PHYSICAL REVIEW B **73**, 035425 (2006)

Ab initio calculations of the stability of a vacancy in Na clusters and correlation with melting

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(Received 29 August 2005; published 23 January 2006)

We report results of *ab initio* calculations on Na_N, $N=55$, 147, and 309 clusters that show icosahedral growth to be most favorable in agreement with the recent photoelectron spectroscopy data. The icosahedral structures are found to be significantly compressed in the central region. However, a vacancy at the center or the first shell is found to cost much higher energy compared to other sites in the clusters. The vacancy formation energy is the lowest at the vertex sites followed by the edge sites on the cluster surface. These results show that disordering is easier to happen at the surface region of the clusters. Recent experiments on sodium clusters also suggest surface premelting. Furthermore, we obtain a higher value of the vacancy formation energy for $N=55$ compared to the case of $N=147$ or 309. This is in agreement with the experimental finding of a higher melting temperature for Na_{55}. The perturbation due to a central vacancy is found to be mainly confined to two atomic shells similar to the phenomena at surfaces of bulk metals.

DOI: 10.1103/PhysRevB.73.035425 PACS number(s): 61.46.−w, 36.40.−c, 64.70.Dv

I. INTRODUCTION

Vacancies are common defects in bulk materials and play an important role in processes such as diffusion, disorder, mixing, and melting. Therefore much attention has been paid to understand vacancy formation in bulk materials.[1–3] However, the energetics of vacancies in nanomaterials that are currently of great interest, is not much explored. Such a knowledge is highly relevant to several technologically important phenomena such as mixing and high diffusion in nanomaterials as well as lower melting temperatures of nanoparticles compared with the corresponding bulk. Clusters of sodium have been widely studied since the pioneering work of Knight *et al.*[4] and have been used as a bench mark to understand the electronic properties of free electronlike simple metal clusters.[5–7] Recently, studies of the melting of sodium clusters have attracted much attention from both experiments[8–10] and theory.[11–15] Clusters and nanoparticles have a large fraction of atoms on the surface and phenomena such as creation of vacancies, disordering, roughening, and premelting that occur on surfaces of bulk materials before melting, could occur in clusters as well. Quantum effects may play an additional important role because of the size dependent properties of clusters. Moreover, clusters and nanoparticles could have atomic structures quite different from that of the bulk and this could make a further difference in the behavior of vacancies and melting phenomenon in such systems. Here we present the results of an *ab initio* study on the stability of a vacancy in large Na_N, $N=55$, 147, and 309 clusters which show that the lowest vacancy formation energy can be correlated with the trends observed[9,10] in the melting temperature.

The stability of sodium clusters can be understood within a jellium model[5–7] according to which clusters with 2, 8, 20, 40, 58, 92, … atoms are magnetic due to the filling of $1s,1p,(1d,2s),(1f,2p),1g,(3s,2d,1h),\ldots$ electronic shells. In a jellium model one replaces the ionic distribution by a uniform positive background and therefore the atomic structures of clusters are considered to be unimportant. A vacancy at the center of such a jellium sphere has been shown[16] to have a large value of formation energy for magnetic Na_N, $N=8$, 20, 40, and 92 clusters. However, melting temperatures of Na clusters do not correlate with electronic shells and cannot be understood by using only the electronic shell structure as *melting is related to the disordering of the atomic structure*.[7–10,14,15] Moreover the jellium model does not provide the answer to a basic question: Are vacancies stable in clusters? For the understanding of the stability of a vacancy an atomistic approach is needed that incorporates ionic relaxations around a vacancy.

Elemental as well as doped clusters of many materials often have an icosahedral growth but in crystalline materials icosahedral symmetry is forbidden. Therefore there could be a different behavior of a vacancy in clusters compared with bulk. In particular in a regular icosahedron (consider a hard ball model) the nearest vertex to vertex distance is about 5% longer than the center to vertex.[17] The different interatomic bond lengths in an icosahedron create increasing strain in packing as the number of balls increases. In a metal cluster the repulsive interaction is softer compared with hard balls and the strain in the bonding between surface atoms can be reduced to some extent by compression as the cluster size grows. Also intuitively the strain could be reduced if the central region in the cluster is occupied by a smaller atom. For large icosahedral clusters one could expect that significant strain could build up so that even a vacancy at the center could become favorable. Indeed studies on homonuclear icosahedral clusters using Lennard-Jones potential[18] show that the energy per atom of a cluster with a vacancy at the center is lower than the value for a cluster without a vacancy beyond a size of about 1000 atoms. However, for metal clusters such a pair potential based approach is not appropriate to understand their bonding behavior and a study based on *ab initio* methods is necessary.

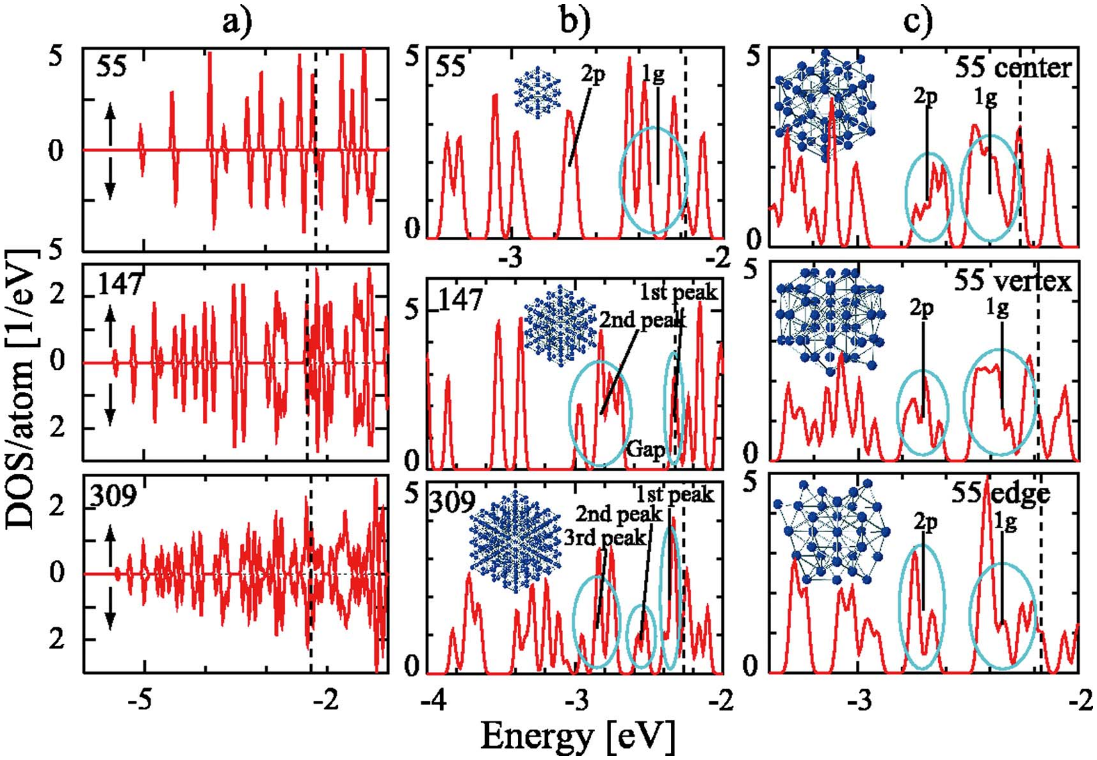

FIG. 1. (Color online) (a) The electronic density of states (DOS) obtained by Gaussian broadening of the electronic spectra of icosahedral Na_N clusters. The arrows show spin-up and spin-down spectra while the broken line shows the HOMO. (b) The total DOS near the HOMO. The inset shows the atomic structures of the clusters. States for $N=55$ near the HOMO are marked using a spherical jellium model for comparison with the PES experimental result (Refs. 10 and 19). For $N=147$ and 309, "1st peak," etc., mean the first peak, etc., seen in PES (Ref. 10). (c) The total DOS and the structures of a Na_{55} cluster with a vacancy at the center, vertex, and edge cites. The splitting of the states and broadening can easily be noticed.

Recent experiments on photoelectron spectra (PES) and melting behavior[9,10,19] of Na_N, $N=55$, 147, and 309 clusters suggest icosahedral growth that corresponds to the Mackay icosahedral structures[17] of these clusters with 2, 3, and 4 icosahedral atomic shells, respectively, and an atom at the center. Similar evidence was obtained from the mass abundance of large sodium clusters.[20] Our results also show icosahedral growth to be the most favorable. However, for the understanding of the behavior of clusters at nonzero temperatures as well as phenomena such as disordering, melting, and the possibility of structural vacancies, one would need to study site specific vacancy formation energies since in a cluster the local environment around different atoms is often different. In this paper we present results of such a study on sodium clusters.

In Sec. II we present our computational approach. The results are given in Sec. III and are discussed in the light of the data available from PES as well as melting experiments.

II. COMPUTATIONAL METHOD

We use an ultrasoft pseudopotential method[21] with a plane wave basis and spin-polarized generalized gradient approximation for the exchange-correlation energy.[22] The cutoff energy for the plane wave expansion is taken to be 48.7 eV. A large cubic unit cell with edge length ranging from 2.5 nm to 4.5 nm is used to study clusters of up to about 3 nm diameter. For such large unit cells, Brillouin zone integrations are performed with only the Γ point. For understanding the stability of a vacancy in Na_N clusters, we performed calculations by (1) removing an atom from an N-atom cluster to have $N-1$ atoms and a vacancy and (2) then placing the removed atom on the surface to have an N atom cluster with a vacancy. In both cases several vacancy sites are considered. All structures are optimized without using any symmetry constraint until the absolute value of each Cartesian component of the force on each ion becomes less than 0.005 eV/Å. In all cases different spin-multiplicities have also been considered.

III. RESULTS

For Na_{55} an icosahedral isomer is found to be distinctly stable with $3\mu_B$ magnetic moment. The decahedral isomer lies 0.803 eV higher in energy while a cuboctahedron transforms to the icosahedral structure. The electronic states of Na_{55} [Fig. 1(a)] near the highest occupied molecular orbital (HOMO) level can be labelled as $1g$ type within a spherical jellium model and the other occupied states as $1s, 1p, 1d, 2s, 1f$, and $2p$ type. In icosahedral symmetry $1g$ state splits into H_g and G_g states. The up-spin states and the down-spin H_g state are fully occupied while the down-spin G_g state has only one electron. This leads to small distortions in the structure that lift the degeneracies of these states but a high-spin isomer with $3\mu_B$ magnetic moment is still energetically favored. The Gaussian broadened spectrum (up- and down-spin states summed up) near the HOMO is shown in Fig. 1(b) and the $1g$ and $2p$ occupied states are marked. Wrigge *et al.*[19] have measured PES spectra from cation sodium clusters and they found $1g$ states for Na_{55}^{+} near the HOMO similar to the results of neutral Na_{55} obtained by us as well as earlier by Akola *et al.*[11] from *ab initio* local density functional calculations. Itoh *et al.*[23] have also performed a comparative study of the electronic structures of Na and Cu clusters and the general features of the electronic structures are found to be similar in the two cases near the HOMO. The PES spectrum of Cu_{55}^{-} has been measured[24] and the splitting of the $1g$ state into H_g and G_g is clearly seen followed by the $2p$ states as obtained by us for Na. These results point to more significant effects of temperature on the broadening of the electronic spectra of Na clusters as it can be expected from much lower binding energies of sodium clusters compared with those of copper. It is to be noted that due to the odd number of electrons in neutral clusters, the calculated up- and the down-spin states are also split by the lifting of the degeneracy due to small distortions.

Further calculations on icosahedral Na_{147} and Na_{309} clusters show $1\mu_B$ and $3\mu_B$ isomers to have the lowest energy, respectively. The calculated electronic spectra [Figs. 1(a) and 1(b)] agree well with the PES data of Haberland *et al.*[10] For Na_{147} the PES data shows a peak near the HOMO followed by a significant gap and then a broad main peak [marked in Fig. 2(b)] in the occupied states. All these features as well as the shape of the peaks are well reproduced from our calculations. Similarly for Na_{309}, a large peak near the HOMO followed by a small peak and then a broad peak with splitting [marked in Fig. 2(b)] agree well with the PES results[10] and lend support to the icosahedral growth.

An important feature of the optimized structures is the compression (Table I) at the center that increases with the cluster size. Alkali metals are highly compressible and icosahedral growth has been suggested[25] to be favorable for such systems. We find that in the icosahedral structure of Na_N clusters the center (C) to the first atomic shell vertex (V1) mean bond length decreases from 3.58 Å for $N=55$ to 3.46 Å for $N=309$ compared with the calculated bulk value of 3.64 Å. For the outer atomic shells, say nth shell we distinguish between the 12 vertex atoms (Vn) that lie on top of the vertex atoms in the inner shells and the remaining atoms. Among the latter, we denote atoms on the edges as En. Atoms on edge centers are denoted as ECn and the others (edge off-center) as EOCn. The remaining atoms on the faces are represented as Fn. The mean bond length between the nearest vertices in the outer two atomic shells, V1-V2 for $N=55$ contracts (3.46 Å) compared with C-V1 but for $N=309$, V3-V4 expands (3.59 Å) compared with C-V1 though it is shorter than the bulk value. However, V2-V3 (3.65 Å) becomes longer than the bulk value, showing an oscillatory behavior. Also for $N=147$, V2-V3 expands (3.66 Å) compared with bulk. On the other hand the mean nearest neighbor bond length between neighboring atomic shells (Sn-S$n+1$), excluding the Vn-V$n+1$ bonds, shows elongation in all cases as one goes outwards from the center (see Table I).

A vacancy at the center further contracts the first shell but there is an expansion between the first and the second shells [Table I and Fig. 2(a)]. Beyond the second shell the changes are much less. This is similar to the oscillatory atomic relaxations on metal surfaces due to the Friedel oscillations in the electronic charge density that are often significant in the top few layers.[26] For clusters, a vacancy creates an internal surface. Interestingly the diameter of the cluster shrinks only slightly for $N=55$ and 147 and remains nearly the same for $N=309$ (Table I). Therefore *the effects of a vacancy in metal clusters are also local as it is the case in bulk systems and with increasing cluster size, shells away from the vacancy have only minor effects because metallic systems have good screening. Therefore, at least in large icosahedral clusters of metals, a central vacancy may not lead to better cohesion between the surface atoms.*

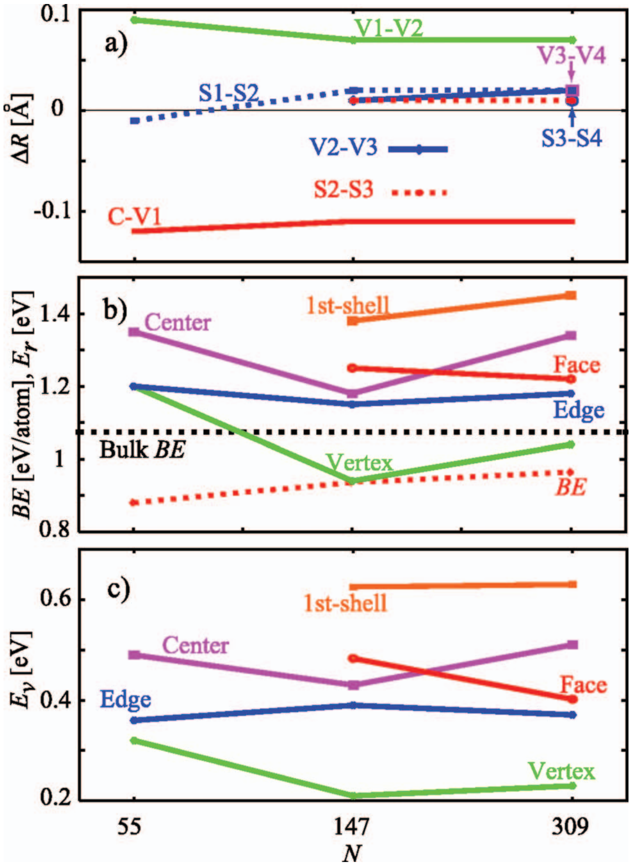

FIG. 2. (Color) (a) The bond length change after an atom is removed at the center (ΔR) for Na_N clusters. The differences between the values for clusters without and with a vacancy are shown. C-V1 is the average bond length between center (C) and vertex (V1), Vn-V$n+1$ are the mean nearest neighbor bond lengths between vertices Vn and V$n+1$, while Sn-S$n+1$ are the mean nearest neighbor bond lengths between shells Sn and S$n+1$ excluding vertex-vertex bond lengths for each icosahedral isomer. As an example, C-V1 shows 0.12 Å decrease in average distance from center to first shell vertex atoms in going from Na_{55} to Na_{54} due to the creation of a vacancy at the center in the latter case. These numbers are easily obtained from Table I. (b) The binding energy (BE) of the clusters without a vacancy and atom removal energy E_r, and (c) the lowest vacancy formation energy E_v for vacancies at different sites in a cluster.

TABLE I. Average bond lengths (Å) between center (C) and vertex (Vn) on the nth atomic shell (Sn) from the center, Vn and Vn+1, Sn and Sn+1 excluding the bonds between the nearest vertices, C and edge (En), C and face (Fn), C and edge center (C-ECn), C and edge off-center (C-EOCn) for each icosahedral isomer. Structures of N=54, 146, and 308 correspond to a vacancy at the center. Bulk value is 3.64 Å.

N	C-V1	V1-V2	V2-V3	V3-V4	S1-S2	S2-S3	S3-S4	C-V2	C-E2	C-V3	C-E3	C-F3	C-V4	C-EOC4	C-EC4	C-F4
54	3.46	3.55			3.61			7.01	6.07							
55	3.58	3.46			3.62			7.04	6.13							
146	3.40	3.62	3.67		3.60	3.65		7.02	6.02	10.69	9.32	8.61				
147	3.51	3.55	3.66		3.58	3.64		7.06	6.05	10.72	9.35	8.63				
308	3.35	3.66	3.67	3.61	3.63	3.66	3.67	7.01	6.02	10.68	9.32	8.63	14.29	12.84	12.22	11.80
309	3.46	3.59	3.65	3.59	3.61	3.65	3.66	7.05	6.06	10.70	9.36	8.65	14.29	12.84	12.23	11.81

Figure 3 shows the electronic charge density variation in an approximately two-fold symmetric plane of Na$_N$ icosahedron passing through the center of the cluster. In all cases the most significant changes occur near the centers of the clusters. In going from N=55 to 147, there is an increase in the electronic charge density at the center and the maximum value is achieved for N=309 which is expected from the compression. The oscillatory behavior of the electronic charge density can clearly be seen. When a vacancy is created at the center as for the 54-atom cluster, the electronic charge density shows a dip near the center but away from it the change in the electronic charge density is quite small showing the perturbation to be quite localized.

The binding energy of a cluster is defined as

$$E_c = -E(N,0)/N + E_{\text{atom}}. \tag{1}$$

Here $E(N,N_v)$ and E_{atom} are the energies of a relaxed cluster with N atoms and N_v vacancies and a sodium atom, respectively. As shown in Fig. 2(b), E_c increases with the cluster size and in the limit $N\rightarrow\infty$, it extrapolates to the bulk value E_{bulk}=1.07 eV/atom following the relation:

$$E_c = E_{\text{bulk}} - AN^{-\frac{1}{3}} \tag{2}$$

in a liquid-drop model.[5–7] Here A is a constant related to the surface energy. The extrapolated value of E_{bulk} agrees well with the calculated value of 1.07 eV/atom. To understand the stability of a vacancy in Na$_N$ cluster, we first calculated the energy E_r needed to remove an atom from a cluster,

$$E_r = -E(N,0) + E(N-1,1) + E_{\text{atom}}. \tag{3}$$

Here $E(N-1,1)$ is the energy of a cluster in which an atom is removed from the desired site and the cluster structure is relaxed. In order to choose the initial structures with a vacancy, we neglected small distortions from complete I_h symmetry for each cluster size. This leads to only a few

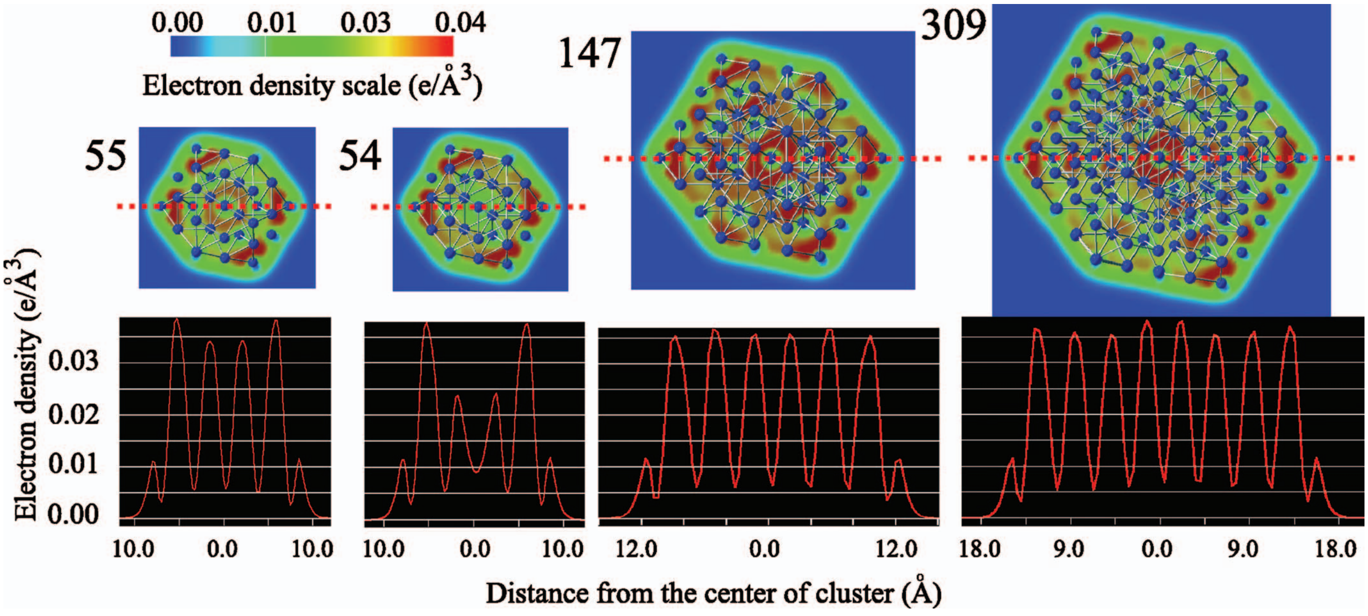

FIG. 3. (Color) The electronic charge density variation for Na$_N$, N=55, 147, and 309 clusters in an approximate two fold symmetric plane passing through the center. The density scale is shown by using different colors. The lower graphs also show the electronic charge density variation along the dotted line. The electronic charge density variation is also shown for Na$_{54}$ cluster with a vacancy at the center. The oscillatory behavior of the density can be seen.

inequivalent sites for a vacancy. For example, only four inequivalent sites are enough to cover all possibilities of a vacancy in Na_{55}. In the second step the vacancy formation energy E_v is calculated for the optimized atomic strcuture of Na_N cluster without a vacancy by removing an atom at the desired site and placing it on the surface of the cluster. The site at which the atom is placed is selected to be a hollow site on a face because such Na clusters are expected to construct tetrahedral packing from our studies on many cluster sizes.[23] After optimizing these structures, we obtained site dependent E_v. Practically E_v can be obtained from the relation

$$E_v = E(N,1) - E(N,0). \tag{4}$$

Approximate form of this equation is frequently used for the calculation of bulk vacancy formation energy.[27] We tried several different sites for a vacancy and different sites to place the removed atom on the surface and in each case the structure has been relaxed to find the local minimum. In the limit of large N, E_v is the vacancy formation energy in bulk but in a cluster it depends on the site at which the vacancy is created.

For Na_N with $N=55$, 147, and 309, E_r at the center of the cluster is calculated to be 1.35, 1.18, and 1.34 eV, respectively. The $N-1$ atom cluster with a vacancy has 4, 2, and 2 μ_B magnetic moment. Further calculations on removal of an atom from the surface and other sites inside the clusters show [Fig. 2(b)] that E_r has the lowest value for a vertex on the surface in each case (1.20, 0.94, and 1.04 eV for $N=55$, 147, and 309, respectively, with the $N-1$ atom cluster having 4, 0, and 4 μ_B magnetic moment). The next favorable site for an atom removal is an edge site on the surface with $E_r=1.20$, 1.15, and 1.18 eV for $N=55$, 147, and 309, respectively. As it can be expected, the value of E_r for a vacancy on a face site is higher than on a vertex or edge site [see the results for $N=147$ and 309 in Fig. 2(b)]. It is higher than a vacancy at the center for $N=147$ but becomes lower in the case of $N=309$. Our calculations show that it costs maximum energy to remove an atom from the first icosahedral shell and the values for $N=147$ and 309 are 1.36 and 1.45 eV, respectively. The next largest value of E_r is for the center of $N=55$ cluster as mentioned above followed by 1.34 eV at the center of Na_{309} and 1.25 eV for a face on the surface of $N=147$ [Fig. 2(b)]. For $N=55$, a vacancy in the first shell is found to be unstable and it migrates to the surface when the structure is relaxed.

For further calculating E_v, we removed an atom from the optimized icosahedral structure and then placed it on the suface of the cluster in a tetrahedral arrangement to have clusters with N atoms and a vacancy as we discussed before. This case is relevant to the understanding of melting. For Na_{55} we optimized 47 vacancy-adatom configurations that included different sites at which the vacancy was created in the cluster and different positions on the surface where the removed atom was placed. It is found that a vacancy on the first atomic shell migrates to the surface in all cases. In four cases the structure continues to relax such that even the surface vacancy is filled up. The latter happens for three cases in a manner that an atom at the nearest second atomic shell edge moves to the vacancy site on the first shell. Simultaneously, the adatom on the face moves to the vacancy site on the edge leading to an icosahedral structure without a vacancy. In the fourth case, the vacancy at the first shell is filled with an outer edge atom. Then the new vacant site at the edge is filled by another outer edge atom and thus another new vacancy is created. Finally, the adatom filled the new vacant second shell site on the edge leading to an icosahedral structure without a vacancy. The vacancy formation energy E_v at the center with the removed atom occupying a three fold coordinated site on a face is 0.49 eV while the vacancy formation energy at the vertex (edge) site on the surface lies in the range of 0.32–0.37 (0.36–0.39) eV which is lower than the value for the central site.

In Na_{147} and Na_{309} the number of structural isomers with different vacancy-adatom configurations increases much more and vacancies inside the clusters at sites other than the center exist. We calculated E_v for a few representative sites and the results of the lowest value for size and site dependency are shown in Fig. 2(c). Similar to the values for E_r, we find that E_v at a site on an inner atomic shell in the cluster has higher value of 0.63 and 0.63 eV, while the value of E_v for the center is 0.43 and 0.52 eV for $N=147$ and 309, respectively. On the other hand, the vacancy formation energy on a surface vertex site of Na_{147} and Na_{309} is only 0.21 and 0.22 eV, respectively, as compared to 0.32 eV for Na_{55}. These results show that *though the binding energy of the cluster increases [Fig. 2(b)] with increasing size, vacancy creation at the surface becomes more likely for* $N=147$ *and 309 clusters at least on vertices.* For edges the variation in E_v with size is small while for a face site E_v decreases in going from $N=147$ to 309. However, once a vacancy is created at a vertex, another lower coordination site is created and it is anticipated that disordering at such sites would become energetically more favorable than on other edge sites. *Accordingly clusters with* $N=147$ *and 309 are likely to be disordered at lower temperatures than* Na_{55} in agreement with the recent experimental findings of higher melting temperature for Na_{55} compared with the values for Na_{147} and Na_{309}.[10] It is to be further noted that in most cases the site dependencies of E_r and E_v are similar. Therefore, E_r itself could provide important information for the melting behavior.

Our calculations show that E_v for a vertex site does not decrease monotonically with increasing cluster size. However, the melting temperature decreases monotonically in going from $N=55$ to 147 and then to 309 (≈ values being 290, 260, and 230 K, respectively[9,10]). This could be due to solid to solid structural changes in $N=309$ cluster 40 K below the melting temperature suggested from the experimental results. Therefore, while E_v is a good indicator of the melting behavior, there could be other factors playing an important role. Our results show that with increasing temperature, disordering in clusters should occur more in the surface region preferentially at vertices and edges while the interior of clusters could remain structurally intact except for thermal vibrations. For $N=309$ even disordering at faces becomes energetically very competitive and it agrees well with the conclusion of surface structural transition. Also recent molecular dynamics simulations[15] on sodium clusters also show edge vacancy diffusion while from experiments Haberland *et al.*[10]

conclude surface premelting in clusters—a phenomenon where surface disordering would play an important role.

We also studied clusters with $N=56$, 148, and 310 in which an atom was placed on the surface of $N=55$, 147, and 309 icosahedron, respectively, in order to calculate the second order difference in energy,

$$\Delta(E_N) = E(N+1,0) + E(N-1,0) - 2E(N,0). \qquad (5)$$

A positive value of $\Delta(E_N)$ shows that two Na_N clusters are stable against fragmentation into two clusters with $N+1$ and $N-1$ atoms. We find $\Delta(E_N)$ to be 0.263, 0.189, 0.148 eV for $N=55$, 147, and 309, respectively. This is interesting because Na_{55}, Na_{147}, and Na_{309}, all have an odd number of electrons, yet these are magnetic and this magnetic behavior is strongest in Na_{55}. In a jellium model clusters with odd number of electrons are not magnetic. Therefore, the magnetic behavior of the three clusters studied here again reflects the importance of the icosahedral atomic shell structure.

We studied the effects of a vacancy on the electronic spectrum for the different vacancy-adatom configurations and obtained two broad behaviors. (1) The creation of a vacancy at a site other than the center reduces the approximate icosahedral symmetry of the cluster and this leads to the splitting of the states. (2) When the removed atom is placed on a face, the states are purturbed further and slightly more spread due to further reduction in symmetry. Figure 1(c) shows three representative spectra for Na_{55} in which the vacancy was created at the center, vertex, or an edge. The main effect is the broadening of the peaks as compared to the case of clusters without a vacancy. Qualitatatively the same results are also obtained for Na_{147} and Na_{309}.

IV. SUMMARY

In summary we find that a vacancy is stable in sodium clusters in the size range studied here and that the perturbation due to a central vacancy is mostly confined to two atomic shells. Therefore a vacancy at the center of a metal cluster may not improve bonding between the surface atoms as it has been found for large Lennard-Jones clusters. The vacancy formation energy is found to be the highest in the central region and the lowest at the vertices followed by edges and faces in icosahedral clusters. Therefore disordering can be expected to start at such low coordinated sites in clusters upon heating. Also the vacancy formation energy at a surface vertex is higher for Na_{55} as compared to Na_{147} and Na_{309}. This correlates well with the higher melting temperature of Na_{55} cluster compared with the values for $N=147$ and 309. The calculated electronic structures of the clusters agree with the photoelectron spectroscopy data and support overall icosahedral growth of these clusters. A vacancy leads to the broadening of the electronic spectra of clusters. It is hoped that our results would help in advancing the understanding of the thermal behavior of clusters.

ACKNOWLEDGMENTS

One of the authors (V.K.) acknowledges support from NAREGI Nanoscience Project funded by the Ministry of Education, Culture, Sports, Science and Technology, Japan and the hospitality at IMR, Tohoku University, and RICS, AIST. The authors are grateful to the staff of the Center for Computational Materials Science, IMR for allowing the use of the Hitachi SR8000/64 supercomputing facilities. The authors also acknowledge Noriaki Matsuoka of KGT and Dr. Hiroaki Kawamura for their help in the visualization of charge density using AVS.

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