

## Auger-induced valence processes in alkali halides following alkali core-hole creation

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*Ab initio* calculated values are presented for the interatomic Auger and radiative decay rates for initial  $(2p)^2$  and  $2p$  hole states of the Na ion in NaF. A comparison of the rates shows that these hole states decay overwhelmingly by the nonradiative Auger process. The knowledge of the rates makes possible a clarification of the mechanism of photon-stimulated positive-ion desorption presented by Parks *et al.* [Phys. Rev. B **28**, 4793 (1983)]. Following the creation of a Na(1s) hole in NaF, the ensuing Auger cascade results in the creation of four to six valence holes, or one  $F^+$  ion and two to four valence holes, on the neighboring negative fluorine ions within an elapsed time of a few times  $10^{-14}$  s. The majority of the valence holes are produced as hot holes, and are likely to diffuse several tens to hundreds of angstroms in times of the order of picoseconds before self-trapping to form  $V_K$  centers. The fast diffusion of these holes greatly reduces their chance of participating in ion desorption processes. The possibility that a fraction of the holes self-trap immediately and assist in the desorption of positive ions is considered. It is found that positive-ion desorption can occur if enough holes self-trap immediately. However, the required configurations are so special that they may occur with too small a probability to account for the observed positive-ion current. The fast hole diffusion also makes it unlikely that the  $V_K$  centers from the cascade will exhibit the clustering effects which would have been expected had the holes self-trapped in place. An increase in the yield of electron-hole pairs of about 6% is predicted to occur at the Na K edge.

### I. INTRODUCTION

The availability of tunable synchrotron radiation sources in recent years has made it possible to study the consequences of inner-shell ionization in the alkali halides and other systems in an amount of detail not allowed by the use of electron beams or nontunable x-ray sources. In particular, it has been possible to measure the photo-induced yields of defects or of desorbed electrons, ions and neutral particles above and below inner shell excitation or ionization thresholds, and to look for changes, or "edge effects," in these yields as a threshold is crossed.<sup>1,2</sup>

In a light element an inner-shell hole decays primarily by intra-atomic Auger processes within the atom containing the hole. An Auger cascade results in which one new electron and two new holes are produced for each hole filled.<sup>3</sup> The requirement of energy conservation stops the cascade. In alkali halide crystals the last holes are made in the valence band. A newly created pair of valence holes can either be localized on separate halogen ions, producing neutral atoms, or both be localized on the same ion, producing a positive halogen ion. We will refer to a hole associated with a neutral halogen simply as a hole; the positive ions will be referred to in the usual way, for example, as  $F^+$ . Since the valence electrons are localized primarily on the halogen anions, inner-shell holes in the halogen ions decay by intra-atomic processes. An example is the  $F(KLL)$  Auger transition in the K hole containing fluorine ion to produce an  $F^+$ . In contrast, how-

ever, the highest inner-shell states of the alkali ions must decay primarily by interatomic processes as in the Knotek-Feibelman mechanism.<sup>4</sup> While the intra-atomic rates are generally well known, little quantitative information is available on interatomic Auger or radiative rates. As a result it has not been possible to discuss the final step in an alkali-ion Auger cascade with confidence.<sup>1</sup>

We have recently carried out *ab initio* interatomic Auger and radiative rate calculations which make possible a more complete discussion of Auger cascades originating on the alkali ions of alkali halides. The calculations are based on the Hartree-Fock molecular orbitals for a  $(NaF_6)^{5-}$  cluster embedded in the external potential of a large cubic array of point ions.<sup>5-7</sup> References 5-7 were concerned with the electrons and photons resulting from interatomic processes which fill single inner-shell vacancies in the Na ion in NaF and provided a test of the quantitative theory. The present paper is concerned with the consequences of the sodium K-shell Auger cascade in NaF, whose first steps following the creation of a Na K-shell vacancy are the  $Na(KLL)$  Auger transitions.<sup>1</sup> In order to discuss the filling of the double inner-shell vacancies by valence-band electrons, new interatomic Auger and radiative rate calculations were performed for the  $2p^2$  two-hole state of the Na ion. The calculations show that the main Na K-shell Auger cascade produces a  $F^+$  ion and two valence holes, or four valence holes, on the neighboring  $F^-$  ions in a few times  $10^{-14}$  s. The radiative decays are about a million times slower. The radiative decays would terminate the K-shell cascade with ei-

ther one  $F^+$  ion or two valence holes, as was assumed in Ref. 1.

The local generation of four valence holes on this short a time scale is of interest in three contexts. First, the holes might play a role in the desorption of positive ions. Second, the localized production of the holes could lead to clustering effects in the production of  $V_K$  centers, self-trapped excitons,  $F$  centers, and  $H$  centers. Finally, the Auger cascade may lead to an increase in the yield of valence holes, and the subsequently formed defects, as the photon energy is increased through the Na  $K$  edge. These three consequences of the Auger cascade are explored in Secs. III C and III D. The Na Auger cascade edge effect in the yield of valence-band holes is also compared with results for  $F$  center yields from anion Auger cascades.<sup>2</sup> Since the results obtained in Secs. III C and III D are greatly influenced by the diffusion of the valence holes before self-trapping, this diffusion is discussed in Sec. III B. The Auger cascade is discussed in Sec. III A.

The Auger calculations reported here were initiated primarily because of the experimental results on positive-ion desorption reported in Ref. 1. This aspect of our work requires some additional background discussion, which is presented in Sec. II.

## II. BACKGROUND DISCUSSION OF Na $K$ -SHELL PHOTON-STIMULATED POSITIVE-ION DESORPTION

The experimental results reported in Ref. 1 stimulated our interest in alkali-ion Auger cascades. It was shown in Ref. 1 that the creation of a Na  $K$ -shell hole in NaF leads to the stimulated desorption of  $Na^+$  and  $F^+$  ions. In interpreting their data the authors pointed out that the first step in the process must be Na( $KLL$ ) Auger transitions which produce  $Na^{3+}$  ions near the crystal surface. Very fast (picosecond time scale) interatomic one-electron charge transfer processes were then assumed to restore the Na ion to its original charge state, while producing neutral and positive fluorine ions from the initially negative neighbors of the original hole-containing cation. Both radiative and Auger decays were invoked as mechanisms which would allow the transfer of charge while conserving energy. It was concluded that either a  $F^+$  ion, or two valence band holes, would be produced by the cascade. We felt it would be desirable to replace this rough qualitative discussion with the quantitative results of direct calculations. The results already described in the introduction were obtained.

The authors of Ref. 1 emphasized that for desorption to occur the holes created by the Auger cascade, particularly those on the  $F^+$  ion, had to remain localized in place for a sufficiently long time. They also argued that  $F^+$  ions should be ejected most readily from the perfect (100) surface and that  $Na^+$  could be best pushed off the surface by a subsurface  $F^+$  ion if the  $Na^+$  ion were in a minority site of low Madelung energy.

After Ref. 1 was published, Walkup and Avouris published molecular-dynamics calculations of  $F^+$  and  $Na^+$  desorption from NaF.<sup>8</sup> They found that a suddenly created  $F^+$  is not ejected from the perfect (100) surface,

but that a  $Na^+$  in an ad-ion site above the perfect surface could be ejected by a suddenly created  $F^+$  just below it. They also concluded that, for room-temperature experiments, the crystal temperature was not a factor in determining whether positive-ion ejection occurred.

More recently, Walkup and Avouris have shown that electron-stimulated desorption (ESD) of positive ions from NaCl can be accounted for in terms of electron-impact ionization of the desorbed neutrals by primary and secondary electrons.<sup>9</sup> The neutrals are known to arise from the production of  $F$  and  $H$  centers in the bulk of the crystal.<sup>10-12</sup> For the ESD experiment on NaCl (Ref. 9) no appeal was made to the direct desorption of ions from the surface via the Knotek-Feibelman mechanism.<sup>4</sup> In considering the photon-stimulated desorption (PSD) experiment of Ref. 1, the authors of Ref. 9 stated that the electron ionization mechanism appeared to account for the order of magnitude of the desorbed-ion signal. However they did not exclude the direct desorption of positive ions from certain defect sites.

The flux of positive ions resulting from the absorption of photons at the Na  $K$  edge is extremely small.<sup>1</sup> Therefore it is difficult to rule out low-probability scenarios or conclusively demonstrate the validity of the secondary electron-impact ionization mechanism of Ref. 9. One goal of the present paper is to reconsider the positive-ion desorption mechanisms, taking into account the additional holes produced in the Auger cascade. This is done in Sec. III C.

## III. DISCUSSION OF THE SODIUM ION $K$ -SHELL AUGER CASCADE

The discussion will be divided into subsections, following the temporal sequence of events related to the Auger cascade.

### A. Interatomic processes in the Na $K$ -shell Auger cascade

Table I exhibits the radiative and Auger rates needed for our discussion. In Table I and throughout the text the notation Na( $2s$ ) etc., designates the excited electronic state in which a Na( $2s$ ) electron is missing from the ground-state configuration of the cluster. The first four lines describe radiative transitions, the rest describe Auger transitions. The rates for the initial Na( $2p^2$ ) two-hole state are reported here for the first time. These were obtained using the  $\Delta$ SCF (change of self-consistent field) theory of Ref. 7 for the radiative rate, and the Auger theory based on initial-state orbitals of Ref. 6. Since the Hartree-Fock theory may not yield sufficiently accurate transition energies, experimentally determined Auger and radiative transition energies were used for the outgoing electron and photon energies. Also, the theory was used only for the prediction of the total initial-hole lifetime, which is insensitive to the effects of configuration interaction in the manifold of final states.<sup>13</sup>

Table I shows that the Na( $2s$ ) and Na( $2p$ ) holes decay by interatomic Auger processes whose rates are comparable to the Na( $KL_{2,3}L_{2,3}$ ) rate<sup>5</sup> of  $6.86 \times 10^{-3}$  a.u. ( $2.84 \times 10^{14} \text{ s}^{-1}$ ), which is also shown as line 5 of Table I. The sequence of events following the creation of a Na( $1s$ )

TABLE I. Auger and radiative transition rates for the NaF crystal summed over all MO's corresponding to the final-state hole. The interatomic rates for single-hole initial states are taken from Refs. 6 and 7. The interatomic rates for the  $2p^2$  initial hole states are presented here for the first time. The first four lines describe radiative transitions.

	Initial-state holes	Final-state holes	Energy (eV) <sup>a</sup>	Theory rate (a.u.) <sup>b</sup>
1	Na(2s)	Na(2p)	32.7	$5.10 \times 10^{-7}$
2	Na(2s)	F(2p)	55.0	$1.49 \times 10^{-8}$
3	Na(2p)	F(2p)	22.3	$4.08 \times 10^{-8}$
4	Na(2p <sup>2</sup> )	Na(2p) + F(2p)	41.4	$8.15 \times 10^{-8}$
5	Na(1s)	Na(2p <sup>2</sup> )	982.0	$6.86 \times 10^{-3c}$
6	Na(2s)	Na(2p) + F(2p)	16.0	$2.36 \times 10^{-2}$
7	Na(2p)	F(2p) + F(2p)	7.0	$5.57 \times 10^{-3}$
8	Na(2p <sup>2</sup> )	Na(2p) + F(2p) + F(2p)	22.4	$1.56 \times 10^{-3}$

<sup>a</sup>Calculated from Tables I and III of P. H. Citrin, J. E. Rowe, and S. B. Christman, Phys. Rev. B **14**, 2642 (1976).

<sup>b</sup>1 a.u. corresponds to a rate of  $4.134 \times 10^{16} \text{ s}^{-1}$ .

<sup>c</sup>This rate for the Na( $KL_{2,3}L_{2,3}$ ) transition is taken from D. L. Walters and C. P. Bhalla, At. Data **3**, 301 (1971).

hole in the NaF crystal can be described as follows. Auger decays to the Na( $2s^2$ ), Na( $2s,2p$ ), and Na( $2p^2$ ) hole states will occur about 6%, 23%, and 71% of the time, respectively, if we use the relative rates observed for a Ne(1s) hole.<sup>13</sup> The first two double-hole states cannot decay by intra-atomic Auger decay, since these transitions are forbidden by energy conservation. They can decay, however, by the Na(2s) hole interatomic Auger process shown in line 6 of Table I, but with an additional spectator 2s or 2p hole. These energy-conserving decays produce the Na( $2s,2p$ ) and Na( $2p^2$ ) hole states, respectively, along with a neighboring F(2p) hole and a low-energy electron. As indicated by the comparison of a Na(2p) and Na( $2p^2$ ) hole rates shown in lines 7 and 8 of Table I, the rates for these spectator processes should be of the same order of magnitude as that for the Na(2s) state. The end result is the population of the Na( $2p^2$ ) hole state, which decays according to line 8 of Table I with a rate of  $1.56 \times 10^{-3}$  a.u. ( $6.4 \times 10^{13} \text{ s}^{-1}$ ) and produces two F(2p) holes in neighboring fluorine ions. In this case there is sufficient energy available to produce a F<sup>+</sup> ion as an alternative to producing two neutral fluorine atoms. Both of these alternative decay modes have been observed to occur in MgF<sub>2</sub>.<sup>14</sup> The 22.4 eV Auger energy used for this transition was based on the assumption that the holes occurred on adjacent fluorine ions, and the holes were treated as independent particles.<sup>6</sup> In a more sophisticated configuration interaction calculation which we cannot carry out at present, the channel for producing a F<sup>+</sup> ion instead of two neutrals would be treated separately. We will assume that a fraction  $m^+$  of the rate given in line 8 corresponds to the production of F<sup>+</sup> ions. As a reasonable guess we take  $\frac{90}{630} \leq m^+ \leq 1$ . The lower limit corresponds to the relative number of two-hole space and spin states in which both holes occur on one of the six nearest F<sup>-</sup> neighbors; the upper limit allows for the possibility that, with a lower energy Auger electron, the F<sup>+</sup> channel might dominate. After the  $2p^2$

hole decay, the resulting Na(2p) hole state will then decay according to line 7 of Table I, producing two more neighboring F(2p) holes. Energy conservation forbids the production of a F<sup>+</sup> ion in this case.

It is seen that the decay of an initial Na(1s) hole leads to the production of four to six holes, or one F<sup>+</sup> ion and two to four holes, in the neighboring fluorine ions on a time scale of a few times  $10^{-14}$  s. For comparison, the longitudinal-optical-phonon frequency is  $1.3 \times 10^{13}$  Hz. The arguments given in Ref. 1 led its authors to conclude that the decay of a Na(1s) hole would produce two holes or one F<sup>+</sup> on a very fast time scale. Our analysis shows that the creation of a Na(1s) hole leads to a substantially greater perturbation of this atom's neighbors than was envisaged in Ref. 1. This strengthens their arguments for the desorption of positive ions, and makes it clear that the decay of a Na(1s) hole at or adjacent to the crystal surface will leave the surface in a highly imperfect state if the holes do not diffuse away as fast as they are produced.

## B. Hot holes and their diffusion

As shown in Refs. 1 and 8, the task of relating the production of holes and F<sup>+</sup> ions to the desorption of F<sup>+</sup> and Na<sup>+</sup> ions is not straightforward. Since the photon current in the experiments described in Ref. 1 was of the order of  $10^9$  photons per second, only those holes made in a single Auger event can be expected to participate in a related positive-ion desorption event. It is therefore essential to know how fast the Auger-produced holes will diffuse away. It is customary to argue that the lifetime of a F<sup>+</sup> ion is long compared to the time for positive-ion desorption,<sup>15</sup> and that assumption will also be made here. It is also frequently assumed in Auger calculations on solids that valence-band holes propagate nearly as band particles. On this basis the Auger-induced holes delocalize in times of the order of the time corresponding to the reciprocal of the valence-band width, and a ground-state

wave function is used as the final-state wave function rather than the two-hole wave function which would be used in an atom or molecule.<sup>16</sup> Both of these approaches are reasonable. However, more quantitative experimental and theoretical data on valence hole diffusion are available for the alkali halides. These data will now be applied to the hole propagation in NaF.

The most comprehensive discussion of hole propagation in the alkali halides is due to Elango and his collaborators.<sup>17,18</sup> They consider independently diffusing valence-band holes which are distributed according to the valence-band density of states. For NaCl the parameters characteristic of the maximum in the density of states are taken to describe a typical hot hole. A hole mass of twice the electron mass and a typical initial-hole kinetic energy of 1.5 eV are used. It is assumed that the hot holes lose energy via longitudinal-optical phonons of energy 0.033 eV during  $n \sim 48$  scatterings on a random walk during which the hot holes lose their energy. The mean free path between scatterings is designated as  $l_p$  so that the total path length on the walk is  $nl_p$ . After this walk they self trap to form  $V_K$  centers. The diffusion length  $L_{op}$  for the walk is given by  $L_{op} = l_p(n/3)^{1/2}$ . For low concentrations of  $\text{Ag}^+$  impurities, whose hole capture cross section is taken to be  $\sigma_{Ap}$ , the probability of hole capture during the random walk is taken to be  $nl_p \sigma_{Ap} N_A$ , where  $N_A$  is the number density of impurities. The relation between the photon energy dependence of the x-ray generated light sum and the photon energy dependence of the x-ray absorption coefficient is used to deduce the hot hole diffusion length for NaCl. This leads to the result that for NaCl at 80 K,  $l_p \sim 180 \text{ \AA}$ ,  $L_{op} \sim 720 \text{ \AA}$ , and for  $\text{Ag}^+$  impurities  $\sigma_{Ap} \sim 1.5 \times 10^{-15} \text{ cm}^2$ . Using the Ref. 17 hot-hole velocity  $V_p$  of  $3.7 \times 10^7 \text{ cm/s}$ , the self-trapping time is  $2.3 \times 10^{-12} \text{ s}$ . The diffusion length for self-trapping,  $L_{op}$ , is very large indeed.

There are also relevant data on valence hole diffusion before self-trapping for NaI and KI.<sup>19,20</sup> In these experiments the crystals were doped with  $\text{Tl}^+$  impurities, and it was shown that in either crystal, for a  $\text{Tl}^+$  concentration of 0.1 mol %, the probability of hole capture before self trapping was close to 0.1. On the basis of the theory of Elango *et al.*, this leads to the result that  $\sigma_{Ap} nl_p \sim 25a_l^3$ , where  $a_l$  is the lattice constant. The lattice constants for NaI and KI are 6.5 and 7.1  $\text{\AA}$ , respectively, and the number of longitudinal-optical phonons involved in the cooling of typical hot holes in either case is about 80.<sup>21</sup> Therefore  $\sigma_{Ap} l_p$  has a value close to  $1 \times 10^{-22} \text{ cm}^3$  for both KI and NaI. The corresponding value for NaCl from the previous paragraph is  $27 \times 10^{-22} \text{ cm}^3$ . At present there is no definitive way to account for the order of magnitude difference in these values for  $\sigma_{Ap} l_p$ . If  $\sigma_{Ap}$  for  $\text{Tl}^+$  is of the order of  $10^{-15} \text{ cm}^2$ ,  $l_p$  is of the order of 10  $\text{\AA}$ , and  $L_{op}$  is of the order of 50  $\text{\AA}$ . A smaller cross section would lead to a longer diffusion length.

There is another possible approach to obtaining the diffusion length in terms of the theory of Refs. 17 and 18. Williams, Bradford, and Faust<sup>22</sup> have shown that in NaCl the self-trapped exciton develops within less than 5 ps of electron-hole pair generation. On this basis the hot holes

have self-trapped in less than 5 ps while traveling a total path  $nl_p$  with velocity  $V_p$ . Since the hot-hole lifetime from Refs. 17 and 18 is less than this value, these two sets of measurements on NaCl are compatible. The self-trapping time from Ref. 22 is also compatible with the results of Refs. 19 and 20.

In the present case of NaF,  $a_l = 4.6 \text{ \AA}$  and  $n \sim 40$ . The many similarities in the properties of the alkali halides make it likely that significant hole diffusion occurs before self-trapping in NaF, and that the diffusion length is many lattice constants. A more definite conclusion cannot be reached until the validity of the theory of Refs. 17 and 18 has been tested further and more experimental data are available.

The holes produced by the interatomic  $\text{Na}(2p^2)$  and  $\text{Na}(2p)$  Auger processes are produced in pairs, and the cluster calculations of Ref. 6 do not determine how the holes are distributed in the valence band of the solid. In the experiment of Refs. 17 and 18 the  $\text{Na}(2s)$ ,  $\text{Na}(2p)$ , and  $\text{Cl}(2p)$  levels are the main levels ionized by the 60–220 eV x rays. Since these levels also decay via Auger processes, we can assume that the hole diffusion data of Refs. 17 and 18 relate to the Auger processes under consideration here.

The repulsion of the holes, which has been neglected so far in our discussion, is of the order of 2.5 eV.<sup>14</sup> This tends to decrease the time the holes spend on their sites of creation, and increases the extent to which the holes remain apart during their valence-band motion.

### C. The desorption of positive ions

The simplest approach to the Na *K*-edge Auger-induced positive-ion desorption is to argue, on the basis of Sec. III B, that all the holes disperse so quickly that, apart from effects due to the  $\text{Na}(KLL)$  Auger electron, a surface Na Auger event disturbs the surface only if it produces a  $\text{F}^+$  ion. We then return to the situation contemplated by the authors of Refs. 1 and 8. According to Ref. 1, the conditions for  $\text{F}^+$  desorption should be most favorable at sites on the perfect (100) surface. The size of the fluorine *K*-shell photoionization cross section near the Na *K* edge,  $\sim 1.5 \times 10^{-19} \text{ cm}^2$ , guarantees that about  $10^{-4}$  surface  $\text{F}^+$  ions are produced per photon, compared to the approximately  $10^{-8}$  ions observed to be desorbed per photon. The smallness of the positive-ion current is a strong confirmation of the molecular-dynamics simulations, since according to Ref. 8  $\text{F}^+$  ejection does not occur from (100) sites. The problem remains, however, of accounting for the small but nonzero current of positive ions which is observed.

Given that we are looking at a process with a yield of only about  $10^{-4}$ , it is possible that a small fraction of the time the Auger-induced holes remain localized where they are created. These holes would be in the process of self-trapping. The theory of Elango *et al.* describes the typical valence hole, but the holes which might self-trap immediately are those created at the top of the valence band. Calculations for the alkali halides<sup>23,24</sup> show a very flat valence dispersion curve, and presumably a non-negligible fraction of states, at the top of the valence

band. The small curvature of the dispersion curve allows holes in these levels to have large masses. Unfortunately, Refs. 23 and 24 do not present densities of states from their calculations. These would make a more quantitative discussion possible. Aluminum  $K\alpha$  x-ray photoemission studies of the valence band do not show any particular structure near its top. The electron energy distributions are roughly triangular in shape with a peak about 1.5–2 eV below the top of the band.<sup>21</sup> However, these spectra correspond to a resolution of about 0.6 eV, and cannot reveal the structure of the top of the band. It is conceivable then that in a fraction of the cases, holes are produced which satisfy the energetic and geometrical requirements for immediate self-trapping. Could this self-trapped minority of the holes lead to ion desorption? This question has been studied in Ref. 25, using the same type of molecular-dynamics approach used in Ref. 8, but with additional two-body potentials to represent the interactions between a neutral fluorine atom at and just outside of the alkali halide surface and the other particles in the simulation. The dielectric image potential induced by an ion leaving the crystallite is largely accounted for in the simulation, since all the ions in the crystallite are allowed to move. The contribution to the image potential arising from the polarizability of the ions is not included in the simulation. However, it is of secondary importance since the zero and infinite frequency dielectric constants of NaF are 5.3 and 1.75, respectively, relative to the vacuum.

As discussed in Sec. III A, an alkali Auger cascade in the second plane can produce a  $F^+$  ion above it and two to four neutral neighbors in the second plane. This is the most favorable scenario for the desorption of an  $F^+$  ion from the perfect (100) surface by the Knotek-Feibelman mechanism. Simulations involving a  $F^+$  ion and two to four localized holes were carried out in Ref. 25. The  $F^+$  ion was found to desorb only if four localized holes were created with the  $F^+$  ion as the result of an Auger cascade which started with the  $Na(KL_1L_1)$  Auger transition. It was also found that a subsurface  $F^+$  ion would eject a surface  $Na^+$  ion only when accompanied by four localized surface holes which were nearest neighbors of the  $Na^+$  ion. Since the branching ratio for the  $Na(KL_1L_1)$  transition which produces this many holes is about 0.06, a four-hole self-trapping probability of about  $1.7 \times 10^{-3}$  is required to produce an ion desorption probability of  $10^{-4}$  per Auger cascade. This corresponds to an independent-particle, single-hole self-trapping probability of about 0.2, a value which is much larger than would be inferred from the experimental data. Analogous results were found for special sites on top of a perfect surface, such as ad-ion sites at the edges and corners of partial monolayers. Only if about half of the nearest-neighbor negative ions were replaced with F atoms could a positive ion be ejected. For example, a suddenly created  $F^+$  ion in an ad-ion site above a surface  $Na^+$  is ejected only if two localized surface holes are created with it.

Currently, the probabilities for immediate hole self-trapping and for the occurrence of special sites on a vacuum-cleaved (100) surface are unknown. However, the very special circumstances required for positive-ion

ejection make it plausible that even a yield as small as  $10^{-4}$  ions per absorbed photon is too large to be explained by the Knotek-Feibelman mechanism. The mechanism of electron ionization of desorbing neutral atoms appears to predict a positive-ion current of the right order of magnitude.<sup>9</sup> Its consequences should be worked out in detail.

#### D. The contribution of alkali Auger cascades to electron-hole pair and defect production

In Sec. III B it was argued that the typical holes from an Auger cascade would have a diffusion length for self-trapping somewhere in the range of 50–700 Å, and that the mutual repulsion of the holes should tend to reduce the likelihood of self-trapping on neighboring sites. Thus it cannot be expected that the opening of the Na  $K$ -shell ionization channel for photoabsorption will lead to  $V_K$  centers and successor defect clustering effects of the kind which might have been anticipated had the Auger-produced holes self-trapped in place. It can be asked, however, if the production of four holes in a single Auger cascade might produce an edge effect in the yield of valence holes. An increase in the yield of valence holes should translate directly into an increase in the yields of  $V_K$  centers, self-trapped excitons,  $F$  centers, and  $H$  centers.

This question can be answered using the atomic photoabsorption cross sections near the Na  $K$  edge,<sup>26</sup> and the electron-hole pair formation efficiency for electrons.<sup>27</sup> Near the Na  $K$  edge the dominant photoabsorption occurs in the sodium and fluorine  $K$  shells; contributions from the higher  $L$  shells and the valence band are less than 10% of those from the  $K$  shells. These will be neglected to simplify the discussion. Then below the Na  $K$  edge only F absorbs and above it both Na and F absorb. From the atomic densities  $4.02 \times 10^{22} \text{ cm}^{-3}$  and the photoabsorption cross sections  $2.6 \times 10^{-19}$  and  $1.4 \times 10^{-19} \text{ cm}^2$ , just above the Na  $K$  edge for Na and F, respectively, the total absorption coefficients below and above the edge are  $5.63 \times 10^3$  and  $1.61 \times 10^4 \text{ cm}^{-1}$ , respectively. As the edge is crossed the absorption mean free path decreases from 1.8 to 0.62  $\mu\text{m}$ . The mean free path of the 400–1000 eV electrons from Auger and photoprocesses at the edge is about 15 Å and so they lose most of their energy in the crystal. Above the Na  $K$  edge 65% of the photons are absorbed by Na and 35% by F. In our approximation all the photons are absorbed by F below the edge.

Let us estimate how many electron-hole pairs are produced below and above the edge at 1077 eV. Below the edge the photoabsorption yields a 382-eV photoelectron, a 650-eV  $KL_{2,3}L_{2,3}$  Auger electron, and a  $F^+$  ion, if we consider only the most intense of the  $KLL$  lines. Above the edge we obtain these products from F photoionization 35% of the time. From Na photoionization we obtain, 65% of the time, a very low energy photoelectron, a 982-eV  $KL_{2,3}L_{2,3}$  Auger electron, four holes from the dominant interatomic Auger decays, a 21-eV electron, and a 7-eV electron. To estimate the number of electron-hole pairs produced by the high-energy elec-

trons, we use the empirical rule that it takes about 3 times the band-gap energy  $E_{\text{gap}}$  to make an electron-hole pair in slowing down electrons.<sup>27</sup> This amounts to about 31 eV. Therefore below the gap we expect about 33 electron-hole pairs per absorbed photon from the two high-energy electrons. Above the edge we expect this 35% of the time. From the Na decays we expect about 32 plus 4 or 36 pairs 65% of the time. On the average we expect about 35 electron-hole pairs above the edge. The anticipated edge effect is therefore about 6%. If the three  $E_{\text{gap}}$  rule of Alig and Bloom<sup>27</sup> were simply applied to the photon, and all the details of the Auger cascades were ignored, about 35 pairs would be expected both above and below the edge.

It is seen that the interatomic Auger processes are efficient producers of electron-hole pairs. However, with over a kilovolt of energy absorbed in the crystal per photon, the effect of interatomic Auger hole production on the production of  $V_K$  centers, self-trapped excitons,  $F$  centers, and  $H$  centers will be hard to observe. The energy deposition depth ( $\sim 3$  absorption mean free paths) decreases as the Na  $K$  edge is crossed. However, since the absorption mean free path in our case is still 6200 Å, it does not appear that proximity of the energy deposition to the surface should lead to an apparent increase in the yields for defect production.

The foregoing discussion is consistent with the results of Brown *et al.* for  $F$  centers generated in KCl and KBr by photons in the energy range 100–1200 eV.<sup>2</sup> However, in light of our discussion, we find the factor of 8 in the edge effect associated with  $F$ -center production which was observed for 13475-eV photons at the Br  $K$  edge in KBr to be surprising.<sup>28</sup> The absorption mean free path above the edge is about 33  $\mu\text{m}$  and the electron scattering mean free path at 10 keV is about 50 Å. The three  $E_{\text{gap}}$  rule of electron-hole pair production for KBr corresponds to about 23 eV per electron-hole pair and this leads to an estimate of about 600 electron-hole pairs per absorbed photon. These should swamp the estimated 6–7 extra electron-hole pairs associated with the Auger cascade following Br  $K$ -shell absorption.<sup>28</sup> Brown has presented similar but less detailed estimates in Ref. 29.

Although we have no explanation at present for the factor of 8 increase in  $F$ -center yield which was observed, one may be considerably more likely to find a factor of 8 change in stabilization of the defects than to find such an increase in primary yield. It has been shown that in KBr and KCl about 0.15  $F$  center per electron-hole pair (i.e., about 0.06  $F$  center per eV of ionizing radiation) is produced at low temperature ( $\sim 80$  K), but that most of these annihilate by the recombination of  $F$  centers with  $H$  centers within a few microseconds.<sup>22,30,31</sup> In KCl, for which somewhat more detailed data are available, the yield of stable  $F$  centers (surviving long enough for conventional spectrophotometer measurement) is  $1.5 \times 10^{-4}$   $F$  center per eV of ionizing radiation at 80 K,<sup>32</sup> a factor of 400 lower than the primary defect yield.<sup>22</sup> In Ref. 22 the ratio of  $F$ -center concentration at 10 s to that at 46 ps after  $e$ - $h$  pair generation in KCl at 80 K was measured to be 0.09. In KBr at 8 K, the fraction of initial  $F$ - $H$  pairs surviving for “a few minutes” is found<sup>30</sup> to be 0.02. The

stable defect yield can be expected to be somewhat lower than this at 80 K. Thus the  $F$  centers that would have been counted in Ref. 28 belong to a rather small minority of the primary (initially formed)  $F$ -center population. If something associated with crossing the Br<sup>-</sup>  $K$  edge can markedly alter the stabilization of  $F$ -center and  $H$ -center defect pairs, there is certainly room for a factor of 8 change in stable defect yield. One such mechanism might occur if a new defect production channel opening at the core threshold could eject the halogen interstitial ( $H$  center) to a larger distance than can valence electron-hole recombination, and so lead to a significantly larger survival rate of the  $F$  centers.

The authors of Ref. 28 had avoided concluding that the Varley mechanism<sup>33</sup> or other core-hole defect formation process was supported by their results because the overall yield of three  $F$  centers per x-ray photon, coupled with the factor of 8 step at threshold, seemed inconsistent with the maximum Varley-type yield of one  $F$  center per x-ray photon. However, since the departing Auger electrons resulting from a Br<sup>-</sup>  $K$ -shell hole can make several hundred additional electron-hole pairs, the total yield is not inconsistent, and we have seen how the factor of 8 might come from stabilization (but not from increased primary yield, even if the new channel were 100% efficient in making primary defects).

#### IV. SUMMARY

The interatomic processes involved in the Na  $K$ -shell Auger cascade in NaF have been discussed. Following  $K$ -shell photoabsorption and the Na( $KLL$ ) Auger transitions, either an  $F^+$  ion and two to four valence holes, or four to six valence holes, are produced on neighboring halogen sites by interatomic Auger decay. It is shown that most of the holes diffuse from 50 to 700 Å in times of the order of picoseconds before self-trapping to form  $V_K$  centers. Fast diffusion of all of the holes away from the site of the Auger cascade would leave only the  $F^+$  ion to cause positive-ion ejection by the Knotek-Feibelman mechanism. However this mechanism was found not to result in positive-ion ejection from the perfect (100) surface in NaF at room temperature.<sup>8</sup> Using results from Ref. 25, the possibility that a fraction of the holes self-trap immediately and assist in the desorption of positive ions is considered. It is found that positive-ion desorption can occur if sufficiently many holes self-trap immediately. However the required configurations are so special that they may occur with too small a probability to account for the observed positive-ion current. This makes further investigation of the electron-impact ionization mechanism of Ref. 9 of particular interest.

The diffusion of the Auger-produced holes and their mutual repulsion make it unlikely that the initial clustering of the holes produced by their creation in a single photoabsorption event will lead to clustering effects in the formation of  $V_K$  centers, self-trapped excitons,  $F$  centers, and  $H$  centers. A small ( $\sim 6\%$ ) increase in the yield of electron-hole pairs at the Na  $K$  edge is predicted.

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