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Theoretical study of Na-atom emission from NaCl (100) surfaces

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Several models for the elementary processes causing the emission of alkali atoms by electronic excitation of NaCl (100) surfaces have been investigated theoretically. First, the desorption of a Na atom neighboring an electronically excited F center on the surface is simulated using a quantum-mechanical embedded-cluster technique. It is shown that emission of a Na atom is energetically favorable. The kinetics of this process is shown to be controlled by the probability of a nonradiative transition between the two states: the excited state of the F center and that corresponding to a Na atom desorbing from the surface. The potential barrier for desorption of an excited Na atom from the excited F-center state is found to be 2.1 eV. It is also found that the energy for emission of a Na atom from a cluster of F centers (the F_3 center) is considerably reduced (for a certain configuration of the defect) with respect to the similar energy for a single F center. The energy barrier for emission of a Na atom neighboring an F' center on the surface is calculated to be 1 eV. It is shown that the electronic excitation of kinklike sites, with a Na atom at the edge, can lead to a barrierless emission of a Na atom, leaving a V_k-type defect behind. The results of calculations are discussed critically on the basis of existing experimental data.

I. INTRODUCTION

Emission of alkali and halide atoms and ions induced by ionizing irradiation and photoexcitation of alkali halides has been a topic of extensive experimental studies.[1-3] The mechanisms of emission have general interest because of their relevance to the radiation processes in the bulk and near the surfaces of insulating materials. In particular, it is well established that electronic excitation in the bulk of alkali halides produces pairs of Frenkel defects in the anion sublattice.[4-7] The micromechanisms of these processes are reviewed in several recent publications.[6,8,9] There are suggestions that electronic excitation can also produce Frenkel defects in the alkali sublattice,[10] although this process is probably either not primary, or not significant in the bulk. However, despite the large number of experimental studies,[11-18] our understanding of electronic and ionic processes near surfaces, and particularly those leading to surface decomposition is not well established.

Experimentally it has been shown that the surface is gradually enriched in alkali metal as irradiation proceeds.[19-21] Therefore, it is generally believed that electronic excitation induces emission preferentially from the halogen sublattice. However, recent high sensitivity measurements of alkali atom emission from NaCl surfaces[22] have revealed that the emission of alkali atoms induced by electron pulses is observed at extremely small doses of irradiation when the surface is not damaged. The yield of this emission is not enhanced by repeated irradiation. These results demonstrate that the irradiation of the nominally clean alkali halide surfaces induces the emission of both halogen and alkali atoms; although the number of emitted alkali atoms is smaller than that of halogen. It is shown that the alkali atoms are emitted with a delay of several microseconds after irradiation by electron pulse below 100 °C; the delay time increases with decreasing temperature.[20,22]

Electronic excitation is known to induce the emission of not only ground-state alkali and halogen atoms but also ions and excited alkali atoms.[20,21] The emission yield of excited alkali atoms or alkali ions is enhanced as the surface is enriched by alkali,[23] indicating that this emission is a secondary effect. It is also established that enrichment of the surface with alkali atoms leads to the reduction of both the halogen and alkali emission yield.[1,22]

Theoretical studies have proved to be very useful in gaining a deeper insight into the mechanisms of radiation-induced processes in the bulk of alkali halides.[6,8,9] However, few studies deal with processes near surfaces.[24-26] Recent quantum-mechanical calculation of the micromechanisms of the surface decomposition due to electronic excitation[24] have demonstrated that the self-trapping of excitons within the surface plane is accompanied by emission of halogen atoms, and that the decay of the self-trapped excitons (into primary Frenkel defects) near the surface may also cause the emission of a halogen atom. These results suggested that the primary processes associated with the conversion of the energy of electronic excitation into the creation of defects in the anion sublattice are similar in the bulk and on surfaces. Theoretical predictions concerning the mechanisms of emission of alkali atoms are less straightforward. The F centers created on the perfect surface of NaCl as a result of the exciton decomposition have been shown to be stable in their electronic ground state toward the emission of a nearest alkali atom. However, such alkali emission is calculated to be energetically favorable from the first excited electronic state of the F center.[24] The results

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of theoretical calculations[24] suggest that the emission of an alkali atom due to exciton localization on perfect surface sites is energetically possible but highly unlikely due to the rapid relaxation in the halogen sublattice leading to emission of a halogen atom.

Recent experiments have observed clear evidence of the mechanism of the emission of ground-state alkali atoms.[22] It has been shown that alkali atoms are emitted by an optical excitation of NaCl samples previously irradiated by electron pulses. The excitation spectrum of the photoinduced emission is close to that of the F-center excitation. These experimental results prove that the decay of the excited F centers on the surface may be a source of alkali atoms, and confirm the theoretical result.[24] However, the detailed mechanism of this process is still unresolved. On the mechanism of Na emission under ionizing radiation, emission from excited F centers is a possible route, although the cross section of the excitation of the F centers under ionizing radiation is not known. Moreover, it still remains uncertain whether it is possible that at least some part of the emitted alkali atoms are produced directly during the process of electron-hole recombination at the perfect surface.

In this paper we will focus on several possible mechanisms for alkali atom emission from defect sites (as is the case for the excited F centers). In particular, it seems plausible that defects at the surface (other than F centers) having loosely bonded electronic states, may in principle be the source of alkali-atom emission, either in the ground state or in an excited state. The reason is twofold. First, the alkali ions have a significant electron affinity (e.g., 5.2 eV for Na^+), and second, the crystalline potential decreases exponentially as the distance from the neutral surface increases. Therefore, under certain conditions cation displacement perpendicular to the surface may be accompanied by the trapping of an electron, leading to atomic emission. However, the delay in cation atom emission below 100 °C observed by Postawa *et al.*[18] and Kubo *et al.*[22] suggests the presence of an energetic barrier, or some transitions which have small probabilities.

We have performed theoretical studies of the mechanisms of sodium-atom desorption from the NaCl (100) surfaces using Hartree-Fock calculations at pseudopotential and semiempirical levels. The aim of this study is to suggest qualitative models and to compare these with existing experimental data. First, we carried out further studies of the emission of alkali atoms from the excited F center. Then several conceivable sources of emission of alkali atoms other than the F centers were considered: the F' center (i.e., the F center which has trapped an additional electron), the F_3 center, and low-coordinated surface sites such as corners and kinks.

The paper is organized as follows. The calculation techniques are described in Sec. II, the results of calculations are presented in Sec. III, and the discussion and conclusions are given in Sec. IV.

II. CALCULATION TECHNIQUES

We calculate the adiabatic potential-energy surfaces (APES's) for the model desorption processes using two different quantum simulation techniques. These results may be used in further discussion and analysis of real processes occurring during irradiation of the surface.

The calculations of the F, F', and F_3 centers at the perfect NaCl (100) surface and the study of the mechanisms of the Na atom desorption from these centers were performed using the defects in ionic crystals automated pseudopotential (DICAP) method.[9,24,27] The calculations for kinks and corners at the surface involve several tens of ions and are therefore more time consuming. Therefore these calculations were performed using the semiempirical CLUSTER method.[28] In both methods a defect is treated within the embedded molecular cluster (EMC) model using approaches which were thoroughly described in several recent publications.[9,29] As such, we will focus only on the details of the calculation schemes which have direct relevance to the present study.

In the DICAP method the unrestricted Hartree-Fock equations for the cluster electrons are solved using a parameter-free pseudopotential technique. The cluster is embedded in an infinite two-dimensional slab of five (100) surface planes. The lattice ions are represented by their pseudopotentials. As has been demonstrated in our previous studies,[24,27] in some cases such as the F center, the full-ion pseudopotentials of anions can be well approximated by the point-ion Coulomb potential. This approximation was also used in this work. At the same time, the representation of the cations nearest to the trapped electron by the core pseudopotentials is essential in order to prevent unphysical delocalization of the wave function of the excess electron(s) in their ground and excited states. In this work all cations, including those outside the cluster, interact with electrons localized inside the cluster through their pseudopotentials. Note that the difference between those cations which belong to the cluster and all others is only that the former have a basis set of valence atomic orbitals. The semilocal norm-conserving pseudopotential of Bachelet, Hamann, and Schluter[30] (BHS) was used to represent the cores of Na ions. The summation of the matrix elements of the interaction of the electrons within the cluster with the pseudopotentials of the ions outside the cluster (the analog of the Madelung sum) is performed over the infinite slab using the Ewald technique.[31]

The total energy includes the energy of the interaction of the electrons between themselves and with all the ions in the slab, and the energy of the pair interactions between these ions. The latter includes the Coulomb and short-range contributions. The effective potentials of the short-range interactions between ions were derived from the perfect crystal calculation using the procedure described in Refs. 24 and 27 and represented in the Born-Mayer analytical form. Their parameters are given in Ref. 27. The polarization of ions was not taken into account. Short-range interactions were included only between those ions whose displacements from the perfect lattice sites were considered in the calculation of the APES, and also between these ions and all other ions within a radius defined by the short-range cutoff. (The energy of the perfect lattice is zero.) The total number of these displaced ions typically was 15–20. However, some of these ions which are distant from the defect did not have any basis, and only simulated the lattice distortion.

The split 111*sp* Gaussian valence basis set was optimized for the Na atom with the BHS pseudopotential core. The exponents of the *s* and *p* Gaussians were identical and equal to 0.437, 0.0635, and 0.021. The electron affinity of the Na^+ calculated using this basis set is equal to 5.29 eV, in good agreement with the experimental value of 5.139 eV. The equilibrium distances and the dissociation energies for the Na_2^+ molecular ion and Na_2 molecule were calculated to be 3.41 Å, 2.91 Å and 1.05 eV, 0.09 eV, respectively. These also compare well with experimental results.[32] In order to make the basis set flexible enough to model the trapping of an electron inside the anion vacancy, and also its redistribution in the excited state and during desorption of the cation, *s* and *p* floating orbitals were included, each of which was comprised of one primitive Gaussian. The centers of the *s* and *p* Gaussians were coincident, and their position and exponents were optimized at each point of the APES. The values of the exponents were typically about 0.07.

The CLUSTER method employs both the embedded molecular cluster (EMC) model[33] and the periodical large unit-cell (LUC) method,[34] and is based on the intermediate neglect of differential overlap (INDO) approximation of the unrestricted Hartree-Fock-Roothaan method.[35] It allows us to determine the electronic structure of a quantum mechanically described cluster or unit cell containing several tens of ions. The latter is essential for the present study since we are going to simulate surface irregularities such as corners and kinks. Similar recent calculations of the chemical reactions on the (100) MgO surface[29] have demonstrated that the method gives reliable results for point defects near ionic surfaces, where a correct representation of the crystalline potential produced by the environment, on the defect under study, is most important. However, it employs a minimal valence Slater basis set and uses a single-determinantal approximation for the wave function and is therefore only able to give preliminary results for adiabatic paths and for barriers in dissociative processes.

The calculation scheme of the CLUSTER code and the parametrization of the INDO method are described in Ref. 28. The procedure for a defect study on a crystal surface using the CLUSTER code includes the following steps.

(i) Calculation of the electronic structure, relaxation, and rumpling of the perfect surface are made using periodic boundary conditions where the crystal with the surface is treated as a slab comprised of several atomic planes. For this purpose the LUC method[34,28] is used as both sides of the two-dimensional infinite slab are equivalent. It is therefore necessary for the slab to be thick enough to reproduce both bulk and surface properties of the crystal. As has been shown both in our previous semiempirical calculations,[36] and in recent *ab initio* studies,[37] a slab comprising 5–7 atomic (100) planes of the rocksalt ionic crystal lattice satisfies these requirements.

(ii) A study of defects on the surface is performed in the EMC model. The surface was simulated by a $Na_{25}Cl_{25}$ molecular cluster comprising two planes of 25 ions and embedded in the slab of five lattice planes representing the relaxed surface. Steps and kinks on the surface were simulated by small neutral islands of 16 ions adsorbed on the surface of the basic $Na_{25}Cl_{25}$ cluster. The lattice outside the cluster is constructed from the ions carrying the same basis of atomic orbitals (AO's) as inside the cluster, but with the Lowdin populations[35] of these AO's frozen to those AO populations in the slab simulating the perfect surface. The Coulomb interaction with these ions is calculated exactly up to a distance R, where the Coulomb integral between two interacting ions becomes practically equal to $1/R$. The potential of the crystalline field produced by the rest of the slab is then calculated using the Ewald method.[31] The electronic structure and rumpling of the NaCl (100) surface calculated using the CLUSTER code, the slab model, and the LUC method are in good agreement with the results of the DICAP calculation.[24] Both calculations suggest that the surface rumpling is very small, i.e., the anions displace outwards and the cations displace inwards perpendicular to the ideal surface plane by about $0.01a$ (a is the interionic distance in NaCl, which in our calculations is 2.789 Å).

III. RESULTS OF CALCULATIONS

A. The *F* center

The results of calculations of the electronic ground state of the *F* center on the (100) NaCl surface using the same methods were reported in a previous paper.[24] According to these results the desorption of a Na atom neighboring an *F* center on the surface requires an energy of about 2 eV. However, the unrelaxed excited state of an *F* center on the surface was found to have a much higher energy than the energy required to remove a Na atom neighboring an *F* center leaving a pair of cation and anion vacancies on the surface. Since *F*-center luminescence in the bulk has a large Stokes shift, it is possible that the relaxation of its excited state on the surface could also be significant. Therefore the calculation of this relaxation is necessary in order to comment further upon the energetics of Na-atom desorption from the excited *F* center. Furthermore, extended calculations of the APES of the excited *F* center are required to understand the micromechanism of desorption.

The $2p$ excited state of the *F* center is split on the surface into two states: the degenerate $2p_{xy}$ state, the wave function of which is located within the surface plane, and the $2p_z$ state oriented perpendicular to the surface. The calculated value of the energy split between these two states is dependent on the choice of basis set. In previous[24] calculations, where a contracted basis set on cations was used, the optical transition energy to the $2p_{xy}$ state was found to be lower by about 0.2 eV than that to the $2p_z$ state. In the present study the cation basis set is much more flexible and both states, while neglecting lattice relaxation, are almost degenerate. The optical transition energy is equal to 2.7 eV. This is 0.3 eV smaller than the optical excitation energy of the *F* center in the bulk calculated using the same method and the same basis set.

The unrelaxed $2p$ excited state of the F center on the surface has C_{4v} symmetry. The several modes of relaxation of this state considered in this study are shown in Fig. 1. The relaxation energy for the fully symmetrical C_{4v} mode which is shown in Fig. 1(a) is found to be 0.41 eV. Energy minimization with the symmetry constrained to C_{2v} gives the same configuration and energy as was obtained for the C_{4v} case. Modes d and e with the local symmetry C_s (see Fig. 1) give identical optimized configurations which correspond to the global minimum of the APES. A cross section of the crystalline lattice along the symmetry plane, showing the ionic displacements and the electron density distribution at the energy minimum, is presented in Fig. 2. At the equilibrium atomic configuration one of the Na ions neighboring the excited F center is displaced by $0.45a$ perpendicular and $0.21a$ parallel to the surface. A significant part of the electron density is transferred to this Na ion. The relaxation energy to this state is 0.7 eV, and the vertical transition energy into the ground state (the luminescence energy) is 1.0 eV. The latter is close to the experimental value of the F-center luminescence energy 1.1 eV (Ref. 38) in the bulk of NaCl.

The large energy gain for the asymmetrical relaxation is due to several complementary factors. In particular, the electron affinity of the Na ion increases when it is displaced out of the surface plane because of the decrease in the crystalline potential. This displacement also significantly disturbs the potential well in the nearby anion vacancy and favors electron transfer to the Na ion. The latter effect is enhanced by the polarization of the lattice which is partly reproduced in our calculation by the displacements of the surrounding ions. Some of these displacements can be seen in Fig. 2. In particular, the anions closest to the Na_1 ion are shifted from their lattice sites by about $0.06a$. On the other hand, the displacement of the Na ion requires a significant energy which counters this effect.

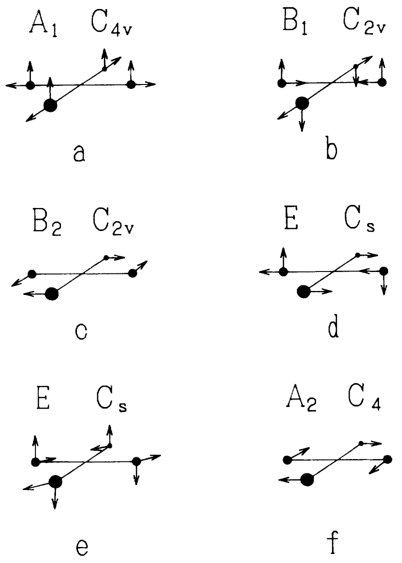

FIG. 1. Sketch of the relaxation modes of the $2p$ excited state of the F center on the NaCl (100) surface. The left symbol above each scheme identifies the irreducible representation of the group C_{4v}, whereas the right symbol shows the symmetry group of the relaxed state.

The excited state of the F center may decay in several ways: (i) radiatively into the ground state (luminescence); (ii) nonradiatively into the ground state (thermal quenching of the luminescence); (iii) nonradiatively into the $Na+(V_a+V_c)$ state; (iv) dissociatively into the excited Na $+(V_a+V_c)$ state; and (v) via thermal excitation of the electron into the conduction band. In order to study some of these possibilities in more detail, we first calculate the sections of the APES's for both the $Na+(V_a+V_c)$ and $Na^*+(V_a+V_c)$ states. The former corresponds to a Na atom emission from the ground electronic state of the F center, whereas the latter corresponds to the emission of a Na atom in the $3p$, i.e., excited state, from the excited electronic state of the F center. The following procedure was used in both cases. The Na ion was displaced to a certain distance perpendicular to the surface in the plane containing both cation and anion vacancies, and the total energy of the system was minimized relative to the coordinates of the surface ions and the position of that Na ion parallel to the surface. The relaxed surface ions include the nearest-neighbor cations and anions to the anion and cation vacancies, respectively. In all cases we checked that the displacement of the Na_1 ion in the perpendicular direction does not lower the total energy. The energy curves corresponding to the trajectories of the minimal energies for both ground and excited states of the system are presented in Fig. 3, whereas both trajectories in real space are depicted in Fig. 4.

From the energy curves one can conclude that emission of a Na atom from the ground state of the F center requires about 2 eV. The energy required to emit the excited Na atom from the excited state of the F center is about 2.1 eV. The energy of the relaxed excited state of the F center is very close to that of the ground state $Na+(V_a+V_c)$ configuration (see Fig. 3). The ionic displacements and the electron-density distribution in the symmetry plane when the Na ion is displaced by about

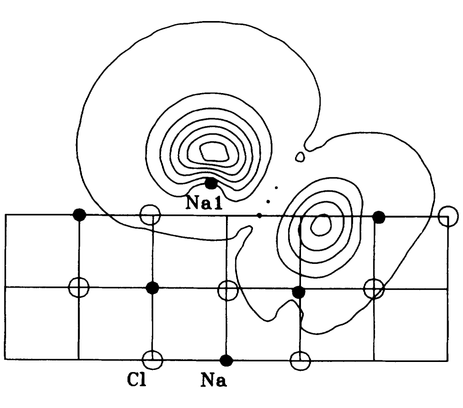

FIG. 2. The section of the crystalline lattice in the symmetry plane at the equilibrium configuration of the $2p$ excited state of the F center on the NaCl (100) surface. The isolines show the section of the electron density. The outer isoline corresponds to a density of 10^{-5} a.u.; the distance between the isolines is equal to 5×10^{-4} a.u.

1.4a from the ideal surface plane are shown in Fig. 5. Two features can clearly be seen. First, at this distance the electron is almost equally delocalized between the Na ion and the vacancy, and, second, there is a significant displacement of the nearest Cl ion out of the surface. Note also the p-like antibonding character of the electron wave function. The repulsion between the Na atom and the F center in this state determines the striking difference between the trajectories for the ground (s-like bonding) and excited (p-like antibonding) states of the system. The polarization of the lattice by the divacancy left on the surface is only partly taken into account in our calculation. It is dependent on the position of the desorbing atom and may slightly change the character of the adiabatic curves. However, we believe that this effect is relatively small and does not affect our qualitative conclusions.

The energies of all other paths corresponding to the decomposition of the ground state into the Na atom and the two vacancies have higher energies. They form a continuum in both the energy spectrum and the real space of possible trajectories. One extreme case which corresponds to the same coordinates as those for the excited state, but for the ground electronic state, is shown in Fig. 3 (curve c). It is the potential energy of the system after the Franck-Condon transition from the excited state. One can see that when the Na atom is displaced by more than one lattice constant from the surface plane both curves become extremely close, suggesting a high probability of the nonradiative transition into the ground state. Similarly, there is a great variety of other trajectories in the ground electronic state of the system which resonate with the energy of the excited state. However, the probabilities of these transitions depend strongly on particular trajectory. In an adiabatic approximation these are determined by a Franck-Condon factor. Since the minimum-energy paths for the ground and excited states differ significantly, one can expect that the trajectories providing the highest probability for the nonradiative transition into the ground state and corresponding to Na-atom emission from the surface may have much higher energies than curve a shown in Fig. 3. Therefore there are two bottlenecks in this process: the probability of the nonradiative transition between the two states, and some energy barrier either in the excited or the ground state (Fig. 3 gives a qualitative idea of possible variants).

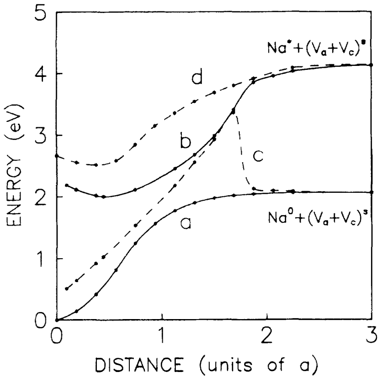

FIG. 3. The adiabatic potential-energy curves for the desorption of a Na atom from a site nearest to an F center on the NaCl (100) surface along the z coordinate (perpendicular to the surface) of the two trajectories of minimum energy (see Fig. 4). Curve a shows the ground electronic state of the F center, b shows the relaxed 2p excited electronic state of the F center, c shows the ground electronic state with the configuration of the excited state (the Franck-Condon transition), and d shows the unrelaxed 2p excited electronic state. For curves a and b at each z coordinate of the Na atom, the x and y coordinates of this atom, and the positions of several ions in the cluster, were optimized. At small displacements of the Na_1 atom at the excited state of the F center the relaxation follows the C_{4v} mode shown in Fig. 1(a). Therefore curves b and c start only at the distance from the surface plane at which the displacement of the Na_1 atom begins to determine the relaxation.

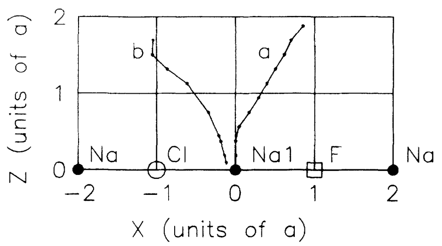

FIG. 4. The trajectories of the minimal energy for the desorption of a Na atom from a site nearest to an F center on the (100) NaCl surface, in the symmetry plane perpendicular to the surface. Abscissa corresponds to the x axis within the surface plane. (a) The F center in the ground electronic state. (b) the F center in the 2p excited electronic state. The ions are schematically shown at their perfect lattice sites.

We did not attempt to calculate any other trajectories due to the nonconclusive character of such calculations. However, we believe that the qualitative result is clearly demonstrated. That is, the emission of the Na atom from the site nearest to the excited F center is energetically feasible. However, the probability of this process may be strongly dependent on temperature. Experiments[22] demonstrate that the emission of a Na atom after optical

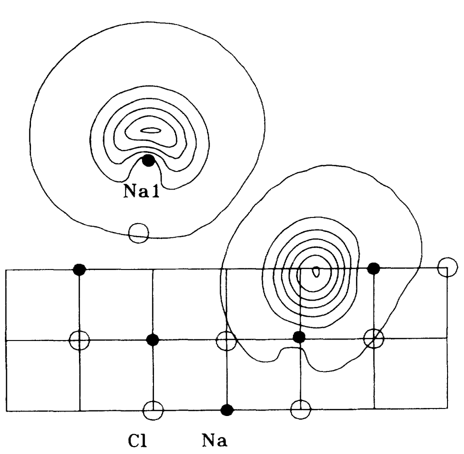

FIG. 5. The section of the crystalline lattice in the symmetry plane at an intermediate position of a Na_1 ion desorbing from a site nearest to the F center in the 2p excited electronic state. The isolines show the section of the electron density. The distance between the isolines is the same as in Fig. 2.

excitation of *F* centers in NaCl samples previously irradiated by an electronic pulse occur after a delay of several microseconds below 100 °C, but this delay becomes much smaller or disappears at higher temperatures. These results can qualitatively be understood on the basis of this model. However, this explanation is oversimplified since it does not take into account thermal ionization of the excited *F* centers which certainly takes place at these temperatures. Note also that the probability of Na-atom desorption may be enhanced during the relaxation of the optically excited *F* center or after formation of this excited state by electron trapping by the anion vacancy. Therefore the real kinetics of the desorption process may be more complicated.

Another point concerns the possibility of forming more complex electronic centers, such as the F' (Ref. 39) or aggregates of several *F* centers. The F' centers are quasistable in NaCl at room temperature and can be formed temporarily, for instance, due to secondary electron trapping by the existing *F* center. We have studied these centers based on results obtained in this section which suggest that diffuse and loosely bonded electronic states may generally have a higher probability for cation atom desorption from the surface.

B. The F' center

The F' center is charged relative to the lattice, and therefore the lattice polarization in this case is much more important than in the case of the *F* center. We assume that this polarization does not change much when we compare the following two cases: the F' center on the surface, and the Na atom at infinity and the *F* center with a cation vacancy in the nearest-neighbor position. However, in order to take into account the effect of polarization as much as possible, five neighboring cations and 12 anions closest to the vacancy were included in the calculation of the lattice distortion. The section of the cluster used in this study is shown in Fig. 6. Two electrons are trapped in the slightly distorted *s*-like state, and the relaxation of the lattice is symmetrical. The cations nearest to the vacancy are displaced inwards as shown in Fig. 6 by about $0.06a$. The nearest anions displace outwards the center by about $0.02a$. The displacements of all other ions are less than $0.01a$. The relaxation energy relative to the ionic configuration corresponding to the *F* center is 0.94 eV, whereas the total energy of the F' center is by 0.2 eV lower than that of the relaxed *F* center. The wave function of the F' center is much more delocalized, and its one-electronic energy is higher than similar characteristics of the *F* center by about 3.4 eV. However, since the center is negatively charged, a more comprehensive treatment of the electronic polarization of the lattice could lower this energy by several tenths of an eV. The desorption energy of the Na atom from the nearest-neighbor position on the surface, i.e., the energy difference between the F' center, and the relaxed configuration of the Na atom at infinity and the F-V_c pair on the surface, is equal to 1 eV. This is much less than the corresponding value for the *F* center and qualitatively reflects the expected tendency.

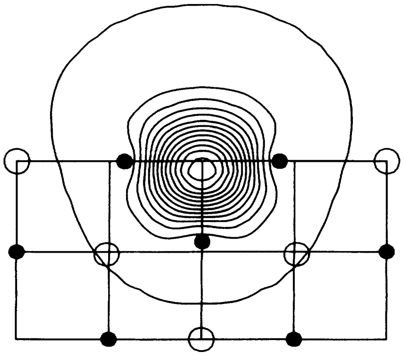

FIG. 6. The section of the crystalline lattice in the symmetry plane at the equilibrium geometry of an F' center. The isolines show the section of the electron density. The distance between the isolines is 10^{-3} a.u.

C. The F_3 centers

Results of previous calculations[24] have demonstrated that there is little difference between the Na desorption energies for the *F* center and the simplest possible aggregate of *F* centers—the F_2 center. However, the experimental data[20,23] suggest strongly that the desorption of excited alkali atoms increases as larger *F*-center aggregates and small metal particles are formed at the surface. For instance, the optical absorption bands of *F*, F_2, and F_3 centers and small metal colloids were clearly observed in LiF- and NaF-irradiated samples which showed desorption of excited alkali atoms.[40] In order to investigate whether *F*-center aggregation enhances alkali-atom desorption for the smallest aggregates, we have studied several possible configurations of the F_3 center at the surface. These configurations are the following: all three *F* centers situated in the surface plane; only two *F* centers in the surface plane and one in the next plane; and vice versa.

The desorption energy of an alkali atom depends significantly not only on the initial configuration of the centers, but also on the most stable configuration in the final state. As such, the calculations become very time consuming. In order to obtain a qualitative result, we first considered all configurations without thorough optimization of the displacements of the ions surrounding the complex. This analysis revealed that the trend is essentially irregular: in some cases the desorption energy of a Na atom decreases, but in some cases it remained close to that obtained for the *F* center. A significant gain in energy was obtained only for the case with two *F* centers (or the *M* center) situated in the surface plane and one in the next plane. They form a triangle, and the most unstable cation is surrounded by three *F* centers and two anions. Detailed calculation including optimization of the positions of the ions nearest to all centers revealed that the desorption energy of this atom is about 1 eV. In the final state the two remaining electrons are redistributed almost homogeneously between the three vacancies.

D. Electron and exciton trapping by corners and kinks

The experimentally observed correlation between desorption of alkali atoms and radiation damage of surfaces[20,21,41] suggests another possibility which has not been considered thus far in the literature. That is, as the desorption of alkali and halide atoms progresses, the number of divacancies at the surface increases. They may form larger vacancy clusters and thus produce homogeneously distributed low-coordinated ionic sites at the surface. These sites may have some peculiar properties regarding the trapping of electrons, holes, or excitons, which may differ from those of the perfect surface. Although the number of possible defective structures at damaged surfaces is enormous, we restricted our study to two simplified model systems shown in Fig. 7: the outer cation corner of a terrace on the surface, and the inner anion corner of the terrace, or the kink.

Both systems were modeled using the CLUSTER code by adsorbing an island of 16 ions on the surface of the basic $Na_{25}Cl_{25}$ molecular cluster embedded in an infinite slab of five surface layers. Some of the ions in the islands were fixed in perfect lattice sites in order to simulate the continuous nature of both the terrace and kink. The positions of other ions were optimized and the directions of the displacements obtained are shown in Fig. 7. The character of the relaxation is qualitatively very similar to that obtained for the analogous structures on the surface of MgO using classical atomistic simulation techniques.[42] The least-coordinated Na ion at the corner is displaced toward the terrace by about $0.15a$. The displacements of other ions are typically about $0.04-0.05a$.

The low coordination of the Na ion at the corner suggests that it may have a localized electronic state of lower energy than the bottom of the conduction band, i.e., it provides a shallow trap for an excess electron. In fact this state is seen in the one-electron spectrum of the system. However, since the quality of the unoccupied electronic states in the Hartree-Fock technique is known to be poor, this point requires additional study. Therefore we performed the calculation using a configuration interaction (CI) technique which gives a better quality of the wave function for the excited states.[43] All one-electron excitations from the electronic states forming the valence band in our cluster into those forming the conduction band were taken into account. In this calculation the wave function of the excited state is a linear combination of the Slater determinants corresponding to each transition. The spectrum of cluster excitations thus obtained revealed that indeed there is an electronic state localized on the three-coordinated cation with an energy about 0.5 eV lower than that of the lowest electronic state within the terrace, and about 1 eV lower than the bulk electronic states. Despite the cluster character of this calculation and the localized basis set, this result appears to be very reasonable.

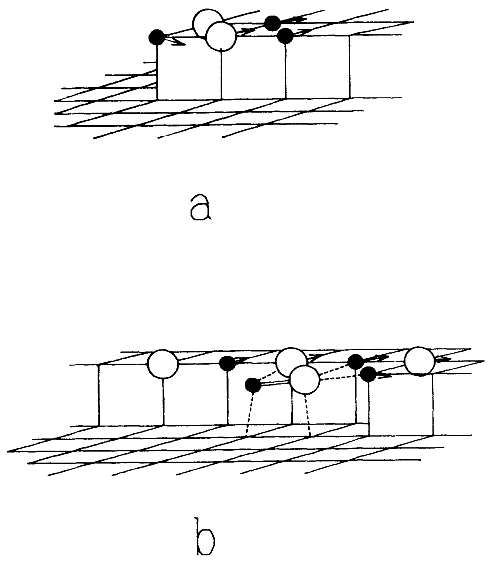

FIG. 7. Sketch of rocksalt [100] terraces, with a corner (a) and kink (b). The arrows show the directions of the lattice relaxation.

It is plausible to assume that at a certain level of surface damage the cross section of such low-coordinated sites towards the trapping of extra electrons may become significant. Such electrons are always present in the surface area during electronic irradiation. We simulated this process by adding the extra electron into the cluster. It localizes completely on the corner cation. This is accompanied by additional lattice relaxation since the neutralization of the ion produces a large perturbation of the surrounding lattice. The calculated desorption energy of the Na atom from this relaxed state is equal to 0.8 eV. This is even smaller than similar energies obtained for the F' and F_3 centers, and suggests that low-coordinated cation sites at the surfaces may be effective sources for the desorption of alkali atoms.

Another point concerns the electronic excitation of low-coordinated sites. Two extreme cases have been studied experimentally: an isolated alkali halide molecule,[44] and small cubic clusters.[45] In the former case the excitation energy is much smaller than that of the bulk crystal, and the excited states of the molecule are essentially dissociative. In the latter case the desorption of halide atoms has been observed to be similar to that in bulk samples. In this study we considered a somewhat intermediate case which may be represented as a kink at the surface ledge shown in Fig. 7(b). These are usually considered as the most important sites which determine crystal growth[46] and evaporation.[47] In phenomenological theories the last two ions of the kink are usually considered as an alkali halide molecule,[46,48] although very few atomistic calculations treating this system exist so far.[49]

The calculation for the equilibrium geometry of the system gives positions of ions at the kink [see Fig. 7(b)] which are very similar to those obtained in the previous study using pair potentials.[49] The electronic excitation of the cluster was treated similarly to our previous studies of excitons[9,27] as a transition into the triplet state which was calculated self-consistently using the unrestricted Hartree-Fock technique.[35] The excited state appeared to be completely localized on the last cation and anion of the kink. The vertical excitation energy was calculated to be equal to 5.2 eV. This is much smaller than the 7.4 eV calculated using the same technique for the similar transition in the cluster simulating the bulk of the crystal. The geometry optimization for the excited state has shown that the total-energy minimum corresponds to the configuration when the Na atom is desorbed from the surface and the Cl atom forms a chemical bond with another chlorine at the corner of the kink [see Fig. 7(b)]. The structure of this latter configuration is similar to a slightly distorted V_k center. Interestingly, the energy of this relaxed configuration is slightly lower than that of the vertically excited state, suggesting that the desorption of the Na atom in this case does not require any additional energy. Another point is that the energy of the bulk crystal excitation, if transferred to this site, is enough to produce the higher excited state of the molecule in which the Na atom will be excited. Although we are unable to calculate this situation, it seems plausible to assume that desorption of the excited atom will also not require additional energy. These results qualitatively demonstrate the low-coordinated sites at the surface may be an effective source for desorption of excited alkali atoms.

IV. DISCUSSION AND CONCLUSIONS

In this paper we have studied theoretically several conceivable models for the emission of alkali atoms from the NaCl (100) surface. These include the decay of the excited state of the *F* center, and the desorption of the alkali atom neighboring other electronic centers on the surface such as small *F*-center aggregates: the F_2 and F_3 centers, and the F' center. We also considered electron and exciton trapping by the defective surface sites such as corners and kinks. In the following discussion we will compare the results of these calculations with the experimental data.

First, we summarize the experimental results relevant for alkali emission. When the emission of alkali is induced from an initially undamaged cleaned surface, the yield is not dependent on the level of radiation damage, as long as the damage is small, and is proportional to the electron current density.[22] The number of halogen atoms emitted is more numerous than the number of alkali atoms, producing alkali-rich surfaces as irradiation progresses. There is a delay in the alkali emission after the excitation pulse at temperatures below 100 °C. Similar delay has been observed for the alkali emission after the excitation of *F* centers by a laser beam. Excited atoms and even ions are emitted after the surface is damaged or enriched by alkali. Practically no emission of excited alkali atoms is observed for undamaged surfaces.

Both the occurrence of the emission and the existence of the delay for the emission of Na atoms from the optically excited *F* centers can be qualitatively understood on the basis of the results of this work. That is, as was demonstrated in Sec. III A, the decay of the excited state of the *F* center on the surfaces into the Na atom and the divacancy on the surface is energetically feasible. However, there is a clear bottleneck for the transition from the excited state of the *F* center into the final state of emission.

Whether the decay of the excited *F* centers on the surface can be the cause of the emission induced by an electron pulse is less straightforward. Suppose that the emission of Na atoms arises from excited *F* centers on the surface. The proportionality of the yield of Na atoms to the electron current density can be explained only by assuming that the creation of the *F* center and its excitation leading to the emission is induced by the same incident electron. Since an incident electron with an energy of 1 keV has a penetration depth of an order of 100 lattice constants and produces about 100 electron-hole pairs, a kind of electron-hole plasma is generated around the incident electron trajectory. The *F* center produced by an incident electron can be excited in an electron-hole plasma by successive trapping of a hole and an electron by the *F* center: the trapping of a hole produces an anion vacancy and the trapping of an electron is known to produce an excited *F* center.[50] Since the *F* center on the surface can be formed in a time range of an order of 0.01 ps,[51] the probability that an *F* center on the surface can be excited in the electron-hole plasma is considered to be high. Thus some fraction of the *F* centers on the surface produced by an incident electron can be transformed into the excited state during the lifetime of the electron-hole plasma. Therefore it is likely, although not conclusive, that excited *F* centers are also the cause of the emission of alkali induced by electron irradiation.

According to the results of present calculations, desorption of a Na atom neighboring an F' center requires about 1 eV, i.e., a half of that for the *F* center in the ground state. Thus, trapping of an electron on the *F* center makes the barrier to the emission of a Na atom smaller. Similarly, we demonstrated that the energy required to emit a Na atom is smaller for the F_3 center of a certain configuration, and for a low-coordinated site such as a corner. Combining these results, it is likely that the energy necessary to emit an alkali atom from a defect on the surface reduces as the ionization energy of the defect, or the degree of coordination of the cation decreases. We should note, however, that this conclusion is mainly qualitative. In particular, it is not yet clear whether the emission of an alkali atom can really be induced by an F' center during its lifetime, since the second electron on an F' center can be stable only at relatively low temperatures [lower than 300 K for NaCl (Ref. 39)].

The result that the energy for the emission of an alkali atom is reduced by combining of three *F* centers gives us an understanding of the experimental observation that the yield of excited Na atoms becomes higher as the surface is enriched with alkali. Emission of an excited alkali atom from an *F* center on the surface, excited to the 2*p* orbital, seems highly unlikely, since the calculated potential barrier for this process is about 2.1 eV. For the F_3 center, which has electron-excited states nearly of the same energy as the *F* center, there is a residual 1 eV, which is still smaller than the excitation energy of a Na atom (2.1 eV). However, the qualitative trend obtained indicates that the emission of excited atoms may even be easier from larger electronically excited *F*-center clusters. Another possible source of excited Na atoms is the exciton trapping in the proximity of the *F*-, F'-, and *F*-aggregate centers on the surface. In this case the probability of the emission of an excited alkali atom from a defect will increase as the energy for the emission of an Na atom in the ground state decreases. Thus experimental results for the emission of excited alkali atoms can be explained qualitatively. We note that this model is similar to that discussed by Bunton *et al.*[52]

Our results also suggest that the three-coordinated sodium atoms at the corners of the steps on the surface can trap electrons, and that the energy for their emission from the surface is about 0.8 eV. Moreover, it is shown that the energy of the crystal excitation, transferred to the kinklike sites, may cause emission of alkali atoms without any barrier. On the basis of these results, we assume that excited alkali atoms may be desorbed without additional barrier if the kink site is excited into the higher excited state. These mechanisms probably do not play a significant role for undamaged surfaces, where the concentration of low-coordinated sites such as corners and kinks is very small. Moreover, in the case of the kink excitation there is no thermal barrier to the emission, and hence the delay in emissions cannot be explained by this mechanism. Note, however, that the emission of excited atoms is observed only for surfaces which are already heavily damaged by irradiation. In the latter case, the concentration of low-coordinated sites may be high due to aggregation of divacancies, and both processes may become important. Note also that after the emission of an alkali atom, the edge of the kink site is now occupied by a hole, which will trap an electron produced by the next electronic excitation. This will produce an exciton, which will decay with emission of a halogen atom. Thus a kink site with a configuration similar to that at the beginning appears. Therefore the exciton relaxation on the kink sites of this type will be induced as long as the surface is substantially damaged. In the latter case the kink sites can be the source of emission of not only alkali, but also of halogen atoms.

We have presented several conceivable models for Na-atom emission by electronic excitation. Although the present calculation cannot differentiate the dominant processes, all of these processes are considered to play roles. A crucial experiment to decide whether excited *F* centers contribute to desorption of alkali is to observe the emission yield of Na atoms by two-photon excitation as a function of the density of excitation. If these excited processes play a role, the dependence will be quadratic.

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