PHYSICAL REVIEW B VOLUME 47, NUMBER 16 15 APRIL 1993-II

Theoretical studies of atomic emission and defect formation by electronic excitation at the (100) surface of NaCl

V. E. Puchin,* A. L. Shluger,* and N. Itoh

Department of Physics, Faculty of Science, Nagoya University, Furo-cho, Chikusaku Nagoya 464-01, Japan

(Received 20 October 1992)

The F and H centers and self-trapped excitons near the (100) surface of NaCl have been simulated using the embedded-cluster Hartree-Fock calculation technique. An F center in the ground state in the top surface layer is shown to be stable. The activation energy of 1.94 eV is needed to emit a neighboring Na atom, while a Na atom can be emitted spontaneously when an F center is excited to the lowest excited state. The H center in the first two surface layers is found to be decomposed into a Cl^- ion on the lattice site and a Cl^0 atom physisorbed on an anion with a binding energy of 0.14 eV. The H center located below the third layer is stable. The self-trapped exciton in the top and second layers is found to be unstable and decomposes into an F center and a Cl^0 atom in the vacuum, while that below the third layer is relaxed similarly to those in the bulk. Existing experimental results on photoinduced emission of alkali and halogen atoms are discussed based on the results of calculations.

I. INTRODUCTION

Emission of atoms and ions induced by ionizing radiation of alkali halides has been a topic of general interest.[1-3] Extensive studies of emission of halogen and alkali atoms and ions have been carried out using electron, ion, uv-photon and laser beams. The linear dependence of the number of emitted atoms on the number of excitations[4-6] indicates that a single-crystal excitation, namely formation of an exciton or an electron-hole pair, can lead to emission. The mechanism of single-crystal excitation, however, is still controversial.

It is well established that excitons or electron-hole pairs in the bulk alkali halides are localized by interaction with phonons to form self-trapped excitons (STE's). According to the currently accepted model, the STE consists of an electron and an off-centered X_2^- molecular ion (where X denotes a halogen atom) occupying two lattice sites [see Fig. 1(a)]. Further displacement of the X_2^- molecular ion along the molecular axis transforms a part of the self-trapped exciton into a primary Frenkel pair in the halogen sublattice. The latter comprises a vacancy [the F center, Fig. 1(b)] and an interstitial atom (the H center: an X_2^- molecular ion occupying a halogen lattice point) [see Fig. 1(c)]. The dynamics of the process of exciton relaxation from free exciton to self-trapped states is not fully understood.

On the surface, because of the presence of additional freedom, the relaxation process of an exciton may be different from that in the bulk. In particular, we expect that the formation of excitons or electron-hole pairs near the surface leads to particle emission. We shall call this type of mechanism the excitonic mechanism. The key issue for this process is the localization of the electronic-excitation energy by virtue of electron-lattice interaction and subsequent conversion of this energy into the energy of atomic migration and emission.

A variety of experimental techniques have been employed for studies of the STE's and their evolution to the F-H pairs in the bulk. These include optical absorption and luminescence spectroscopy,[7,8] magnetic resonance,[7] Raman spectroscopy[9] femtosecond,[10] and picosecond,[11,12] and nanosecond time-resolved optical spectroscopy. All these techniques cannot be employed presently for studies of the self-trapped excitons and their evolution to atomic emission near the surfaces. The reason for this is twofold: the self-trapped excitons near the surface are small in number, and secondly the evolution to atomic emission occurs usually in a short time. Thus, the experiments carried out so far have focused on measuring the emis-

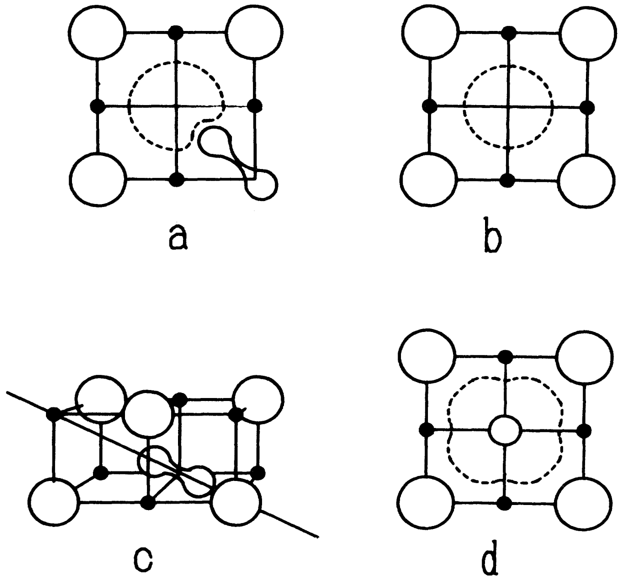

FIG. 1. Schematic diagrams of (a) the self-trapped exciton, (b) the F center, (c) the H center, and (d) the one-center exciton in the bulk. The small closed circles denote Na ions, and large open circles Cl ions; dotted lines schematically represent the electron orbitals, small circles indicate the preferable location of the hole.

sion yield and the velocity distribution of the emitted atoms in various conditions of excitation.

Halogen atoms emitted near room temperature exhibit both thermal and nonthermal velocity distributions (fast component), while alkali atoms exhibit only thermal distributions.[13] These results are consistent with the concept that the instability of the self-trapped excitons near the surface is the cause of desorption: halogen atoms should be emitted primarily, and emission of alkali atoms follow. Furthermore, the number of halogen atoms included in the fast component decreases only slightly with increasing temperature.[14] If the deexcitation of an exciton is the cause of emission of a halogen, the yield should be determined by the branching ratio between two different deexcitation processes: one leading to desorption, the other leading to nonradiative and radiative transitions to the ground state. The rate of the nonradiative transitions increases with increasing temperature. Thus the emission of the fast component may be ascribed to the decomposition of the excitons formed near the surface layer.

Based on the recent experimental observation that halogen atoms are emitted preferentially perpendicular to the (100) surface, Szymonski *et al.*[15] concluded that the deexcitation of excitons near the surface is not the cause of emission. The H center evolved from a self-trapped exciton in the bulk is known to be transferred by a replacement sequence along the $\langle 110 \rangle$ direction. Thus, if the termination of the replacement sequence at the surface causes the emission, the atoms emitted from the surface should be directed along the $\langle 110 \rangle$ direction. Consequently, Szymonski *et al.*[15] have suggested an alternative model where generation of hot holes near surfaces leads to emission. However, without determination of the orientation of the H center near the surface, the excitonic mechanism cannot be excluded on the basis of the angular distribution observed by Szymonski. Further studies are needed to reveal the mechanism. No theoretical studies of desorption from an exciton or a hole near the alkali-halide surfaces has been carried out, but Itoh, Stoneham, and Harker[16] have pointed out the possibility of emission of a halogen atom from a self-trapped exciton near the surface.

In addition to the instability of self-trapped excitons near the surface, emission may take place because of Frenkel pair formation in the subsurface layers. In particular, one can suppose that an H center near the surface is decomposed into a halogen ion in the lattice site and an emitted halogen atom. Since the H centers are coagulated into clusters above liquid-nitrogen temperature,[17] the emission due to the instability of an H center near the surface is governed by the branching into the coagulation and the emission. In order to see whether the emission of this origin takes place, more information on the stability of an H center near the surface is needed.

It is generally considered that emission of alkali atoms follows the emission of halogen atoms. Tolk *et al.*[18] observed a delayed emission of alkali atoms near room temperature and ascribed it to the decomposition of the F centers, which approach the surface by diffusion. Again, it is not yet clear whether emission of an alkali atom from an F center near the surface is energetically feasible. It has been shown that overall emission yield is reduced when the surface stoichiometry is changed by preferential emission of halogen atoms.[19] Furthermore, the emission yield of excited alkali atoms is enhanced when the surface is enriched by alkali atoms.[20–22] However, microscopic origin of the effects of surface stoichiometry change on the exciton relaxation near the surfaces is not yet understood, and hence the phenomena described above remain unexplained.

Useful information concerning the basic properties of the point defects, such as F centers, H centers, V_k centers, and self-trapped excitons near surfaces can be derived from a theoretical simulation. Several theoretical calculations of the F centers near the surfaces of alkali halides and MgO have been carried out recently using semiempirical quantum chemical techniques.[16,23–26] However, to our knowledge no calculations exist for stability of the H and V_k centers and self-trapped excitons near the alkali halide surfaces. The possibility of self-trapping for the hole and the exciton on the surface of MgO has been simulated by Shluger *et al.*[27] These calculations have demonstrated that a single excitonic excitation of the MgO (100) surface cannot lead to the surface disintegration due to O^--ion emission, but produces a metastable state, a complex consisting of an F^+ center and an O^- ion. Further excitation of the F^+-O^- metastable state causes oxygen-atom emission.

The purpose of the present study is to provide basic information on defects of the NaCl (100) surface relevant to particle emission induced by electronic excitation, using the *ab initio* electronic structure calculation technique. An embedded-molecular-cluster model was employed in order to calculate the adiabatic potential energy surface (APES) for emission of an alkali atom from an F center on the surface, for the H center as a function of its position relative to the surface, and for emission of a halogen atom from an exciton. The V_k centers on the surface are not considered in this paper because the crystal polarization, which should be taken into account, is not included in the present method of the calculation. The results are used to discuss existing experimental information, and it is pointed out that the instability of a self-trapped exciton near the surface and formation of Frenkel pairs near the surface layers can be the main cause of emission of halogen atoms. The conditions for emission of alkali atoms are also discussed.

II. METHOD OF CALCULATION

The main assumption of an embedded-cluster approach is that the whole system, in our case the semi-infinite crystal with the point defect on the surface, can be separated into two parts: a molecular cluster and the remainder of the crystal, which has almost perfect structure. Accurate quantum chemical methods are usually used for the calculation of the atomic and electronic structures of the molecular cluster, which is embedded in the field of the rest of the crystal treated more approximately.

A. Total energy

In the present study the wave function of the cluster was treated in a single-determinant approximation. The restricted Hartree-Fock method was used for the singlet closed-shell case (the ground state of the crystal), and unrestricted Hartree-Fock (UHF) method for the open-shell doublet and triplet states. In order to obtain the energy of the singlet state of the cluster containing two F centers (like an *M* center), which cannot be described by the closed-shell wave function, the open-shell UHF approach was employed for both singlet and triplet states. Then the standard formulas were used[28] to project out the triplet component of the wave function. Up to 12 Cl^- anions were included in the molecular cluster. Cl^{+7} and Na^+ cores (cations) were replaced by the norm-conserving pseudopotentials.[29]

The crystal remainder was treated using the pair interaction approximation. The wave functions of the ions, including those situated on the surface, were the same as in the bulk of the perfect crystal.[30] The electrons localized inside the cluster interact with Na^+ ions of the remainder by means of the same pseudopotential as inside the cluster. The pure Coulombic potential ($1/r$) was used for the electron interaction with the Cl^- ions outside the cluster. The effective potentials of the pair interactions between the ions outside the cluster and those between cores of ions in the molecular cluster and ions in the remainder were derived from the perfect crystal calculations. They satisfy the following criteria: (i) the equilibrium geometry of the molecular cluster simulating the perfect lattice coincides with the corresponding fragment of the infinite lattice; (ii) the total energy of this cluster behaves symmetrically with respect to the displacement of the ions both inward and outward from the border of the cluster. In this way the inequivalence between the interactions of the ions on the border of the cluster, namely the interaction between the quantum-mechanical ions inside the cluster and the ions represented by frozen pseudopotentials outside the cluster, is corrected. The analytical expression of the Born-Mayer form was used afterwards to fit the pair potentials. The polarization of ions was not taken into account. Therefore, the effective pair potentials, which were derived from the perfect lattice calculations, are slightly different from those for the lattice constructed of polarizable ions.

The sum of pseudopotentials and effective pair potentials constitutes both the short- and long-range parts of the embedding potential of the lattice, which was incorporated in the Fock matrix of the cluster. We used the conventional Ewald technique in order to calculate the long-range (Madelung) potential and corresponding electron matrix elements. The summation was performed over the infinite two-dimensional periodic slab of ions, comprising five parallel layers. The upper layer corresponds to the surface. It was shown that the potential produced by such a slab in the cluster area is the same as that of the semi-infinite crystal. This model was implemented in a DICAP (defect in ionic crystal automated pseudopotential) computer code, described in detail in a previous paper,[31] which contains the complete set of the parameters of the pair potentials for LiCl, NaCl, and KCl crystals. It was successfully applied to the study of the structure and properties of the STE in the bulk of NaCl.[31] Due to the complete compensation of the cluster boundary effect, the shape of the APES does not depend on the size of quantum cluster. This feature of the model allows us to study the complicated processes of point defects diffusion and interaction.

B. Basis sets

The split 511*sp* and contracted (minimal) 7*sp* basis set on chlorine ion were employed in the present study. Both sets were obtained by the independent variation of the exponents of the seven *sp* Gaussian primitives for the Cl^- in the crystalline field. They were then contracted with the corresponding coefficients to the 511*sp* and 7*sp* form. It was found that the basis-set contraction leads to the almost parallel shift of the APES of about 0.65 eV in the open-shell cases and gives a negligible effect on the ground state of the crystal. A substantial difference exists at the dissociation limit of the Cl_2^- molecular ion. At large distances an artificial broken-symmetry solution, which is characteristic of the unrestricted Hartree-Fock method, leads to the Cl_2^- dissociation energy of 0.54 eV (Fig. 2), while the symmetrical solution gives the value of 1.17 eV, which compares well with the previous calculation.[32] This is due to the difference in the treatment of electron correlation for the symmetrical and broken-symmetry solutions. We should note that in the minimal basis set, where only the symmetrical solution can exist, the dissociation energy of Cl_2^- is 1.21 eV, because the symmetry breaking cannot appear in this case. The equilibrium distance of the Cl_2^- molecular ion does not depend on the basis-set contraction and is 2.70 Å. The error compensation effect of the same kind appears also in the chlorine electron affinity calculation: The unrestricted Hartree-Fock method gives a value 2.59 eV, the restricted one a value of 2.80 eV, and both calculations are

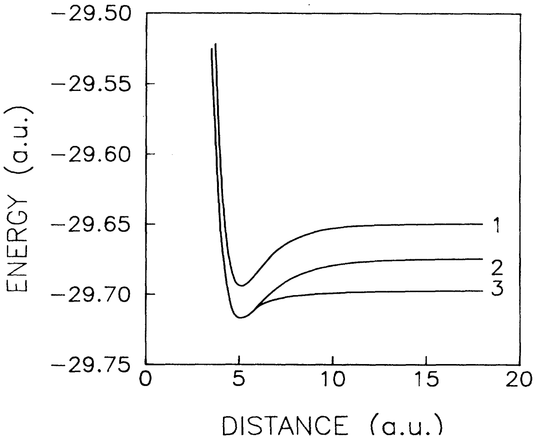

FIG. 2. The adiabatic potential-energy curves of a Cl_2^- molecular ion calculated using minimal (1) and split basis sets; 2 and 3 show symmetrical and broken-symmetry solutions, respectively.

close to the Hartree-Fock limit. Using our minimal basis set we obtained 3.53 eV, in reasonable agreement with the experimental result (3.617 eV). This is another reason why we used the minimal 7*sp* basis for studying emission of atoms by electronic transition from the surface.

For Na atoms, we employed the 3*s* basis,[31] augmented by *p* Gaussians with the same exponents in the cases of the excited state and when the polarization effect was considered important. In this basis set, the sodium ionization potential is 5.29 eV, which is close to the experimental value of 5.139 eV.

The rumpling of the perfect (100) surface, calculated using the 7*sp* basis set, corresponds to the inward displacement of both cations and anions by $0.012a_0$ and $0.008a_0$, respectively, where a_0 is the lattice constant for the three-dimensional lattice ($a_0=2.789$ A). We did not take it into account in further calculations of the defects.

In order to simulate the *F* center, the basis set was extended by an *s* floating Gaussian orbital centered in the anion vacancy. The position and the exponent of this orbital occupied by the *F*-center electron was optimized at each point of the APES; the value of exponent was typically about 0.07 a.u. A *p*-type floating Gaussian orbital with the same exponent was added at the same position for the calculation of the *F*-center excitation energy.

As was shown in previous calculations of the structure and properties of the self-trapped exciton in the bulk NaCl, which were performed using the DICAP code, the overall accuracy of the calculated APES is about 0.3 eV. The main sources of errors are (1) neglect of the polarization of the lattice ions outside the cluster and of the polarization of the cores in the cluster, and (2) underestimation of the electron correlation effects in the unrestricted Hartree-Fock approximation, which are significant in some special cases.[31]

III. RESULTS OF CALCULATION

A. The *F*-center formation energy

The atomic structure of the *F* center on the surface is found to be almost the same as in the bulk. The displacements of the nearest cations from their sites are less than 1% of the lattice constant. The one-electron level of the electron localized to the *F* center shifts by about 0.35 eV upwards for both the ground *s*-like state and the excited p_z-like states directed perpendicular to the surface. This is the consequence of the lack of coordination and lowering of the Madelung potential at the surface layer. The energy of the p_x and p_y excited states located in the surface plane changes only slightly. Thus the excitation energy of the *F* center on the surface splits by about 0.2 eV.

We found that the *F*-center formation energy on the surface is 5.35 eV and is higher by 0.02 eV than that in the bulk. This result implies that the perfect ⟨100⟩ surface does not attract the *F* centers, although the accuracy of the present calculation does not allow us to address this point definitely.

We calculated the formation energy of an additional *F* center on the surface at the nearest and next-nearest lattice sites to the first *F* center; we call the former the surface *M* center and the latter the 2*E* center. The results are shown in Table I. We found that the singlet state is lower than the triplet state by 0.23 eV for the *M* center and by 0.01 eV for the 2*F* center. The latter result shows that the exchange interaction between two electrons localized in each of the two vacancies becomes negligibly small when the distance between the *F* centers is larger than two lattice constants. The energy of the *F*-center attraction estimated as the difference between *M*-center and 2*F*-center energies is 0.16 eV.

TABLE I. The energetics of the *F* and *H* centers and the exciton (eV). The asterisk indicates that the formation energy of the first *F* center is subtracted.

Center	Energy of formation with respect to the perfect lattice Split basis set	 Minimal basis set
On the surface		
F	5.35	6.15
M		5.99*
2*F* centers at the next-nearest neighbor		6.18*
V_a+V_c		1.94*
V_k+V_c	7.21	7.91
STE in the	7.04	
second layer	7.04	
In the bulk		
F	5.33	6.13
H	2.46	3.31
Separated *F*-*H* pair	7.79	
STE	7.33	

B. Stability of Na atoms near the *F* and F_2 centers on the surface

We found that the energy required for Na-atom desorption from the nearest-neighbor position to the *F* center on the surface is 1.94 eV. This value also includes the relaxation energy of the ions surrounding the divacancy that is left on the surface. The adiabatic potential energy along the reaction path for the ground and the lowest excited states of the *F* center is shown in Fig. 3. At the dissociation limit, the upper curve corresponds to the *F* center in its ground state near the cation vacancy on the surface and a Na^+ ion on the infinity, while the lower curve corresponds to the divacancy left on the surface and a Na atom on the infinity. The quasicrossing of two curves appears when the distance between the Na atom and its former lattice site is about a lattice constant. Thus the excitation of the *F* center can result in desorption of a Na atom. The energy for desorption of the Na atom between two *F* centers at the next-nearest neighbors is found to be 2.00 eV, almost the same as that from a single *F* center. The energy is even higher for Na atoms near an *M* center.

C. Stability of the *H* center near the surface

We calculated the APES for an *H* center near the surface as a function of the position relative to the surface.

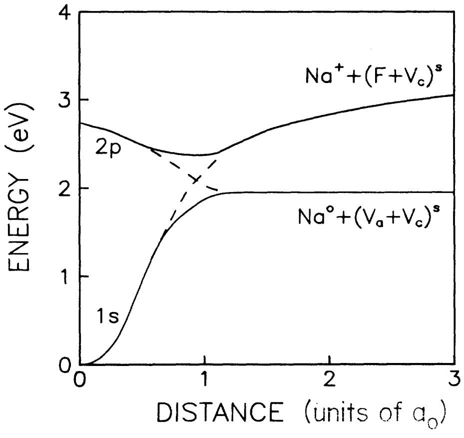

FIG. 3. The adiabatic potential-energy curves for the desorption of a Na atom from a site nearest to an F center on the ⟨100⟩ NaCl surface; 1s shows that for the ground state and 2p shows that for the excited state. The coordinate is the distance between Na and its lattice site on the surface.

The cut of this APES by the ⟨001⟩ plane perpendicular to the surface is shown by curve 1 in Fig. 4. In the figure the ordinate is the energy of the H center. The abscissa in the negative range is the projection of the center of the spin density of the H center to the ⟨001⟩ axis, while that in the positive range is the distance from the surface of a halogen atom dissociated from the H center. The hole is equivalently shared by two anions of the Cl_2^- molecular ion in the bulk, while the H center in the top layer of the surface decomposes into a Cl^- ion occupying a lattice point and a Cl atom physically adsorbed on the surface anion. The H center in the second layer is strongly polarized, and the hole tends to be localized on the anion located closer to the surface. The energy of the adsorption is 0.14 eV, and equilibrium distance is 2.8 Å. Qualitatively, this result does not depend on the basis set. Splitting of the Cl basis, which should describe the contribution of Cl^0 polarization to the physical adsorption more accurately, leads to even lower adsorption energy (0.03 eV).

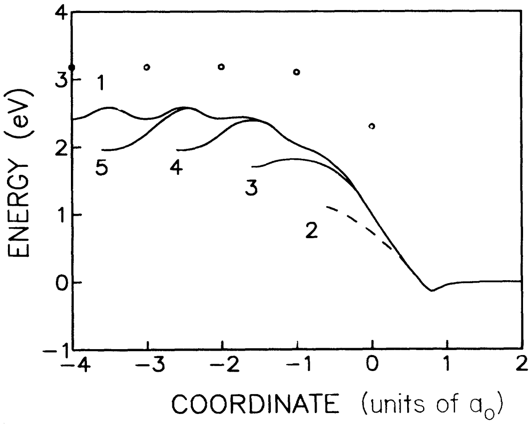

FIG. 4. The adiabatic potential-energy curves for a Cl atom physically adsorbed and diffused further into the bulk-forming an H center. The coordinate is the projection of the center of the spin density of the hole to the ⟨100⟩ axis crossing the surface and is shown in units of lattice constant. Curve 1 is for an isolated H center (doublet state), curves 2, 3, 4, and 5 are for the self-trapped exciton in the second, third, fourth, and fifth layers, respectively (triplet state). The energy of the F-center formation is subtracted for curves 2, 3, 4, and 5. The circles denote the energies of one-center unrelaxed excitons formed in the corresponding layers.

There is no adiabatic potential barrier for the H-center diffusion from the second layer to the surface top layer. The H center placed in the third layer possesses an extremely low activation energy for diffusion toward the surface. The energy for the H-center diffusion backwards to the bulk direction is 0.17 eV and is the same as that for the H center in the bulk, obtained using the same method of calculation.[31] The H center in the third layer is oriented along a ⟨111⟩ direction. This preferential orientation has been proved experimentally in the bulk[33,34] and predicted theoretically.[31] When the H center diffuses from the third layer to the second layer, the Cl_2^- molecular ion rotates from the ⟨111⟩ direction to the ⟨110⟩ direction in the plane perpendicular to the surface. The H center takes an orientation intermediate between the ⟨110⟩ and ⟨100⟩ directions as it approaches the surface top layer. The deviation of its molecular axis from the ⟨001⟩ axis is about 20°. However, we should stress that the adiabatic potential for the H-center rotation is extremely soft, and its reorientation within 10° relative to this direction does not change the total energy beyond the accuracy of our calculations.

According to the calculation, the energy of H-center formation is 2.44 eV, as shown in Table I. This energy contains three main contributions: the binding energy of the Cl_2^- molecular ion, which is negative, the deformation energy of this bond in the Madelung field of the lattice, and the energy of the elastic deformation of the surrounding lattice.

D. Decomposition of the exciton at the surface

We first calculated the lowest triplet excited state of the cluster with the perfect crystal atomic structure. We found that the excitation energy is 8.51 eV. The excited state, irrespective of the cluster size has a hole localized on the Cl p function and an electron distributed over the nearest cations and outermost (diffuse) s orbital of Cl. We call this excited state the one-center or unrelaxed exciton. If the cluster includes more than one chlorine ion, we obtained the corresponding number of broken-symmetry solutions; each represents the one-center exciton located on the halogen sites in the cluster. The energies of these solutions are almost the same within an error of about 0.05 eV, which is caused by the difference in the atom position with respect to the cluster boundary. The first excited state for the cluster simulating the surface is different from that in the bulk: the exciton is localized on the surface ion, with the hole on a p_z orbital perpendicular to the surface, and has an excitation energy of 7.53 eV, lower than the bulk value by 1 eV. The energies of the one-center exciton in the first five layers from the surface are shown by circles in Fig. 4. Since all the lattice sites are equivalent, the excited state of the perfect crystal should be a Bloch state, having a proper translation symmetry. The excited states of the crystal, which we can obtain in our cluster model, are localized in the cluster area, and thus cannot be directly interpreted as the excited states of the crystal. The energy $E(k)$ of the band state may be obtained by the projection of the cluster state to the crystal symmetry group.[35] The wave function of the band state will be a linear combination of such broken-symmetry Hartree-Fock solutions, each corresponding to an exciton localized on the different lattice sites. The dispersion of the band is determined by the interaction matrix element between one-center excitons localized on the nearest sites, and the energy of one-center excitation corresponds somewhat to the middle of the exciton band.

The APES that describes the relaxation of the one-center exciton is a multidimensional function of several modes of lattice relaxation. The self-trapping process of a one-center exciton in the bulk is governed by coupling with two major modes of relaxation: the symmetrical relaxation mode (Q_1), which reduces the distance between two neighboring halogen ions to form a Cl_2^- molecular ion, and the translational displacement mode (Q_2) of the Cl_2^- molecular ion. (Note that both modes include the cation motion.) For the one-center exciton on the surface, in addition to these two coordinates, the mode Q_S, representing the distance of the emitted halogen atom from the surface, is involved.

The cuts of the APES by coordinate Q_2 for the triplet self-trapped exciton formed in the second, third, fourth, and fifth layers below the surface are depicted in Fig. 4 by curves 2, 3, 4, and 5, respectively. Note that the calculation includes the relaxation of all ions in the cluster and optimization of the position and exponent of the floating orbital (see Ref. 31 for more details). Curve 2 is drawn rather arbitrarily, since no minimum appears. Curves 3, 4, and 5 coincide with curve 1 for the migration of the *H* center, except near the local minima of the STE, which occurs since the attraction between the electron and hole components of the STE exceeds the attraction of the hole component (the *H* center) to the surface. The energy gain due to this attraction in the bulk can be evaluated by taking the difference in the energy of a self-trapped exciton and a separated *F*-*H* pair. In our calculation, the value is 0.46 eV (practically this value can be evaluated by taking the difference between the energy of the minima of curve 1 and of curve 5 in Fig. 4). The exciton binding energy in the third layer is almost compensated by the attraction of the *H* center to the surface, and hence the barrier for the emission is much lower for curve 3 than for curves 4 and 5. The energy of the self-trapped excitons in the third layer is 7.04 eV, while that below the fourth layer is 7.33 eV and is the same as that in the bulk. These numbers are shown in Table I for comparison.

The positions of atoms near the surface at several stages, starting from a self-trapped exciton in the third layer and ending with emission of a halogen atom, are shown in Fig. 5. The atomic configurations at the minimum of the APES and at the saddle point for the exciton decomposition are depicted in Figs. 5(a) and 5(b), respectively. Figures 5(c) and 5(d) show two intermediate stages for the halogen-atom emission. Similar to the *H* center, the emitted atom is oriented almost perpendicular to the surface.

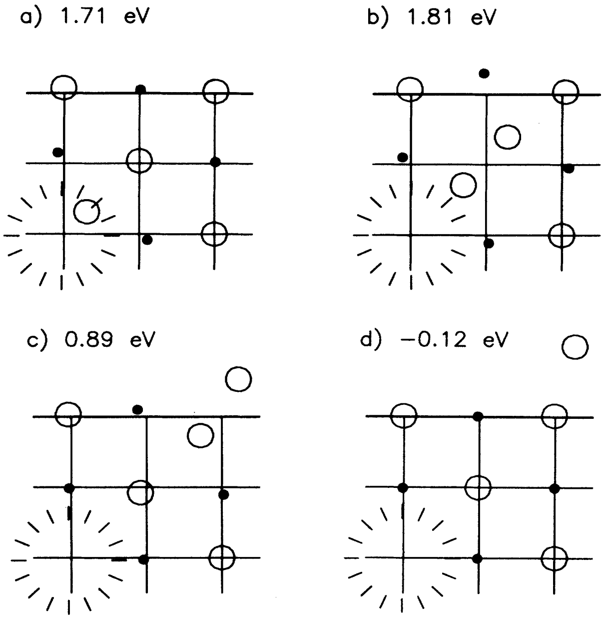

FIG. 5. The atomic configurations at several stages of evolution leading from a self-trapped exciton in the third layer to emission of a halogen atom, following curve 3 of Fig. 4. (a) shows the atomic configuration of the self-trapped exciton in the third layer from the surface, (b) that at the saddle-point configuration, (d) at the physisorbed configuration, and (c) an intermediate stage. The numbers in the figure show the relative energy at each configuration (see Fig. 4). The small closed circles denote Na ions and the large open circles denote Cl ions.

The cut of the APES by coordinate Q_S for the crystal

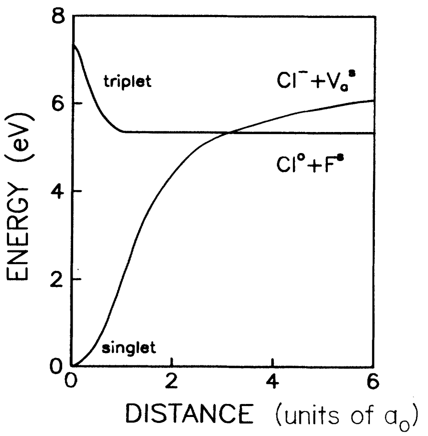

FIG. 6. The adiabatic potential-energy curves for the Cl desorption from the ⟨100⟩ surface of NaCl, for (1) the singlet ground state and (2) the triplet excited state. Zero distance corresponds to the perfect surface.

ground state (singlet) and for the lowest one-center excited state (triplet one-center exciton) is shown in Fig. 6. The crossing of the singlet term corresponding to the ionic configuration ($Cl^- +$ vacancy) with the triplet term (Cl^0+F center) takes place at the distance of three lattice constants. The excitation of the one-center exciton near the surface can lead to emission of a halogen atom. A similar result for alkali-halide clusters has been obtained recently.[36]

IV. DISCUSSION

According to Table I, the energy required to remove a halogen atom from the (100) surface, namely the formation energy of an *F* center on the surface, is smaller than the energy of the one-center excitation 8.51 eV and of a self-trapped exciton 7.33 eV in the bulk. The calculated one-center excitation energy is larger than the experimental value (7.96 eV).[37] If we subtract the difference between the calculated and experimental energies of the one-center excitation from the calculated energy of the self-trapped exciton, the remainder is still larger than the energy required to remove an atom from the surface. Similar arguments lead to a conclusion that the surface self-trapped exciton on the surface also has sufficient energy to emit an atom. According to the semiempirical evaluation by Itoh, Stoneham, and Harker,[16] the energy of the self-trapped exciton in KCl is only slightly smaller than the energy necessary to emit a halogen atom. This contradicts the present calculation. Although the one-center exciton apparently has an energy much larger than that necessary to remove a halogen atom, whether emission can occur after self-trapped exciton is formed is still controversial.

Whether the atomic emission takes place after the crystal excitation is governed by the pathway of the relaxation from the initial excited state. We are going to discuss the possible channels of this relaxation based on the results shown in Figs. 4 and 6. Suppose that the one-center excitation is formed on the surface top layer. Because of the large force acting on the halogen atom, as shown in Fig. 6, it is likely that the halogen atom is desorbed, leaving an *F* center behind. The upper limit for the kinetic energy transferred to the emitted Cl is 2.18 eV as calculated for the split basis set and 1.96 eV for the minimal basis set.

Several pathways are conceivable, if one-center excitation is formed in the second layer. Since the one-center excitation energy in this case is higher by 0.98 eV than that in the first layer, the exciton may jump from the second layer to the top layer (transition from the bulk exciton to the surface exciton) and eventually cause the emission described above. Alternatively, if the Cl_2^- molecular ion is first produced by the Q_1 relaxation, the Q_2 relaxation can then proceed following curve 2 in Fig. 4. In both cases, crystal excitation in the second layer relaxes into an *F* center and a halogen atom emitted from the surface.

Let us consider now the consequence of the exciton formation in the third layer under the surface. The APES (curve 3 in Fig. 4) has a local minimum, but only with a small potential barrier for Cl_2^- molecular ion migration toward the surface. Thus formation of an exciton in the third layer can lead to desorption. The electronic energy which can be imparted to the emitted atom may be estimated to be 2.94 eV [the energy (1.76 eV) of the STE plus the difference (1.18 eV) in the energy of a free exciton and the STE].

Since all processes described above are dynamical, the electronic energy is only partly converted into the kinetic energy of the emitted atoms. We consider the fact that these processes induce the fast component of the emission, where the emitted atoms possess a kinetic energy of approximately 0.3 eV.[15] The difference in the observed kinetic energy and the electronic energy may be imparted to the partner forming the halogen molecular ion and to the surrounding alkali and halogen ions.

Formation of an exciton below the third layer may not necessarily be the source of the dynamic emission. For instance, if the replacement sequence is not oriented toward the surface, it will terminate in the bulk, leaving an *F*-*H* pair. Thus the *F* and *H* centers may be accumulated in the subsurface layers. At room temperature, the *H* centers are known to be coagulated to the interstitial aggregates, as observed most extensively for iodides.[38,39] We suggest that the thermal component of the atomic emission is originated from the surface layers containing *F* centers and interstitial aggregates. According to the present results, the halogen molecular ion of the *H* center tends to reorient along a ⟨001⟩ direction as it approaches the surface. If one-center excitation is generated in the first layer, the force acting on the halogen atom on the surface is also directed perpendicular to the surface. Thus experimental observation by Szymonski[14] that the emission is perpendicular to the surface cannot exclude the excitonic mechanism of emission.

We found that the *F* center at the ground state on the surface is stable: emission of the neighboring alkali atom requires an energy of 1.9 eV. Green, Loubriel, and Richards have observed delayed emission of alkali atoms after termination of a pulsed irradiation. According to our calculation, these results cannot be explained in terms of either the arrival of an individual *F* center or the formation of two *F* centers on the surface by diffusion, but most probably can be explained in terms of formation of *F*-center clusters or Na-atom clusters. We note that Na atoms can be emitted from electronically excited *F* centers. Experimental observation of the consequences of double-beam irradiation, one to produce band-to-band transitions and the other to produce *F*-band excitation, is of interest. Enhancement of second-harmonic generation due to laser-induced distortion by simultaneous *F*-band excitation observed by Reif[40] for BaF_2 can be interpreted in terms of atomic emission by *F*-band excitation.

The phonon-kicking process, atomic emission by the impartition of nonradiative electronic transition energy to the reaction mode, is known to be the cause of atomic emission of electronic origin in a certain solid, such as rare-gas solids.[41] The results of the present calculation exclude the phonon-kicking process, which was suggested originally by Pooley,[42] as the cause of emission as far as alkali halides are concerned. For alkali halides, the phonon-kicking process should result in emission of a halogen ion instead of a halogen atom. According to the calculation, the APES for the lowest relaxed excited state leads to the decomposition of an exciton into an *F* center and an emitted atom. Emission of a halogen ion needs an energy larger than the emission of an atom by about 1 eV. Moreover, the energy of the self-trapped exciton in the bulk, 7.33 eV (calculated), is close to the energy (6.20 eV) to remove a halogen ion. It is unlikely that the energy of the nonradiative transition is imparted to that of ion emission so efficiently.

V. CONCLUSION

The following conclusions have been drawn from the present calculations.

(i) A force acting on the halogen atom of the excited state generated on the surface top layer is applied along the ⟨001⟩ direction. This force can induce emission of energetic halogen atoms, leaving *F* centers behind.

(ii) There is no stable relaxed atomic configuration corresponding to the self-trapped exciton located in the first two layers of the surface.

(iii) The self-trapped excitons below the third surface layer may be stable at low temperature. They possess an energy higher than that required to emit a halogen atom. Therefore, it is unlikely that dynamic emission of halogen atoms is induced from self-trapped excitons formed in near-surface layers.

(iv) An *H* center, as it approaches the surface, tends to orient along the ⟨100⟩ direction perpendicular to the surface and decompose into a halogen ion on the lattice site and an emitted atom. Similarly, the *H* centers evolved from the self-trapped excitons formed in near-surface layers are reoriented along the ⟨001⟩ direction perpendicular to the surface.

(v) An *F* center on the surface is stable at the ground state: an energy of 1.9 eV is needed to emit a neighboring alkali atom. A neighboring alkali atom may be emitted when the *F* center is electronically excited.

The results of present calculation are in favor of the excitonic mechanism for emission of atoms induced by photoexcitation of alkali-halide surfaces. High-sensitivity measurements of emitted atoms, in which the damage of the surface during measurements is minimized, may reveal further basic excitonic processes emission of atoms induced by electronic excitation.

ACKNOWLEDGMENTS

The work is partially supported by the Grant-in-Aid for International Collaboration Program by the Ministry of Education, Science and Culture, Japan. A.L.S. is grateful to the Cannon Foundation in Europe, and to the Royal Society for financial support.

---

*Permanent address: Department of Condensed Matter Chemical Physics, University of Latvia, Rainis Blvd., 19, Riga 266089, Latvia.

[1] P. D. Townsend and F. Lama, in *Desorption Induced by Electronic Transition,* edited by N. H. Tolk, M. M. Traum, J. C. Tully, and T. E. Madey (Springer-Verlag, Berlin, 1983), p. 220.

[2] N. Itoh, Nucl. Instrum. Methods **132**, 201 (1976).

[3] M. Szymonski, J. Ruthowski, A. Poradzisz, and Z. Postawa, in *Desorption Induced by Electronic Transition II,* edited by W. Brenig and D. Menzel (Springer-Verlag, Berlin, 1985), p. 160.

[4] D. J. Elliot and P. D. Townsend, Philos. Mag. **23**, 249 (1971).

[5] A. Schmid, P. Braunlich, and P. K. Rol, Phys. Rev. Lett. **35**, 1382 (1975).

[6] H. Kanzaki and T. Mori, Phys. Rev. B **29**, 3583 (1984).

[7] R. T. Williams and K. S. Song, J. Phys. Chem. Solids **51**, 679 (1990).

[8] N. Itoh and K. Tanimura, J. Phys. Chem. Solids **51**, 717 (1990).

[9] K. Tanimura, T. Suzuki, and N. Itoh, Phys. Rev. Lett. **68**, 635 (1992).

[10] T. Tokizaki, T. Makimura, H. Akiyama, A. Nakamura, K. Tanimura, and N. Itoh, Phys. Rev. Lett. **67**, 2701 (1991).

[11] R. T. Williams, W. L. Faust, and B. B. Craig, Cryst. Lattice Defects Amorphous Mater. **12**, 103 (1985).

[12] M. Hirai, Rev. Solid State Sci. **4**, 431 (1990).

[13] Z. Postawa and M. Szymonski, Phys. Rev. B **39**, 12 950 (1989).

[14] M. Szymonski, in *Desorption Induced by Electronic Transitions IV,* edited by G. Betz and P. Varge (Springer-Verlag, Berlin, 1990), p. 270.

[15] M. Szymonski, J. Kolodziej, P. Czuba, P. Piatkowski, A. Paradzisz, N. H. Tolk, and J. Fine, Phys. Rev. Lett. **67**, 1906 (1991).

[16] N. Itoh, A. M. Stoneham, and A. H. Harker, Surf. Sci. **217**, 573 (1989).

[17] N. Itoh, Cryst. Lattice Defects **3**, 115 (1972).

[18] T. A. Green, G. M. Loubriel, P. M. Richards, N. H. Tolk, and R. F. Hagland, Jr., Phys. Rev. B **35**, 781 (1987).

[19] Y. Al Jammal, D. Pooley, and P. D. Townsend, J. Phys. C **6**, 247 (1973).

[20] E. Tagulauer, N. Tolk, R. Riedel, E. Colavita, G. Margaritondo, N. Greshenfels, N. Stoffel, J. A. Kelber, G. Loubriel, A. S. Bommanavar, M. Bakshi, and Z. Huric, Surf. Sci. **169**, 267 (1986).

[21] P. H. Bunton, R. F. Haglund, Jr., and J. L. Rose, in *Desorption Induced by Electronic Transitions IV* (Ref. 14), p. 305.

[22] P. Wurz, J. Sarnthein, W. Husinsky, and G. Betz, in *Desorption Induced by Electronic Transitions IV* (Ref. 14), p. 289.

[23] R. R. Sharma and A. M. Stoneham, J. Chem. Soc. Faraday Trans. II **72**, 913 (1976).

[24] H. A. Kassim, J. A. D. Matthaw, and B. Green, Surf. Sci. **74**, 109 (1978).

[25] E. A. Kotomin, A. L. Shluger, and R. Yu. Dzelme, Phys. Status Solidi B **98**, 427 (1980).

[26] E. V. Stefanovich, A. L. Shluger, and Yu. E. Tiliks, Chemical Physics (Russian) **7**, 815 (1988).

[27] A. L. Shluger, R. W. Grimes, C. R. A. Catlow, and N. Itoh, J. Phys. Condens. Matter **3**, 8027 (1991).

[28] See, for example, R. Pandey, J. Zuo, and A. B. Kunz, Phys. Rev. B **39**, 12 565 (1989).

[29] G. B. Bachelet, D. R. Hamann, and M. Schluter, Phys. Rev. B **26**, 4199 (1982).

[30] A. L. Shluger, N. Itoh, V. E. Puchin, and E. N. Heifets, Phys.

Rev. B **44**, 1499 (1991).

[31] V. E. Puchin, A. L. Shluger, K. Tanimura, and N. Itoh, Phys. Rev. B **47**, 6226 (1993).

[32] P. W. Tasker, G. G. Balint-Kurti, and R. N. Dixon, Mol. Phys. **32**, 1651 (1976).

[33] A. Ch. Luschchik, Yu V. Kolk, N. E. Lushchik, and A. G. Fropir, Tr. Inst. Fiz. i Astron. Akad. Nauk Est. SSR, Ser. Fiz. **58**, 7 (1986).

[34] K. Tanimura (unpublished).

[35] R. Broer and W. C. Nieuwpoort, Theor. Chim. Acta **73**, 405 (1988).

[36] X. L. Rainer, D. Beck, and R. L. Whetten, Phys. Rev. Lett. **68**, 3420 (1992).

[37] T. Miyata and T. Tomiki, J. Phys. Soc. Jpn. **24**, 1286 (1968).

[38] A. M. T. Allen and J. D. Comins, Nucl. Instrum. Methods B **46**, 240 (1990).

[39] A. M. T. Allen and J. D. Comins, J. Phys. Condens. Matter **4**, 2701 (1992).

[40] J. Reif, Opt. Eng. **28**, 1122 (1989).

[41] J.Schou, Nucl. Instrum. Methods B **27**, 188 (1987).

[42] D. Pooley, Solid State Commun. **39**, 241 (1965).