -43.90 eV, -43.13 eV, and -43.09 eV, respectively.

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