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LETTER TO THE EDITOR

The excitonic mechanism of Na-atom desorption from the (100)NaCl surface

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Abstract. We report the results of *ab initio* Hartree–Fock calculations of the exciton relaxation in the second layer of the (100)NaCl surface which demonstrate a possible mechanism of the alkali-atom emission in the primary process of decay of an electronic excitation in alkali halides.

The atomic emission induced by electronic excitation of alkali halides has been studied both experimentally and theoretically [1–3] (see [4] for a recent review). Experimentally, it has been observed that the surface is gradually enriched by alkali metal as the irradiation at room temperature proceeds [5, 6]. Therefore it is generally accepted that electronic excitation leads to a preferential emission of halogen atoms. According to a time-of-flight analysis, the energy distribution of emitted halogen atoms has two components [7]: a non-thermal component, of which the most probable kinetic energy is 0.3 eV, and a thermal component characterized by a Maxwellian distribution of energies of emitted atoms. The emission of alkali atoms was considered to be due to a thermal evaporation from the alkali-rich surface created by emission of halogen atoms [8]. Recent high-sensitivity measurements of the emitted alkali atoms [9] have indicated, however, that the emission of alkali occurs at the very beginning of the irradiation of the undamaged surface. Thus it is also likely that the alkali atoms can be emitted primarily by electronic excitation, although the yield of this emission is much lower than that of the halogen atoms.

It is generally believed that the atomic emission induced by electronic excitation of alkali halides is related to the strong electron–lattice coupling that induces the self-trapping of excitons and holes similar to that in the bulk [10]. Theoretical modelling of localized electronic excitations near the (100)NaCl surface revealed two possible types of process leading to the emission of halogen atoms [11]. A free exciton trapped in the top surface layer can relax to a configuration in which a halogen atom is emitted out from the surface leaving an F centre on the top layer. This type of exciton relaxation is specific to the surface where there is asymmetry and additional freedom for atomic relaxation out from the surface. It is substantially different from that in the bulk where the F centre and the halogen interstitial atom (H centre) are formed. The maximum exciton relaxation energy that can be imparted to the emitted halogen atom was evaluated to be 2.2 eV. It has been suggested that this relaxation channel causes the non-thermal component of the halogen emission [11]. The difference between the energy gain evaluated theoretically and the observed kinetic energy of the non-thermal component has been attributed to the energy loss to other phonon modes near the surface. On the other hand, the self-trapping of excitons localized in the third and

deeper layers was shown to lead to a configuration similar to that in the bulk, comprising an F centre (a halogen-ion vacancy with a trapped electron) and an H centre (a halogen molecular ion occupying a halogen site). However, the H centres arriving to the top surface layer are metastable and can decay with desorption of a halogen atom. The calculated adiabatic barrier for the latter process is about 0.12 eV. Decomposition of the H centres created as a result of self-trapping of the excitons near the surface and arriving at the surface with thermal energies has been suggested to induce the thermal component of the halogen emission [11].

The cause of the emission of alkali atoms induced by electronic excitation is not yet clear, although several mechanisms have been suggested and studied theoretically for the (100)NaCl surface [12]. It has been shown that the non-radiative deexcitation of the lowest electronically excited state of the F centre on the surface can cause alkali-atom emission. F' centres and F-centre aggregates can decompose at the surface with emission of a neighbouring alkali atom trapping one of the extra electrons. However, in all of these cases the theoretical calculations [12] predicted the existence of substantial adiabatic barrier for the atom emission which depends on the defect configuration. The presence of the barrier can cause a certain time delay for the emission, which has indeed been observed experimentally [9, 13].

Although the emission of alkali atoms has been shown to be induced from a radiation-undamaged surface, it is not yet possible to exclude the possibility that it arises from the surface steps and kinks [12]. Nevertheless it is of interest to explore the effect of the lower symmetry on an exciton relaxation near the surface in greater detail and to try to find any possible mechanism for the emission of alkali atoms not related to surface defects. The purpose of this work is to report the results of theoretical calculations of the exciton relaxation in the second surface layer which demonstrate a possible mechanism for the alkali atom emission in the primary process of decay of an electronic excitation.

We have simulated the (100) NaCl surface using the *ab initio* Hartree-Fock embedded-molecular-cluster method implemented in the DICAP computer code [11, 12, 14]. A quantum cluster, Na_6Cl_5 , having C_{4v} symmetry was used in the calculations. It contains six Na ions surrounding a Cl ion in the second layer and four more Cl ions nearest to the Na ion on the (100) surface. Equations of the unrestricted Hartree-Fock (UHF) method [15] were solved for the 40 active valence electrons using a pseudopotential technique. The cluster was embedded in the potential of the infinite lattice. The lattice potential included three components: (i) a Madelung term produced by summing up to infinity the Coulomb potentials of point ions; (ii) a term produced by the semilocal pseudopotentials of Bachelet, Hamann and Schluter [16] of the ions nearest to the cluster boundary, preventing unphysical delocalization of the cluster wave-function; (iii) a short-range repulsion between the ionic cores in the quantum cluster and the ions of surrounding lattice. The latter is necessary to compensate for the absence of the exchange and resonant interactions between the electrons inside the cluster and those of the surrounding lattice, and to reproduce the perfect lattice structure [14]. The dependence of the results of calculations on the size and shape of the cluster, basis sets, pseudopotentials and pair potentials as well as other details of the method were thoroughly discussed in recent publications [11, 12, 14].

As discussed in [11], the solution of the UHF equations for the triplet state of a cluster simulating the bulk perfect lattice corresponds to the electronic excitation from the double-occupied anion states to the unoccupied cation states with a hole localized on the *p* atomic orbitals of a single anion and electron distributed over the nearest cations. The energy of this state, which we will from now on call an unrelaxed one-centre exciton, corresponds to the middle of the free-exciton band. It can be reasonably considered in the cluster model as

a precursor for an estimate of the lattice relaxation energy into the self-trapped state [17].

Due to the lower symmetry, for the surface simulated by the Na_6Cl_5 cluster we found two different solutions for the triplet excited state, i.e. unrelaxed one-centre excitons. The lowest state has an energy of 7.53 eV with respect to the ground state of the cluster and a broken-symmetry (C_s group) wave-function. In this state the hole is localized on one of the four Cl ions in the surface top layer. The relaxation of this state leads to the formation of an F centre in the surface layer and to the emission of a Cl atom with extra kinetic energy [11]. The second excited state corresponds to the one-centre unrelaxed exciton formation in the second layer below the surface. This state has an energy of 8.47 eV, which is only 0.04 eV smaller than the energy of the one-centre exciton in the bulk. The atomic relaxation of this exciton state is found to be very different from that in the third layer below the surface and in the bulk, and from that in the top surface layer. It is accompanied by a strong outward displacement perpendicular to the surface of the Na atom situated in the surface layer above the excited Cl atom as shown in figure 1. Let us now consider this state in more detail.

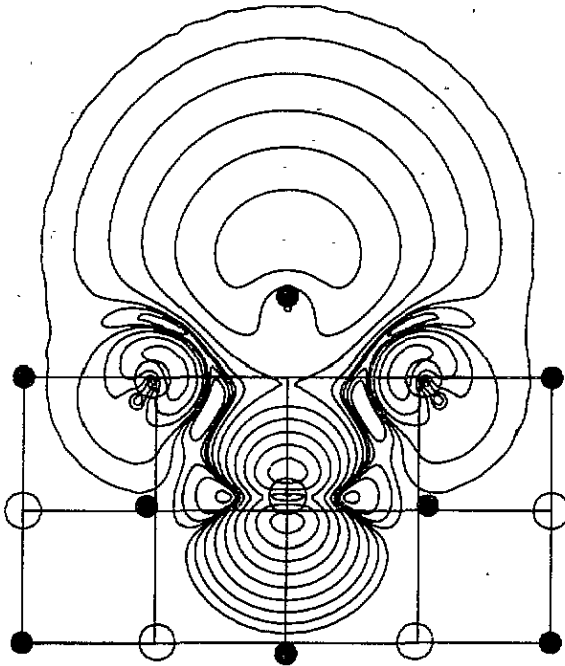


Figure 1. The section of the crystalline lattice in the symmetry plane perpendicular to the (100) surface and of the spin density of the triplet self-trapped exciton in the second layer below the surface. The spin-density isolines are shown in geometrical progression with a factor 3 with absolute initial values equal to 10^{-5} au^{-3} . Open circles denote chlorine ions and closed circles denote sodium ions. The centres of the circles correspond to the relaxed atomic configuration of the exciton.

In the relaxed atomic configuration, the Na atom is displaced from the surface plane by 1.7 Å. The energy at the minimum is 6.76 eV with respect to the ground state of the perfect surface. This gives an estimate for the relaxation energy from the one-centre exciton state of 1.7 eV. In this configuration the energy of binding of the Na atom to the surface is only 0.4 eV. The latter value agrees with an experimental estimate for the activation energy for the Na-atom emission from the undamaged NaCl surface [9, 13]. In figure 1 we also

present the contour plot of the spin density distribution in the relaxed triplet exciton. As one can see, the electron is localized on the Na atom and the hole occupies the p_z atomic orbital of the Cl atom in the second surface layer. The spin density on the Cl^- ions in the surface layer is small. The hole orbital (the lowest unoccupied beta-spin molecular orbital) has a bonding character with respect to the Cl atom and four nearest-neighbour anions in the surface layer. It is strongly polarized towards the Cl atom in the second layer due to the difference in the Madelung potential on these sites. This corresponds to the anti-bonding state of the Cl atom with the surface anions. Thus, the formation of chemical bonds between a Cl atom in the second layer and one of the surface anions in this excited metastable state seems highly unlikely.

Table 1. Energies (in eV) of the unrelaxed one-centre excitons and relaxed excitons in the bulk and in the three top layers of the NaCl (100) surface.

Position	Bulk	Third layer	Second layer	First layer
Unrelaxed exciton	8.51	8.51	8.47	7.53
Relaxed exciton	7.33	7.04	6.76	5.33
Configuration	$(\text{Cl}_2^- + e^-)$	$(\text{Cl}_2^- + e^-)$	$(\text{Cl}^0 + \text{Na}^0)$	$(\text{F} + \text{Cl}^0)$

In table 1 we summarize the calculated energies of the unrelaxed and relaxed excitons in the three surface layers and in the bulk of NaCl. The lowest energy corresponds to the unrelaxed exciton in the surface layer. Lower excitation energies for the surface with respect to the bulk have recently been observed experimentally for several alkali fluorides [18]. Unlike transfer of the unrelaxed excitons in the bulk, which can be considered as a resonant process occurring between equivalent lattice sites, transfer from the second to the first surface layer should be accompanied by phonon emission. Hence the unrelaxed excitons approaching the surface from the bulk can be reflected back or trapped in the second layer with probability higher than that of transfer into the surface layer. The energy difference between the two excitons in their unrelaxed configurations is related to the difference between the Madelung potentials of the first and second surface layers. However, the relaxed configurations are completely different: the one-centre exciton in the second layer relaxes in the configuration shown in figure 1 which may decay with emission of the alkali atom, whereas that in the first layer relaxes with emission of the halogen atom.

Since the exciton configuration in the first surface layer has lower energy, there is probability for the non-radiative transformation of the exciton from the second layer into the first layer during the relaxation process. Besides this, the exciton in the second surface layer can possibly relax into the F-H configuration located within this layer or that oriented deeper into the bulk. Study of these processes, which would enable us to make a more quantitative estimate of the probability of creation of the configuration shown in figure 1, requires a thorough calculation of the multidimensional adiabatic potential including electron correlation. The effect described in this paper is much simpler. It is based on the large (5.29 eV [19]) electron affinity of the free Na^+ ion. In the bulk the Na^+ electron affinity is reduced because of the Madelung potential. However, the surface ion can displace out from the surface where the crystalline potential is much smaller, which favours the localization of the excited electron upon this ion. The magnitude of this displacement and the barrier for the Na-atom desorption are determined roughly by the interplay between the energy gain due to the electron localization on Na and the energy loss due its displacement from the surface. The overall energy gain in this type of the exciton relaxation is larger than that in the bulk (see table 1). A very similar effect has been obtained in recent calculations for

the excited F centre on the NaCl surface [12]. It is clearly induced by the surface and we expect that the emission of alkali atoms due to the exciton relaxation shown in figure 1 will prove feasible.

In conclusion, the results of present calculations demonstrate that the primary emission of alkali atoms from the perfect (100) surface of alkali halides is energetically possible and can result from the thermal decomposition of the configuration shown in figure 1. The presence of the adiabatic barrier will cause delay for the emission at low temperatures. The probability for the primary alkali-atom emission induced by the surface photoexcitation should be lower than that for the halogen atoms because of the presence of competing non-radiative channels for the exciton relaxation. This process will compete also with other channels of alkali-atom emission related to the surface defects. It would be of great interest to study the dependence of the yield of this emission on the surface roughness.

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