Competition between face-centered cubic and icosahedral cluster structures

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The binding energy of atoms in icosahedral and face-centered-cubic clusters is calculated numerically for pairwise Morse-potential interactions between atoms and for clusters containing from 561 to 923 atoms, which corresponds to gradual filling of the sixth layer of the icosahedral cluster. Perturbation theory is used to calculate the cluster binding energy, in which the small parameter is the ratio of the interaction energy between non-nearest neighbor atoms to the interaction energy between nearest neighbors. Values of the Morse interaction potential parameter are found for which the energies of clusters with different structures coincide. Under the conditions used in these computations, the strain energy of a cluster can be neglected. Although the contribution of the interaction energy between non-nearest neighbors to the total cluster energy is small, it turns out to be important in finding the level crossing parameter. © *1997 American Institute of Physics.* [S1063-7761(97)02009-X]

1. INTRODUCTION

Two-hundred thirty crystal structures are known to occur naturally at low temperatures.[1–3] The variety of cluster structures is still more extensive. For example, condensed-matter systems consisting of atoms with pairwise interactions form close-packed crystal structures, which include hexagonal and face-centered cubic (*fcc*) structures.[3,4] Clusters of atoms with pairwise interactions can condense into these structures as well, but they also can form icosahedra.[5] Geometrically, the icosahedron has a surface consisting of 20 equilateral triangles. The internal atoms of an icosahedral cluster have 12 nearest neighbors, like a close-packed structure in which all the distances between nearest neighbors are the same. However, in an icosahedral cluster the distance between nearest neighbors belonging to the same layer exceeds the distance between nearest neighbors belonging to adjacent layers by roughly 5%. Therefore, the structure of an icosahedron is unsuitable for macroscopic systems. However, for systems made up of a finite number of bound cluster atoms it can turn out to be preferable at low temperatures.

The advantage of the icosahedral structure compared to the close-packed structure lies in the larger number of bonds between nearest neighbors. Therefore, this structure will be energetically more favorable for small clusters. In particular, for clusters of inert gases a transition from an icosahedral structure to an *fcc* structure occurs when the numbers of atoms in the cluster reaches $n=1000-3000$.[6–8] For clusters of atoms interacting via a Lennard–Jones potential, the transition from the icosahedral structure to a cuboctahedron—one of the *fcc* structures—occurs when the number of atoms in the cluster satisfies $n\sim10^4$ (Refs. 9,10), while for clusters with short-range interactions between atoms the transition between the icosahedral and *fcc* structures takes place for $n=200-500$.[11,12] This extreme sensitivity of the transition region to the type of atomic interaction requires a more careful analysis of the competition between these structures. In this paper we carry out this analysis using the method developed in Ref. 13 for a Morse-potential interaction between atoms. We then illustrate the competition between structures by using a ''phase diagram'' (see Ref. 13) on which we plot the Morse-potential parameter at which the *fcc* and icosahedral structure energies cross versus the number of atoms in a cluster. Constructing this phase diagram is in fact the main task of this article.

Note that we have excluded clusters with hexagonal structure from the discussion. This structure competes with the *fcc* structure for small-sized clusters, when the icosahedral structure is preferred, but in the range of atom numbers where the icosahedral and *fcc* structures compete, both these structures characteristically bind atoms to the cluster with higher binding energies than the hexagonal structures do.[14,15] In what follows we identify as ''icosahedral'' those clusters whose core has the structure of an icosahedron, although their surface occupied layers can have either *fcc* or icosahedral structures,[6,7,16] depending on the degree of occupation of the layer. We specify the structure of the surface layer of atoms by choosing the structure with the larger atomic binding energy for the given number of atoms.

A cluster with *fcc* structure grows by filling its planar facets.[14,17] Such structures come in pairs, depending on whether the core of the cluster does or does not contain a central atom. Of these two possible structures for a cluster we choose the one with the larger atomic binding energy for the given number of atoms in the cluster. Thus, when we compare *fcc* structures with icosahedra, we first choose the optimal configuration of atoms among the *fcc* structures, i.e., the one that ensures the maximum binding energy. In reality, each of the optimal atomic configurations will correspond to the maximum number of bonds between nearest neighbors.

We then compare the energies of optimal configurations of atoms with *fcc* and icosahedral structures for clusters with

numbers of atoms $n=561-923$, which corresponds to gradual filling of the sixth layer of the icosahedral structure. This comparison allows us to understand the distinctive features of the competition between these structures.

Note that the variety of crystal structures observed in nature is determined by the way the type of interactions between atoms differs from system to system. The assumption that this interaction is pairwise for a system of bound atoms in which the atoms retain their individuality is correct if the interaction potential between two atoms does not depend on the positions of the surrounding atoms of the system. This will be the case when the interaction potential between two atoms is small compared to characteristic single-atom quantities, in particular the ionization potential of an atom. Hence, our analysis will apply primarily to clusters consisting of inert-gas atoms or gas molecules. In other types of interactions the atoms lose their individuality when they enter the cluster, which complicates the analysis of the cluster structures. However, even the simple case under discussion here, i.e., pairwise atomic interactions, admits multiple cluster structures and their hybrids, such that the optimal cluster structures have *fcc* or icosahedral cores.

2. ENERGETICS OF LARGE CLUSTERS

The Morse-potential interaction between two atoms has the following form as a function of the interatomic distance R:

$$U(R)=D\{\exp\,[2\alpha(R_e-R)]-2\exp\,[\alpha(R_e-R)]\},\quad (1)$$

where the potential minimum corresponds to the equilibrium distance R_e between atoms for a diatomic molecule. In what follows we set the dissociation energy of the diatomic molecule equal to $D=1$. We used a standard computer program to determine the energy of a cluster for a given configuration of its atoms, so that the total binding energy of the cluster atoms is defined as

$$E=-\sum_{i,k} U(r_{ik}),\quad (2)$$

where i,k label the atoms and r_{ik} the distances between them.

We must take into account that the interaction with non-nearest neighbors changes the distance between nearest neighbors to a value different from the equilibrium distance R_e for a diatomic molecule. In doing do we make use of the standard method[4] for the Morse interaction potential, writing the total energy of the cluster atoms Eq. (2) in the form

$$E=2\exp\,(\alpha R_e)F(\alpha a)-\exp\,(2\alpha R_e)F(2\alpha a),\quad (3)$$

where

$$F(\alpha a)=\sum_{i,k}\exp\,(-\alpha r_{ik}),\quad (4)$$

a is the distance between nearest neighbors (the basis for the given cluster), and the sum runs over all bonds. We then take the derivative of this function, which is

$$F'(\alpha a)=\frac{dF}{d(\alpha a)}=\sum_{i,k} r_{ik}\exp\,(-\alpha r_{ik}).\quad (5)$$

Once we have optimized the energy of the cluster E, we find the optimum distance a between nearest neighbors from the ratio

$$\exp\,(\alpha R_e)=g(\alpha a)=F'(\alpha a)/F'(2\alpha a),\quad (6)$$

so that the optimum binding energy of the cluster under study is

$$E=g(\alpha a)F(\alpha a)-\frac{1}{2}g^2(\alpha a)F(2\alpha a).\quad (7)$$

We then separate in the sum Eq. (4) the terms that involve nearest-neighbor F_{nn} and non-nearest neighbor interactions F_{nnn}, so that $F=F_{nn}+F_{nnn}$. This allows us to conveniently divide up the cluster energy in the standard way[13] into a nearest-neighbor interaction energy E_{nn}, a non-nearest neighbor interaction energy E_{nnn}, and a strain energy $E_{\rm str}$:

$$E=E_{nn}+E_{nnn}+E_{\rm str}.\quad (8)$$

Here

$$E_{nn}=2\exp\,(\alpha R_e)F_{nn}(\alpha a)-\exp\,(2\alpha R_e)F_{nn}(2\alpha a).\quad (9)$$

We define the interaction energy of non-nearest neighbors in the same way:

$$E_{nnn}=2\exp\,(\alpha R_e)F_{nnn}(\alpha a)-\exp\,(2\alpha R_e)F_{nnn}(2\alpha a).\quad (10)$$

In these expressions, the quantity a acts as the basis for the short-range interaction, which includes only the interaction between nearest neighbors. The strain energy arises from the change in the nearest-neighbor distance in the cluster from a to its optimal value.

Let us first discuss the case of short-range interactions between atoms in the cluster, when only the interaction between nearest neighbors is taken into account. Then for an *fcc* cluster we obtain

$$F_{nn}(a)=K\exp\,(-\alpha a),\quad F_{nnn}=0,\quad (11)$$

where K is the total number of bonds between nearest neighbors for the given cluster. If we take the value of this quantity from Ref. 17, we have $F'_{nn}=-F_{nn}$, so that optimization of the energy gives $g(\alpha a)=\exp(-\alpha a)$ and $a=R_e$ for nearest neighbors. Then we obtain

$$E=K.\quad (12)$$

The interaction energy of non-nearest neighbors E_{nnn} and the strain energy $E_{\rm str}$ both equal zero.

For an icosahedral cluster, there are two distances between nearest neighbors. Let us denote the distance between nearest neighbors belonging to adjacent layers by R, and the distance between nearest neighbors in the same layer by R_0; then $R=0.951R_0$. Introducing A, the number of bonds between nearest neighbors in adjacent layers (bond length R) and B, the number of bonds between nearest neighbors in the same layer (bond length R_0), we obtain

TABLE I. Cluster parameters (m is the number of filled layers of the icosahedral cluster, n the number of cluster atoms.

m	n	A	B	K	$\alpha_* R_e$
3	147	276	420	668	8.21
4	309	648	900	1507	6.60
5	561	1260	1650	2844	6.07
6	923	2172	2730	4809	5.54
7	1415	3444	4200	7527	4.96
8	2057	5136	6120	11118	4.44

$$F_{nn}=A\ \exp\ (-\alpha R)+B\ \exp\ (-\alpha R_0). \tag{13}$$

Optimizing the binding energy of the cluster atoms, we find for the optimum distance between nearest neighbors in neighboring layers[11,12]

$$R=R_e[1-0.047B/(0.904A+B)]. \tag{14}$$

If we limit ourselves only to interaction between nearest neighbors, this leads to the following expression for the total energy of an icosahedral cluster with Morse-potential interactions between atoms:[11,12]

$$E=A+B-0.0024\alpha^2AB/(0.904A+B). \tag{15}$$

Equality of the icosahedral and *fcc* cluster energies for short-range interactions between atoms in the cluster corresponds to the following value of the parameter in the Morse interaction potential:

$$\alpha_*=20.4[(A+B-K)(0.904A+B)/(AB)]^{1/2}. \tag{16}$$

In Table I we compare the parameters of clusters whose number of atoms corresponds to filled layers of the icosahedral structure. Table II lists these parameters versus the number of atoms for icosahedral clusters in which 10 surface triangles are occupied above each filled layer. In these tables we list values of the parameter α_* corresponding to energy level crossing, which is determined by Eq. (16). This comparison identifies the range of values of parameter α in which a competition between the structures takes place.

Next, we include the interaction of non-nearest neighbors as a perturbation, i.e., we construct a perturbation theory for Morse-potential interactions between cluster atoms in which the small parameter is $\Delta=F_{nnn}(\alpha R_e)/F_{nn}(\alpha R_e)$. This perturbation theory is valid for $\alpha>4$. In Table III we list values of this small parameter for *fcc* (Δ_{fcc}) and icosahedral clusters ($\Delta_{\rm ico}$). Table III also lists values of the parameter $\gamma=-d\ \ln F_{nnn}(\alpha R_e)/d\ln(\alpha R_e)$. Since R_e/γ is the characteristic distance between cluster atoms, which determines the value of F_{nnn}, it follows that $\gamma>1$. For this reason, we may neglect the second term in Eq. (10) compared to the first. Actually, in the range of cluster sizes of interest $n=561-923$, the quantity $\exp(\alpha R_e)F_{nnn}(2\alpha R_e)/F_{nnn}(\alpha R_e)$ equals 0.11 when $\alpha R_e=4$, 0.074 when $\alpha R_e=5$, and 0.054 when $\alpha R_e=6$.

TABLE II. Parameters of icosahedral clusters having m filled layers and 10 occupied surface triangles above each filled layer (n is the number of cluster atoms).

m	n	A	B	K	$\alpha_* R_e$
4	216	442	603	1024	5.74
5	420	928	1203	2094	5.31
6	724	1684	2103	3730	4.93
7	1148	2770	3363	6042	4.89
8	1712	4246	5043	9181	4.32

TABLE III. Non-nearest neighbor interaction parameters for clusters with the Morse-potential interaction between atoms.

αR_e	γ_{fcc}	Δ_{fcc}	$\gamma_{\rm ico}$	$\Delta_{\rm ico}$
4	1.68	0.21	1.72	0.23
5	1.61	0.11	1.64	0.12
6	1.56	0.061	1.60	0.071
7	1.52	0.036	1.56	0.042
8	1.50	0.021	1.53	0.026
10	1.46	0.0082	1.50	0.010

Thus, within the framework of this perturbation theory, we obtain for binding energies of atoms of an *fcc* cluster

$$E=2K\ \exp\ [\alpha(R_e-a)]-K\ \exp\ [2\alpha(R_e-a)] +2F_{nnn}(\alpha a)\exp\ (\alpha R_e). \tag{17}$$

Optimizing the cluster energy with respect to distance between nearest neighbors a, we obtain for this distance

$$\alpha(R_e-a)=\gamma F_{nnn}(\alpha R_e)/F_{nn}(\alpha R_e)=\gamma\Delta. \tag{18}$$

From this, we find for the terms in Eq. (8)

$$E_{nn}=K,\quad E_{nnn}=2K\Delta,\quad E_{\rm str}=\gamma^2\Delta^2K. \tag{19}$$

In a similar way we obtain for the total binding energy of atoms in an icosahedral cluster

$$E=A+B-0.0024\alpha^2AB/(0.904A+B)-(A+1.106B) \times(R'-R)^2+2F_{nnn}(\alpha R)\exp\ (\alpha R_e), \tag{20}$$

where the distance R' is given by Eq. (14): $R'=R_e[1-0.047B/(0.904A+B)]$. After optimizing the binding energy of the cluster atoms for a given value of the parameter αR_e according to the parameter R, we obtain for the individual terms of Eq. (8)

$$E_{nn}=A+B-0.0024\alpha^2AB/(0.904A+B),$$
$$E_{nnn}=2F_{nnn}(\alpha R')\exp(\alpha R_e),$$
$$E_{\rm str}=(\gamma\alpha)^2F_{nnn}^2(\alpha R')\exp\ (2\alpha R_e)/(A+1.106B). \tag{21}$$

As in the case of *fcc* clusters, it follows from these expressions that $E_{nnn}/E_{nn}\sim\Delta$, $E_{\rm str}/E_{nn}\sim\Delta^2$.

Note that for a given value of the parameter αR_e the specific quantities F_{nn}/n and F_{nnn}/n are smooth functions of the number of atoms n in the cluster. For example, in the interval of cluster sizes we are interested in the quantity K changes from 2844 for $n=561$ to 4809 for $n=923$. Accordingly, the quantity K/n changes from 5.07 to 5.21, i.e., by a few percent. In contrast to the smooth function that describes this quantity, the number of bonds between nearest neighbors as a function of n is discontinuous at magic numbers of atoms in the cluster; however, the difference of these functions even for the magic numbers of atoms does not exceed

TABLE IV. Parameters for competition between *fcc* and icosahedral structures.

n	A	B	K	$\alpha_* R_e$
561	1260(ic)	1650	2844(nc)	7.1
606	1395(fcc)	1740	3093(nc)	6.8
636	1485(fcc)	1800	3255(nc)	6.4
681	1620(fcc)	1890	3490(c)	6.2
688	1592(ic)	1996	3529(c)	6.7
724	1677(ic)	2103	3730(c)	6.7
760	1774(ic)	2210	3934(c)	6.6
817	1916(ic)	2385	4234(c)	6.8
874	2058(ic)	2564	4575(c)	6.5
923	2172(ic)	2730	4809(c)	7.1

20, i.e., is relatively small compared to the total number of bonds. The function F_{nnn}/n is a smoother function of the number of atoms in the cluster, since it describes the interaction of non-nearest neighbors. Thus, in calculating the binding energy of atoms in a cluster we may assume that the specific energetic parameters do not depend on n within a certain range of n. However, this assumption can lead to errors in analyzing the competition between *fcc* and icosahedral structures.

Actually, it follows from the data of Tables I, II that the numbers of bonds between nearest neighbors are close for optimal configurations of atoms in *fcc* and icosahedral structures, so that their relative difference is a few percent over a wide range of cluster parameters. From Table III it is clear that the non-nearest neighbor interaction energies are also close. Table IV summarizes the results of a comparison of clusters with different structures, for each of which the optimum configuration of atoms has been chosen. While the core of the cluster can have only an icosahedral structure, its (outermost) filling layer can have either *fcc* or icosahedral structure. The structure of this surface layer is indicated next to the number of bonds between nearest neighbors by the letters *ic* or *fcc* respectively. An *fcc* structure is preferred for the surface layer of an icosahedral cluster as long as no more than eight surface triangles of the cluster are occupied. For larger numbers of occupied triangles a surface layer with icosahedral structure becomes energetically more favorable.

As for *fcc* clusters, there is also a competition between structures with and without a central core atom. As the number atoms in the cluster increases, these structures are found to alternate. Within the range of cluster sizes under discussion here, the structure with a central core atom turns out to be energetically favorable for the most part. The preferred core structure of the *fcc* clusters is indicated in Table IV by the letters *c* or *nc* in brackets next to the number of bonds K between nearest neighbors of the cluster, denoting the presence or absence of a central atom in the cluster core.

Table IV lists values of the parameter $\alpha_* R_e$ at which the binding energy of a cluster consisting of this number of atoms becomes the same for *fcc* and icosahedral cluster structures for optimum configurations of atoms. Equations (19), (20) were used for the *fcc* and icosahedral cluster energies. The parameters for the optimum configuration of an icosahedral cluster with short-range interactions between the atoms were taken from Refs. 11, 12, while the parameters for the optimum configuration of an *fcc* cluster are from Refs. 14, 17. The parameters for long-range interactions between cluster atoms, including the interaction between non-nearest neighbors, were calculated for a Morse-potential interaction by numerical methods using Eq. (4). Note that for the interval of cluster sizes $n=561-923$ being analyzed, the values of the parameter $\alpha_* R_e$ of interest in the range in which these cluster structures compete are concentrated in the range $\alpha_* R_e = 6-7$, so that the interaction between nearest neighbors gives the primary contribution to the total binding energy of the cluster atoms. This justifies our method, in which we choose the optimum configurations of atoms for short-range atomic interactions. Nevertheless, the interactions of non-nearest neighbors are important in analyzing the competition between structures.

Actually, the data of Tables I, II, IV imply that the numbers of bonds between nearest neighbors are similar for the *fcc* and icosahedral clusters. Hence, although the non-nearest neighbor interaction potential in the cluster is small compared to the interaction between nearest neighbors, it can turn out to be comparable to the difference between the nearest neighbor interaction potentials for these structures. In fact, it follows from Tables I, II, IV that the difference $A+B-K$ entering into Eq. (16) is a few percent of $A+B$. This is the same order of magnitude as the interaction potential between non-nearest neighbors in the range of parameter values $\alpha R_e = 6-7$, where these structures compete (see Table III). For the icosahedral structure the interaction potential between non-nearest neighbors is larger than it is for the *fcc* structure, so that this interaction increases the energy level crossing parameter $\alpha_* R_e$ above its value when the interaction includes nearest neighbors only. Note that in the energy level crossing range the strain energy, according to Eqs. (19), (21), is proportional to Δ^2, and hence is unimportant.

The quantity $A+B-K$ is sensitive to the structure of the clusters, exhibiting local maxima at magic numbers of the icosahedral cluster and minima at magic numbers of the *fcc* cluster. Consequently, in a range of cluster sizes that includes magic numbers the quantity $\alpha_* R_e$ will be an irregular function of n. The non-nearest neighbor interaction makes this function smoother, since this interaction is insensitive to the magic numbers.

Note that the popular Lennard–Jones potential corresponds to a Morse potential with the parameter $\alpha R_e = 6$. Then our analysis implies that for atoms interacting via the Lennard–Jones potential these cluster structures will compete for $n > 1000$, which corresponds to Ref. 11.

3. CONCLUSION

Thus, we have shown that the competition between icosahedral and *fcc* cluster structures for optimal configurations of atoms, equal numbers of atoms, and pairwise interaction potentials between these atoms, is conveniently analyzed in terms of the parameter αR_e of the Morse-potential for which the energies of these clusters coincide.[13] We have calculated these cluster energies numerically for clusters containing $n=561-923$ atoms, which corresponds to filling

of the sixth layer of an icosahedral cluster. It follows from these calculations and our analysis that our energy level crossing parameter $\alpha_* R_e$ is determined by interactions between both nearest neighbors and non-nearest neighbors in the cluster. In the range of cluster sizes of interest, this parameter varies in the range $\alpha_* R_e = 6-7$ and is a nonmonotonic function of the number of atoms in the cluster. Within this range of values of the parameter αR_e the primary contribution to the cluster energies of both structures comes from the interaction between nearest neighbors, so that the interaction of non-nearest neighbors is a few percent of the total cluster energy. Nevertheless, since the number of bonds between nearest neighbors turns out to be close for the optimal configurations of atoms of both structures, it is important to include the interaction between non-nearest neighbors when determining the parameter $\alpha_* R_e$ at which the energies of these structures coincide. Interactions between non-nearest neighbors increase the value of $\alpha_* R_e$ and make the dependence of this parameter on the number of atoms in the cluster smoother.

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