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Nickel-Aluminum Alloy Clusters - Structural and Dynamical Properties

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Structural and dynamical properties of mixed Ni_nAl_m alloy clusters mimicked by a many-body potential are studied computationally for all the possible compositions n and m such that $n+m=13$. It is shown that the manifold of the usually very large number of the different possible structural forms can be systematized by introducing classes of structures corresponding to the same concentration of the components, geometry and type of the central atom. General definitions of mixing energy and mixing coefficient are introduced, and it is shown that the energy ordering of the structural forms within each class is governed by the mixing coefficient. The peculiarities of the solid-to-liquid-like transition are described as a function of the concentration of the two types of atoms. These peculiarities are correlated with and explained in terms of the energy spectra of the structural forms. Class-dependent features of the dynamics are described and analyzed.

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Understanding of properties of different materials and, even more so, design and fabrication of novel materials require a microscopic (i.e., atomic level) description of the fundamental characteristics of these systems. The field of atomic and molecular clusters grew out of an effort to provide such a description. Clusters are a tool for arriving at understanding of how properties of individual atoms and molecules (gas phase) evolve into those of solids and liquids (condensed phase) as the number of atoms or molecules in a cluster increases. It has been realized along the way that clusters themselves form a class of extremely interesting and important, from the applied point of view, objects. Cluster research evolved into a sovereign discipline with its own methodologies and techniques. At its present stage it already begins to have a noticeable impact on bordering disciplines, such as materials science, chemistry and physics, and on a variety of modern technologies, such as microelectronics, catalysis, nucleation and growth of particles and layers, etc.

One of the well-known ways of obtaining materials with superior properties is to mix different elements. Alloys (mixes of metals) are known to the mankind for millennia (at least from the bronze age). A promising novel approach to design and fabrication of materials with predefined mechanical, thermal, electrical, optical, magnetic and other properties emerges in the cluster field. The idea is to use clusters with special properties as building blocks for manufacturing so-called cluster-assembled (1-4) and nanophase (5-7) materials. It is clear that different (in size, structure, type and relative concentration of the component elements, etc.) clusters will have to be used to manufacture cluster-assembled and nanophase materials tailor-made to meet special-purpose needs and specifications. Clusters of mixed composition stand the best chance of becoming the optimal building blocks of such novel materials. In this respect, alloy clusters are of especial interest because they are natural "laboratories" both for furthering our understanding of the traditional (bulk) alloys and for searching for building blocks of novel metal-cluster based materials.

Here we give a description and analysis of some of the structural and dynamical properties of two-component metal clusters (8-18). We use as a paradigm the Ni_nAl_m system with all the possible values of n and m such that $n+m=13$. In the next section, we specify the potential energy function representing the microscopic (interatomic) interactions and describe the necessary theoretical and computational tools. Then we present an analysis of the structural properties of the mixed clusters and formulate a classification scheme, which allows for systematization and rationalization of the energy ordering of the different structural forms of the alloy 13-mer. The discussion of the structural and energy characteristics is followed by a description of the dynamical properties of the mixed clusters. It is shown that these properties correlate with and can be understood in terms of the classes of structural forms. A brief summary is given in conclusion.

Theory and Methodology

All the structural and dynamical properties of alloy clusters, as of any physical system, are ultimately defined by the interactions between the constituent atoms. We mimic these interactions in a mixed 13-atom Ni-Al cluster by a Gupta-like potential of the form (19)

$$V = \sum_{i=1}^N \left\{ \sum_{j=1(j \neq i)}^N A_{ij} \exp \left(-p_{ij} \left(\frac{r_{ij}}{r_{ij}^0} - 1 \right) \right) - \left[\sum_{j=1(j \neq i)}^N \xi_{ij}^2 \exp \left(-2q_{ij} \left(\frac{r_{ij}}{r_{ij}^0} - 1 \right) \right) \right]^{1/2} \right\}, \quad (1)$$

where N is the total number of atoms in the cluster; A_{ij} , ξ_{ij} , p_{ij} , q_{ij} , and r_{ij}^0 are adjustable parameters, the values of which depend on the type of the i -th and the j -th atoms; and r_{ij} is the distance between the i -th and the j -th atoms. The values of the parameters for the Ni-Ni, Al-Al and Ni-Al pairs of atoms are adopted from ref. (19) and are listed in Table I. These parameters are fitted in such a way that in the cases $n=0$ or $m=0$ the potential describes the pure Al_{13} or Ni_{13} clusters, respectively [for details see ref. (19)]. As has been established in earlier studies, the lowest energy structure of both Ni_{13} (20-24) and Al_{13} (16) is an icosahedron. The distance from the center of the icosahedron to its surface, as obtained from the potential, equation (1), is 2.43 Å and 2.66 Å for Ni_{13} and Al_{13} , respectively. These values are in good agreement with those obtained in other studies (25-32). The average binding energy per atom is 2.67 eV in Ni_{13} and 2.60 eV in Al_{13} . The corresponding values obtained in electronic structure calculations vary from 2.91 to 4.26 eV in Ni_{13} (25-27) and from 2.77 to 3.21 eV in Al_{13} (28-32).

A possible way to obtain different structural forms of the mixed Ni_mAl_n , $n+m=13$, clusters, is to perform simulated thermal quenches from a variety of initial configurations. These can be generated, for example, by a sufficiently high energy and sufficiently long molecular dynamics trajectory that accomplishes a sufficiently complete sampling of the configuration space of the cluster of interest. A distinguishing feature of two-component clusters is that the total number of their different structural forms is much larger than that corresponding to their one-component counterparts. The reason for this is that the structural forms of mixed clusters can differ not only by the geometry (packing), as in the case of one-component clusters, but also by different distributions of the two types of atoms between the sites of a chosen geometry. We retain the term *isomers* to label the different geometric forms of a mixed cluster of a given size and introduce the term *homotops* to label a subset of the structures of a cluster with a given composition that belong to the same isomer, but differ by the distribution of the two types of atoms between the sites of that isomer. The total number of the different possible structural forms (isomers and homotops) of mixed clusters is usually very large. For example, the number of ways, in which one can distribute six Al atoms and seven Ni atoms (or seven Al atoms and six Ni atoms) in a single isomer of a 13-atom cluster is $13!/(6!7!)=1716$, although, because of the possible symmetry of an isomer, not all the 1716 distributions necessarily form different homotops. Instead of performing a comprehensive search for the possible structures of Ni_nAl_m through the thermal quenching procedure mentioned above, we carried out a search for all the homotopic forms corresponding to six isomers. These isomers were chosen as the first six lowest energy structures of the pure Al_{13} (Figure 1). (The search for the structures of Al_{13} was performed using the simulated thermal quenching technique; it produced a total of 129 different isomers.) For each composition, i.e. fixed n and m , $n+m=13$, all the possible replacements of n Al atoms by

n Ni atoms were considered in each of the six chosen isomers of Al_{13} . The so formed mixed Ni_nAl_m clusters were then allowed to relax to their corresponding equilibrium configurations. The technical details of the applied relaxation procedure are given in ref. (14). We consider all the stable equilibrium structures that differ only by small local relaxations in the positions of the individual atoms, but have the same geometric packing, as the same isomer. A normal mode analysis was applied to each resulting configuration to filter out those structures that represent saddles, rather than minima, of the corresponding potential energy surfaces. In general, not necessarily all the stable isomeric forms of the pure clusters survive as equilibrium geometries of the corresponding mixed clusters (at least, not necessarily for all the compositions of the latter), and, vice versa, some stable isomers of the mixed clusters may not survive as equilibrium geometries of their one-component counterparts [cf. refs. (14,16)].

An important structural aspect of two-component clusters is mixing vs segregation of the component materials and the quantification of the degree of mixing. It has been suggested (11) to use as a measure of the degree of mixing the total number of bonds between first neighbor atoms of unlike type. The shortcomings of this measure in establishing a correlation between the preference for mixing (or segregation) and the configurational energy of a mixed cluster are obvious. Such a correlation exists only when and if 1) the total interaction energy can be represented as a sum of the pairwise interactions (pairwise-additivity) and 2) the interatomic interactions do not extend beyond the first nearest neighbors of each atom. Neither of the two assumptions holds for many systems. The inherently many-body character of the interatomic interactions in metals is one of the most distinguishing features of these systems.

A physically meaningful and general definition of the mixing energy V_{mix} of a two-component cluster A_nB_m in a given configuration, as specified by the coordinates of its atoms, where A and B are the types of the atoms, is given by (14)

$$V_{mix} = V_{A_nB_m} - \left[V_{A_n}^{(A_nA_m)} + V_{B_m}^{(B_nB_m)} \right], \quad (2)$$

where $V_{A_nB_m}$ is the energy of the A_nB_m cluster, $V_{A_n}^{(A_nA_m)}$ is the energy of the A_n subcluster in the A_nA_m cluster, and $V_{B_m}^{(B_nB_m)}$ is the energy of the B_m subcluster in the B_nB_m cluster. In the above definition the one-component A_nA_m and B_nB_m clusters have the same configuration as A_nB_m , and the configurations of the n -atom and of the m -atom subclusters are the same in A_nB_m , A_nA_m and B_nB_m . Since

$$V_{A_nB_m} = V_{A_n}^{(A_nB_m)} + V_{B_m}^{(A_nB_m)}, \quad (3)$$

where $V_{A_n}^{(A_nB_m)}$ and $V_{B_m}^{(A_nB_m)}$ are the energies of the A_n and B_m subclusters in the A_nB_m cluster, the mixing energy can be written as

$$V_{\text{mix}} = \left(V_{A_n}^{(A_n B_m)} - V_{A_n}^{(A_n A_m)} \right) + \left(V_{B_m}^{(A_n B_m)} - V_{B_m}^{(B_n B_m)} \right). \quad (4)$$

V_{mix} is, therefore, a measure of the total change in energy experienced by the A_n and B_m subclusters (or, alternatively, their individual atoms) when they are removed from the one-component $A_n A_m$ and $B_n B_m$ clusters, respectively, and are brought together to form the $A_n B_m$ cluster. It is clear that for pairwise-additive potentials which include only first-neighbor interactions our definition of V_{mix} becomes equivalent, more precisely, proportional, to the number of bonds between first-neighbor atoms of unlike type. (The proportionality is obtained rigorously only if one neglects the possible small differences, caused by the relaxations, in the distances between the nearest neighbor atoms of unlike type.) The (global) mixing coefficient M can be defined as (14)

$$M = \frac{V_{\text{mix}}}{V} \cdot 100\%. \quad (5)$$

The dynamical features of the clusters are derived from microcanonical (i.e., constant energy) molecular dynamics simulations. Long trajectories (up to $8 \cdot 10^6$ steps with a step size of 2 fs) were run on a fine grid covering a broad energy range for all the possible compositions of the mixed Ni-Al 13-mer. The trajectories were generated using the velocity version of the Verlet propagator (33). The initial coordinates and velocities of the atoms were chosen so as to supply no total linear and angular momenta to the cluster. The total energy is conserved, even along the longest trajectories, within 0.01 %. The cluster temperature in a given run is defined as

$$T = \frac{2 \langle E_k \rangle_t}{(3N-6)k}, \quad (6)$$

where E_k is the total (internal) kinetic energy, k is the Boltzmann constant, and $\langle \rangle_t$ stands for time averaging over the entire trajectory. The dynamical features of the clusters are analyzed in terms of the following quantities: 1) caloric curve, i.e., time-averaged kinetic energy (per atom) as a function of total energy (per atom); 2) relative root-mean-square (rms) bond length fluctuation δ ,

$$\delta = \frac{2}{N(N-1)} \sum_{i < j} \frac{\left(\langle r_{ij}^2 \rangle_t - \langle r_{ij} \rangle_t^2 \right)^{\frac{1}{2}}}{\langle r_{ij} \rangle_t}, \quad (7)$$

as a function of total energy (per atom); and 3) specific heat (per atom) (34),

$$C = \left[N - N \left(1 - \frac{2}{3N-6} \right) \langle E_k \rangle_t \langle E_k^{-1} \rangle_t \right]^{-1}, \quad (8)$$

as a function of total energy (per atom).

Structural Properties

The number of homotops corresponding to a given isomer depends on the geometry (degree of its symmetry) and the composition of the isomer. As a rule, a larger number of homotops corresponds to an isomer 1) of lower symmetry and 2) with a more equal concentration of the two types of atoms. For example, 30, 805, 887, 900, 137 and 43 different stable homotops correspond, respectively, to the six isomers of Ni_7Al_6 sequenced in order of increasing energy as defined by the most stable homotop of each isomer. The ordering of the isomers by the energy of the corresponding most stable homotop produces a sequence which is, in general, different from that for the isomers of the pure Al_{13} and which changes with the concentration of the Ni and Al atoms in the 13-mer. However, for all n and m , $n+m=13$, including the cases of $n=0$ or $m=0$, the lowest energy geometry of Ni_nAl_m is the icosahedron. Figures 1-4 display the first four (of the six considered) isomers, each represented by its lowest energy homotop, for the cases of Ni_{12}Al , Ni_7Al_6 , Ni_6Al_7 and NiAl_{12} , respectively. The figures also show the homotop energy diagrams (either in the form of individual energy levels or distributions of these levels), as well as the total number of homotops corresponding to each isomer. The energy diagrams clearly display the features mentioned above. They also show that Ni_{12}Al prefers Al as the central atom, whereas Ni_7Al_6 , Ni_6Al_7 and NiAl_{12} prefer Ni as the central atom. In fact, $n=12$, $m=1$ is the only composition of the Ni_nAl_m 13-mer for which it is energetically favorable to place an Al atom in the center of the cluster. With the exception of the case of Ni_{12}Al , the homotop energy spectra of the individual isomers are bimodal. As is clear from the figures, the lower energy branches of the distributions correspond to homotops with Ni in the center, whereas the higher energy branches represent homotops with Al in the center. The branches become better separated as the number of the Al atoms in the mixed 13-mer increases. In the case of NiAl_{12} the lower energy branch degenerates into a single energy level - that of the homotop with Ni in the center. This level is separated by a large gap from the manifold of levels corresponding to homotops with Al in the center. The degree of bimodality of the homotop energy spectra of a given isomer can be quantified by the difference between the energies of the two most stable homotops of this isomer, representing the branches with Ni and Al, respectively, as the central atom. Figure 5 shows the graph of this difference as a function of the number m of the Al atoms for the icosahedral isomer of the mixed 13-mer.

The features discussed above suggest that one can introduce a classification of the manifold of the structural forms of mixed clusters of a given size and chosen materials (which in the case of the six isomers of the mixed NiAl 13-mer considered here includes 13603 such stable structures) based on the isomeric form, composition, and the type of the central atom. What defines then the energy ordering of the homotops within each class specified by these three attributes? The answer to this question is - the mixing coefficient. Figure 6 displays the graphs of the mixing coefficient as a function of the homotop energy for four classes representing two isomers of the Ni_6Al_7 cluster. The feature to notice is the monotonicity of the graphs, which is either absolute (exact), as in the case of the icosahedron, or global (overall), as in the case of the second isomer. The higher the degree of mixing of a homotop, the lower its energy within its class. The monotonicity is exact when the energy gap between neighboring homotops within a class is larger than the energy changes caused by the local relaxations in the structures of the individual homotops. The reason for the local violation of the monotonicity in the case of

the second isomer is that the energy gap between neighboring homotops in the two classes corresponding to it is very small: 338 homotops with Ni in the center and 438 homotops with Al in the center fall into energy ranges with width of 0.557 eV and 0.722 eV, respectively. The defining role of the mixing coefficient as an ordering index in a given class of homotops holds for all isomers and all compositions of the mixed Ni-Al 13-mer.

All the structural and energy properties of the Ni_nAl_m clusters discussed above are, of course, imbedded in the parameters, cf. Table I, of the potential, equation (1). A model which transparently displays and explains the role of the *homo* (i.e., Ni-Ni and Al-Al) vs *hetero* (i.e., Ni-Al) interactions in defining these properties is discussed elsewhere (17,18).

Dynamical Properties

A sample of the dynamical properties of the clusters is given in Figure. 7, which displays graphs of the caloric curve, rms bond length fluctuation δ , and specific heat C , all considered as a function of the cluster energy, for three compositions of the mixed Ni-Al 13-mer. The icosahedral isomer is chosen to represent the zero-temperature geometries of the clusters, and two cases - one corresponding to Ni and the other to Al as the initial central atom (each is represented by the homotop of the lowest energy in the corresponding class) - are considered for each composition. The global features of the graphs are typical of those corresponding to a solid-to-liquid-like transition in clusters induced by increase of their internal energy [cf., e.g., refs. (22-24,35-37)]. The details - stages and mechanism(s) - of this transition, however, depend on the class as defined by the zero-temperature structure of the cluster.

Consider first the cases when the zero-temperature icosahedra have the energetically preferred type of atom in the center (cases A in Figure. 7). Whereas two abrupt changes characterize the δ graphs of the Ni_{12}Al and Ni_7Al_6 clusters, only one such change is present in the δ graph of the NiAl_{12} cluster. In contrast, the specific heat graphs display only one peak for the Ni_{12}Al and Ni_7Al_6 clusters, but two peaks for the NiAl_{12} cluster. These peculiarities of the dynamical features can be correlated with and explained in terms of the peculiarities of homotop energy spectra associated with the individual isomers of different compositions (cf. Figures. 1-4). As the energy of a mixed cluster is increased, it begins to sample its higher energy isomeric and homotopic forms. The order in which additional structural forms become accessible depends on their energy and/or the height of the barriers separating them from the other structures. Any homotopic rearrangement within the icosahedral geometry would require overcoming very high barriers. It is energetically easier to convert the complete icosahedron into geometric forms of higher energy. The cluster, therefore, first undergoes isomerization transitions that destroy the completeness of the icosahedral shell. The isomerizations that require the least extra energy are those that involve only the surface atoms. These "surface isomerizations" leave the central atom in the central position, and they are the ones that are responsible for the first abrupt change in the δ graphs. As the energy of the Ni_{12}Al and Ni_7Al_6 clusters with the preferred type of the atom in the center is increased, they sample, through surface isomerizations and homotopic transitions, an increasing number of structural forms. The reason for this is that in these clusters the most stable homotop of each isomer with incomplete shell is separated from the higher energy homotops, either in the same or the other class of either the same or similar isomers, only by small or at most moderate energy gaps (cf. Figures 1 and 2). Further increase of the energy (by about

0.1 eV/atom over that needed to trigger surface isomerizations and homotopic transitions) results in that also global structural changes, i.e., ones that involve permutations between the central atom and a surface atom, become observable on the time scale of our simulations. In Ni_{12}Al such permutations imply replacing the Al atom by a Ni atom in the central position. In Ni_7Al_6 these permutations may or may not change the central Ni by an Al. It is these global structural rearrangements that cause the second abrupt change in the δ graphs. When the preferred central atom in Ni_{12}Al and Ni_7Al_6 gets replaced by an atom of the other type, the clusters sample also their icosahedral homotop(s) of higher energy (i.e., those with Ni in the center of Ni_{12}Al and with Al in the center of Ni_7Al_6); both homotops of the icosahedral Ni_{12}Al and most of the icosahedral Ni_7Al_6 have energies that are lower than those of the homotopic forms of the corresponding higher energy isomers of these clusters. Further increase of the energy leads to an increase in the rate of the surface and global structural transitions and eventually produces a liquidlike state [22-24,35-37] of the Ni_{12}Al and Ni_7Al_6 . The single peak in the graphs of the specific heat of these clusters is the signatures of transition to this state.

The overall sequence in which the different structural transitions (surface and global) become observable in the NiAl_{12} cluster with Ni as the initial central atom is the same as described above for the Ni_{12}Al and Ni_7Al_6 clusters. The factor that makes the dynamical behavior of NiAl_{12} , as exhibited by the graphs of Fig. 7, different from that of either Ni_{12}Al or Ni_7Al_6 is the large energy gap separating the most stable homotop of its higher energy isomers from the higher energy homotop(s) of these isomers. The abrupt change in the δ graph of the NiAl_{12} cluster is caused by surface isomerizations, which convert the lowest energy homotop of the icosahedral isomer into the lowest energy homotops of the higher energy isomers. The global isomerizations and homotopic transitions (i.e., the ones that replace the Ni atom by an Al atom in the center) remain unobservable on the time scale of our simulations until an extra energy of about 0.18 eV is deposited into the cluster. Before the global isomerizations become observable, however, the extra energy makes the rate of the surface isomerizations so high that the cluster attains the state of surface melting. The twelve Al surface atoms form a highly mobile shell, which is not necessarily completely closed at all times, but which overall encages the single Ni atom. The signature of surface melting is the first peak in the corresponding graph of the specific heat. The minimum between the two peaks in this graph corresponds to the energy at which the replacement of Ni by Al in the central position becomes observable on the time scale of our simulation runs. The rapid increase of the rms bond length fluctuation due to surface melting masks the distinct signature of the onset of global rearrangements in the corresponding δ graph. The second peak in the graph of the specific heat corresponds to complete melting of the NiAl_{12} cluster. In the state of complete melting the Ni atom executes frequent excursions to the surface of the cluster.

Comparison of pairs of graphs A and B of a given quantity in Figure 7 corresponding to the same composition but different types of the central atom in the zero-temperature structure of the mixed 13-mer allows one to analyze the class-dependence of the dynamics as defined by the initial type of the central atom. Inspection of the graphs shows that for each composition there is an energy above which the two dynamics, one associated with Ni and the other with Al as the initial central atom, become identical. Above this energy the clusters loose memory of the fact that their zero-temperature icosahedral structure may have been prepared with the energetically less favorable type of atom in the center. Clearly, this composition-dependent energy is one at which structural changes that alter the type of the central atom are feasible. An important and

tantalizing observation is that this energy, as defined by the graphs B - they correspond to dynamics associated with the classes with the less preferred type of the central atom, - is lower than the energy at which global structural changes become observable, as defined by the corresponding graphs A (cf. the discussion above). This "paradox" is apparent, rather than real, in that it is based on long but finite observation (simulation) times, and it can be explained either by different extents ("volumes") of the parts of the configuration space ("basins of attraction") associated with the different structural forms (especially those with the more preferred type of the central atom, on the one hand, and those with the less preferred, on the other), or by peculiarities of the topography of the corresponding potential energy surfaces that make the transition over a barrier in a given direction more probable than in the reverse direction, or both.

The way the clusters loose memory of the initial less preferred central atom depends on their composition (cf. graphs B of Figure 7). This composition dependence also can be explained through the features of the corresponding homotop energy spectra. When one energizes an icosahedral NiAl_{12} with Al initially in the central position, the surface isomerizations become observable at the energy of about -2.52 eV/atom, which is approximately 0.04 eV/atom higher than the corresponding energy in the case when Ni is initially in the central position (cf. graphs B and A for NiAl_{12} in Figure 7). Very little additional energy (less than 0.02 eV/atom) leads then to a replacement of the initially central Al atom by the energetically more preferred Ni atom. After this replacement the cluster behaves as if it were originally prepared with Ni in the center - the A and B graphs become identical. The first replacement of Al by Ni in the central position takes place early on along the trajectory of the corresponding energy, and after it occurred the cluster never revisits in the course of the same trajectory structures with Al in the center. The homotops with Ni in the center completely dominate the dynamics, and, as a consequence, the time-averaged kinetic energy of the cluster drastically increases because the configurational energies of these homotops are much lower than those of homotops with Al in the center. The change is so abrupt that it appears as a discontinuity in the B-labeled graphs of the caloric curve and specific heat of the NiAl_{12} cluster. Similar arguments explain also the quite rapid but smaller increase in the B-labeled caloric curve of the Ni_7Al_6 cluster. In this case, however, the change in the time-averaged kinetic energy is not as drastic, and it translates into an additional sharp local peak (represented by a single point), rather than a discontinuity, at the energy of about -2.59 eV/atom in the B-labeled graph of the specific heat of this cluster. The dynamical replacement of an initial Al atom by a more preferred Ni atom in the center of Ni_7Al_6 triggers a less abrupt change in the time-averaged kinetic energy because 1) the homotops of this cluster with Ni in the center are separated from the corresponding (i.e., belonging to the same isomer) homotops with Al in the center by smaller energy gaps, and 2) the number of homotopic forms participating in the switchover from Al to Ni as the central atom increases gradually as the cluster energy is increased. In the B-labeled δ graph of the Ni_7Al_6 cluster this is reflected by a less distinct (as compared to the corresponding A graph) representation of the two changes associated with the onsets of the surface and of the global structural transformations, respectively. In the case of Ni_{12}Al , the small difference between the configurational energies of the homotops with Ni in the center and the corresponding homotops with Al in the center makes the replacement of an initial Ni central atom by the more favorable Al atom essentially unnoticeable, as gauged by the B-labeled graphs of the caloric curve and specific heat of this cluster. The only noticeable effect of this replacement is some blurring of the distinction between the two rapid increases in the B-labeled δ graph of Ni_{12}Al (as compared to the corresponding A graph),

which is caused by inclusion in the sampling of additional homotops participating in the switchover from Ni to Al in the central position as the energy of the cluster is increased.

Summary

Mixed metal (alloy) clusters are systems with an enormous, yet unexplored, potential for fabrication of novel materials and other applications. The richness of their properties, - not only structural and dynamical considered in this study, - but also other (e.g., electronic, optical, magnetic, chemical, etc.), and the ability to control and shape these properties through rational selection of their sizes, types and concentrations of their component elements, as well as conditions (e.g., temperature, etc.) of their preparation, make them ideal for arriving at materials tailor-made to unique and demanding specifications. For this, however, an understanding of the fundamental properties of these systems and of how these properties change with the "control variables", e.g., those listed above, is necessary. Theoretical and numerical simulation studies are the means of arriving at a microscopic level of description and understanding of these properties. The two major ingredients of such studies are 1) adequate description of the many-body interatomic interactions and 2) conceptually adequate and efficient analysis tools. An example of the latter is the concept of mixing energy and mixing coefficient, as implemented for systems characterized by interactions that are of inherently many-body character. The finding that the usually very large manifolds of the possible different structural forms of mixed clusters can be subdivided into classes, within which the energy of the different structural forms changes monotonically with the degree of mixing of the component elements, suggests in the case of the Ni-Al clusters considered here that annealing will produce clusters with a higher degree of mixing of the Ni and Al atoms, whereas rapid thermal quenching will preferentially yield clusters with higher degree of segregation of the two metals. Clusters of the same size, as well as type and concentration of the component elements, but different degree of mixing of these elements, most certainly exhibit differences in many, if not all, of their physical and chemical properties. It is the very rich spectrum of these properties that makes two-component clusters, especially alloy clusters, so challenging and attractive both from the fundamental cognitive and applied points of view.

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Table I. Parameters of the Gupta-like potential (19).

Parameters	Ni-Ni	Al-Al	Ni-Al
A (eV)	0.0376	0.1221	0.0563
ξ (eV)	1.070	1.316	1.2349
p	16.999	8.612	14.997
q	1.189	2.516	1.2823
r^0 (Å)	2.4911	2.8637	2.5222

Figure Captions

Figure 1. Four isomeric forms and energy diagrams of the corresponding to them homotops for the Ni_{12}Al cluster (the darker spheres represent Ni, the grays Al). The diagrams are separated into classes defined by the type of the central atom. The total number of homotops in each class is also shown. Each isomer is depicted by its lowest energy homotop. The isomers are shown in the order of increasing energy and are labeled by roman numerals, which indicate the isomer of Al_{13} with the same geometry (see text). The number labeling each energy level represents the position of the Al atom in the homotop corresponding to that level.

Figure 2. The same as Figure 1, but for Ni_7Al_6 . Because of the large number of homotops that correspond to each class, distributions of the homotop energy levels are shown instead of the levels themselves. The distributions are obtained with an energy box size of 0.03 eV. The homotops of the lowest and the highest energy in each class are labeled. The numbers forming a label of a homotop represent the positions of the Ni atoms in it.

Figure 3. The same as Figure 2, but for Ni_6Al_7 . The numbers in parenthesis indicate the number of additional stationary homotops that correspond to saddles, rather than to minima, of the potential energy surface.

Figure 4. The same as Figure 1, but for NiAl_{12} . The number labeling each energy level represents the position of the Ni atom in the homotop corresponding to that level.

Figure 5. The energy difference between two icosahedral homotops, one of which is the most stable structure in the class with Ni in the center, and the other with Al in the center, as a function of the number of Al atoms in the cluster (see text).

Figure 6. Mixing coefficient as a function of the homotop energy for four classes of Ni_6Al_7 . The pictures show the lowest and the highest energy homotops of each class. The darker spheres represent Ni, the grays Al.

Figure 7. Caloric curves, rms bond length fluctuations and specific heats for Ni_{12}Al , Ni_7Al_6 and NiAl_{12} . Two cases are considered for each composition - one corresponds to the class with Ni in the center, the other - with Al in the center. The pictures represent the lowest energy homotop in each class. These homotops are used as the initial zero-temperature structures of the corresponding dynamics.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7