Electron-Stimulated Emission of Na Atoms from NaCl Nanocube Corners

D. Ceresoli\textsuperscript{a,b}, T. Zykova-Timan\textsuperscript{a,b}, E. Tosatti\textsuperscript{a,b,c,*}

\textsuperscript{a}International School for Advanced Studies (SISSA), via Beirut 2, 3414 Trieste, Italy
\textsuperscript{b}Democritos National Simulation Center, Trieste, Italy
\textsuperscript{c}International Center for Theoretical Physics (ICTP), Strada Costiera 11, 3414, Trieste, Italy

Abstract

We performed first principles density functional calculations and simulations of magic-size neutral NaCl nanocubes, and computed the extraction of a Na neutral corner atom after donating an electron. The atomic structure of the resulting Na corner vacancy is presented.

Key words: Alkali halides, Nanoclusters, Density Functional Theory, Surface energy, Atom emission

1 Introduction

Alkali halide compounds such as NaCl form very stable ionic crystals. Their binding energy consists almost entirely of Coulomb attraction of the excess electric charges of oppositely charged ions. In this respect, extraction of ions, or of neutral molecules, from a bulk alkali halide crystal is a very endoenergetic process. For instance, the energy required to remove a NaCl molecule from bulk NaCl is 2.25 eV per molecule. Following addition or removal of an electron, individual neutral atoms can also be extracted from a surface. That process however is expected to be energetically less expensive.

For the extraction of halogen atoms, the energy scale is set by the exciton energy of NaCl – roughly 8 eV. In fact, once the solid is primed with one

* Corresponding author.

Email address: tosatti@sissa.it (E. Tosatti).
(surface) exciton it is known to emit a halogen atom with creation of a surface F-center [1]. Recent experiments with STM tips on NaCl(100) thin films [2,3], also showed that it is possible to extract halogen atoms under conditions of applied voltage.

Here we are concerned with the emission of neutral Na atoms upon donation of electrons. Experimentally, it is observed that some neutral NaCl nanoclusters become negative through electron attachment or positive via photoemission. [4] Earlier semi-empirical estimates on NaCl nanoclusters indicates neutral Na atom emission with a small activation energy of 0.4 eV [5,7,6]. In nanocube clusters, such low detachment energies can arise from the weakly bound corner atoms. Availability of cheap reactive alkali atoms might prove of considerable practical importance in the future. Motivated by this observation, we addressed the problem of calculating – now from first principles – the energy necessary to detach a neutral corner alkali atom after donation of an electron to an alkali halide crystalline nanocube.

Let us begin by considering an infinite surface first. An electron added to an infinite NaCl(100) surface will presumably go into a surface state just below the conduction band bottom $\sim 1$ eV below the vacuum level. By calculating the electronic structure of a neutral NaCl(100) slab, we find the empty surface state of NaCl(100) to be a linear combination of surface Na $3s$ and $3p_z$ orbitals. The added electron could remain delocalized over the surface, or else it could lead to a local deformation and become localized and self-trapped. If it became self-trapped near a single Na$^+$ surface ion, the added electron would neutralize it, thus canceling the coulomb attraction that binds the now neutral Na surface atom in its lattice place. As a result, this Na atom will remain bound to the surface only by weak induced-dipole and dispersion forces, making it relatively easy to detach. For this reason, emission of neutral Na atoms after electron addition can be expected to happen with a relatively modest energy cost. The final outcome after neutral atom emission, will be a surface atom vacancy, associated with a large characteristic rearrangement of the surrounding lattice ions.

The amount of energy required for extraction of an atom is expected to decrease for atoms located in less favorable positions, such as at surface steps and kinks, where the local coordination is smaller. The most favorable case of all should be represented by corner atoms of alkali halides cubes, where the ionic binding is weakest. Moreover, there is in this case no question of self-trapping, since the corner atoms naturally trap the carrier preferentially over all other atoms.
2 Computational details

NaCl nanoclusters were built by cutting out cubelets from a perfect NaCl crystal, with initial interatomic Na–Cl distance of 2.82 Å.

Previous calculations of electron attachment to a NaCl nanocluster exist based on a quantum path-integral molecular dynamics method, using classical interatomic potentials, and treating the quantum nature of the extra electron in an effective way [8,9].

We performed total energy calculations of NaCl(100) and of cubic NaCl nanoclusters in the first principles framework of density functional theory (DFT). We used the plane wave pseudopotential method [10,11], with norm-conserving pseudopotentials [12] and a plane wave cutoff of 40 Ry. Nonlinear core corrections [13] were included in the pseudopotential for Na. All calculations were spin polarized and the gradient-corrected BLYP exchange-correlation functional [14] was used.

Initially electron selfconsistency and full zero-pressure equilibrium was generated as a starting point of the neutral cluster. Donation of an electron was simulated by adding an electron in the LUMO, and by neutralizing the system by a uniform compensating background. The total energy change resulting by adiabatically pulling the appropriate surface or corner Na atom away from its initial location gives the desired extraction energy. We note that the energetics of this system may in principle be affected by finite-size effects and by self-interaction if the extra electron is localized. The finite size effects can be checked by comparing results for increasing size. The self-interaction error will only be large if the localization is extreme, and can still be be minimized when dealing with initial and final adiabatic states with similar levels of electron localization. In our case, we explicitly checked the ionization energy of an isolated Na atom and found it to be 5.3 eV, which is close to the experimental value 5.139 eV indicating that self-interaction is not an important problem.

3 Results and discussion

It is known from experiment [6] that ionized NaCl nanoclusters have “magic numbers” corresponding to small cubelets exposing (100) facets, whose general formula is [Na\textsubscript{n}Cl\textsubscript{n−1}]\textsuperscript{+} or [Na\textsubscript{n}Cl\textsubscript{n+1}]\textsuperscript{−}. Even if neutral clusters cannot be detected in mass-spectroscopy experiments, they are also predicted [6] to be of the cubic shape, with general formula Na\textsubscript{2n}Cl\textsubscript{2n}. Charged clusters have an odd number of ions on the cubic edges, whereas neutral clusters have an even number of ions. Positively charged clusters, in this idealized picture, have Na\textsuperscript{+}...
corner ions. Negatively charged clusters have Cl\(^{-}\) corner ions. On the contrary, neutral clusters will have four Na\(^{+}\) and four Cl\(^{-}\) corner ions.

We studied neutral nanocubes of two sizes: the small one just made up of 8 atoms or 4 molecules (Na\(_4\)Cl\(_4\)); the large one of 64 atoms or 32 molecules (Na\(_{32}\)Cl\(_{32}\)). The nanocubes were periodically repeated in a cubic box of 10 Å and 20 Å of side, respectively, where the residual interaction with periodic replicas is negligible. One Na atom was displaced gradually from one corner in the (111) direction of the cubic supercell. The displacement was measured from the ideal corner coordinates of the perfect cube, taken as the reference geometry. The geometry was relaxed for outwards displacements of the extracted corner atom of 0.1 Å, 0.2 Å and 5.0 Å. In order to simulate the mechanical rigidity of a much bigger cube, only ions closest to the resulting corner vacancy were allowed to relax, whereas the remaining nanocube ions (roughly 1/2 of the total) were kept fixed as indicated by different coloring in Fig. 1. Γ-point sampling was used in all calculations.

The total energy was found to increase monotonically as a function of displacement, leveling off for an outward displacement of \(\sim 4\) Å and higher. The extraction energy is evaluated as a difference between the total energy for a displacement of 5.0 Å and the total energy for zero displacement.

As anticipated, initially the energy for zero displacement may not be directly comparable to the final distorted energy because of the different self-interaction energy. For example one added electron would in the perfect cubic cluster be perfectly delocalized, because of symmetry, over the four Na corner atoms. Due to this in the initial (delocalized) state the electron self-interaction is much lower than in the distorted (localized) state, and the total
energy difference may be affected. However as soon as one corner Na atom is even slightly displaced outwards, the four-fold degeneracy is removed and the extra electron wave function strongly localizes on that Na atom. In this manner the error is approximately eliminated. The effective initial state energy is therefore calculated by assuming a very small displacement breaking the cubic symmetry in the initial state too, and then extrapolating to zero the initial displacement. For an appreciation of the effect mentioned above, the perfect cubic Na$_{32}$Cl$_{32}$ cluster energy is $E_0 = -1687.173$ eV, that with a slight distortion (extrapolated to zero) is $E'_0 = -1687.211$ eV, and the final one after full Na atom extraction $E'_5 = -1686.531$ eV. As one can see, the difference $E_0 - E'_0 = 38$ meV (which also contains the self-interaction), is negligibly smaller compared the Na extraction energy $\Delta = E'_5 - E'_0 = 0.68$ eV.

Our preliminary calculated energies for removal of neutral corner Na atoms are shown in Tab. 1 for the small and large cubes. The near coincidence of results of the small and large clusters indicates that finite-size errors arising from various sources, including interactions between replicas, are relatively unimportant. The energy required to extract a neutral Na atom, by addition of an electron is calculated to be $\sim 0.6$ eV, in fairly good agreement with the previous estimates of 0.4 eV [6,5,7] The relaxation pattern near the corner defect is shown in Fig. 2: the three first neighbors Cl$^-$ ions relaxed outwards in such a way as to minimize their repulsion. The extra electron goes into the Na 3s level, which falls in the middle of the NaCl cluster energy gap.

|               | small cube (Na$_4$Cl$_4$) | large cube (Na$_{32}$Cl$_{32}$) |
|---------------|----------------------------|---------------------------------|
| Na extraction energy $\Delta$ | 0.62 eV | 0.68 eV |

Table 1
Energy necessary to extract a Na neutral atom from the corner of a nanocube.
4 Conclusion

We calculated the extraction process of a neutral Na corner atom from NaCl nanoclusters to which one electron has been donated. A relatively low extraction energy of the order of half an eV previously suggested \([5,7,6]\) is essentially confirmed by the calculation. This implies that neutral Na atoms will be to some extent thermally emitted by corner sites of negatively charged NaCl nanocubes. In conclusion the nanocube corners seem to be an energetically cheap source of very reactive Na atoms.

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