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Structure and energetics of $Na_{n-x}Li_x$ ($n \leq 21$) clusters

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Hohenberg-Kohn-Sham density-functional theory is used to obtain the energy of valence electrons in a spherically averaged external ionic potential for $Na_{n-x}Li_x$ ($n \leq 21$) clusters. By adding the ion-ion interaction and minimizing the total energy with respect to the ion positions, we then obtain the equilibrium geometry of the cluster. Strong similarities are found to exist between the characteristics of clusters with a common n and varying x. The substitution of Na atoms by Li atoms is a favorable reaction and appears to justify the Li enrichment observed in the experiments. The importance of low-lying metastable geometries for the interpretation of the abundance spectrum is stressed.

I. INTRODUCTION

Alkali-metal clusters are the most widely studied class of clusters both from the experimental and the theoretical sides. The evident reasons are practical advantages, as, for example, low melting points and simple electronic structure. Since the shell-model interpretation[1] of their relative stability in terms of well-known and strongly supported facts of bulk phases (nearly free-electron picture) and atomic phases (spherical self-consistent field), much effort has been devoted to guarantee the adequacy and limits of that interpretation. For example, temperature effects on abundance spectra have been discussed.[2-4] Also, the effects of mixing different alkali metals,[4-6] and doping an alkali-metal cluster with impurities,[7-11] have been analyzed. It emerges from those studies that the shell model has a wide range of applicability and is not restricted to pure clusters.

However, as the simplest shell model, jellium is a one-parameter model and not too flexible to accommodate heteroclusters, except perhaps in the case of a single impurity.[11] With no substantial increase in computational difficulties the authors have developed the spherically-averaged-pseudopotential model[12] (or SAPS model), which is also a shell model but flexible in the sense that each atom in the cluster is explicitly considered through its valence, pseudopotential, and spatial coordinates.

As a first application of the SAPS model the stability of Na_n, Mg_n, Al_n, and Pb_n clusters have been studied[12] (n indicates the number of atoms in the cluster). The model was then extended to consider H impurities in Al clusters[13] and to preliminary studies of enrichment and segregation effects in $Na_{n-1}Li$ and Na/Cs heteroclusters.[14] The present paper is concerned with a comprehensive study of $Na_{n-x}Li_x$ clusters with different Li concentrations.

II. MODEL

Only a brief description of the model will be given here. More details can be found by consulting Refs. 12 and 13. In the SAPS model the electron density (of the valence electrons) is calculated by solving the self-consistent Kohn-Sham equations of the density-functional formalism[15,16] with the local density approximation for exchange and correlation effects. The ionic core of each atom is replaced by an empty-core pseudopotential[17] v_{EC} and the equilibrium geometry of the cluster is calculated by minimization of the total energy with respect to the positions $\{\mathbf{R}_i\}$ of all the atoms. However, in the step of calculating the electron density during the iterative process of searching for the equilibrium geometry, the real three-dimensional external potential of the ions

$$V_I(\mathbf{r}) = \sum_i v(\mathbf{r}-\mathbf{R}_i) \tag{1}$$

is substituted by its spherical average $V_I^{av}(r)$ about the center of ionic charge of the cluster. The validity of this assumption, which largely simplifies the numerical procedure, is justified by the experimental evidence in favor of the shell model.

The empty-core radii chosen here are $r_{EC}(\text{Li}) = 1.61$ a.u. and $r_{EC}(\text{Na}) = 1.74$ a.u. These values have been obtained from density-functional calculations for isolated atoms using also the empty-core pseudopotential, and varying r_{EC} to fit the experimental ionization potential

In the process of calculating the equilibrium geometry of the cluster, the ions are first located at random positions (the whole process is repeated several times with different starting random geometries) and then follow the direction of the steepest descent of the total energy. Since no kinetic energy is given to the ions, the calculations are of significance for very low temperatures. At the end of the geometry-optimization process, rigid equilibrium geometries result. We stress that the final electron density is self-consistent with the equilibrium geometry, subject to the approximation of using V_I^{av} as indicated above

III. RESULTS AND DISCUSSION

A. Geometries

To begin with our presentation of results we report some interesting conclusions about the geometries of $Na_{n-x}Li_x$ heteroclusters. In the size range $n=3$–21, and for all values of x studied in this paper (we have restricted our analysis to $x \leq 10$), three types of equilibrium geometries have been found: (a) all atoms sharing a common spherical layer, (b) one central atom plus a surface layer, and (c) two atomic layers, the inner one with two or three atoms and the rest of them on the surface layer. A layer is defined here as a group of atoms at a similar distance from the cluster center, and well separated from other layers.

Figure 1(a) shows, first of all, the sequence of ground-state geometries as a function of cluster size, for $x=1$ and 2. A single layer is obtained for the very small sizes ($n \leq 6$). At a critical size, $n=7$, one single atom occupies the center of the cluster, whereas the rest form the surface layer. This configuration persists as n increases further. Then, a second critical size is reached, $n=20$, when the central atom is replaced by an inner layer which begins to grow itself. We stress that the above sequence is found for both $x=1$ and 2. Even more, the same sequence of ground-state geometries as a function of size was found for pure Na clusters.[12] This remarkable fact follows from the identical valence and the similarity between the empty-core radii of Li and Na. The only apparent consequence of the small difference (0.1 a.u.) in core size is that Na_6 is noncentered.

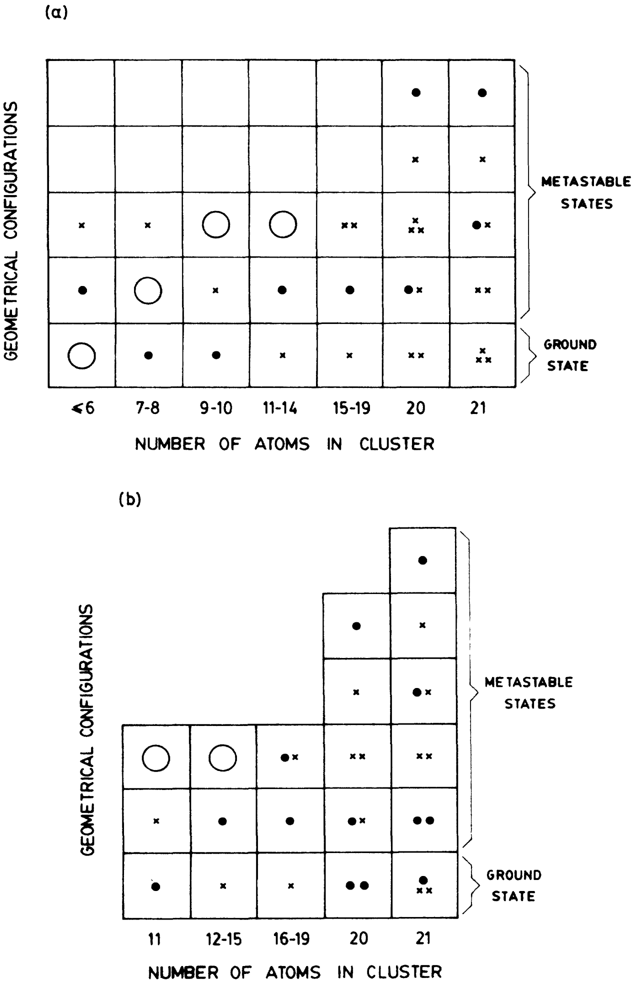

FIG. 1. (a) Types of equilibrium and metastable geometries for $Na_{n-x}Li_x$ ($x=1,2$; $n \leq 21$), ordered upwards by decreasing stability (increasing energy). A large circle represents a unique layer. Clusters with one or several atoms in the inner region are indicated by crosses and/or solid circles. The number of crosses and circles indicates the number of Na atoms and Li atoms, respectively, in the inner region of the cluster. Energies of the different structures are given in Fig. 4 for $x=1$. (b) Same as (a) but for $x=10$.

Figure 1(a) also shows that, for a given value of n, the two clusters $Na_{n-1}Li$ and $Na_{n-2}Li_2$ have not only the same type of geometry but also the same atomic species in the inner region of the cluster. Even more striking is that, again for a given value of n, the energy sequence of metastable geometries is the same for both compositions. From a naive point if view one might expect a Li atom to prefer the inner part of the cluster in order to maximize the number of Li-Na bonds. This occurs for very small clusters, $7 \leq n \leq 10$, but not for $11 \leq n \leq 19$. This is, to a large extent, a size effect. A large atom like Na fills better the increasingly large central hole as n increases. Furthermore, Li has a slightly more attractive pseudopotential than Na and it tends to be in regions of high electron density in the cluster. These regions are not necessarily in the central part of the cluster since the electron distribution depends on the configuration of electronic shells.

The picture for other values of x larger than 2 is rather similar to that shown in Fig. 1(a), although some differences of detail exist. The critical size for the transition from a single layer to a configuration with one central atom is always between $n=7$ and 9. The second critical number, for the transition from one single inner atom to two inner atoms, occurs at $n=20$, independent of x. Also, with reference to metastable states, we find that the sequence of metastable geometries for a given n, is roughly independent of the number x of Li atoms in the cluster.

To illustrate that some differences of detail exist, we give in Fig. 1(b) the ground and metastable geometries for $x=10$, which should be compared with the cases $x=1,2$ of Fig. 1(a). Notice that, for n close to 10 these clusters are rich in Li. However, the similarity with the trends in Fig. 1(a) is evident, as a consequence, we stress, of the similarity between Li and Na.

Figure 2 shows the radial distribution of atoms (measured with respect to the cluster center) in several representative clusters: $Na_{11}Li_2$, $Na_{11}Li_5$, $Na_{10}Li_{10}$, and $Na_{13}Li_2$. Considering the surface shell of these clusters, we observe a tendency for the Li atoms to be slightly displaced inwards. This can be understood from the lower surface energy of Na metal with respect to Li,[18] evidently related to the difference in atomic size. The same effect appears to operate in small atomic aggregates and promotes segregation of Na to the cluster surface. The segregation effect is, however, not large, as seen from a

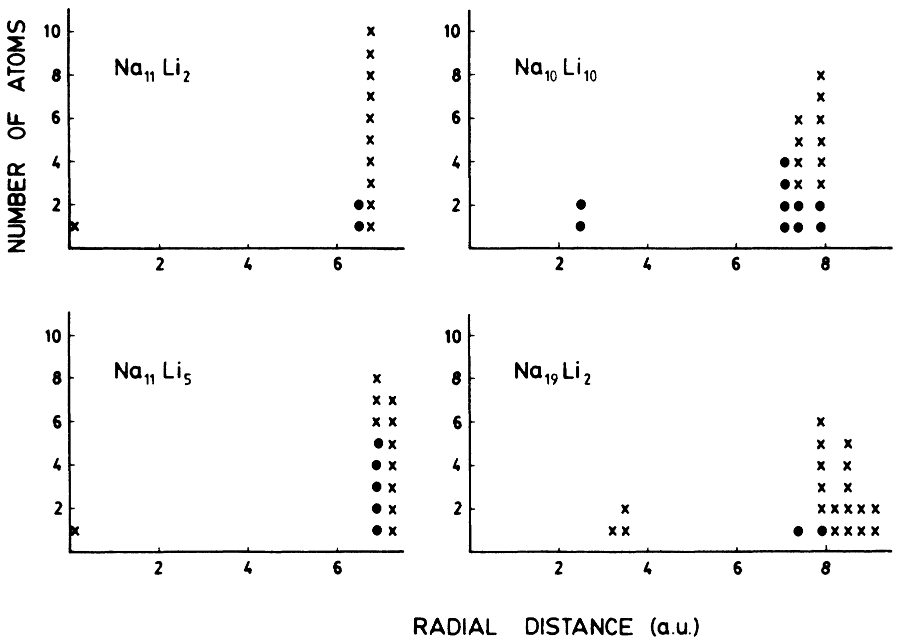

FIG. 2. Radial distribution of atoms in different $Na_{n-x}Li_x$ clusters, measured from the center of ionic charge of the cluster. Solid circles and crosses represent Li and Na atoms, respectively.

comparison with the Na/Cs system.[14] In this system, and for clusters of composition Na_mCs_m, Na and Cs atoms occupy well-separated layers, an strong segregation of Cs atoms to the cluster surface is predicted. The atomic size (or ionic size) difference is larger in Na/Cs than in Na/Li, which explains the different qualitative behavior.

B. Magic numbers

Figure 3 shows the energy per atom in $Na_{n-x}Li_x$ as a function of n, each curve corresponding to a given value of x. The trend shown by the different curves is independent of x. Well-defined maxima occur for $n=2$, 8, and 13 and an abrupt drop at $n=20$. It is customary to correlate magic numbers of stability with sharp variations of the ground-state energy as a function of size. The stability effects at $n=2$, 8, and 20 are due to the electronic shell-closing effect. These shell-closing numbers are independent of x due to the similarity between Li and Na (equal valence and similar ionic radius) and have been observed in the experimental mass spectra of the $Na_{n-x}Li_x$ clusters.[5,19] The cluster with 13 atoms is a particularly stable one from structural considerations. It is an icosahedron with an atom and its center. Some evidence of the enhanced stability of icosahedral 13-atom clusters of alkali-metal elements has been obtained in the experiments of Saito and co-workers[20,21] on Li and Na clusters generated by the liquid metal ion source technique. However X_{13} is not an abundant cluster in the mass spectra of alkali-metal clusters obtained by vapor expansion techniques.[1] This makes the nature of the 13-atom alkali-metal clusters somehow controversial.

Figure 4 shows the energy per atom of $Na_{n-1}Li$ as a function of cluster size. Energies for the ground state and metastable geometries are given. These are easily identified with reference to Fig. 1(a). Consideration of the metastable states of finite clusters may be important for a full undersanding of the magic numbers of abundance since clusters are always produced in a state of high internal excitation.[3,22]

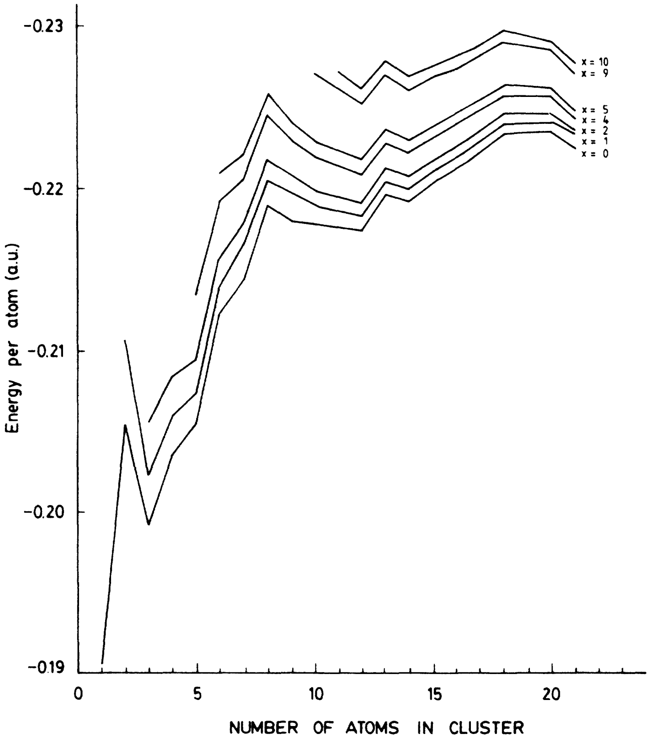

FIG. 3. Energy per atom of $Na_{n-x}Li_x$ clusters as a function of n and x.

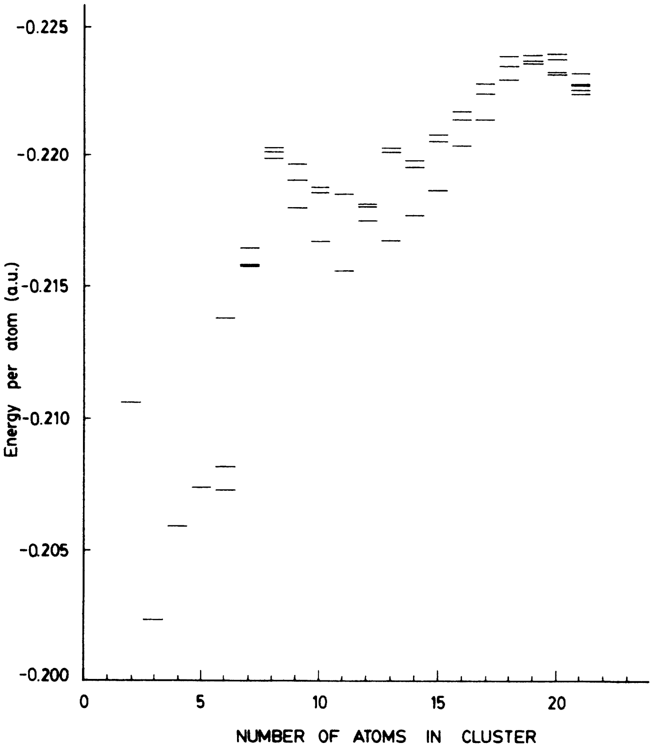

FIG. 4. Energy per atom of $Na_{n-1}Li$ clusters as a function of size. Ground states and metastable geometries are included. Each geometry can be easily identified with reference to Fig. 1.

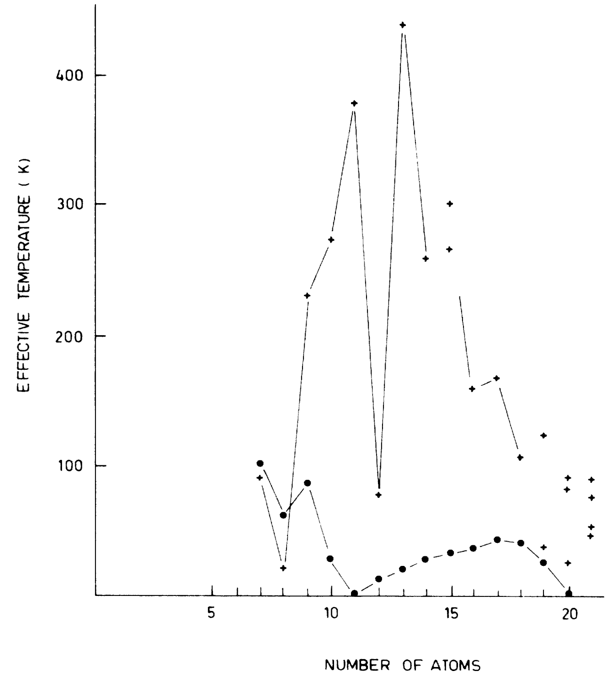

FIG. 5. Difference between the energy of metastable states and ground states of $Na_{n-1}Li$ clusters as a function of cluster size. The energy difference has been converted to an internal temperature, using Eq. (2). Solid circles correspond to exchanging a Li and a Na atom in the central region of the cluster. Crosses correspond to real geometrical changes [see Fig. 1(a)]. Lines are drawn to guide the eye.

In Fig. 5 we show the difference in energy ΔE between the ground state and the metastable geometries of Fig. 4. However, rather than ΔE we have plotted the average internal energy per mode, expressed as a temperature T, defined as

$$T = \frac{\Delta E}{(3n-6)k_B} , \qquad (2)$$

where $3n-6$ is the number of modes in a cluster of size n and k_B is the Boltzmann constant (trends are similar for $x \neq 1$). The solid circles in Fig. 5 correspond to metastable clusters with the same underlying geometry as the ground state, but differing from this one only in the interchange of the positions of the Li atom and one Na atom. On the other hand, the crosses represent metastable states with a drastic change in geometry, for instance, the migration of the central atom to the surface of the cluster for $7 \leq n \leq 14$. In some cases, the energy needed to produce a drastic change in geometry is large; much larger, in fact, than that to simply interchange the positions of the Li atom and one Na atom. This occurs for clusters with $n=9$, 10, 11, 13, 14, 15, 16, and 17. For the rest of the clusters the energy for a drastic geometrical change is small, and similar to the energy for the Li-Na positional interchange.

Clusters of a size such that several low-lying states are available may fluctuate between the ground state and those metastable states at finite temperature. These clusters, having low structural stability, can easily absorb the excess energy acquired during the process of cluster formation in vapor-expansion experiments, and attain a fluid or liquid-like state. Clusters with $n=7$, 8, 12, and $n \geq 18$ provide good examples of this behavior. In contrast, clusters without several low-lying metastable states are too rigid and resistant to internal deformation. In this case excess energy cannot be easily absorbed by the cluster, and evaporation of atoms can provide the way to liberate the excess energy. The clusters with 11 and 13 atoms provide the best examples of this behavior. It is striking that, being $Na_{12}Li$ and Na_{13} highly stable clusters in the calculations at $T=0$ K, they are, nevertheless, not particularly abundant in the vapor-expansion experiments.[1,5] The reason is, in our opinion, that the clusters produced in the experiments have substantial excess internal energy.[3] This energy cannot be accommodated in clusters like Na_{13} or $Na_{12}Li$ because of their rigidity. The excess energy will then be spent in evaporating atoms, a process that lowers the population of $n=13$. The magic clusters $n=8$ and 20 are not only highly stable at $T=0$ K, these are also highly stable at finite T because they are soft clusters, and this enhances their magic character.

C. Relation between electronic structure and geometry

Table I gives the difference in energy between two particular states of the cluster $Na_{n-1}Li$. In both states the

TABLE I. Difference between the energies of $Na_{n-x}Li_x$ ($x=1,2$) clusters formed by a surface shell and a single Li or Na atom occupying the central site. See Eqs. (3) and (4).

n	$10^3\,\Delta E_{\mathrm{exch}}(\mathrm{Na}_{n-1}\mathrm{Li})$ (a.u.)	$10^3\,\Delta E_{\mathrm{exch}}(\mathrm{Na}_{n-2}\mathrm{Li}_2)$ (a.u.)
6	−5.4	−5.9
7	−4.9	−4.9
8	−3.6	−3.4
9	−5.8	−5.6
10	−2.2	−2.1
11	0.002	0.2
12	1.3	1.4
13	2.2	2.7
14	3.4	3.6
15	4.2	4.5
16	5.1	5.7
17	6.3	6.3
18	6.5	6.8
19	4.5	4.5
20	1.5	2.1
21	2.4	2.8

structure of the cluster consists of a surface layer and a single central atom, and the only difference is that the central atom is Li in one case and Na in the other; that is, this interchange energy is given by

$$\Delta E_{\mathrm{exch}}(\mathrm{Na}_{n-1}\mathrm{Li})=[E(\mathrm{Na}_{n-1}\mathrm{Li})]_{\mathrm{Li\,central}}-[E(\mathrm{Na}_{n-1}\mathrm{Li})]_{\mathrm{Na\,central}}\ . \tag{3}$$

The corresponding interchange energy for clusters with the same structure as above (surface layer and single central atom) and composition $Na_{n-2}Li_2$ is also given in the table:

$$\Delta E_{\mathrm{exch}}(\mathrm{Na}_{n-2}\mathrm{Li}_2)=[E(\mathrm{Na}_{n-2}\mathrm{Li}_2)]_{\mathrm{Li\,central}}-[E(\mathrm{Na}_{n-2}\mathrm{Li}_2)]_{\mathrm{Na\,central}}\ . \tag{4}$$

For a given value of n the two values of ΔE_{exch} for $x=1$ and 2 are very similar.

The larger stabilization of the Li-centered cluster with $n=9$ with respect to neighbor sizes arises from the outermost electronic level (2s) in the electronic configuration of the cluster with $n=9$. This configuration is $(1s)^2(1p)^6(2s)^1$. The 2s orbital penetrates into the central region of the cluster, providing an attractive site for the Li atom, which is more electronegative than the Na atom.

D. Enrichment

Recent experiments[5,6] give evidence of a thermodynamic enrichment in the lighter alkali metals for $Na_{n-x}Li_x$ and $K_{n-x}Na_x$ heteroclusters. In other words, Na/Li clusters detected in supersonic expansion experiments are enriched in Li with respect to the initial composition of the mixed atomic vapors. It has been proposed that the detected clusters are formed after many cycles involving atom aggregation, atom evaporation, and reactions of substitution of a Na atom by a Li atom.[5] To connect with these experimental results we have calculated the heat ΔH for the reaction of substitution of a Na by a Li atom.

$$\mathrm{Na}_{n-x+1}\mathrm{Li}_{x-1}+\mathrm{Li}\rightarrow\mathrm{Na}_{n-x}\mathrm{Li}_x+\mathrm{Na}\ . \tag{5}$$

ΔH calculated from the corresponding total energies

$$\Delta H=E(\mathrm{Na}_{n-x}\mathrm{Li}_x)+E(\mathrm{Na})-E(\mathrm{Na}_{n-x+1}\mathrm{Li}_{x-1})-E(\mathrm{Li}) \tag{6}$$

is given in Fig. 6 for $x=1$, 2, 5, and 10. ΔH is always negative, that is, substitution of a Na atom by a Li atom is favorable (with the exception of $n=21$ for $x=2$). This, in our view, can explain the enrichment in Li observed in the experiments.

It is evident that the values of ΔH are rather similar for the different x and a common n, except for a few cases discussed immediately below. This is due to the geometrical similitude between the clusters involved in the substitution reactions. An indication of the affinity of Li for the central site in very small clusters is also appreciated in the behavior of ΔH for $x=1$. When the Li impurity is in the center (cases $n=7-10$) then ΔH is more negative than for other cases. Also, an electronic effect plays a role for $n=9$. Na_8Li is particularly stable with respect to Na_9 in response to a change of electronic configuration: $(1s)^2(1p)^6(1d)^1$ in Na_9 versus $(1s)^2(1p)^6(2s)^1$ in Na_8Li. In effect, the energy difference between the ground-state electronic configuration of Na_8Li and the excited electronic configuration $(1s)^2(1p)^6(1d)^1$ (with the ground-state geometry) is 0.004 a.u. which accounts for the drop in ΔH at $n=9$, $x=1$. In contrast, for $x=2$, ΔH is smooth at $n=7-10$, because the second Li atom sits on the surface and electronic configurations of the clusters with one and two Li atoms are similar. A relevant feature of the experiments of Kappes *et al.*[5] concerns the binomial distribution for abundance of $Na_{n-x}Li_x$ for

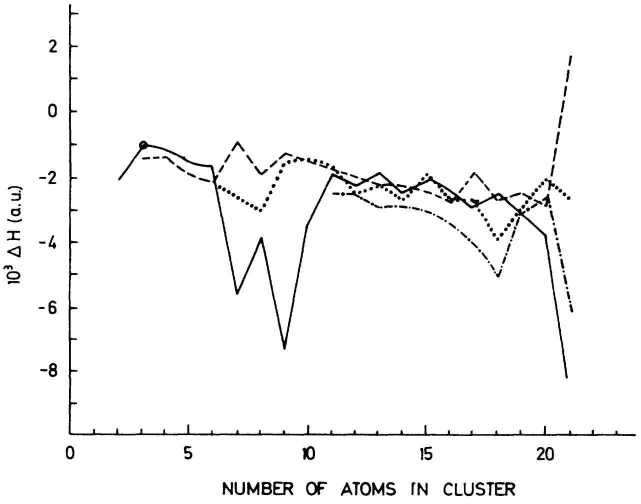

FIG. 6. Heat of the substitution reaction $Na_{n-x+1}Li_{x-1}+Li\rightarrow Na_{n-x}Li_x+Na$ for $x=1$ (——), $x=2$(— — —), $x=5$(· · · ·), and $x=10$(—·—·—·). The circle is an experimental result for $x=1$.

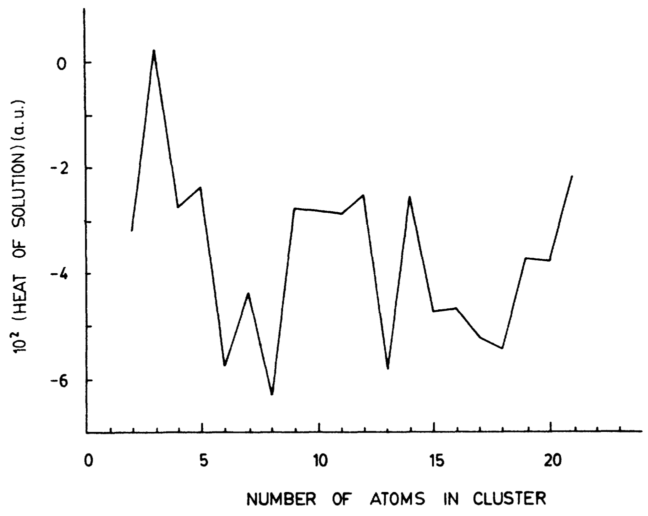

FIG. 7. Heat of solution of Li in Na_{n-1} as a function of n.

fixed n and varying x. According to these authors the binomial distribution reflects the fact that, for given n, ΔH is roughly independent of x. Except for the few exceptions already discussed, our results also display this feature and are consistent with the interpretation of Kappes *et al.*

The only quantitative experimental data[5] known to us is for the reaction $Na_3+Li \rightarrow Na_2Li+Na$. The heat of this reaction is $\Delta H=-0.001$ a.u. which is in rather close agreement with our prediction, although this agreement should not be overemphasized.

Another quantity of interest is the heat of solution of a Li atom in the Na cluster. This is defined

$$\Delta E_{\text{sol}}=E(Na_{n-1}Li)-E(Na_{n-1})-E(Li) . \tag{7}$$

This quantity has been plotted in Fig. 7 as a function of n. The heat of solution is negative (except for $n=3$) and its magnitude displays large oscillations as n grows.

The phase diagram of the bulk Li/Na alloy[23] indicates complete immiscibility in the solid phase and a large miscibility gap in the liquid phase. This indicates that the heats of solution of Li in Na and Na in Li are positive in the bulk. The contrast with respect to the negative values calculated for small clusters is striking and it is, in our view, consistent with the experimental information available: immiscibility in the bulk, but miscibility (enrichment effect) in small clusters. The oscillations of the heat of solution in Fig. 7 indicate that a strong size effect, linked to the orbital character of the electron wave functions, dominates the behavior of ΔE_{sol} at small n and that very large clusters are needed for ΔE_{sol} reaching its value for bulk alloys. In fact, previous calculations performed some time ago in our group,[24] using also the Hohenberg-Kohn density-functional formalism and the empty-core pseudopotential (and a model explicitly aimed to bulk phases), give indeed a positive heat of solution in the bulk Li/Na alloy.

IV. SUMMARY AND COMMENTS

In summary, by using the Hohenberg-Kohn-Sham density-functional formalism and a convenient computational simplification in the treatment of the ionic potential, we have arrived at some interesting conclusions concerning Na/Li clusters: (a) The cluster geometries depend mainly on the total number of atoms and not much on the relative concentration of Na and Li. (b) There is segregation of Na atoms to the cluster surface, consistent with the lower surface energy of Na metal. (c) The observed magic numbers are due to electronic shell-closing stabilization. On the other hand, some stable clusters from a geometrical point of view, like the 13-atom icosahedron, appear to be unobservable due to their rigidity, which promotes fragmentation as a way to employ any excess energy. (d) The reaction of substitution of a Na by a Li atom is a favorable one, and it explains, in our view, the enrichment effect observed in the experiments of Kappes *et al.*[5]

The available experimental information on Li/Na clusters is in agreement with our predictions. To have more confidence in the results we can consider how our model performs as one goes to the bulk limit.

Considering the cohesive energy, previous calculations for Na_n and Cs_n clusters using the SAPS model[25,26] give, for a size $n \simeq 100$, a difference in cohesive energy (per atom) of 0.3 eV, which is equal to the difference between the experimental bulk cohesive energies of these two metals.[27] Since the alkali metals are well described by a one-parameter pseudopotential we can expect a similar good description of the difference in cohesive energy between any two of these metals. In the same line of argument we can expect a good description of the difference in surface energy of very large (or macroscopic) clusters of pure alkaline elments using the SAPS model. In fact, a density-functional calculation of the surface energy of macroscopic metals based on the jellium-background model, corrected by the introduction of the ionic lattice in a perturbative way, leads to such a result.[28] Evidently, the surface-energy difference is the main factor controlling segregation effects in alloys.

Finally we stress the different behavior between Na/Li clusters and the corresponding bulk alloys. Na and Li are miscible in clusters but immiscible in the bulk alloy. This miscibility is, on the other hand, perfectly consistent with the tendency for Na to be in the outer part of the cluster to minimize the surface energy.

ACKNOWLEDGMENTS

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