Theory of lithium islands and monolayers: Electronic structure and stability

S. Quassowski and K. Hermann

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

(Received 1 September 1994; revised manuscript received 7 October 1994)

Systematic calculations on planar clusters and monolayers of lithium are performed to study geometries and stabilities of the clusters as well as their convergence behavior with increasing cluster size. The calculations are based on *ab initio* methods using density-functional theory within the local-spin-density approximation for exchange and correlation. The optimized nearest-neighbor distances $d_{\rm NN}$ of the Li_n clusters, $n = 1, \ldots, 25$, of both hexagonal and square geometry increase with cluster size, converging quite rapidly towards the monolayer results. Further, the cluster cohesive energies E_c increase with cluster size and converge towards the respective monolayer values that form upper bounds. Clusters of hexagonal geometry are found to be more stable than square clusters of comparable size, consistent with the monolayer results. The size dependence of the cluster cohesive energies can be described approximately by a coordination model based on the concept of pairwise additive nearest-neighbor binding. This indicates that the average binding in the Li_n clusters and their relative stabilities can be explained by simple geometric effects which derive from the nearest-neighbor coordination.

I. INTRODUCTION

The physical properties of bulk lithium and thin layers of lithium have attracted considerable interest among theorists as well as experimentalists. This lightest of all alkali metals exists in different bulk crystal structuresclose-packed rhombohedral structures¹ at low tempera-tures below 70 K and bcc structures¹⁻³ above 70 K which are characterized by relatively large lattice constants leading to rather low average valence-electron densities. The open crystal lattice, together with the electronic structure, gives rise to interesting physical and chemical features such as easy penetration of oxygen into the bulk⁴ and high reactivity for oxidation. In fact, oxygen-lithium systems are of technological importance for the construction of nuclear fusion reactors.^{5,6} On the other hand, lithium as a simple sp-band metal constitutes a prototypical system where many of the theoretical concepts developed in connection with free-electron-gas and jellium models^{7,8} can be tested. The electronic structure and the derived properties of bulk lithium have been studied extensively by both band-structure⁹⁻¹⁵ and cluster¹⁶⁻²⁰ methods. These studies identify the hcp crystal structure to be energetically favored compared to bcc and fcc structures. Further, the calculated nearest-neighbor distance, the bulk modulus, and the work function values agree quite well with experiment.

Unsupported ultrathin lithium films of monolayer up to a few layers thickness have been considered in theoretical studies of quantum size effects and structural properties in comparison with the bulk.^{21,22} For hexagonal monolayers it was found that while the nearest-neighbor equilibrium distance gets quite close to the bulk value $[d_{\rm NN} = 5.70$ a.u. (Ref. 3) for bcc crystals], the electronic structure and binding are different. Cohesive energies of the monolayer amount to 1.1-1.4 eV (Refs. 21 and 22) and are below the bulk value of 1.66 eV.^{10,23} Further, monolayer results of the work function are about 0.6 eV larger than the bulk value²² and the width of the occupied part of the *sp* band increases considerably from monolayer to bulk.²¹ All these results can be rationalized mainly by the reduced nearest-neighbor environment in the film compared to the bulk. Thin lithium films supported on Ru(0001) substrate have been studied experimentally^{24,25} as examples of alkali-metal surface systems in order to investigate reactive oxygen chemisorption and oxide formation. These studies confirm the open structure of the alkali-metal film, which allows oxygen to penetrate below the surface. However, a detailed lithium film geometry could not be derived from this study. Moreover, experimental results on well-ordered thin lithium films do not seem to exist due to preparational difficulties.²⁶⁻²⁸

At very low coverages lithium atoms deposited on a substrate will migrate on the surface and can form a lattice gas or local islands. Here it is interesting, both from structural and energetic points of view, to understand how the atoms nucleate. This requires systematic studies on (supported) lithium clusters^{4,17,29} as well as isolated islands modeled by planar clusters. Calculations on planar Li_n clusters of different size (up to Li_{11}) have been reported recently,³⁰ where the systems are chosen as sections of fcc (111) and (100) lattice planes without further geometry optimization. These calculations based on ab initio Hartree-Fock theory suggest that the relative stability of the clusters varies strongly with size and shape indicating the occurrence of magic numbers for planar clusters. However, the study is restricted to relatively small clusters and the geometry optimization does not include nearest-neighbor distance variations. This allows only limited conclusions concerning the cluster growth energetics and a possible transition from finite islands to monolayers as the lithium surface coverage increases.

In the present study we have performed systematic calculations on finite planar clusters (islands) and monolayers of lithium in order to obtain detailed information

<u>51</u> 2457

about geometries and relative stabilities of the clusters as well as about possible convergence behavior with respect to the monolayer results as the cluster size increases. The calculation of energetic quantities and geometry optimizations are performed using ab initio methods based on density-functional theory within the local-(spin-)density approximation for exchange and correlation.^{31,32} The optimized nearest-neighbor distances d_{NN} of Li_n clusters, $n = 1, \ldots, 25$, of both hexagonal and square geometries are found to increase with increasing cluster size and converge towards the d_{NN} value of the respective monolayers. The convergence is quite rapid and the monolayer value is reached at rather moderate Li_n cluster sizes of $n \approx 10$. The cohesive energies E_c of the larger planar clusters increase with cluster size with a clear convergence towards the E_c value of the respective monolayer which forms an upper bound. The calculations do not yield Li_n clusters of preferred relative stability for *n* between 1 and 25 and thus do not support the existence of magic numbers for two-dimensional planar clusters.³⁰ Further, clusters of hexagonal geometry are always found to be slightly more stable than square clusters of comparable size, which is consistent with the monolayer results where the hexagonal geometry is energetically preferred.^{21,22} The size dependence of the cluster cohesive energies can be reproduced almost quantitatively by a rather simple coordination model based on the concept of pairwise additive nearest-neighbor binding. This indicates strongly that the average binding in the Li_n clusters reflected in their relative stability can be explained to a major extent by simple geometric effects which derive from the nearest-neighbor coordination of the cluster atoms.

Section II discusses theoretical details and methods used in this study, while Sec. III presents the numerical results and discussion. Finally, Sec. IV summarizes the conclusions, stressing those features which are relevant for the real surface situation.

II. COMPUTATIONAL DETAILS

Bulk lithium of bcc or fcc crystal structure is characterized by densest net planes which are hexagonal, fcc(111); rectangular centered, bcc(110); or square, fcc(100) and bcc(100). This suggests monolayer lattice structures of hexagonal and square geometry. The rectangular centered geometry can be thought of as intermediate between hexagonal and square and will not be dealt with in the following. While the hexagonal structure is considered to be most stable and has been discussed quite frequently, 21,22,33,34 the present calculations include hexagonal and square monolayers. For each system the nearest-neighbor distance d_{NN} is optimized to yield the lowest total energy. Planar lithium clusters of different size and shape representing isolated surface islands are constructed as finite sections of the respective monolayers. However, in all clusters the nearestneighbor distance d_{NN} is reoptimized at the given symmetry to yield the lowest cluster total energy. The validity of this optimization procedure as compared to a full planar optimization has been checked by test calculations

as discussed below. Figure 1 shows the complete set of clusters considered in this study that are cut from the hexagonal monolayer (hexagonal clusters). They range from Li₂ to Li₂₄ and are labeled Hnp according to cluster size (*n* denotes the number of atoms in the cluster) and shape (clusters of equal size, but different shape are discriminated by label p if needed). While most of the smaller clusters form open structures, the larger clusters are chosen to be compact, reflecting closed atom shells with a maximum number of nearest neighbors per atom. These compact clusters are likely to be candidates for two-dimensional magic clusters discussed recently.³⁰ Figure 2 contains all clusters considered in this work that are cut from the square monolayer (square clusters). They range from Li₂ to Li₂₅ and are labeled Snp accordingly.

The electronic structures and energetic quantities needed in the geometry optimization are calculated using ab initio methods based on density-functional theory (DFT) within the local-density approximation (LDA) as well as the local-spin-density approximation (LSDA) for exchange and correlation. 31,32 For the monolayers (described by slab geometries) we applied the nonrelativistic full-potential linearized augmented plane wave (FPLAPW) method implemented in the WIEN93 computer code³⁵ and using the exchange-correlation energy functional from Refs. 31 and 32. The calculation of reliable energy quantities requires fairly large Kohn-Sham orbital basis sets. Thus the energy cutoff value for the planewave basis expansion in the interstitial region was 6.85 hartree for the hexagonal monolayer and 8.68 hartree for the square monolayer, while the highest angular momentum component for the wave-function expansion inside the atom spheres was $l_{max} = 12$. The irreducible Brillouin-zone scan was performed with 90 k points in the irreducible wedge and the distance between adjacent layers in the slab system was set to 20 bohrs to guarantee electronic layer separation. Test calculations on the monolayers were carried out also with nonlocal gradient corrections in the exchange-correlation functional (the GGA-II approach¹⁴). They show that while the total energies per lithium layer atom can differ by as much as 0.13 hartree due to gradient corrections, cohesive ener-



FIG. 1. Geometric structures of all hexagonal Li_n clusters of the present study. Compact clusters are those labeled (H2),H3,H7,H10,H14,H19,H24.



FIG. 2. Geometric structures of all square Li_n clusters of the present study. Compact clusters are those labeled (S2),S4a,S9,S16,S20,S25.

gies determining the layer stability vary only by 0.13 eV and are almost identical between hexagonal and square monolayers; see below.

For the electronic structure of the finite clusters we applied a LSDA cluster calculation scheme implemented recently.^{36,37} This scheme uses Gaussian-type basis sets for Kohn-Sham orbitals and does not rely on additional fitting basis sets for densities and exchange-correlation potentials. Respective matrix elements are evaluated either analytically or by highly accurate numerical realspace integration.³⁶ This guarantees reliable total and binding energies if sufficiently large basis sets are used. The present spin-polarized calculations are performed with the exchange-correlation energy functional taken from Refs. 31 and 32 and with a lithium basis set of contracted Gaussians described by (9s, 4p/4s, 3p) taken from optimizations on the free atom.⁴ The quality of the basis set can be tested by comparing results for the atom obtained using the cluster code with those of the atom part of the WIEN93 code which uses numerical basis sets. The atomic total energies from the calculations are $E_{tot}^{Gauss} = -7.34161$ spin-polarized hartree and $E_{\text{tot}}^{\text{num}} = -7.34266$ hartree, respectively, and differ by only 10^{-3} hartree, which seems sufficient for the present purpose.

III. RESULTS AND DISCUSSION

Table I lists all lithium atom energy results which are used as a reference in the binding energy calculations of the monolayers and clusters. As mentioned above, the total energy of the free Li atom computed with numerical and Gaussian basis sets differs by only 10^{-3} hartree if the same exchange-correlation functional (LDA or LSDA) is applied, which demonstrates the quality of the Gaussian basis set. The total energy per Li atom in both monolayers E_{tot} (layer) is lower than the free-atom value E_{tot} (atom), which shows the stability of the monolayers. The energy difference

$$E_c = E_{\text{tot}}(\text{atom}) - E_{\text{tot}}(\text{layer}) , \qquad (1)$$

which defines the cohesive energy E_c of the layer atoms, is slightly larger for the hexagonal monolayer than for the square monolayer. This is consistent with the general notion of the hexagonal Li monolayer being overall most stable. The E_c values, 1.23 eV for hexagonal and 1.17 eV for square monolayers, computed for the equilibrium nearest-neighbor distance, are in good agreement with data obtained by other band-structure studies,^{21,22,33,34} as will be discussed later. However, these values are smaller by about 0.6 eV compared to E_c values computed for Li bulk. The present FPLAPW calculations yield bulk cohesive energies E_c of 1.81 eV for fcc and 1.75 eV for bcc lithium, where the increase with respect to the monolayer values is explained by the changed nearest-neighbor environment.

It is interesting to note that if nonlocal gradient corrections are included in the exchange-correlation functional,¹⁴ the atomic total energies are lowered considerably. The respective values in Table I marked as GGA-II differ from their L(S)DA analogs by as much as 3.6 eV. However, the binding of the Li atom in the monolayers seems to be much less affected. Test calculations for the hexagonal and square monolayers yield a reduction in E_c by only 0.13 eV due to gradient corrections. The similarity in the results between the two monolayers suggests further that gradient corrections are likely to affect all Li systems equally such that they can be neglected in estimates of relative stability.

Table II contains results of the optimizations on the hexagonal lithium clusters; see Fig. 1. For each cluster the optimized nearest-neighbor distance d_{NN} is listed to-

TABLE I. Total energies E_{tot} for the free lithium atom and those inside the hexagonal and square monolayers (from FPLAPW calculations). The energies of the free atom are given both for the present Gaussian and for the numerical basis set. For definitions of the cohesive energy E_c and the different exchange-correlation schemes LDA, LSDA, GGA-II, see the text.

System	$E_{\rm tot}$ (hartree)	E_c (eV)
Li atom (LDA, numerical/Gaussian)	-7.33409/-7.33300	
Li atom (LSDA, numerical/Gaussian)	-7.342 66/-7.341 61	
Li atom (spin polarized GGA-II, numerical)	- 7.474 17	
Li monolayer (hexagonal, LDA)	-7.38777	1.23
Li monolayer (hexagonal, GGA-II)	-7.514 55	1.10
Li monolayer (square, LDA)	-7.385 70	1.17
Li monolayer (square, GGA-II)	-7.512 49	1.04

Cluster	d _{NN} (bohr)	$\boldsymbol{E}_{\mathrm{tot}}$ (hartree)	E_b (eV)	E_c (eV)
Li ₂ (H2/S2)	5.13	14.7212	1.034	0.517
Li ₃ (H3)	5.43	-22.0866	1.687	0.562
Li ₄ (H4)	5.53	-29.4749	2.966	0.742
Li ₅ (H5a)	5.57	-36.8551	4.005	0.801
Li ₅ (H5b)	5.40	-36.8470	3.782	0.756
Li ₆ (H6a)	5.59	-44.2423	5.226	0.871
Li ₆ (H6b)	5.59	-44.2404	5.192	0.865
Li ₆ (H6c)	5.54	-44.2010	4.120	0.687
Li ₇ (H7)	5.64	-51.6173	6.153	0.879
Li ₁₀ (H10)	5.66	-73.7493	9.070	0.907
Li ₁₃ (H13a)	5.61	-95.8907	12.242	0.942
Li ₁₃ (H13b)	5.64	-95.8895	12.220	0.940
Li ₁₄ (H14)	5.69	-103.2933	13.902	0.993
Li ₁₈ (H18a)	5.66	-132.8095	17.987	0.999
Li ₁₈ (H18b)	5.69	-132.8209	18.289	1.016
Li ₁₉ (H19)	5.70	-140.2067	19.492	1.026
Li ₂₄ (H24)	5.71	-177.1344	25.469	1.061

TABLE II. Geometric and energetic results for all hexagonal clusters of this study. For definitions of the optimized nearest-neighbor distances $d_{\rm NN}$, total energies $E_{\rm tot}$, atomization energies E_b , and cohesive energies E_c , see the text. The cluster labels coincide with those of Fig. 1.

gether with the cluster total energy E_{tot} and the atomization energy E_b defined by

$$E_b = nE_{\text{tot}}(\text{Li}) - E_{\text{tot}}(\text{Li}_n)$$
(2)

and the cluster cohesive energy E_c defined by

=

$$E_c = \frac{E_b}{n} . aga{3}$$

The equilibrium nearest-neighbor distances $d_{\rm NN}$ of the hexagonal clusters show an overall monotonous convergence with increasing cluster size. This becomes also clear from Fig. 3, where the $d_{\rm NN}$ values of Table II are drawn as a function of the number *n* of Li atoms in the



FIG. 3. Optimized nearest-neighbor distances d_{NN} shown as a function of the number *n* of Li atoms in the hexagonal Li_n clusters. The values for compact clusters (open diamonds) are connected by a line. Crosses refer to open structures; see Fig. 1. The dashed line gives the monolayer result and the full square to the right shows the bulk value of d_{NN} .

clusters. Here the values for compact clusters which form closed convex islands (n = 2, 3, 7, 10, 14, 19, 24; opendiamonds) are connected by a line, while the other values (crosses) refer to more open structures; see Fig. 1. The dashed line gives the monolayer result $d_{\rm NN} = 5.77$ bohr and the full square to the right shows the bulk value $d_{\rm NN} = 5.70$ bohr, obtained by the present FPLAPW calculations. Obviously, the optimized d_{NN} values increase, i.e., the clusters become less dense as their size increases, and there is a clear convergence toward the hexagonal monolayer value. For clusters larger than ten atoms the difference between monolayer and island is below 0.1 bohr. This corresponds roughly to the accuracy of the equilibrium values of $d_{\rm NN}$. The cluster total-energy curves are rather flat about the equilibrium distances and the error bars shown in Fig. 3 reflect an energy range of only $\Delta E_{tot} = \pm 5 \times 10^{-3}$ eV. The scatter in the d_{NN} results for the smaller open clusters is explained by the fact that their shape, together with the size, influences binding, which determines the nearest-neighbor distance, as has been found in other studies on small metal clusters. 4,17,29,30

The above cluster geometries are obtained by a restricted optimization where the hexagonal cluster symmetry is kept fixed and only the nearest-neighbor distance $d_{\rm NN}$ is optimized. The validity of this procedure has been checked in test calculations on several clusters where the cluster symmetry was relaxed and a full planar geometry optimization was carried out using energy gradients of the DEMON computer code.³⁸ As an illustration Fig. 4 compares, for the Li₁₃ cluster, H13a, equilibrium geometries of the restricted and of the full planar optimization. Here the hexagonal equilibrium structure is given by black disks denoting the Li atom positions and the fully optimized structure is overlayed by gray disks with identical radii where the central Li atoms of both structures coincide. Further, the Li₁₃ skeleton of the full op-



FIG. 4. Equilibrium geometries of the Li_{13} cluster H13a. The structure resulting from a restricted hexagonal optimization (black disks denoting the Li atom positions) is overlayed by that of a full planar optimization (gray disks) where all disk radii are identical and the central Li atoms coincide. The Li_{13} skeleton of the full optimization is sketched by lines connecting nearest-neighbor atom centers.

timization is sketched by lines connecting nearestneighbor atom centers. Obviously, the geometries resulting from both optimizations are very similar. A nearestneighbor analysis yields for the full optimization $d_{\rm NN}$ values ranging between 5.49 and 5.79 bohrs with an average of 5.66 bohr, which is very close to that of the hexagonal optimization $d_{\rm NN}$ = 5.61 bohr. Further, the total energies $E_{\rm tot}$ of both geometries differ by less than 0.05 eV. Thus the present optimization procedure is meaningful and can give equilibrium geometries which are quite close to those of the fully optimized planar (perturbed hexagonal) structures.

Figure 5 shows the computed cluster cohesive energies E_c of Table II as a function of the number *n* of Li atoms in the clusters. As in Fig. 3 the results of compact clusters are connected by a line and the dashed line gives the monolayer result $E_c = 1.23$ eV. Analogous to the nearest-neighbor results, the cluster cohesive energies E_c show some oscillatory behavior for smaller sizes, but, in general, increase with cluster size where the hexagonal monolayer value forms an upper bound. Thus the average bond strength of the islands increases with size and the Li atoms inside the monolayer are more strongly bound than those of the finite islands. This result may be rationalized by simple coordination considerations based on pairwise additive binding and the assumption that Li atoms are most stable if they are surrounded by a maximum number of nearest neighbors, six in the case of two-dimensional densest (hexagonal) packing. It explains the increased average binding for larger clusters by the fact that relatively more cluster atoms experience an ideal monolayer environment of six nearest neighbors and the E_c value of the monolayer must be an upper bound. This simple intuitive model can also be used to quantify the size dependence of E_c to some extent, as will be discussed later on. However, it cannot explain the detailed physics that is behind cluster, layer, and bulk cohesion where binding energies of neighbor shells are not strictly additive. This is obvious from the fact that the bulk values $E_c = 1.75$ eV for bcc (eight nearest neighbors) and $E_c = 1.81$ eV for fcc (12 nearest neighbors) are quite similar and considerably larger than the hexagonal monolayer



FIG. 5. Cluster cohesive energies E_c shown as a function of the number *n* of Li atoms in the hexagonal Li_n clusters. The values for compact clusters (open diamonds) are connected by a line. Crosses refer to open structures; see Fig. 1. The dashed line gives the monolayer value of E_c .

result.

Table III gives results of the calculations on the square lithium clusters; see Fig. 2. As in the hexagonal case, the optimized nearest-neighbor distance d_{NN} of each cluster is listed together with the cluster total energy E_{tot} , the atomization energy E_b , and the cluster cohesive energy E_c . The equilibrium nearest-neighbor distances $d_{\rm NN}$ of the square clusters vary much more strongly with cluster size compared to those of the hexagonal clusters, but overall the values for the larger clusters increase and seem to converge to the monolayer result. This can be seen in Fig. 6, which shows the d_{NN} values of Table III as a function of the number n of Li atoms in the clusters. The values for compact clusters forming closed convex island (n = 2, 4, 9, 16, 20, 25; open squares) are connected by a line, while the other values (crosses) refer to more open structures; see Fig. 2. The error bars in Fig. 6 correspond to a total energy uncertainty of $\Delta E_{tot} = \pm 5 \times 10^{-3}$ eV. The monolayer result $d_{\rm NN} = 5.45$ bohr is shown by the dashed line and the full square to the right denotes the bulk value $d_{\rm NN} = 5.70$ bohr of the present FPLAPW calculations. Here the strong variation of d_{NN} with cluster size becomes obvious and there seems no clear trend toward convergence for smaller clusters up to Li_{12} . This is due to the fact that these square clusters form more open structures with "pockets" and corner atoms (see Fig. 2) compared to the small hexagonal clusters such that the cluster shape sensitivity of $d_{\rm NN}$ is more pro-nounced.^{4,17,29,30} However, the optimized $d_{\rm NN}$ values of the larger compact square clusters come rather close to the result of the square monolayer.

The equilibrium nearest-neighbor distance of the square monolayer is smaller by 0.3 bohr compared to that of the hexagonal layer which itself is only slightly larger (0.07 bohr) than the bcc bulk value. The former result can be understood by a simple coordination effect. In the square clusters including the monolayer each Li atom is surrounded by a maximum of four nearest and four next nearest neighbors, yielding a more open structure com-

Cluster	d _{NN} (bohrs)	$E_{\rm tot}$ (hartree)	E_b (eV)	E_c (eV)
Li ₂ (S2/H2)	5.13	-14.7212	1.034	0.517
Li_{3} (S3)	5.18	-22.0867	1.687	0.562
Li_{4} (S4a)	5.43	-29.4606	2.558	0.640
Li₄ (S4b)	5.10	-29.4582	2.503	0.626
Lis (S5)	4.96	-36.8361	3.483	0.697
Li_7 (S7a)	5.29	- 51.5978	5.633	0.805
Li ₇ (S7b)	5.19	51.5716	4.898	0.700
Li_7 (S7c)	5.29	-51.5960	5.578	0.797
Li. (S8)	5.41	- 58.9727	6.531	0.816
Li. (S9)	5.47	-66.3552	7.646	0.850
Li_{12} (S12)	5.29	- 88.5092	11.157	0.930
Li_{14} (S14a)	5.36	-103.2614	13.034	0.931
Li_{14} (S14b)	5.36	-103.2683	13.225	0.945
Li_{15} (S15)	5.40	-110.6440	14.150	0.943
Li_{16} (S16)	5.49	-118.0288	15.320	0.958
Li ₂₀ (S20)	5.42	-147.5430	19.350	0.967
Li ₂₅ (S25)	5.40	-184.4540	24.870	0.995

TABLE III. Geometric and energetic results for all square clusters of this study. For definitions of the optimized nearest-neighbor distances d_{NN} , total energies E_{tot} , atomization energies E_b , and cohesive energies E_c , see the text. The cluster labels coincide with those of Fig. 2.

pared to the hexagonal clusters (and monolayer) with a maximum of six nearest and six next nearest neighbors per atom. Thus, for a given layer density $[\rho(\text{hexagonal})=(2/\sqrt{3})d_{NN}^{-2}=0.035 \text{ bohr}^{-2}$ and $\rho(\text{square}) = d_{NN}^{-2} = 0.034 \text{ bohr}^{-2}$ from the present optimizations], the interatomic distances of the square monolayer are smaller than those of the hexagonal layer. However, the agreement between the hexagonal layer and the bcc bulk results for d_{NN} seems accidental and cannot be explained by a simple coordination model.

The computed cluster cohesive energies E_c of Table III are displayed in Fig. 7 as a function of the number *n* of Li atoms in the square clusters analogous to Fig. 5 for the



FIG. 6. Optimized nearest-neighbor distances d_{NN} shown as a function of the number *n* of Li atoms in the square Li_n clusters. The values for compact clusters (open squares) are connected by a line. Crosses refer to open structures; see Fig. 2. The dashed line gives the monolayer result and the full square to the right shows the bulk value of d_{NN} .

hexagonal case. The E_c values for compact clusters connected by a line increase with cluster size and the square monolayer value $E_c = 1.17$ eV (dashed line in Fig. 7) forms an upper bound. Thus, the average bond strength in the square clusters increases with size and the Li atom inside the monolayer are most strongly bound, which is analogous to the results for the hexagonal clusters. It can also be understood by the incomplete average coordination of the cluster atoms with respect to those of the monolayer as discussed before.

The coordination model can only account for the average stability of the planar clusters. It cannot describe the



51



detailed binding energetics when Li atoms are added to or removed from the cluster, which is important for a microscopic understanding of the cluster and island growth process. This is illustrated in test calculations on the square Li₉ cluster S9; see Figs. 2 and 8. Here the removal of Li corner atom requires an energy

$$\Delta E_{\rm rem} = E_{\rm tot}({\rm Li}_8) + E_{\rm tot}({\rm Li}) - E_{\rm tot}({\rm Li}_9) = 1.11 \text{ eV}$$
, (4)

while the addition of a Li atom at the most favorite site of the cluster rim (see Fig. 8) gains an energy

$$\Delta E_{add} = E_{tot}(Li_9) + E_{tot}(Li) - E_{tot}(Li_{10}) = 1.23 \text{ eV} .$$
 (5)

Both $\Delta E_{\rm rem}$ and $\Delta E_{\rm add}$ are considerably larger than the average binding energy $E_c = 0.85$ eV for Li₉. This confirms that the cluster growth process is determined by details of the electronic structure near the cluster edge and therefore is not quantitatively connected with average binding in the cluster, which is expected. Further, the result of $\Delta E_{\rm add}$ being larger than $\Delta E_{\rm rem}$ suggests that it is energetically favorable to add Li atoms to existing clusters compared to removing atoms. This trend, which favors large Li islands over smaller ones, is already visible in the results for the cohesive energies E_c (see Fig. 7), where the stability increases with increasing cluster size.

A comparison of the binding-energy results reveals close similarities between the hexagonal and square clusters. For both geometries the cohesive energy E_c increases with cluster size and converges towards the respective monolayer value. However, for a given size the E_c values are always larger for compact hexagonal clusters than for square clusters. This is consistent with the monolayer results (see Table I), where the hexagonal geometry is favored energetically over the square geometry. It may be explained by a coordination effect due to the different nearest-neighbor environment in the two geometries. In the hexagonal monolayer each Li atom is surrounded by six nearest neighbors corresponding to maximum coordination and densest twodimensional packing as opposed to the square monolayer with only four nearest neighbors per Li atom.

The concept of pairwise additive nearest and next nearest neighbor binding in the Li_n clusters can be used to quantify the size dependence of the cohesive energies E_c in an approximate way. Here we assume that E_c for a



FIG. 8. Geometry of the square Li_9 cluster with (a) one Li atom removed from the cluster corner and (b) one Li atom added at the most stable site near the cluster rim.

given geometry (hexagonal or square) depends linearly on the number of nearest and next nearest atom pairs in the Li_n cluster, which can be expressed by

$$E_{c}(n, n_{1}, n_{2}) = (\alpha n_{1} + \beta n_{2})/n , \qquad (6)$$

where α, β are energy parameters and n_1, n_2 measure the nearest and next-nearest-neighbor pairs in the cluster defined by

$$n_1 = \sum_{i=1}^n p_i^{(1)}, \quad n_2 = \sum_{i=1}^n p_i^{(2)},$$
 (7)

where $p_i^{(1)}, p_i^{(2)}$ denote the number of nearest and next nearest neighbors of atom *i* in the cluster. Obviously, in the limit of infinite size both n_1/n and n_2/n assume the value 6 (4) for hexagonal (square) clusters. The energy parameters α, β , determined by least-squares fits including all clusters of the present study, are found as

$$\alpha = 0.2778 \text{ eV}$$
, $\beta = -0.0501 \text{ eV}$

(hexagonal clusters) (8)

and

$$\alpha = 0.2977 \text{ eV}$$
, $\beta = -0.0292 \text{ eV}$

(square clusters), (9)

reproducing the computed E_c data of all compact clusters except Li₂ with an accuracy of 0.03 eV. Further, the energy contributions to E_c originating from next nearest neighbors represented by βn_2 in the above fit are always much smaller in size compared to the nearest-neighbor contributions. In fact, if next nearest-neighbor contributions are neglected, which results in a fitting formula

$$E_c(n, n_1) = (\alpha n_1)/n$$
, (10)

where separate least squares fits yield

$$\alpha = 0.2424 \text{ eV}$$
 (hexagonal clusters),
 $\alpha = 0.3252 \text{ eV}$ (square clusters), (11)

the computed E_c results of most compact clusters are reproduced with an error below of 0.05 eV. This can be seen in Figs. 9 and 10, which compare the computed E_c data with fitted E_c data for the hexagonal and square clusters. The overall good agreement gives strong indications that the average binding in the Li_n clusters reflecting their relative stability and quantified by E_c can be explained to a major extent by simple geometric effects, which derive from the nearest-neighbor coordination of the cluster atoms. Details of the electronic structure in the clusters seem to become important only for very small systems such as Li₂. The fitting parameter α may be interpreted as an average energy per Li-Li bond in the clusters where the numerical evaluation yields larger values for the square compared to the hexagonal systems. This may be connected with the smaller equilibrium nearest-neighbor distances d_{NN} in the square clusters, resulting in an increased nearest-neighbor interaction compared to that of the hexagonal clusters. However, such conclusions cannot be quantitative and have to



FIG. 9. Cluster cohesive energies E_c for compact hexagonal Li_n clusters. The computed results (open diamonds, full line, calc.) are compared with the fit based on pairwise nearest-neighbor binding (open triangles, dashed line, appr.); see the text.

be considered with caution due to the simplicity of the present fitting model.

The energetic distribution of the valence electron orbitals of the present systems can be characterized by respective level diagrams of the clusters and by band structures of the monolayers. As examples, Figs. 11 and 12 compare, for the hexagonal and square geometries, level diagrams of the compact clusters with densities of states (DOS's) derived from the respective monolayer band structures. Here the energies of all levels of a given cluster referring to Kohn-Sham valence orbitals of dominant Li 2sp character are shifted rigidly such that the energy of the highest occupied level (Fermi energy) coincides with the energy zero. While the distributions of the finite cluster levels are discrete, with the number of occupied



FIG. 10. Cluster cohesive energies E_c for compact square Li_n clusters. The computed results (open diamonds, full line, calc.) are compared with the fit based on pairwise nearest-neighbor binding (open triangles, dashed line, appr.); see the text.



FIG. 11. Kohn-Sham level diagrams of the compact hexagonal Li_n clusters and DOS of the hexagonal monolayer (full line). The highest occupied level of each cluster and the monolayer Fermi level are defined as energy zero. The dashed line gives a fictitious DOS of the Li₂₄ cluster where a level broadening of 0.08 eV has been applied.

levels increasing with increasing cluster size, the monolayers are described by quasicontinuous level distributions, which are characterized by (energy-dependent) DOS's. Figures 11 and 12 show that for both monolayer geometries the DOS (full line) remains roughly constant within the energy range of the occupied levels. This confirms that the Li monolayers are described approximately by two-dimensional free-electron metals (where the DOS does not depend on energy), which is to be expected from the Li bulk behavior.²¹ Further, the DOS values are very close between the hexagonal and the square monolayers, which is due to the very similar average electron densities determined by the layer geometries. As a consequence, the energy range W of the occupied



FIG. 12. Kohn-Sham level diagrams of the compact square Li_n clusters and DOS of the square monolayer (full line). The highest occupied level of each cluster and the monolayer Fermi level are defined as energy zero. The dashed line gives a fictitious DOS of the Li_{25} cluster where a level broadening of 0.08 eV has been applied.

TABLE IV. Comparison of the electronic structure and binding parameters of the largest Li_n clusters and monolayers. For a definition of the cohesive energy E_c , the equilibrium nearest-neighbor distance d_{NN} , and the occupied bandwidth W, see the text. The hexagonal monolayer results include LDA band-structure data from the literature.

System	d _{NN} (bohrs)	E_c (eV)	<i>W</i> (eV)
Li ₂₄ (hexagonal LSDA)	5.71	1.06	1.81
Li monolayer (hexagonal, LDA)	5.77	1.23	2.10
Li monolayer (hexagonal, LDA, other)	5.74°, 5.78°, 5.73°	1.09 ^a , 1.11 ^b , 1.10 ^c	2.17 ^a , 2.10 ^b , 2.20 ^c
Li ₂₅ (square, LSDA)	5.40	1.00	1.99
Li monolayer (square, LDA)	5.45	1.17	2.01

^aReference 34. ^bReference 21.

^cReference 22.

Kohn-Sham levels defined by

$$W = E_F - E_{\text{bottom}} , \qquad (12)$$

where E_F is the energy of the highest occupied level (Fermi level) and E_{bottom} denotes that of the lowest Li 2s derived level, differs only slightly between the hexagonal (W = 2.10 eV) and the square monolayer (W = 2.01 eV); see also Table IV.

It is interesting to compare the level densities of the largest clusters, hexagonal Li_{24} and square Li_{25} , with the DOS's obtained for the respective monolayers. This is shown in Figs. 11 and 12, where the dashed lines refer to fictitious DOS's determined with a level broadening of 0.08 eV. Clearly, the discreteness of the cluster level distributions results in DOS oscillations, but the center of gravity of the oscillations approaches the respective monolayer DOS value, as one would expect in a simple cluster convergence scheme. The range W of the occupied cluster levels varies with cluster size as can be seen in Figs. 11 and 12. However, there seems to be no gradual convergence. The monolayer values of W are reached already for rather small clusters, hexagonal Li7 and square Li₉, and a further increase in cluster size results only in minor variations by 10-20%. This may suggest that the interaction between the Li atoms in the clusters, which is the origin the level splitting characterized by W, is determined to a major degree by short-range coupling between Li nearest neighbors. This would explain the weak dependence of W on cluster size and would also be consistent with the success of the simple coordination model to reproduce the computed cohesive energy results as discussed above.

IV. CONCLUSIONS

The present study, which combines *ab initio* cluster calculations on finite planar Li_n clusters with bandstructure calculations on Li monolayers of hexagonal and square geometries can give insight into electronic and geometric properties of the systems. It can, in particular, help us understand details of the cluster size dependence of the physical parameters and their convergence behavior with respect to the monolayer results as the cluster size increases. These results are relevant for a microscopic description of growth processes that happen when Li atoms are adsorbed at substrate surfaces and combine to form islands and layers with increasing coverage. Total-energy optimizations on the clusters yield, for both hexagonal and square geometries, equilibrium nearest-neighbor distances d_{NN} which increase with increasing cluster size and converge towards the d_{NN} value of the respective monolayers. The convergence of d_{NN} is quite rapid and the monolayer value is reached at rather moderate Li_n cluster sizes of $n \approx 10$. Assuming weak adsorbate-substrate coupling, this suggests that compact Li_n islands formed at a solid substrate can assume a monolayerlike structure already at moderate sizes and the addition of further Li atoms increasing the islands does not result in major structural changes.

The electronic structures of the clusters are described by Li 2sp derived Kohn-Sham valence orbitals where the levels of the occupied orbitals are confined to an energy range of $W \approx 2$ eV. This value of W is found already for the smaller Li_n clusters $n \approx 7$ and varies only little with size. It coincides with the width W of the occupied part of the 2sp bands of the monolayers. This agreement indicates electronic similarity between the finite Li islands and the monolayer films. However, the discrete level distribution in the finite cluster cannot represent the quasicontinuous distribution of the monolayers as evidenced in comparisons of respective DOS's. While the monolayer DOS's are approximately constant within the energy range of occupied levels, reflecting a twodimensional free-electron-like behavior of the Li 2sp bands, the DOS's for the largest clusters of the present study oscillate about the monolayer value.

The cohesive energies E_c of the planar cluster vary more strongly with size and shape for the smaller clusters, while for the large ones there is a smooth increase of E_c with size and a clear convergence towards the cohesive energy value of the monolayer, which forms an upper limit. The present data do not show any Li_n clusters of preferred relative stability for *n* ranging between 1 and 25 and thus do not support the existence of magic numbers for the two-dimensional planar clusters, as has been suggested in Hartree-Fock studies.³⁰ A comparison between clusters of hexagonal geometry with those of square geometry and comparable size yields hexagonal clusters slightly more stable. This result holds also for the monolayers where the hexagonal layer is found to be more stable than the square layer, in agreement with previous work.^{21,22} The size dependence of the cluster cohesive energies can be reproduced almost quantitatively by a rather simple model based on the concept of pairwise additive nearest-neighbor binding. Here E_c is assumed to depend linearly on the number of nearest atom pairs in the cluster with the proportionality constant used as a fitting parameter. The fits result in E_c being reproduced with an error below 0.05 eV for most of the compact Li_n clusters. This overall good agreement indicates strongly that the average binding in the Li_n clusters reflecting their relative stability can be explained to a major extent by simple geometric effects which derive from the nearest-neighbor coordination of the cluster atoms. Details of the electronic structure in the clusters seem to become important only for very small systems such as Li₂.

The increase of the cluster cohesive energy E_c with size suggests that on real substrate surfaces with Li adatoms

¹A. W. Overhauser, Phys. Rev. Lett. 53, 64 (1984).

- ²A. P. Cracknell, in *Metals: Phonon States, Electron States and Fermi Surfaces*, edited by K. H. Hellwege and J. L. Olsen, Landolt-Börnstein, New Series, Group III, Vol. 13, Pt. c (Springer-Verlag, Berlin, 1984).
- ³M. S. Anderson and C. A. Swenson, Phys. Rev. B **31**, 668 (1985).
- ⁴K. Hermann and P. S. Bagus, Phys. Rev. B 17, 4082 (1978).
- ⁵C. E. Sessions and J. H. DeVan, Nucl. App. 9, 250 (1970).
- ⁶E. F. Cairns, F. A. Cafasso, and V. A. Maroni, in *The Chemistry of Fusion Technology*, edited by D. M. Gruen (Plenum, New York, 1972).
- ⁷N. D. Lang, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1973), Vol. 28, p. 225.
- ⁸N. D. Lang and A. R. Williams, Phys. Rev. B 18, 616 (1978).
- ⁹A. Heilingbrunner and G. Stollhoff, J. Chem. Phys. **99**, 6799 (1993).
- ¹⁰V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Electronic Properties of Metals* (Pergamon, New York, 1987).
- ¹¹J. Callaway, X. Zou, and D. Bagayoko, Phys. Rev. B 27, 631 (1982).
- ¹²J. C. Boettger and S. B. Trickey, Phys. Rev. B 32, 3391 (1986).
- ¹³M. M. Dacorogna and M. L. Cohen, Phys. Rev. B 34, 4996 (1986).
- ¹⁴J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B 46, 6671 (1992).
- ¹⁵J. A. Nobel, S. B. Trickey, P. Blaha, and K. Schwarz, Phys. Rev. B 45, 5012 (1992).
- ¹⁶J. D. Pack, H. J. Monkhorst, and D. L. Freeman, Solid State Commun. 29, 723 (1979).
- ¹⁷B. K. Rao, P. Jena, and D. D. Shillady, Phys. Rev. B **30**, 7293 (1984).
- ¹⁸R. Tang, Phys. Rev. B 43, 9255 (1991).

diffusing without major barriers, large Li islands are formed at low coverage and grow at the expense of smaller islands until a monolayer is built with increasing Li coverage. This would be compatible with Frank-Van der Merwe or Stranski-Krastanov growth modes and exclude Volmer-Weber growth³⁹ where three-dimensional islands are created on the surface. However, the present calculations do not allow definitive conclusions about growth modes and dynamics, which would require larger clusters including three-dimensional islands as well as an account of the interaction between islands and the bulk substrate, which is neglected in this work. Calculations along these lines are presently under way.

ACKNOWLEDGMENT

This study was supported in part by Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 290, Berlin).

- ¹⁹A. D. Zdetsis, Phys. Rev. B 34, 7666 (1986).
- ²⁰R. Car and J. L. Martins, Surf. Sci. **106**, 281 (1980).
- ²¹J. C. Boettger and S. B. Trickey, Phys. Rev. B 45, 1363 (1992).
- ²²E. Wimmer, J. Phys. F **13**, 2313 (1983).
- ²³W. T. Hicks, J. Chem. Phys. 38, 1873 (1963).
- ²⁴T. Greber, K. Freihube, R. Grobecker, A. Böttcher, K. Hermann, and G. Ertl, Phys. Rev. B **50**, 8755 (1994).
- ²⁵K. Hermann, K. Freihube, T. Greber, A. Böttcher, R. Grobecker, D. Fick, and G. Ertl, Surf. Sci. **313**, L806 (1994).
- ²⁶Z. P. Hu and A. Ignatiev, Phys. Rev. B 30, 4856 (1984).
- ²⁷G. M. Watson, P. A. Bruhwiler, E. W. Plummer, H.-J. Sagner, and K.-H. Frank, Phys. Rev. Lett. **65**, 468 (1990).
- ²⁸Y. S. Vedula and V. V. Polplavskii, Pis'ma Zh. Eksp. Teor. Fiz. **46**, 182 (1987) [JETP Lett. **46**, 231 (1987)].
- ²⁹G. Pacchioni, D. Plavsic, and J. Koutecky, Ber. Bunsenges. Phys. Chem. 87, 503 (1983).
- ³⁰A. K. Ray, B. K. Rao, and P. Jena, Phys. Rev. B 48, 14702 (1993).
- ³¹D. M. Ceperley and B. J. Alder, Phys. Rev. B 45, 566 (1980).
- ³²J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).
- ³³J. C. Boettger and S. B. Trickey, J. Phys. Condens. Matter 1, 4323 (1989).
- ³⁴J. C. Boettger, S. B. Trickey, F. Muller-Plathe, and G. H. F. Diercksen, J. Phys. Condens. Matter 2, 9589 (1990).
- ³⁵P. Blaha, K. Schwarz, P. Sorantin, and S. B. Trickey, Comput. Phys. Commun. **59**, 399 (1990); P. Blaha, K. Schwarz, and R. Augustyn, WIEN93 computer code, Technische Universität Wien, 1993.
- ³⁶K. Freihube, Ph.D. thesis, Freie Universität, Berlin, 1993.
- ³⁷K. Hermann and K. Freihube (unpublished).
- ³⁸The LCGTO-LSD-DF program package DEMON was developed by A. St-Amant and D. Salahub at the University of Montreal.
- ³⁹E. Bauer, Appl. Surf. Sci. 11/12, 479 (1982).



FIG. 4. Equilibrium geometries of the Li_{13} cluster H13a. The structure resulting from a restricted hexagonal optimization (black disks denoting the Li atom positions) is overlayed by that of a full planar optimization (gray disks) where all disk radii are identical and the central Li atoms coincide. The Li_{13} skeleton of the full optimization is sketched by lines connecting nearest-neighbor atom centers.