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Molecular-dynamics simulation of positive-ion and neutral halogen desorption following Na *K*-shell Auger cascades in the NaF crystal

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A Na *K*-shell Auger cascade in NaF can produce either four to six neighboring valence holes, or two to four neighboring valence holes and a F^+ ion. If the holes remain localized as neutral atoms where they are created, they will assist the F^+ ion to desorb, or assist in the desorption of Na^+ ions. The neutral atoms themselves may also desorb. We use molecular-dynamics calculations to investigate whether the F^+ ion and neutral F atoms produced by the Na *K*-shell Auger cascade in NaF can in fact lead to the desorption of positive ions and/or neutral F atoms. Simple fits to the Gordon-Kim potentials are used for the ionic interactions. *Ab initio* two-body potentials are developed to describe the interaction between a neutral F atom just outside of the crystal surface and a Na or F ion in the surface plane. The potentials exhibit a repulsive inner wall similar to that found for the diatomic molecules, and a shallow well. The integration time required for a satisfactory simulation of positive-ion desorption by the Knotek-Feibelman mechanism is shown to be 1–2 ps. Using 2-ps simulations, it is shown that only when the F^+ ion is accompanied by four neighboring F atoms from the same Auger cascade does positive-ion desorption occur from the perfect (100) surface. Analogous results are obtained in simulations designed to relate to the imperfect (100) surface. It is concluded that the neutral atoms assist positive ions to desorb only in configurations which appear to be too rare to be of experimental significance. It is shown that crystal temperature, near room temperature, is not a factor in determining whether positive-ion desorption occurs by the Knotek-Feibelman mechanism. This work extends that of Walkup and Avouris on NaF to the case where the Auger-produced F^+ ion is accompanied by neutral F atoms.

I. INTRODUCTION

Auger cascades in alkali halides can produce positive halogen ions at halogen sites. Such ions are subject to forces which tend to move them to an interstitial position in the lattice,[1] or tend to cause them to be ejected from the crystal surface.[2] The positive halogen ions can also exert repulsive forces on surface cations which tend to cause the cations to desorb.[2] Positive Na and F ions were observed by Parks *et al.* to be desorbed from the NaF crystal with increasing yields as the Na *K* edge was traversed in a synchrotron experiment.[3,4] The magnitudes of the positive-ion fluxes were very small; about one positive ion was observed for 10^4 photons absorbed in the surface plane. Parks *et al.* argued that the Auger cascade following each photon absorption should produce either a F^+ ion, or two holes (neutral F atoms), from the F^- neighbors of the initial hole-containing Na ion. They interpreted the increase in yields in terms of the Knotek-Feibelman mechanism,[2] and argued that, owing to the sudden change of charge, a F^+ ion should be ejected most readily from a regular lattice site of maximum Madelung potential in the surface layer of the perfect (100) surface. They also argued that a Na^+ ion could best be pushed off the crystal by a F^+ ion below it if the Na^+ ion were in a minority ad-ion site of low Madelung potential.

After Ref. 3 was published, Walkup and Avouris studied the Auger-induced desorption of F^+ and Na^+ from NaF.[5] They used the technique of molecular-dynamics simulation to allow many of the crystal's ions to share the initial excitation energy given to the system when a negative fluorine ion is suddenly changed into a positive one as a result of the Auger process. They found that a suddenly created F^+ ion does not desorb from the perfect (100) surface. However, a Na^+ ion in an ad-ion site above the perfect surface could be ejected by a suddenly created F^+ ion just below it. A study of the effect of lattice temperature on ion desorption led them to the conclusion that, in their calculations at 300 K, lattice temperature had not been a factor in determining whether desorption occurs. Taken together, the conclusions of Refs. 3 and 5 imply that F^+ desorption from NaF does not occur by the Knotek-Feibelman mechanism.

Recently, an alternative positive-ion desorption mechanism has been demonstrated for electron stimulated desorption in NaCl.[6] It is based on the ionization of desorbing neutral atoms by primary and secondary electrons. In Ref. 6 it was stated that the alternative mechanism could also account for the order of magnitude of the positive-ion fluxes observed in the photon stimulated desorption experiment of Ref. 3. However, the possibility of additional contributions to the ion flux defect sites or other mechanisms was not ruled out.

There is a problem with the discussion of the Na *K*-shell Auger cascade in Ref. 3, which arises from their treatment of the filling of the $2p^2$ hole in the Na ion after the Na(*KLL*) Auger transition. This has consequences for the discussion of the desorption of positive ions. In a recent paper[7] it was shown that the main Na($KL_{2,3}L_{2,3}$) Auger cascade in NaF produces either four valence holes, or one F^+ ion and two valence holes on the neighbors of the Na ion where the cascade originated. Here we use the notation F^+ to designate two $2p$ electrons missing from a single F^- ion and use the word valence hole to designate one $2p$ electron missing from a F^- ion. The Na($KL_{2,3}L_{2,3}$) Auger transition starts the cascade about 71% of the time. The cascade starts with the Na($KL_1L_{2,3}$) transition about 23% of the time, and this produces one additional valence hole. The Na(KL_1L_1) transition starts the cascade about 6% of the time and produces two additional valence holes.[7] The dynamics of these holes must be taken into account in any theory of positive-ion desorption, since the creation of a hole leads to a large change in the Madelung potential seen by other ions. It was shown in Ref. 7 that the majority of the holes should diffuse from 50 to 700 Å from the site of their creation in times of the order of a picosecond, and should therefore not play a role in the ejection of positive ions. However it could not be ruled out that a fraction of the time a hole might localize as a F atom where it was created, because of a combination of low hole energy, large hole effective mass, and favorable atomic geometry. Each of these neutral F atoms can be expected to interact with one of their F^- neighbors to form a V_K center. At the same time, however, the F atoms can participate with a F^+ ion from the same cascade in the ejection of positive ions. In addition, a cluster of several F atoms near a surface Na ion subjects it to net repulsive forces which may cause it to be ejected. Moreover, the F atoms themselves may desorb from the surface. If these localized hole configurations lead to positive-ion ejection, they need only occur with a probability of the order of 10^{-4} per Auger cascade to account for the order of magnitude of the desorbed ion current. It is these presumably rare desorption processes involving neutral halogen atoms which are explored via molecular-dynamics simulation in the present paper. Our methodology is to use molecular-dynamics simulations to determine which configurations of a F^+ ion and/or F atoms lead to positive-ion desorption. It will be shown that only the most unlikely configurations of holes with a F^+ ion lead to its ejection, or to the ejection of a Na^+ ion. Positive-ion desorption involving F atoms may be considered to be desorption from defect sites in the sense of Ref. 6. The results obtained in the present paper were reported briefly in Ref. 7.

II. THE MOLECULAR-DYNAMICS SIMULATION METHOD

In a given electronic state, the Born-Oppenheimer approximation allows us to integrate the classical equations of motion (EOM) of the atoms or ions as they move in the total potential field. Electronic transitions such as the Auger process are effectively instantaneous and are not coupled to the nuclear motion. Other electronic processes, such as the formation of the F_2^- quasimolecules in V_K centers, are strongly coupled to the nuclear motion within the solid. Molecular dynamics (MD), as implemented here, solves for the classical motion in a single electronic state and cannot determine the correct coupling between different electronic states.

We integrate the Newtonian EOM of the isolated crystallite by the second-order central-difference scheme (the "royal road"[8] or Verlet[9] method) with a fixed time step. We choose to examine a rather large isolated crystallite rather than attempt to couple a smaller crystallite to a reservoir because of potential difficulties in the treatment of long-range Coulombic forces.

Our MD program only contains provisions for additive two-body interactions. The neglect of three-body and higher forces is a good approximation for the ground electronic state of the closed-shell alkali halide crystals. The presence of F^+ and F complicates this, as discussed in Sec. III. Our MD simulations are a straightforward numerical integration of the EOM with two-body potentials chosen to approximate the Born-Oppenheimer potentials.

The MD of an isolated crystallite is energy conserving, that is, microcanonical. We cannot address dissipative processes such as phonon relaxation unless the EOM are modified by a reservoir, or the crystallite is sufficiently large that it needs no reservoir during the relevant time period. We have confirmed that the latter is true for our simulations of the post-Auger dynamics. However, the statistical methods of MD are useful to us in order to relax the original (prior-Auger) crystallite to its 0-K state or to select an initial dynamical state characteristic of some nonzero temperature. We use the velocity reset method[10] of thermal simulation to accomplish both these tasks. The velocity reset method as used here is a minor modification[10] of the Andersen method[11] of thermostating. One integrates the EOM for a suitable period, typically one-fifth of a Debye period, selects new particle velocities from a Maxwellian distribution at the appropriate temperature, and continues integration. This cycle of integration and velocity resetting is repeated many times. If the temperature is zero and one is not in a metastable configuration, the crystallite freezes to absolute zero. If metastability is a concern, the temperature should be lowered slowly.

The prior-Auger MD of the crystallite are done with Gordon-Kim interactions.[12] The velocity reset method is used to thermostat the crystallite from the initial, ideal bulk-lattice positions to equilibrium at 0-K or to some state characteristic of a temperature in these potentials. The interactions are then switched to the post-Auger potentials of the new electronic state, which include those of the F^+ and any F atoms. MD is initiated for the new electronic system as previously done by Walkup and Avouris. Numerical output of positions and velocities, as well as graphical representations of the events, are examined.

It would be difficult to treat the simultaneous dynamics of V_K center formation and positive-ion desorption in the Born-Oppenheimer approximation, because there are several electronic configurations (channels) to consider. In the V_K center channel the F atom and one of its neighbor F^- ions are interacting strongly to form a F_2^- molecular ion. The molecular ion is weakly enough bonded to the rest of the crystal that it can be regarded as a perturbed free molecular ion, and the charge on each of the F_2^- ion centers is taken to be $-\frac{1}{2}$.[13] In the desorption channel, however, the F atom is neutral, and sees the rest of the crystal as an array of closed-shell anions and cations to which it is weakly bound. This channel is the one which applies to a desorbing F atom outside the crystal surface. An analogous, but simpler, problem arises in describing a F^+ ion. It also corresponds to a separate electronic configuration in the Born-Oppenheimer sense.

We have chosen to replace the multichannel problem by a single-channel problem which should maximize the probability of positive-ion desorption. This is done by ignoring the V_K-center–formation channel and using only the F-atom potentials applicable to the desorption channel in the molecular-dynamics simulation. In the V_K-center–formation channel the hole on the V_K center is shared equally between its two atoms.[13] As a result, the hole on a V_K center being formed from a F atom which is a neighbor of a surface Na^+ or F^+ ion is usually farther from the Na^+ or F^+ ion than it is in our approximate treatment, where the hole (an effective positive charge) cannot be shared. In a few cases a hole can be shared between two halogen sites at equal distances from the F^+ or Na^+ ion of interest.

The F-atom potential for the desorption channel is a necessary ingredient of the calculation. Since it is not possible to calculate this potential *ab initio* in a completely quantitative manner, two extreme types of potential are considered. The first extreme is that of F atoms which interact only via the short-range repulsion that is left when the charge on the F ion of the Gordon-Kim two-body potential is set equal to zero. This is a nonbonding situation. The other extreme is that of F atoms which are bound to the crystal by a potential which is probably somewhat too strong. The molecular-dynamics program is set up to use two-body potentials, and so we developed two-body potentials for the second extreme case from the interaction of a F atom outside the (100) surface with a surface Na^+ or F^- ion. The F-atom potentials are described in Sec. III.

We conclude this section by discussing the length of time for which the molecular-dynamics simulations need to be carried out in order to conclude that the products of an Auger cascade are not going to lead to the desorption of an ion by the Knotek-Feibelman mechanism, which entails a prompt Coulomb explosion. There are two times to consider. The first is the time for the initial potential energy provided by the sudden conversion of F^- ions to F^+ ions and F atoms to be shared by the crystal ions to the extent that the subsequent emission of particles is governed by the laws of thermal evaporation. The second is the time for the changed halogen ions to recapture some or all of their electrons, thereby reducing or turning off the potential energy which drives the positive-ion ejection. We shall consider the electron-capture processes first.

The first, and probably fastest, electron-capture process is the "capture" of electrons from the valence band, i.e., the association of the F^+ ion or F atom with a neighboring F^- ion. For the F^+ ion, this electronic transition results in the formation of an excited ionic state of the F_2 molecule. It has been considered in connection with the Varley mechanism.[14,15] For the F atom, the corresponding electronic transition is the formation of a V_K center. If we are concerned with the ejection of a F^+ ion, the formation of the F_2 molecule will terminate the existence of the F^+ ion as such.[14,15] If the F^+ ion is supposed to be ejecting a Na^+ ion, its holes become shared with a neighboring F^- ion, analogous to the hole sharing discussed above for V_K-center formation. We need estimates of the capture time for these processes.

On the basis of the vibrational frequency of the F_2 molecule and the crystal longitudinal optical phonon frequency it could be expected that the formation times for F_2 molecules in NaF lie in the range 0.1 to a few picoseconds. For V_K centers, a similar statement has been made by Williams, Bradford, and Faust.[16] In the case of KCl, the V_K-center–formation time is known experimentally to be less than 5 ps.[16] Thus an excited-state F_2 molecule formation time of from 0.1 to 2 ps does not seem unreasonable.

The other electron-capture process is electron recombination from the conduction band. For the V_K center, this process has been discussed in Ref. 16 in terms of two-body recombination. The recombination time is inversely proportional to the electron density, and densities of the order of magnitude of 10^{17} cm^{-3} lead to picosecond capture times. Currently, the diffusion lengths for electrons and holes in NaF are not well enough known to permit a useful estimate of the electron density. Thus the recombination time cannot be estimated at present.

We now consider the time necessary for the initial crystal potential energy to be shared among the crystal ions sufficiently that subsequent particle emission is governed by thermal evaporation. The suddenly created F^+ ion behaves very much like a majority Na^+ ion. Once the sharing of the initial energy has occurred, the rate of positive ion desorption should be about 10^{-8} of the rate of thermal desorption of neutral molecules.[17] The molecular-dynamics simulations allow one to examine the particle motions and kinetic energy distributions as a function of time to see how quickly the ion motions and kinetic energy distribution of the crystallite become nearly random. For the case of a suddenly created F^+ ion on the (100) surface at 0 K, we have studied these quantities as a function of time in simulations on the ion crystallite of size $10\times10\times4$ used for most of our calculations. At time $t=0$, when the F^- ion is suddenly changed into a F^+ ion on the 0-K surface, the crystallite kinetic energy (KE) is zero. At a time of 0.12 ps, the crystallite KE is 7.32 eV. The F^+ ion has a KE of 0.77 eV and the ions adjacent to and below the F^+ ion have KE's of 0.1 or 0.2 eV. Some ions at the crystallite edges are still essentially at rest, while others, at the end of lines of ions leading to the site of the F^+ ion, have KE's of about 0.1 eV. These energies are shared with all the particles of the crystallite by times of 1 or 2 ps. At 2 ps, the average KE of an ion is 0.0165 eV and the maximum KE of an ion is 0.08 eV. The F^+ ion has an energy of 0.048

eV. At this time the most energetic ions appear to be distributed nearly randomly about the crystallite. Additional F^+-ion simulations with 64- and 216-ion cubes led to similar results. A movie of the 64-ion system out to 5 ps shows that it has lost its original crystallite structure. As stated earlier, a F^+ ion behaves like the majority Na^+ ions and it seeks Na^+ sites either in the crystallite or as an ad-ion on the surface. By 1 or 2 ps the F^+ ion's kinetic energy is the same on the average as that of the other ions in the crystallite. On this basis it can be concluded that a 1- or 2-ps simulation is justified for an investigation of the Knotek-Feibelman mechanism. If the ion in question does not desorb within this time, the mechanism is inoperative. As will be seen in Sec. IV, when an ion is ejected, it leaves the crystal in a few tenths of a picosecond.

III. TWO-BODY POTENTIALS FOR A NaF SIMULATION INCLUDING F ATOMS

To describe the interaction of the positive and negative ions of the perfect crystal we adopt the Gordon-Kim two-body potentials used by Walkup and Avouris.[5] In light of their work it was possible to simplify the potentials of NaF somewhat by fitting the tabulated short-range interactions to exponential functions, neglecting the very weak attractive parts of the tabulated functions. One short-range potential was used for the Na^+-Na^+ interaction and one common short-range interaction was used for the Na^+-F^-, Na^+-F^+, F^--F^-, and F^--F^+ interactions. This should not influence the results in any significant way, as we showed by repeating the calculations of F^+ and Na^+ desorption in Ref. 5. For the extreme case of nonbonding F atoms discussed in Sec. II, the second short-range interaction mentioned above was used for all F-atom interactions. The Born-Mayer form of the potential V_1 for the ions is shown in Eq. (1):

$$V_1 = A_1 \exp(-a_1 R) + C/R \ . \tag{1}$$

In Eq. (1), R is the ion-ion separation, and C for a pair of ions arises from the product of the ion charges in Coulomb's law. For nonbonding F atoms, C is set equal to zero.

It is worth noting that since the MD simulation allows for the relative displacement of all the crystallite ions, it accounts for the major part of the crystal polarizability. Thus dielectric image effects on a departing ion are largely accounted for.

To develop potentials for the case of bonding F atoms we proceeded as follows. As a F atom approaches the (100) surface of the perfect NaF crystal from the vacuum side it first experiences the electric field produced by the mainly closed-shell ions of the crystal. The largest long-range forces are due to the atom's ^2P quadrupole moment and its induced dipole moment. With the quadrupole axis appropriately aligned, these forces are attractive. At long range then, the lowest potential-energy surface for a F atom will be attractive. As the atom approaches the nearest ions on the surface it can bond with them. Sufficiently close to any given ion, the F atom will experience a repulsive force. We want to describe this interaction approximately as a sum of two-body potentials. The potential curves for the free F_2^- and NaF^+ molecules are not appropriate since they describe a F atom in the relatively strong electric field of a single ion at large distances. In addition, they do not reflect the fact that the ions we wish to consider are part of the ionic crystal and subject to the crystal's Madelung potential.

In order to incorporate the essential features of the interaction of a F atom with the surface as simply as possible, we represent the crystal by a single F^- or Na^+ ion embedded in the center of the (100) surface of a $10\times10\times10$ cube of point ions so that 999 point ions are

TABLE I. Potential-energy curves for a fluorine atom on three perpendiculars to the (100) surface of a NaF crystal simulated by a $10\times10\times10$ cube of point ions and one or two all-electron ions. The perpendicular passes either through the ion or through the midpoint of the line joining the ion pair. The all-electron clusters are designated as NaF^+, etc.

	NaF^+		F_2^-		F_3^{2-}	
R (Å)[a]	q[b]	V (eV)[c,d]	q	V (eV)	q	V (eV)
1.07	−0.37	20.74	−0.02	13.81		
1.48			−0.27	2.09		
1.53	−0.04	3.21				
1.69	−0.02	1.49	−0.13	0.524	−0.24	1.31
2.00	0.01	0.265	−0.03	−0.0357	−0.06	0.328
2.31	0.01	0.0059	−0.01	−0.1115	−0.02	0.0283
2.51	0.01	−0.0289				
2.62			0.00	−0.0959	0.00	−0.0620
2.70	0.01	−0.0399				
2.91	0.01	−0.0297	0.00	−0.0726	0.00	−0.0744
3.70	0.00	−0.0112	0.00	−0.0258	0.00	−0.0381
4.76	0.00	−0.0039	0.00	−0.0035	0.00	−0.0042
9.24		0.0		0.0		0.0

[a] Distance from F atom to ion. The anion-cation distance was 2.31 Å.

[b] Mulliken charge on F atom.

[c] Potential energy of F atom relative to zero at $R = 9.24$ Å.

[d] There were 999 point ions for the NaF^+ and F_2^- cases, and 998 point ions for the F_3^{2-} case.

used. The F atom is then placed outside the surface on a line perpendicular to it and passing through the ion it is to approach. The model system then consists of a diatomic molecule ion in the external potential of the lattice of point ions. The interaction energy for this system is calculated as a function of position along the perpendicular in the fourth order of Moller-Plesset perturbation theory based on the molecular orbitals from an unrestricted Hartree-Fock calculation.[18] This provides the two-body potentials for the F-F$^-$ and F-Na$^+$ interactions. The F-F$^-$ potential was then also used for the other F-F interactions. As a means of exploring the validity of the description of the atom-surface interaction in terms of two-body interactions, two F$^-$ ions were incorporated into the surface of the point ion array and a F atom was placed on the perpendicular to the surface passing through the midpoint of the line joining the two ions. This provided a potential which could be compared with the sum of two F$^-$-F potentials. The three potentials are exhibited in Table I, where the variable R represents the distance from the neutral atom to the ions. The R values were chosen to allow generalized Morse potential functions to be fitted approximately to the tabulated potentials and to exhibit their shape and depth. The form of the generalized Morse potential V_2 is given by

$$V_2 = A_1 \exp(-a_1 R) + A_2 \exp(-a_2 R) \ . \tag{2}$$

Here R is the particle-particle separation.

The table also shows the Mulliken charge on the atom. The F-atom Mulliken charge is very small until the atom's charge cloud overlaps the surface charge cloud because the Madelung potential keeps the negative or positive charge on the surface ions.

Table I shows that the F-Na$^+$ and F-F$^-$ interactions are much weaker than those of the gas-phase molecules or the V_K center, which have dissociation energies in excess of an electron volt. The well depth of the weakest interactions is of the order 0.04 eV. In all three cases the range of the interaction is somewhat greater than twice the anion-cation distance of 2.31 Å. The NaF$^+$ crystallite was obtained from the F$_2^-$ crystallite by interchanging positive and negative point ions and replacing the F$^-$ ion with a Na$^+$ ion. Therefore the crystallite's electric field and electric field gradients differ only in sign to a good approximation in these two cases. To within the accuracy of our calculations, the difference in the potential curves arises from the orientation of the F-atom quadrupole. It is along the perpendicular to the surface in the F$_2^-$ case, and perpendicular to it in the NaF$^+$ case. The relevant components of the quadrupole tensor differ by a factor of 2. In each case the contrary orientation of the quadrupole leads to a configuration with a repulsive potential energy curve. The small values obtained for the well depths suggest that the potential curves in Table I should not be claimed to be quantitatively correct, even along the NaF$^+$ and F$_2^-$ perpendiculars. The accuracy required for this is probably beyond the capacity of our *ab initio* electronic structure calculations.

TABLE II. Prefactors and exponential decay parameters for Born-Mayer repulsive interactions in Eq. (1), and generalized Morse potentials in Eq. (2). The ionic potentials are the sum of the Born-Mayer repulsive exponential and the Coulomb potential. The F-atom generalized Morse potentials are the sum of the repulsive and attractive exponentials.

Interaction	Prefactor A_1 (K)[a]	Parameter a_1 (Å^{-1})	Prefactor A_2 (K)	Parameter a_2 (Å^{-1})
Na$^+$-Na$^+$	9.0230×10^7	5.8656		
Other ionic[b]	2.7239×10^7	4.0143		
Na$^+$-F^0	3.1678×10^7	4.3464	-6.3972×10^4	1.7008
Other F^0	1.5977×10^7	4.1574	-1.8661×10^5	1.8897

[a] One kelvin unit (K) is equivalent to $8.617\,395\times10^{-5}$ eV.

[b] This repulsive interaction was also used to describe nonbonding F-atom interactions.

It should not be surprising that twice the potential from the F$_2^-$ simulation is not equal to the potential from the F$_3^{2-}$ simulation. The electric field is zero on the perpendicular line in the F$_3^{2-}$ simulation, since the line passes through the center of a hollow surface site equidistant from two F$^-$ ions and two positive point charges. The perpendicular for the F$_2^-$ simulation is a line where the electric field is relatively large. It is interesting to note that for $R = 3.7$ Å, at an energy of about 6 eV above the configuration with two surface F$^-$ ions and one F atom in front of the surface, there is a configuration with a surface F$_2^-$ ion and a F$^-$ ion in front of the surface. The close relation between the V_K-center–formation and desorption electronic channels thus appears in the course of the molecular structure calculations.

The use of two-body potentials to describe the interaction of the F atoms in the molecular-dynamics calculations is a somewhat crude approximation. In view of the foregoing discussion, we expect that the use of two-body potentials taken from the NaF$^+$ and F$_2^-$ results in Table I will overestimate the binding of the F atom to the surface. The values of the parameters used in the potentials V_1 and V_2 are exhibited in Table II.

IV. RESULTS AND DISCUSSION

The presentation and discussion of the results is subdivided into several subtopics. First, some general information about the simulations is presented. With this introduction, the results obtained from simulations at 0 K on the perfect (100) surface are discussed, with emphasis being placed on the effect of localized holes (F atoms) on the desorption of F$^+$ and Na$^+$ ions. Next, simulations concerning the imperfect (100) surface are described. Then the effect of crystal temperature is considered. Finally, from the accumulated information on which configurations of F$^+$ ions and F atoms lead to positive-ion desorption, the likelihood that the Knotek-Feibelman mechanism can account for the observed flux of positive ions from the photoinduced Na *KLL* Auger cascade in NaF is assessed.

The simulations reported here were carried out primarily on lattices of size 10×10×4, following the work of Walkup and Avouris,[5] and using an initial anion-cation separation of 2.31 Å. The crystal was thermostated approximately to either 0 or 293 K, or initialized at 2930 K, after which the fluorine anions participating in the Auger cascade were changed to F atoms or F^+ ions. The 0-K thermostating for all cases, and the 293-K thermostating for the unchanged crystallite, were accomplished with 100 velocity reset cycles. In these cases the crystallite temperature and the thermostating temperature correspond closely. The thermostating in the other cases was accomplished with 6–10 reset cycles and the temperature correspondence is only to within about 20%. The changed ions were located near the center of the largest face. The classical equations of motion for the system were then integrated for 2 ps. The output consisted of the tabulated positions and velocities of all the lattice atoms. It could be observed that the large perturbation caused by the ion changes did not disrupt the basic lattice structure at the lattice edges or on the face opposite that where the perturbation was centered.

Thermostating the lattice to 0 K from the initial configuration, lowered the system energy by 1.77 eV to a value of −1870.5 eV. This corresponds to a binding energy of 9.35 eV per ion pair, relative to the separated ions. The calculations of Kim and Gordon for the infinite solid led to a cation-anion equilibrium separation of 2.31 Å and a binding energy of 9.64 eV.[19] Our relaxed lattice is distorted inwards at the corners by about 0.26 Å. In the middle of the short and long edges, the inward distortion is about 0.07 and 0.01 Å, respectively. In the center of the faces the distortion is about 0.09 Å outward. These displacements are all relative to the unrelaxed rectangular parallelopiped.

We first compare simulations done with nonbonding F atoms on the one hand, and bonding F atoms on the other. The first preliminary calculations confirmed the idea

TABLE III. Tabulation of molecular-dynamics simulations on a 10×10×4 NaF crystallite for times out to 2 ps.

Case	Description[a]	Remarks[b]	Initial lattice temp. (eV)	Final average ion kinetic energy (eV)[c]
1	Unchanged crystal		0.0252	0.0334
2	$F^+(1)$	F^+ and two F^- rise[d]	0.0	0.0165
3	F^+ (1)	F^+ and F^- go together to ad-ion sites; eight other ions rearrange	~0.22	0.2413
4	$F^+(1)+2F(2)$	F^+ to ad-ion site, two F^- rise	0.0	0.0399
5	$F^+(1)+2F(2)$	~ eight ions rearrange	~ 0.025	0.0751
6	$F^+(1)+2F(2)U$	F (0.06 eV) and F (0.31 eV) desorb ~ eight ions rearrange	~ 0.025	0.0726
7	$F^+(1)+2F(2')$	F^+ replaces Na^+ and Na^+ goes to ad-ion site; several F^- rise	0.0	0.0414
8	$F^+(1)+3F(2)$	F^+ and one F^- approach and rise	0.0	0.0573
9	$F^+(1)+3F(2)$		~ 0.025	0.0918
10	$F^+(1)+4F(2)$	F^+ (3.69 eV) ejected	0.0	0.0916
11	$F^+(1)+2F(1)+F(2)$		0.0	0.0579
12	$F^+(2)+2F(1)$		~ 0.025	0.0747
13	$F^+(2)+3F(1)$	Na^+ rises, F^+ takes its place; fourth F^- approaches Na^+ and rises	0.0	0.0619
14	$F^+(2)+4F(1)$	Na^+ (5.07 eV), two F (0.076 eV) ejected	0.0	0.0867
15	$F^+(2)+F(1)+F(2)$		0.0	0.0427
16	$F^+(2)+F(1)+2F(2)$	F(1) (0.48 eV) desorbs	0.0	0.0620
17	$F(1)+3F(2)$		~ 0.025	0.0615
18	$F(1)+3F(2)U$	F(1) (1.03 eV) desorbs	~ 0.025	0.0665
19	$F(2)+4F(1)$		0.0	0.0488
20	$F(1)+4F(2)+F(3)$	two nonadjacent F atoms added to case 17	~ 0.025	0.1003

[a] The final state of the changed F^- ions is given. The numbers 1 and 2 in parentheses designate a location in the first plane (surface) or second plane, respectively. A 2′ denotes adjacent F sites in the second plane; otherwise the sites are nonadjacent. All changed ions are neighbors of the Na ion where the Auger cascade started. A surface F^+ ion always starts with nominal (x,y,z) coordinates (0.0,2.31,0.0). A subsurface F^+ ion always starts with nominal coordinates (0.0,0.0,−2.31). In this case an attempt is being made to eject the surface Na ion with nominal coordinates (0.0,0.0,0.0). The positive z axis is the normal to the crystallite (100) 10×10 surface. The range of nominal x and y values is −9.24 to 11.55. The unit of length is angstroms. A trailing U on the description indicates that the calculation was carried out with unbound F atoms.

[b] Particles are not ejected unless noted. Ejected particle kinetic energies are given. Bonding F-atom potentials are used unless noted.

[c] In the simulations at 0 K, the initial kinetic energy is zero.

[d] The word "rise" signifies that the average positions of the ions lie above the crystallite surface.

that if the charge on a F^- ion is suddenly set equal to zero, leaving only its short-range repulsive interaction with the rest of the ions in the crystallite, the newly created F atom will leave the crystal if it is on the surface. If it starts below the surface it will usually be kept in its original relative position by the ions around it. Preliminary studies of clusters of four F atoms showed that the surface F atoms desorbed, but that no positive ions desorbed. At this point the bonding F-atom potentials described in Sec. III were developed. With the bonding F-atom potentials, a suddenly created F atom on the surface remains at the site where it is created. Most of our subsequent calculations were performed with the bonding F-atom potentials because these are more realistic. Table III exhibits two comparisons of calculations done with bonding and nonbonding F atoms. In cases 5 and 6 the Auger cascade occurred in a Na^+ ion in the plane just below the (100) surface, producing a F^+ ion in the first plane and two F atoms in the second plane, on opposite sides of the Na ion. Even though they start in the second plane, the nonbonding F atoms desorb. There are substantial and different ion rearrangements in the two cases, but no ion desorption occurs. In cases 17 and 18 of Table III, the Auger cascade occurred in the same Na ion as above, but this time four F atoms were produced, one of which was in the surface plane. Case 18 shows that with nonbonding F atoms, only the surface atom desorbed. No ions desorbed in either case. We conclude that the strength of the F-atom binding is not a factor in determining whether positive ions are ejected as a result of the Auger cascade.

Let us now consider a sequence of 0-K simulations which involve a F^+ ion in the first plane and an increasing number of F atoms in the second plane. The Auger cascade occurred in the second plane just below the ion which becomes the F^+ ion. In these simulations the initial kinetic energy of the ions is zero, but the crystallite has increasing amounts of potential energy which ultimately gets shared by the crystal ions. This is reflected in the average ion kinetic energies in the last column of Table III. For comparison a room-temperature simulation on the unchanged crystallite is recorded as case 1. Case 2 is one of the cases treated by Walkup and Avouris.[8] [A single F^+ ion is also created by the intra-atomic $F(KLL)$ channel, which is also open and has a photoabsorption cross section comparable to that for the Na K shell.] No ions are ejected. However, the F^+ ion rises about 3 Å above the surface and two adjacent F^- ions rise about half this distance. The F^+-ion trajectory is shown as a function of time in Fig. 1, which exhibits the oscillations which are occurring about the ion's average position. One of the F^--ion trajectories is shown in Fig. 2. The system has a vertical plane of symmetry passing through a diagonal in the 10×10 face. Thus there is a second F^- ion executing a mirror image motion to the one shown in Fig. 2. The KE of the F^+ ion at 2 ps is 0.048 eV. Cases 4 and 7 describe Auger processes which produced a F^+ ion and two F atoms. In the first case the F^+ ion goes to an ad-ion site, in the second case it replaces the Na^+ ion next to it, while the Na^+ ion moves to an ad-ion site. In both cases F^- ions rise about 0.5 Å above the surface around the displaced positive ions. In cases 8 and 10 the F^+ ion is accompanied by three and four F atoms, respectively. This could only occur if the Auger cascade started with the $Na(KL_1L_{2,3})$ or $Na(KL_1L_1)$ processes, which produce one or two extra valence holes, compared to the main $Na(KL_{2,3}L_{2,3})$ transition. With four F^- ions replaced by F atoms, the F^+ ion is ejected. The F^+-ion trajectories are shown in Figs. 3 and 4. In the three-hole case the F^+ ion is accom-

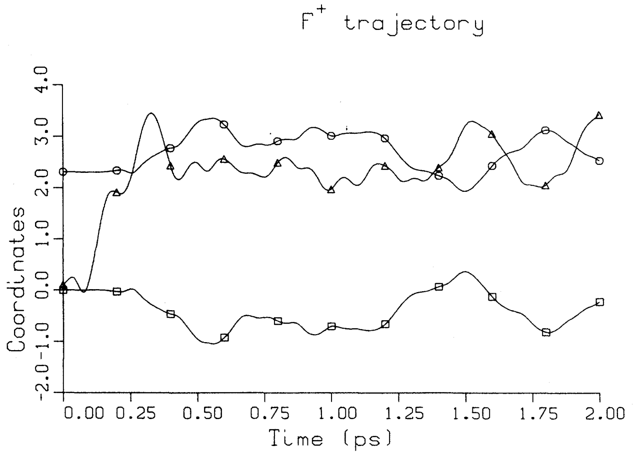

FIG. 1. F^+-ion x,y,z coordinates in angstroms vs time following the sudden change of a F^- ion to a F^+ ion on the 0-K (100) surface of NaF. This trajectory corresponds to case 2 of Table III. The x,y,z coordinates are indicated by squares, circles, and triangles, respectively. The z axis is normal to the surface, which is the 10×10 face of a $10\times10\times4$ crystallite. See footnote a of Table III for the location of the coordinate origin on the 10×10 face. The small-amplitude high-frequency oscillations reflect collisions of the F^+ ion with adjacent ions.

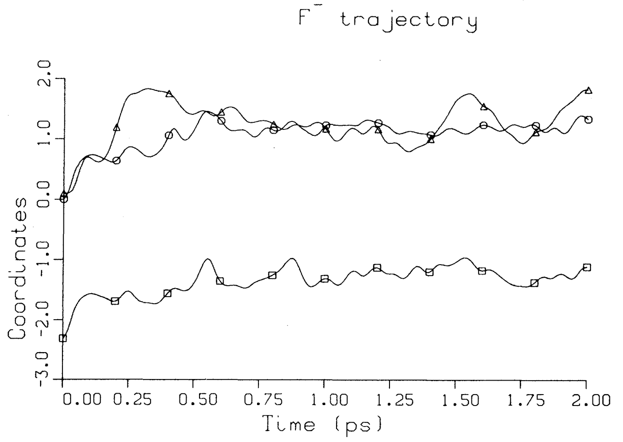

FIG. 2. Neighboring F^--ion x,y,z coordinates in angstroms vs time following the sudden change of a F^- ion to a F^+ ion on the 0-K (100) surface of NaF. This trajectory corresponds to case 2 of Table III, and the F^+ trajectory is shown in Fig. 1. The coordinate definitions are the same as those used in Fig. 1. The correlation between the z coordinate motions in Figs. 1 and 2 should be noted. As explained in the text, there is a second neighboring F^- ion executing a mirror image motion to the one shown in Fig. 2.

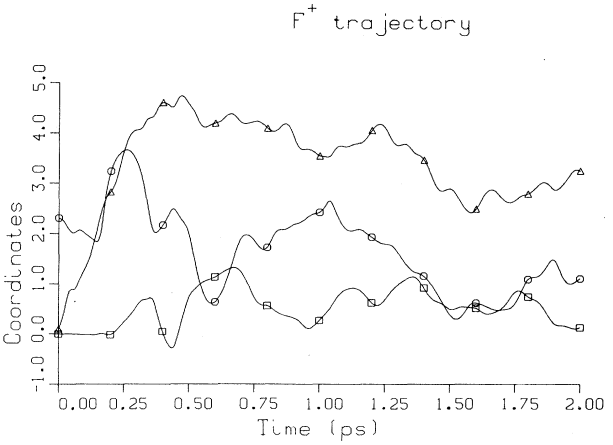

FIG. 3. F^+-ion x,y,z coordinates in angstroms as functions of time following the sudden creation of the F^+ ion and three F atoms at the 0-K (100) surface of NaF. This trajectory corresponds to case 8 in Table III. See Fig. 1 for the coordinate definitions, and see the discussion in the text.

panied by a F^- ion which also rises above the surface. Case 11 concerns an Auger cascade in a surface Na^+ ion rather than one in the second plane.

This series of simulations illustrates the strong correlations in the motions of the positive and negative ions which arise out of the strength and long range of the Coulomb interaction. When a F atom replaces a negative ion, a strong long-range interaction is replaced by a weak short-range one. The surface F^+ ion has eight nearest F^- neighbors to keep it from being ejected. They are so effective that only when half of them are replaced with F atoms does ejection occur.

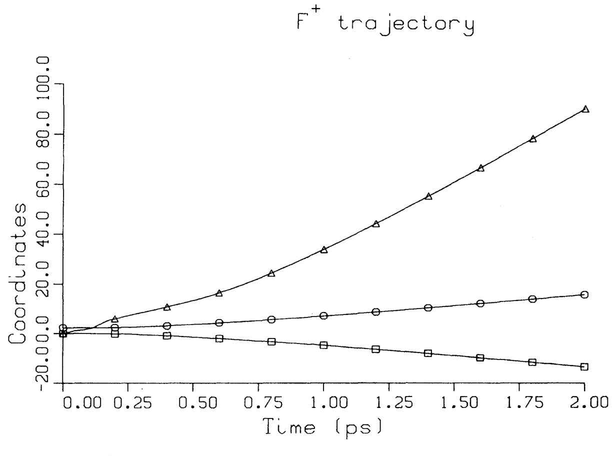

FIG. 4. F^+-ion x,y,z coordinates in angstroms as functions of time following the sudden creation of the F^+ ion and four F atoms at the 0-K (100) surface of NaF. This trajectory corresponds to case 10 in Table III. See Fig. 1 for the coordinate definitions, and see the discussion in the text. The replacement of four strongly binding F^- neighbors of the F^+ ion by weakly binding F atoms prevents the F^+ ion from being captured by the crystallite at times of about 0.25 ps, as is the case in Figs. 1 and 3.

We now consider the simulations which concern an Auger cascade in a surface Na^+ ion, which produces an F^+ below it and surface F atoms. We show the 0-K simulations for three and four holes as cases 13 and 14. As in the case of a surface F^+ ion, no ejection of positive ions occurs until four F^- ions are replaced by F atoms. In this case two F atoms desorb along with the Na^+ ion. The results for F^+- and Na^+-ion ejection are very similar. Cases 15 and 16 concern simulations for the ejection of a surface Na^+ ion due to an Auger cascade which starts in a Na^+ ion in the second plane and produces a F^+ ion below the surface Na^+ ion. There is no ion desorption. The Auger cascade cannot produce another hole adjacent to the surface Na^+ ion which is above the F^+ ion.

Case 19 records the simulation which is the analogue of case 14, with the F^+ ion replaced by a F atom. A surface Na ion started the Auger cascade with the $Na(KL_1L_{2,3})$ transition. It was not ejected. In case 20 the extension of the case-17 simulation to the maximum of six F atoms is reported. The last two cannot be adjacent to the surface Na^+ ion which is next to the surface F atom and above one of the F atoms in the second plane. The added, more distant, F atoms do not cause the Na^+ ion to be ejected.

In Ref. 3 it was stated the most favorable site for the ejection of a F^+ ion from a nominally (100) surface should be a regular surface site in the perfect surface. This follows from the fact that such sites have a larger Madelung energy than the minority surface sites one might imagine to occur. This argument does not incorporate the geometrical and dynamical factors which should be taken into account. We are not aware of specific information on the surface morphology of the vacuum cleaved surfaces used in ion desorption studies. With such information in hand molecular-dynamics studies of the relevant minority sites could be undertaken. Lacking such information we decided to study sudden F^- to F^+ changes on four types of site.

The first was a site in the middle of the edge of a monolayer step created by covering half of the 10×10 (100) surface. A F^- ion on this edge lacks one adjacent Na^+ ion and two F^- ions compared to the (100) surface. When this F^- ion was changed to a F^+ ion in the presence of two or three surface F atoms, the F^+ ion was not ejected. The creation of four surface F atoms with the F^+ ion suffices to cause the F^+ ion to be ejected. This result is analogous to that in case 10.

To obtain the second site, six ions were added to the above step edge, to form a partial row. The regular row has ten atoms. When the changed F^- ion is at the sixth position in the full row of the step edge and the added row ends in a Na^+ ion, the suddenly formed F^+ ion "sees" its normal four surface Na^+ ions, but only three of its normal four F^- ions at the adjacent surface positions. The inclusion of three surface F atoms in the simulation does not suffice to result in the ejection of a suddenly created F^+ ion. These are minority sites which arguably might be found on the cleaved crystal. However they do not provide an improved opportunity for F^+-ion ejection over the perfect (100) surface.

The third site was a F^- ad-ion site above a Na^+ ion lying in the perfect (100) surface. Ejection of a F^+ ion does not occur from these sites, and the creation of one surface F atom along with the F^+ ion does not lead to ejection either. However, if two neutral F atoms are produced in the surface plane along with the F^+, the F^+ ion is ejected.

The last site we considered was the corner of a $6\times6\times6$ cube. At 0 K the system has a threefold symmetry axis, and the newly created corner F^+ ion "sees" three Na^+ ions closest to it. It is not ejected. The replacement of two of the three F^- ions by F atoms in the plane below that containing the three Na^+ ions causes the corner F^+ ion to be ejected. The replacement of a single F^- ion does not suffice.

The above results for possible sites on an imperfect (100) surface are completely analogous to those obtained for the perfect (100) surface. Unless half or more of the neighboring F^- ions adjacent to the positive ion we are trying to eject are replaced with F atoms, no positive-ion ejection occurs. In considering the yield of positive ions from such a site, the probability of its occurrence must be taken into account along with the Auger branching ratio and the hole self-trapping probabilities.

We now discuss the possible influence of temperature on our results, assuming that the experiments are carried out in the vicinity of room temperature. This question was addressed in Ref. 8, where it was concluded that the crystal temperature, near room temperature, was not a factor in whether positive ions desorbed or not. The authors reached this conclusion by doing simulations at different temperatures, and they pointed out the essential fact the kinetic and potential energies available to the crystal ions near room temperature, a few hundreths of an electron volt, are very small compared to the potential energy change, about 11 eV, which occurs as the result of the creation of a F^+ ion from a F^- ion. Using the relation $\exp(-E/k_BT)=10^{-4}$ to get an energy E associated with a fluctuation with a 10^{-4} probability at room temperature, we find E to be a few tenths of an electron volt. Here k_B is Boltzmann's constant. This is still very small compared to 11 eV. It is also very small compared to the binding energy, ~4.5 eV, of a F^--F^+ ion pair at the normal anion-anion distance in the crystal. This convinces us of the correctness of the conclusion reached in Ref. 8. The inclusion of suddenly created F atoms in the simulations involving F^+ ions has shown that very large changes in the Madelung energy do not suffice in and of themselves to cause positive ion desorption in NaF. Thermal fluctuations equivalent to these changes must be very rare indeed. In an attempt to consider the effect of initial ion kinetic energies on the Knotek-Feibelman mechanism, we carried out the simulation described in case 3 of Table III. A lot of ion rearrangement, but no ion ejection occurs. Several simulations were carried out in order to insure that initially, the F^+ ion's velocity had substantial components either parallel to or antiparallel to the surface normal. The crystallite has enough energy to be above its melting temperature, and ultimately evaporation will occur. The Knotek-Feibelman mechanism was not conceived as a thermally activated process,[2] and the conclusions reached first in Ref. 8 and in the present paper support this point of view.

In order to predict the yield of positive ions ejected from the (100) surface by the Knotek-Feibelman mechanism per absorbed photon via Na K-shell Auger cascades, it is necessary to know the probability for the immediate self-trapping of the four holes produced along with a F^+ ion by the $Na(KL_1L_1)$ transition. Also, one can envisage minority sites such as the multilayer corner or the ad-ion site. In this case the probability of occurrence of an Auger cascade in these sites along with the probability for the immediate self-trapping of a pair of valence holes is required. The values of these quantities are not likely to become available soon. However, the circumstances which allow positive ion ejection in NaF have been shown here to be very special. Therefore it is quite plausible that the yield of desorbed F^+ ions by the mechanisms discussed here is too small to account for the yield of 10^{-4} ions per absorbed photon which was found experimentally.

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