PHYSICAL REVIEW B VOLUME 57, NUMBER 23 15 JUNE 1998-I

Metal segregation and electronic properties of lithium suboxide clusters

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(Received 9 March 1998)

The structural and electronic properties of neutral lithium suboxide clusters $Li_{4+p}O_2$ $(0 \leqslant p \leqslant 9)$ are studied by means of *ab initio* molecular dynamics simulations. For few excess Li atoms Li-O bonds are formed which progressively weaken as the O coordination number increases. Then Li attachment proceeds around nonstoichiometric ionic cores and results in metal segregation. The evolution of the growth mode correlates with a change of the electronic properties, some of which can be probed experimentally to obtain structural information. We predict that at small p $Li_{4+p}O_2$ clusters have ionization potential much lower than pure Li_p. A generalization of our results to oxidized alkali-metal surfaces and bulk suboxides is proposed. [S0163-1829(98)04624-4]

Reduction of oxides or oxidation of metals are important processes often related with profound modifications of the electronic properties, potentially useful for technological applications. However, a basic understanding of these phenomena is still lacking. When depositing metal atoms onto their oxides, the transition to a metallic behavior may sensitively depend on the amount of deposited atoms and their structural organization.[1] Symmetrically, oxidation of alkali-metal films is accompanied by an increase of the photoelectric yield,[2,3] which has been correlated to the lowering of the work function with respect to the pure metal, a fact that plays a role in the activation of photocathodes. Electron energy loss spectra and work-function measurements taken on oxidized Cs films show a strong sensitivity to the degree of oxidation.[4] Despite their structural complexity at a microscopic scale, these systems show photoemission spectra very similar to those obtained from bulk alkali-metal suboxides.[2] These compounds, whose building blocks are nonstoichiometric oxide clusters,[5] display a wide variety of electronic properties, due to the coexistence of both ionic and metallic bonding as a function of the actual stoichiometry. They have also served as model systems to explain the lowering of the work function Φ of alkali-metal surfaces upon oxidation on the basis of a quantum-size effect.[6] Nevertheless, in Cs compounds, work functions as low as 0.9 eV[4] are not yet fully explained by the analogy with bulk suboxides, whose Φ is about 50% higher.

The interest in oxide clusters grew when photoionization spectra of unsupported, mass-selected Cs_mO_n clusters were obtained[7] and showed the same qualitative behavior already observed on films. Moreover, evidence of the existence of electronic shell structure for the metal-rich clusters was provided in this study. Further experimental investigations on $Li_{2n+m}O_n^+$ clusters focused on the energetics of the cluster fragmentation and/or evaporation,[8] and raised the question of whether the electronic and thermodynamical properties of alkali-metal suboxide clusters could be described in terms of the coexistence of a ''metallic'' and ''ionic'' part inside the same microscopic object. However, the direct observation of the structure of small unsupported clusters is presently not feasible.

In order to understand the relation between atomic structure and electronic properties in suboxide systems and provide complementary information to experimental data, we choose to study the systematics of the Li enrichment of lithium dioxide clusters $Li_{4+p}O_2$ with $0 \leqslant p \leqslant 9$, by means of a combination of *ab initio* molecular dynamics simulations[9] and electronic structure calculations. Our computations are performed within the density functional theory, by using both the local density approximation (LDA) and local spin density approximation (LSDA) for the exchange and correlation energy. In particular, LSDA is used for clusters with an odd number of electrons, and for some even-numbered clusters that could present a non-spin-paired ground state. This approach has already been tested for stoichiometric clusters[10] and detailed elsewhere.[11] In addition to the calculations reported in Ref. 11, further tests are performed on pure Li_m clusters $(m=4,5,6,7)$, and on Li_nO molecules $(n=3,4,5)$. In both cases, the calculated cohesive energies $E_{\rm coh}$ and interatomic distances agree within at most 2% with previous calculations.[12–14] For instance, in T_d Li_4O, we find $E_{\rm coh}=3.31$ eV, and an Li-O bond length equal to 1.74 Å.

In order to find the equilibrium geometries of $Li_{4+p}O_2$ clusters, we carry out simulated annealing runs. From the geometries resulting from the dynamic runs, we obtain starting configurations through an educated guess on other possible topologies of the clusters. These geometries are then optimized until the atomic forces do not exceed 5 meV/Å. The calculated electronic structures always refer to stable geometries optimized in a fully self-consistent way. The stability of all the configurations issued from the local minimizations is checked against a random displacement of the atomic coordinates.

In spite of the existence of many competing low-energy isomers, whose thorough description will be the subject of a future report,[15] the essential features of cluster growth can be conveniently characterized by looking at the most stable $Li_{4+p}O_2$ isomers as found in our simulations, for $p \leqslant 9$ (Figs. 1 and 2).

In the first stage $(p \leqslant 3)$ the excess Li atoms bind to O (Fig. 1), increasing its coordination number from 3 (Li_4O_2) up to 5 (Li_7O_2). In the resulting $Li_{4+p}O_2$ most stable isomers, the two oxygens are bridged by either two or three lithiums, giving rise to Li_2O_2 or Li_3O_2 inner structures, which are both present in the low-energy configurations of

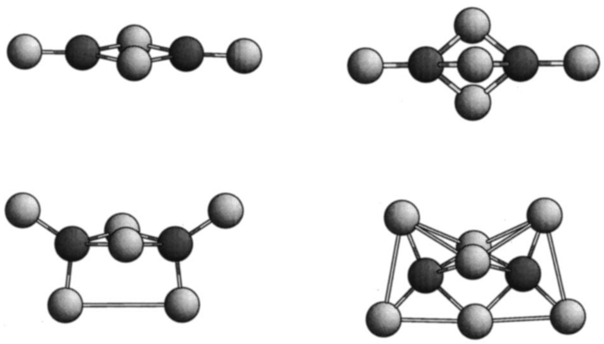

FIG. 1. First stage of growth of a $Li_{4+p}O_2$ cluster ($0 \leqslant p \leqslant 3$) by attachment of lithiums on oxygens. From left to right and from top to bottom, Li_4O_2, Li_5O_2, Li_6O_2, and Li_7O_2. Li atoms are drawn in light grey and O atoms in dark grey in all ball and stick representations.

the stoichiometric Li_4O_2 parents.[10] The alternation of Li_2O_2 and Li_3O_2 cores is explained by considering that equivalent environments for the two oxygens favor larger electron delocalization and lower total energy.

By analyzing the Li-O mean bondlengths $\bar{d}$, and the energy associated with the attachment of an Li atom to $Li_{4+p}O_2$, forming a new Li-O bond ($E^{\mathrm{att}}_{\text{Li-O}}$), we observe a correlated increase of $\bar{d}$ and decrease of $E^{\mathrm{att}}_{\text{Li-O}}$ as the number p of excess Li atoms grows. The growth of $\bar{d}$ induced when the coordination number increases has already been stressed in stoichiometric $Li_{2n}O_n$ clusters[10] and is a rather general phenomenon. In suboxide clusters, however, the Li-O bond weakens more quickly, and $E^{\mathrm{att}}_{\text{Li-O}}$ rapidly decreases as a function of p,[11,13] thus showing that these effects are mostly due to the reduction of the oxide clusters. When $E^{\mathrm{att}}_{\text{Li-O}}$ falls below a critical value of about 1.5 eV, which is close to the attachment energy of Li on pure Li_m clusters[16] and to the cohesive energy of bulk lithium (1.63 eV per Li atom), a second growth mechanism prevails (Fig. 2). Li addition takes place through Li-Li bond formation, without noticeable change of the ionic core of the cluster, which contains the two oxygens and all the lithiums bound to them.

It is worth introducing the notation $Li^{(n)}$ to distinguish among Li atoms n-fold coordinated with O. In the first stage of $Li_{4+p}O_2$ reduction by Li attachment, a growing number of $Li^{(1)}$ is formed. Configurations having only $Li^{(1)}$ and $Li^{(2)}$ are found up to $p=6$, but from $p=4$, the most stable isomers show $Li^{(0)}$-type atoms, whose number grows as a function of p (see Fig. 2), while the ionic core contains O, $Li^{(2)}$, and $Li^{(1)}$ only.

For $4 \leqslant p \leqslant 8$, the most stable $Li_{4+p}O_2$ isomers can be described as a Li_7O_2 ionic core, similar to the Li_7O_2 isomer shown in Fig. 1, surrounded by an increasing number of $Li^{(0)}$ as a function of p. This attachment process results into weak modifications of the ionic part, and a large rearrangement of $Li^{(0)}$ atoms when passing from p to $p+1$, with a clear trend towards $Li^{(0)}$ segregation. Metal segregation has also been reported in nonstoichiometric alkali-halide clusters[17] and, very recently, in Li_mO clusters.[13]

Finally, for $p=9$, the most stable $Li_{13}O_2$ isomer is built from a Li_9O_2 core plus four $Li^{(0)}$ atoms on top arranged in a tetrahedral configuration. The Li_9O_2 central block is formed by two O-centered distorted octahedra sharing a face; the same structural motif characterize a metastable configuration of a Li_9O_2 lying $\simeq 0.5$ eV above the most stable isomer.[11] It is interesting to note that it is isostructural to the building block of Rb_9O_2 and Rb_6O suboxides, synthetized by Simon and co-workers.[5] In our simulation, this structure was obtained through simulated annealing runs, by imposing no constraints on the atomic motion. The largest oxygen coordination number found among all the isomers is 6, thus confirming that the octahedral environment for O as found in Rb suboxides is particularly stable not only in bulk,[5] but also in alkali-metal suboxide clusters above a critical size.

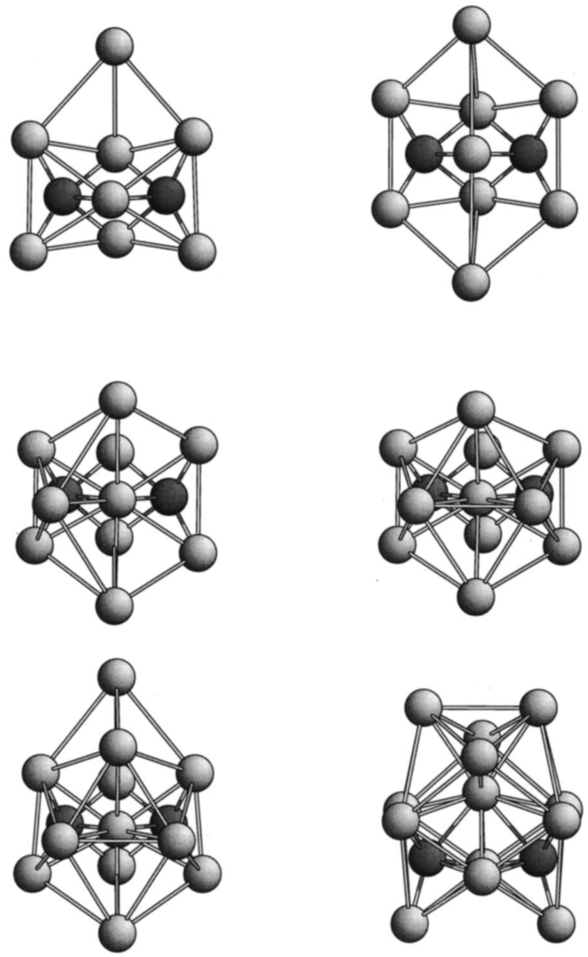

FIG. 2. Second stage of growth of a $Li_{4+p}O_2$ cluster ($4 \leqslant p \leqslant 9$) by attachment of lithiums on other lithiums. From left to right and from top to bottom, Li_8O_2, Li_9O_2, $Li_{10}O_2$, $Li_{11}O_2$, $Li_{12}O_2$, and $Li_{13}O_2$.

The trends observed in the cluster growth can be rationalized by considering the changes in the electronic structure as a function of the number p of excess Li atoms. For $p=0$ (stoichiometric cluster) a large electron transfer from Li to O takes place, and the resulting electrostatic potential increases the gap between the levels of occupied O-derived states and empty Li-derived states. As a general trend, in stoichiometric as well as in nonstoichiometric $Li_{4+p}O_2$ clusters, $Li^{(n)}$ atoms with the smallest n experience the smallest electrostatic potential and are thus associated to the lowest lying occupied antibonding states. For small p, the p excess electrons are thus mainly redistributed within the $Li^{(1)}$-O antibonding

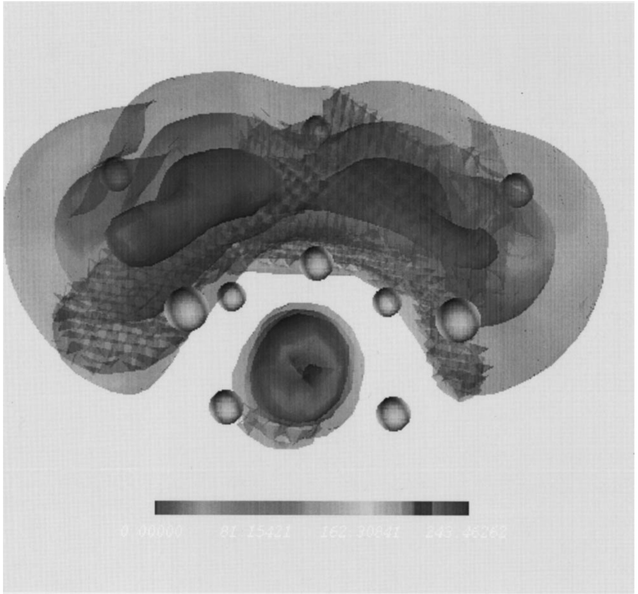

FIG. 3. Surfaces of equal density for the distribution of *excess* electrons in $Li_{10}O_2$. The view is taken along the O-O axis. Oxygen (in the lower central part of the figure) and surrounding lithium atoms are represented by small dark spheres and larger light spheres, respectively.

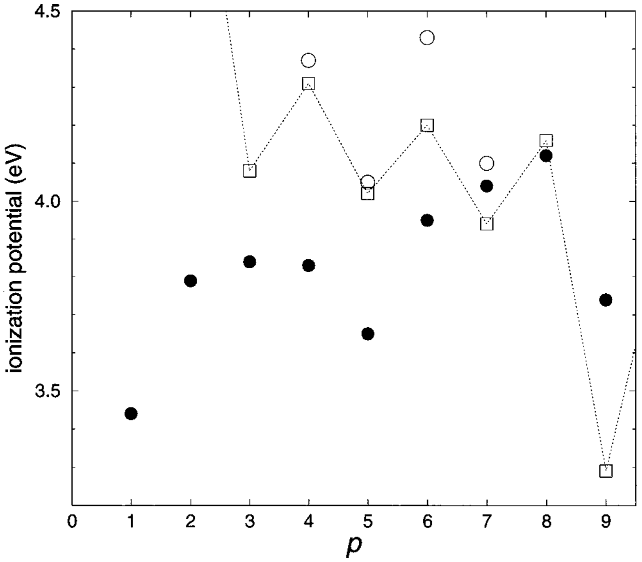

FIG. 4. Full circles: computed vertical ionization potential Φ_v of the most stable neutral $Li_{4+p}O_2$ isomers, as a function of p. Open circles: computed Φ_v for pure Li_p clusters. Open squares: experimental ionization potential for Li_p clusters, from Ref. 20.

states. As a consequence, the ionic Li-O bond weakens.

This picture is, however, insufficient to describe the second growth regime ($p \geqslant 4$), in which the existence of $Li^{(0)}$ suggests the presence of some *covalent* bonding between Li, such as in the dimer or in pure Li clusters. It is therefore crucial to distinguish the ionic from the covalent bonding within the same cluster, since a short Li-Li distance is not necessarily a signature of a covalent bond (CB).[18] Rather, a CB is formed between two lithiums when the valence electronic density shows a local maximum between them. Because they do not directly transfer electrons to oxygens, the $Li^{(0)}$'s are in a much more favorable situation to form CB's with other lithiums than $Li^{(1)}$ or $Li^{(2)}$. That they actually do so is exemplified in Fig. 3, where the distribution of the excess electrons in $Li_{10}O_2$ shows a clear covalent bonding among the lithiums. We find that the larger the number of CB's, the larger the energy gain $E^{\mathrm{att}}_{\text{Li-Li}}$ for the attachment of a $Li^{(0)}$ to the cluster. Typical values of $E^{\mathrm{att}}_{\text{Li-Li}}$ lie between 1.5 and 1.6 eV. Two consequences follow: (i) the crossover between the first and second growth regime happens when $E^{\mathrm{att}}_{\text{Li-Li}} > E^{\mathrm{att}}_{\text{Li-O}}$, around $p=4$ according to our numerical results and (ii) the Li-Li attachment process is reinforced as the number of $Li^{(0)}$'s increases and finally results into segregation of $Li^{(0)}$.

When segregation takes place ($p \geqslant 6$), a simple tight-binding (TB) model can account for the eigenenergies of all filled excess states: wave functions are expanded on the $2s$ atomic states of the $Li^{(0)}$ atoms, and constant resonance integrals and atomic energies are considered for all values of p. The eigenvalues of the model Hamiltonian turn out to be in remarkable agreement with those calculated from first principles, and the TB eigenvectors account well for the observed spatial behavior of LDA eigenstates. The model confirms that the $Li^{(0)}$'s can be roughly considered as lithium atoms in a pure Li_n cluster, and that a clear distinction exists between $Li^{(2)}$, $Li^{(1)}$, which play the role of cations, and $Li^{(0)}$, around which the electronic charge in excess is mostly localized. This conclusion is in agreement with the interpretation of photoemission experiments from alkali-metal suboxides.[2]

It is of interest to determine whether measurable electronic properties can probe the change of growth mode and thus assess the existence of a structural transition from a suboxide cluster to a metal cluster over a suboxide cluster in $Li_{4+p}O_2$, when p grows. To address this issue, we calculate the vertical ionization potential Φ_v of the most stable neutral isomers as a function of p, as the total energy difference $E_{\mathrm{tot}}(Li_{4+p}O_2) - E_{\mathrm{tot}}(Li_{4+p}O_2^+)$ in the LSDA.[19]

A dramatic decrease takes place from a large value (6.12 eV) in the stoichiometric parent D_{2h} Li_4O_2 to 3.44 eV in C_{3v} Li_5O_2. Then, as shown in Fig. 4, Φ_v increases up to 4.12 eV for $p=8$, apart from two local minima, to which we will return later. In the limit of very large p, Φ_v will eventually pass by a maximum and reach the value of the work function for elemental Li (3.4 eV).

We note the following. (i) For $p<6$, $\Phi_v(Li_{4+p}O_2)$ is smaller than both the experimental[20] and our calculated ionization potentials for the most stable isomers of pure Li_p clusters. This is due to the presence of O, and can be explained on the basis of a quantum size effect.[6] (ii) At variance with the usual behavior for pure metal clusters,[21] $\Phi_v(Li_{4+p}O_2)$ shows a general increasing trend in the range $1 \leqslant p \leqslant 8$. The existence of a minimum for nearly stoichiometric suboxide clusters ($p=1$) is a peculiar feature of the first and intermediate growth regimes ($p \leqslant 5$) in which $Li^{(0)}$ have not yet segregated. Indeed, in this regime, there are not enough low-energy $Li^{(0)}$-derived states to accommodate all excess electrons. The HOMO's are thus $Li^{(1)}$ derived. Located at higher energies, they are associated with lower values of Φ_v . However, when $p \geqslant 6$, most of the excess charge can be accommodated around the segregated $Li^{(0)}$. The HOMO, then, is $Li^{(0)}$ derived, Φ_v is higher and slightly increases towards its value for pure Li_p clusters. A similar argument may be used to explain the two minima shown by Φ_v for $p=5$ and $p=9$: $Li_9O_2^+$ and $Li_{13}O_2^+$ present an enhanced stability because there are as many $Li^{(0)}$ as excess electronic states, which all have a $Li^{(0)}$ character (see Fig. 2).

We thus conclude that the onset of metal segregation in alkali-metal suboxide clusters $A_{2n+p}O_n$ can be detected through ionization potential measurements, as the composition for which $\Phi_v(A_{2n+p}O_n)$ approaches $\Phi_v(A_p)$. In addition, we find that the lowest ionization potentials can be achieved close to the stoichiometric composition, i.e., for $0<p<n$, in agreement with experimental data for cesium oxide clusters.[7] By generalizing our model to oxidized alkali-metal surfaces, we also predict that the lowest values of the work functions can be achieved whenever the oxidation process results in suboxide compounds having the largest number of A-O bonds and the smallest number of segregating alkali atoms. We thus explain the behavior observed for Cs oxidized thick films[4] as a function of the surface oxidation. Our findings confirm the existence of an excluded region of space for the excess electrons as proposed by Burt and Heine,[6] but clarifies on more quantitative grounds the connection between the microscopic bonding configuration and the change of the electronic properties.

We conclude this paper with a peculiarity of the transition between the two growth regimes, namely, the occurrence of electronic instabilities. Some of the metastable Li_8O_2 isomers found in the simulations have a HOMO-LUMO gap ϵ_g smaller than 0.2 eV. In particular, this is the case for the most stable one, represented in Fig. 2. Although in density functional calculations ϵ_g is affected by systematic error,[22] its closing is an indication of a marked instability. Indeed, for all the clusters having a small ϵ_g, spin-unrestricted calculations unambiguously predict[23] a magnetic ground state with a net polarization of two spin units and a net spin density largely delocalized around the cluster. Interestingly, the magnetic configurations have a higher point symmetry than the spin-paired ones, on which a small geometrical distortion takes place.[24] A magnetic ground state for some alkali-metal clusters has already been predicted on the basis of a ellipsoidal jellium model,[25] as opposed to pure geometrical deformations. For $Li_{4+p}O_2$ clusters, spin-unpaired configurations are found only for $p=4$, at the transition between Li-O and Li-Li attachment.

Calculations for this work were performed at the IDRIS/CNRS computational center in Orsay (Project No. 970109). We acknowledge technical assistance by Thierry Goldmann, and thank Paul Walker for a careful reading of the manuscript. Laboratoire de Physique des Solides is ''Unité Associée au CNRS.''

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[16] It is defined as the energy of the reaction $Li_{m-1}+Li\rightarrow Li_m$. For $m=5,6,7$, we obtain 1.20, 1.55, and 1.51 eV, respectively, when considering the most stable isomers in the reaction.

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[18] Even in antifluorite Li_2O, the Li-Li interatomic distances are shorter than in the Li dimer. This is due to steric effects and is not a signature of chemical bonding between neighboring lithiums.

[19] The total energy of charged systems has been calculated by using a compensating background (B), and includes the B-B electrostatic interaction. Tests on pure Li_p clusters compare well with experiments (see Fig. 4) and existing calculations [see, e.g., I. Boustani *et al.*, Phys. Rev. B **35**, 9437 (1987)].

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[23] The energy gain due to spin polarization turns out to be in the range 0.05–0.1 eV, depending on the isomer.

[24] The distortion is not a Jahn-Teller effect, since the point group of the clusters does not contain irreducible representations of dimension greater than one. However, for these configurations, HOMO and LUMO are hybrids localized on Li atoms with the same chemical environment and are thus very close in energy.

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