Laser-induced reactions in crystals: Femtosecond pump-probe spectroscopy and *ab initio* calculations of self-trapped excitons and holes in KBr

Alexander L. Shluger

Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom

Katsumi Tanimura

Department of Physics, Nagoya University, Furo-cho, Chikusa, Nagoya 464-01, Japan

(Received 12 October 1999)

We used an embedded cluster Hartree-Fock method that self-consistently accounts for lattice polarization to calculate adiabatic potential energy surfaces of the ground and excited states of the self-trapped exciton and to model its decomposition into Frenkel defect pairs in KBr. The characteristic optical excitation and lumines-cence energies of the self-trapped exciton and basic Frenkel defects are calculated. We present the experimental results of femtosecond pump-probe spectroscopy, which demonstrate the time evolution of the optical absorption of the KBr crystal excited by an 8-eV pulse at 80 K. These results reveal that Frenkel-defect pairs are formed in KBr prior to the holes relaxing into their most stable V_K center state. Contrary to these results, the femtosecond spectroscopy of the V_K-center formation in NaBr demonstrates that this is an extremely fast (< 1 ps) process. Theoretical modeling is used to show that the fast process of the F center (electron trapped by a halogen vacancy) and H center (interstitial halogen atom) pair formation in KBr prior to the hole self-trapping can happen in the ground electronic state of the exciton. This process is driven by the interaction of the relaxing hole with electron. We conclude that the speed of the hole vibrational relaxation prior to recombination with an electron and formation of an exciton is an important factor that determines the speed and effectiveness of exciton decomposition into Frenkel defects in alkali halides.

I. INTRODUCTION

Self-trapped holes and excitons, and Frenkel defects are among the most well-documented products of relaxation of excited states in condensed matter.[1–3] However, the rapid self-trapping process is less well understood. In particular, the mechanisms and the temporal evolution of self-trapping and of the electron-hole interaction during exciton transformation into Frenkel defects are far richer and more diverse phenomena than were previously appreciated, as has been revealed by time-resolved spectroscopic studies of these processes.[3–8] In this paper we present the results of a combined experimental and theoretical study of these phenomena in KBr.

It is well known that photoinduced processes have a very diverse character even within the seemingly uniform family of alkali halide crystals.[1–3] Models of some of the fundamental species involved in these processes are shown schematically in Fig. 1. In very broad terms, dependent on excitation energy, one can excite excitons and/or electron-hole pairs. Holes self-trap in alkali halides, forming a polaron state localized on two halogen ions displaced from their lattice sites, the V_K center. The electrons and holes can recombine, producing singlet and triplet excitons. These excitons can localize on several perfect lattice sites and become immobile at low temperatures, which is called self-trapping. The localization of excitons is accompanied by significant lattice relaxation manifested in a Stokes shift of exciton luminescence, which is particularly large for triplet, so-called off-center excitons (see Fig. 1). In the process, or afterwards they can decompose into a pair of neutral Frenkel defects: an F center (an electron trapped by a halogen vacancy) and an H center

(an interstitial halogen atom in the form of X_2^- at a single halogen site, where X is a halogen). The H center is much more mobile than the F center, and the two defects can separate either in the process of creation or afterwards by diffusion. If the separation distance is larger than several lattice constants, these defects are stable at low temperature.[9] The
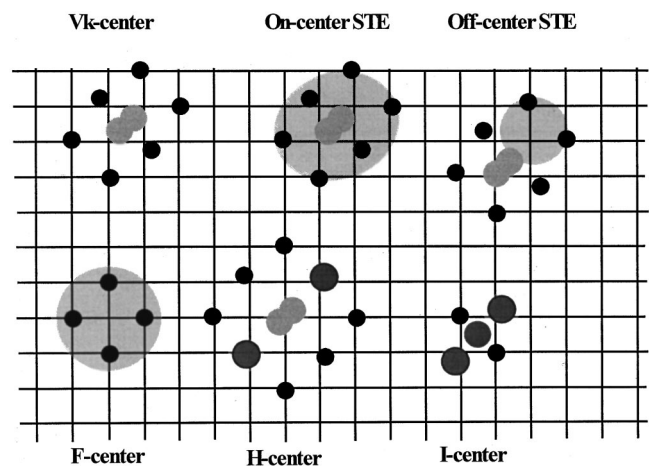

FIG. 1. Schematic of several basic self-trapped exciton and defect structures. Small black balls represent K ions. Gantell-like structures represent the Br_2^- ion, which is the stable form of hole localization in alkali halides. Displacements of ions from lattice sites qualitatively reflect projections of these displacements around particular defects on the (100) plane. Note that in the case of the I center the Br ion is situated in the body-center lattice position. The diffuse circle qualitatively indicates the mode of electron localization in the STE and F center.

PRB <u>61</u>   5392

electron tunneling from the F center to the H center leads to formation of another pair of basic defects: an α center (a positively charged anion vacancy) and an I center (an interstitial halogen ion). Recombination of these defects restores the perfect lattice. These basic stable defects are well characterized theoretically and using a variety of spectroscopic techniques.[1–3,10,11] Under different irradiation conditions there are many other processes involving these and other crystal species,[1–3] but they are not in the scope of this paper.

In spite of a long history of research, many new details of temporal evolution of these effects started to emerge only recently. In particular, it has been shown that in KBr and RbBr the generation of a Frenkel pair (see Fig. 1) consisting of an F center and an H center takes place through two different processes: the fast process, which terminates within a few picoseconds after the excitation, and the slow process, which continues after the fast process has terminated for over 100 ps at low temperatures.[4,5] Similar results have also been obtained in KCl and RbCl crystals.[7] The mechanism of the fast process, which plays a central role in formation of the F-H pairs at low temperatures,[5,7] remains unclear. The two-photon excitation with an energy of about 8 eV employed in these experiments produces electron-hole pairs in the bulk of the crystals. The electron is shown to be initially delocalized in the lattice[12] for several picoseconds before recombining with the hole. One of the characteristic features of the fast process is that it takes place before the relaxation of the holes into their most stable configuration, the V_K center, is completed.[4,5] Therefore it has been suggested that the fast process of the F-H pair formation is due to the interaction of the electrons with relaxing holes.[4,5] However, the nature of the relaxing holes and excitons and the mechanism of the fast process of the F-H pair formation has not yet been clarified. These issues, which are in the focus of our current experimental and theoretical studies, are discussed in this paper.

The understanding of dynamical properties requires dynamical means of analysis. Although modeling of the whole process of the exciton self-trapping and decomposition in real time is possible, it requires a lot of effort. For example, a somewhat similar process of electron solvation has been modeled in finite molecular clusters in the one-electron approximation (see, for example, Refs. 13–16). However, with complex many-electron systems such as self-trapped excitons (STE's), we are still even further from full understanding of their static properties. The current qualitative atomistic model of STE's in alkali halides has been proposed by Leung, Brunet, and Song[17] and further developed using the effective potential one-electron calculations, as reviewed in Ref. 3. It has then been elaborated using *ab initio* Hartree-Fock methods in the series of papers.[18–22] The results of these calculations have been reviewed in Ref. 23. More recently, the effect of electron correlation in the STE calculations has been explored in NaCl.[24] Together with the previous calculations,[22] these results present a comprehensive set for the NaCl crystal. However, there has been no detailed *ab initio* study of the STE and defect pairs in KBr, which shows quite different properties. Such a comprehensive picture is needed in order to compare different crystals, to assess the main factors that determine the accuracy of the model, and to develop dynamic simulations of exciton self-trapping and de-

composition. It can also give some clues for further understanding of the temporal evolution of this process.

From a more general perspective, one can view the process of transformation of electronic excitation in insulators into localized excitons and transient and stable defect pairs as an example of a fundamental photoinduced reaction in a solid that reflects its electronic and vibrational properties. There is, however, a significant difference between this process and the photoinduced transformations of, for example, the NaI molecule in solution[25] or the I_2^- molecule in solutions[26–28] and in small clusters,[29,30] which are now extensively discussed in the literature. In particular, excitons and defect pairs can be viewed as ''molecules'' embedded in some media only to a very limited extent. Due to the equivalence of crystal sites, the very nature of their localization from delocalized states and the mechanisms of their diffusion are the collective property of crystal atoms.

In this paper we report the results of a comprehensive theoretical analysis of the electronic structure and properties of the triplet self-trapped exciton and nearest-neighbor defect pairs in KBr. We check the robustness of our results by calculating the properties of individual Frenkel defects: the F and H centers and the α (anion vacancy) and I (interstitial Br ion) centers. We also present the time-resolved optical absorption spectra of NaBr and KBr irradiated by femtosecond laser pulses that reflect the hole relaxation and transformation of electron-hole pairs into Frenkel defects, and suggest their qualitative interpretation on the basis of our theoretical model.

The paper is organized as follows. In the next section we describe the calculation technique. Then in Sec. III the results of calculations of the STE and the Frenkel defects are presented and discussed. In Sec. IV we present the time-resolved spectra of the KBr crystal after femtosecond laser excitation and suggest their qualitative interpretation. The results of this work are discussed in Sec. V.

II. METHOD OF CALCULATIONS

To model the STE and the Frenkel defects, we have made many-electron embedded-cluster calculations using the ICE-CAP computer code,[31] which employs the *ab initio* Hartree-Fock method. It has been used in some of our previous STE calculations[21,22] and is thoroughly described in Refs. 21–23, 32, and 33.

In this code, the lattice polarization is treated self-consistently with the charge-density flow in the course of the exciton and defect transformations. This is achieved by splitting the crystal with a defect roughly into three regions. Region I consists of a quantum cluster (QC) treated quantum mechanically and/or of classical ions represented in the shell model,[34] i.e., by point cores and massless shells connected by a spring. The core and shell charges and the spring constant of each ion are parameters of the model. The sum of the core and shell charges is equal to the charge of the ion in the perfect lattice. Shells of different ions are interacting via interatomic potentials. By the dipole approximation, the polarization of the ions outside the quantum cluster by the defect is represented by the displacement of their shells relative to the cores. The lattice distortion outside the quantum cluster is simulated by the core's displacement from their lattice site

positions. In region I, these displacements are calculated explicitly. Region I is surrounded by another finite region II in which ions are also treated in the classical shell model, but their polarization is calculated in a linear approximation with respect to the electric field produced by a defect at each lattice site. The finite regions I and II are embedded in the infinite region III. Polarization of that region is treated in the dielectric continuum approximation. Ions in the region III and cores and shells in the region II produce a crystalline potential in region I.

If the defect is treated classically, region I consists only of classical ions and this Mott-Littleton model[35] is calculated using the HADES code,[36] which is a part of the ICECAP package. The parameters of interatomic potentials, cores, and shells are optimized in order to reproduce the elastic and dielectric crystal properties and the energies of formation of some basic crystal defects.[37] For the quantum-mechanical defect presentation, part of the ions in region I are substituted by quantum-mechanical ions, i.e., by QC. The electronic structure of the QC embedded in the potential of the surrounding classical lattice and the lattice polarization by the defect are treated sequentially as different steps of the computational procedure. Basically, each new charge distribution in the QC produces a new response by the polarizable lattice. To achieve consistency between these two factors, the quantum-mechanical charge distribution is mapped on the classical distribution, which is then used in the HADES code to calculate the lattice polarization. In order to achieve that, the dipole, quadrupole, and octopole moments of the new charge density in the QC is calculated after each successive Hartree-Fock (HF) calculation of the electronic structure. They are compared with the moments produced by the charges of the shell-model ions located in the same positions as the cluster ions. The difference in the multipole moments is then compensated by generating additional charges situated in the core locations of the cluster ions. This procedure is repeated until the relative change of calculated multipole moments is typically less than about 10^{-5}.

The quantum-mechanical calculations for open-shell systems were performed using the unrestricted Hartree-Fock (UHF) method. Electrons are treated in the valence approximation using the semilocal norm-conserving pseudopotentials of Bachelet, Hamann, and Schluter[38] (BHS). The interaction of Br electrons with the core of K ion represented by the BHS pseudopotential is overestimated leading to unrealistically short equilibrium separation, e.g., in a free KBr molecule. To correct this effect, a repulsive exponential pair potential has been introduced, as in Refs. 21 and 22.

According to our previous experience,[21,22] the split $511sp$ valence basis set on anions provides a reasonable compromise between our computer facilities and the accuracy of calculations. The basis set for the Br ion has been obtained by independent variation of the exponents of the split set of $7sp$ Gaussians in the crystalline field, which then has been contracted into the $511sp$ form. In our previous calculations we have also checked that the addition of d orbitals does not affect the results for STE and point defects in similar crystals. For K ions we employed the $(3s)$ Huzinaga-type basis set and also that augmented by one split p orbital (with the exponent equal to 0.039) from our previous calculations in KCl.[21,22] The Huzinaga basis has been additionally optimized for the BHS pseudopotential by minimizing the total energy of an isolated K atom.

As has been demonstrated in Refs. 21–24, this basis set is not enough to treat the electron component of the STE even in the most localized state. The electron localization changes strongly during formation of the STE and its decomposition into Frenkel defects. The flexibility of the basis set to accommodate these changes is achieved by using a set of floating Gaussian orbitals (FGO's) centered in different positions within the QC. This approach proved to be very robust and has been thoroughly discussed in Refs. 22 and 23. To model the STE localization, in this work we used a set of up to five $1s$FGO's. Their positions and exponents were optimized at each new position of nuclei within the QC. To calculate the optical absorption of the STE and F-H pairs, as well as of the F and α centers, we also used the $511sp$ basis of the Br ion centered in the center of anion vacancy.

Some of the typical quantum clusters used in these calculations are shown schematically in Fig. 2. They were built along the $\langle 110 \rangle$ crystal axis in such a way that each Br ion was always surrounded by a complete shell of the nearest K ions. The largest clusters included up to 6 Br ions and 26 K ions. First, the consistency between the quantum-mechanical interaction between the ions within the QC and those with the ions outside the cluster was checked by calculating the positions of ions in the clusters representing the perfect lattice. This ''perfect lattice test'' worked remarkably well and all the quantum ions remained in their perfect lattice sites with the polarization energy very close to zero. This basically results from the fact that an ionic model works well for this crystal in this basis set.

The excitation or luminescence energies are calculated as the difference between the total energies of the self-consistently calculated ground and excited states. The Franck-Condon approximation was taken into account where necessary by allowing only shells to respond to the change of the electronic state. This models the electronic response of the rest of the crystal, where all cores remain fixed in the initial state. In this study, only the triplet STE was considered. It was modeled by computing the triplet state of an appropriate cluster.

III. STATIC PROPERTIES OF STE'S AND FRENKEL DEFECTS

Most of the experimental data on the lowest state of the triplet STE in alkali halides are well described in the so-called off-center model of STE's proposed by Leung, Brunet, and Song,[17] which is supported by all recent HF calculations.[18–22] The recent study[24] of the STE in NaCl has demonstrated that the electron correlation does not significantly affect the geometric and electronic structures of the STE at its equilibrium position. Not surprisingly therefore, the structure of the STE in KBr obtained in this study is not much different from that obtained in chlorides using the same method.[21,22] It is qualitatively depicted in Fig. 2(A). The Br_2^- molecular ion is shifted from its symmetrical position in the lattice corresponding to the V_K center with one of the Br ions located just in the middle of the lattice square. The equilibrium distance between the two Br ions in this
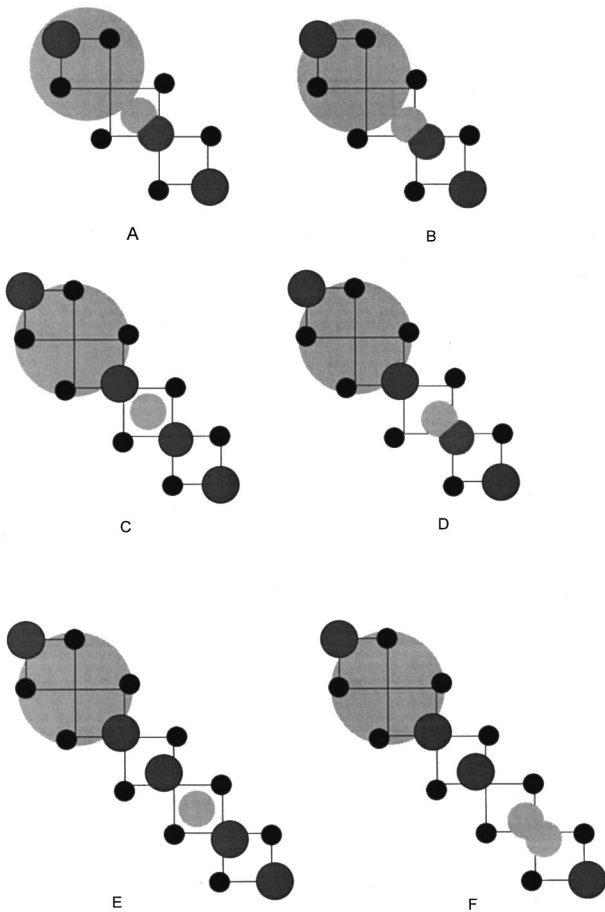
FIG. 2. Schematic of different stages of conversion of the off-center STE(A) into the NN F-H pair (F) in KBr. Part (A) qualitatively depicts the equilibrium off-center STE configuration and the characteristic displacements of surrounding ions. The polarization of the hole component of the STE and the hole localization in other cases is shown by different colors of the anions, lighter meaning stronger hole localization. Part (B) corresponds to the nascent F-H pair, which is unstable in our calculations. Part (C) is the barrier configuration for the transformation into the nearest stable F-H pair in part (D). Similarly part (E) represents the barrier configuration for the H-center diffusion along the $\langle 110 \rangle$ axis and the system transformation into the NN F-H pair in part (F).

configuration is equal to 2.86 Å. The electron is localized around the nascent anion vacancy. The hole component of the STE is polarized towards the vacancy. The electron-density distribution and the geometrical parameters of the STE are similar to those calculated in Refs. 21, 22, and 24.

We have also calculated the fully adiabatic potential energy curve corresponding to the displacement of one of the Br ions of the STE along the $\langle 110 \rangle$ axis and all other ions in the lattice allowed to adjust their positions. Several characteristic configurations are shown in Figs. 2(B)–2(F) and their relative energies are given in Table I. Note that this coordi-

TABLE I. Relative energies (eV) of the STE and several F-H configurations shown in Fig. 2.

A	B	C	D	E	F
0.00	0.20	0.28	0.25	0.27	0.25

TABLE II. Optical absorption energies (eV) of the STE and several defects considered in this work.

	STE	α center	F center	F' center	I center	F-H	(NN) F-H
Theory	2.0	6.2	2.6	1.2	6.3	2.6	2.7
Experiment	1.8[a]	6.14[b]	2.1[b]	1.2[b]	5.4[c]		

[a]Reference 39.
[b]Reference 10.
[c]Reference 2.

nate makes sense only before we reach configuration C in Fig. 2 where the hole switches from one bromine ion to another. In the calculations, we then were moving that last atom and allowed all other atoms to relax until we reached configuration E where the hole switches again. One can see that stable defect pairs correspond to configurations D and F, which we will call the nearest and the next-nearest (NN) neighbor F-H pairs, correspondingly. The Br_2^- molecule in the isolated H center is symmetrical with respect to the lattice site (see Fig. 1). The H center in the nearest F-H pair is shifted from this position towards the F center and polarized in such a way that the hole density is larger on the ion closer to the F center. However, the geometry of the H center in the (NN) F-H pair was found to be already close to that in the isolated state. The calculated barrier for the transformation of the STE into the nearest F-H pair is equal 0.28 eV. The energy of the nearest F-H pair is higher than that of the STE by 0.25 eV, reflecting the exciton bonding. However, the energy of the NN F-H pair is the same as that for the nearest pair within the accuracy of our calculations. One can see that our calculations predict very small barriers for recombination of the nearest F-H pair back into the STE and for the H-center diffusion. These barrier configurations are shown schematically in Figs. 2(C) and 2(E). Note that, due to the hole transfer, the actual displacements of bromine ions during the separation of the F and H centers are much smaller than the final F-center and H-center distance.

How can we assess the accuracy of these predictions? One way is to look at the spectroscopic parameters of the STE, its characteristic optical absorption, and luminescence energies. The energy of the so-called triplet π luminescence is calculated as the Franck-Condon (FC) difference between the total energies of the triplet and singlet states with the positions of nuclei and cores fixed at the STE minimum and only the electronic polarization taken into account. The obtained value of 2.45 eV is close to the experimental value of 2.28 eV. To calculate the electronic excitation, instead of FGO's we used the $511sp$ basis set centered at the same position as the main FGO located in the anion vacancy. The energy of the ground state of the STE with this basis set is lower only by about 0.04 eV, which demonstrates that the electron in the vacancy is already well described by one $1s$ Gaussian and the basis of surrounding cations. Due to the strong interaction of the p_x and p_y atomic orbitals (AO's) of the electronically excited state with the p hole states, we were unable to converge the excited state of this symmetry. Therefore only the transition to the perpendicular p_z state has been successfully calculated. One can see in Table II that it is also in reasonable agreement with the experimental value. To

check some of the previous qualitative predictions regarding the character of the STE excited state,[39,40] we have calculated several points of the adiabatic potential of the excited p_z state along the displacement of one Br atom. The energy of the excited state goes down as the off-center displacement of the hole component of the STE decreases.

As the H center shifts forward along the $\langle 110 \rangle$ axis towards configurations C and D, the energy of the FC transition to the ground singlet state decreases sharply. However, the singlet state is still lower than the triplet state by about 0.25 eV even in configuration D corresponding to the nearest F-H pair. The FC energies of these two states become equal after the system has passed the nearest F-H minimum. The FC singlet state is already much higher than the triplet state in the NN F-H pair. This crossing point, which we were unable to locate precisely, has that significance that it corresponds to the configuration where the nonradiative transition to the ground crystal state happens with the highest probability. Therefore it is partly responsible for the thermal quenching of the triplet STE luminescence (another channel being the further separation of the F and H centers). Although our result is very similar to that obtained for NaCl in Ref. 22, the fact that the crossing in both systems happens past the nearest F-H pair has been overlooked previously.

Let us try to understand this result in simple terms. The FC transition between the triplet and singlet states corresponds to the electron transfer from the F center to the H center at fixed positions of nuclei. Therefore the energy of this transition is essentially determined by the difference in the vertical ionization energy of the F center and the electron affinity of the H center, correspondingly. Another important term is the Coulomb interaction of the interstitial Br ion still in the H-center configuration with the positively charged anion vacancy. The vertical ionization energy of the F center in the NN F-H pair was calculated to be 4.3 eV. The calculated electron affinity of the individual H center is about 2 eV. The positive difference of about 2.3 eV at the nearest F-H pair distance can be compensated by the Coulomb attraction between the $H+e$ center and the anion vacancy.

The results of our calculations are summarized in Figs. 2 and 3. The latter represents the energy curves plotted against a coordinate that can be thought of as a center of gravity of the hole localization. Although it has clear meaning, it is not easily quantifiable; therefore we use this schematic rather to summarize the results in customary terms. In order to have a more comprehensive picture of relative energies of different states and to further assess the accuracy of our model, we have calculated the structure and properties of individual F, H, α and I centers using different cluster sizes and basis sets. The calculated optical excitation energies of different centers are given in Table II.

The relative electron affinity of the anion vacancy and that of the Br_2^- ion as it shifts from the V_K-center configuration play a crucial role in the off-center STE model. Therefore let us first discuss different charge states of the anion vacancy. They have been calculated using three basis sets: (i) $3s$ on K and one FGO centered in the vacancy; (ii) $3s$ on K and the $511sp$ basis centered in the vacancy; and (iii) $3s$ augmented with one diffuse p AO on K and $511sp$ centered in the vacancy. The ground-state energy of the defects depends very little on the basis set. The optical absorption en-
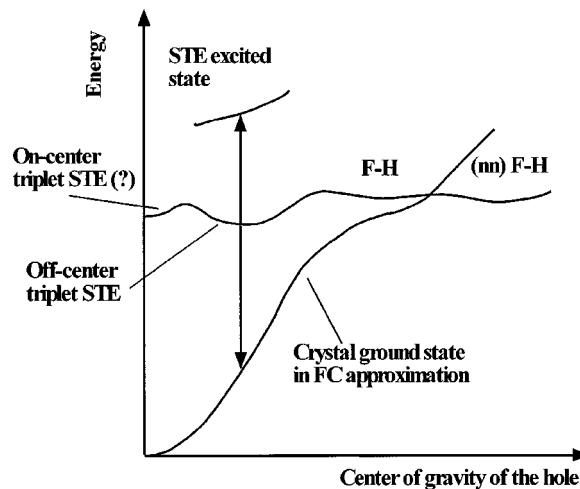

FIG. 3. Schematic presentation of the section of the adiabatic potential of the excited KBr crystal based on the results of this work. The x coordinate formally corresponds to the center of gravity of the hole (see text). For the ground and excited STE state, all other crystal ions were allowed to relax. The curve for the crystal ground state corresponds to the same positions of nuclei as in the STE state and only electrons allowed to relax. Several atomic configurations corresponding to the adiabatic curve of the STE→F-H transformation are shown in Fig. 2.

ergies calculated in the basis (ii) and (iii) are also very similar. Therefore the results shown in Table II are for the basis set (ii), which has also been used in calculating the STE and F-H pair properties. One can see that the optical excitation energy of the anion vacancy, which was calculated as a transition into the triplet state, is in good agreement with the experimental value. This excitation corresponds to the electron transfer from the anions surrounding the vacancy onto the local state in the vacancy and surrounding cations. This in some cases is called the excitation of an exciton near vacancy. The vertical electron affinity of the α center with respect to the vacuum level was calculated to be 1.85 eV. The experimental value is unknown. To assess whether this is a realistic number, one can make a rough estimate. The sum of the vacancy excitation energy and the vertical electron affinity calculated at the same geometry, $6.2+1.85 = 8.05$ eV, should be about the energy of the top of the valence band with respect to the vacuum level. If we consider that the experimental band-gap energy in KBr is 7.4 eV, then our calculations predict the position of the bottom of the conduction band at -0.65 eV, which does not look unrealistic.

The calculated optical absorption energy of the F center is by about 0.5 eV larger than the experimental value. The calculated electron transition energy to the state delocalized by surrounding cations is 3.3 eV. In order to examine further how our method can describe the properties of an anion vacancy in KBr, we have modeled trapping of the second electron by the vacancy, i.e., formation of the F' center. The calculated optical excitation energy of this defect into the triplet state was found to be close to the experimental value.

The relaxed I center occupies the body center interstitial position in the lattice with the four nearest-neighbor Br ions displaced outwards by about $0.11\sqrt{3}a_0$, where a_0 is the in-

teratomic distance (3.262 Å in our calculations). The amount of outward displacements of the four nearest-neighbor cations is only about $0.02\sqrt{3}a_0$. The calculated excitation energy of the I center is by 0.9 eV higher than measured experimentally (see Table II). This excitation is from the anion onto the local state formed by the strongly perturbed nearest-neighbor cations and can depend on the cluster size. We should also note at this point that our method allows us to calculate only singlet-triplet transitions for closed-shell systems, such as the neutral vacancy, F' center, and I center. They generally have smaller excitation energies than allowed singlet-singlet transitions; however, we were unable to calculate the singlet-triplet splitting.

Knowing the energies of individual defects we can now calculate the relative energies of different states at large defect separations. In particular, the energy of a pair of noninteracting F and H centers is by 1.3 eV higher than that of the pair of α and I centers. This energy difference should be even larger at close distances where there is Coulomb attraction between the charged defects. On the other hand, the FC energy difference between the separated F and H pair and the F-e and $H+e$ pair is -2.6 eV, the latter state being higher in energy. This result is close to that calculated for configuration F in Fig. 2. The large difference in energy between this state and the relaxed $\alpha+I$ state reflects the very strong lattice distortion that accompanies the transformation from the initial FC ($H+e$) state into the I center.

These results demonstrate that although our model is not free from limitations, some of which will be discussed in more detail below, broad consistence of the results makes a good basis for further discussion of dynamics of the exciton self-trapping and defect formation.

IV. DYNAMICS OF FRENKEL-DEFECT FORMATION IN THE FIRST STAGE

We start by presenting the results of our recent time-resolved measurements of optical spectra after the femtosecond pulse excitation of KBr. Specimens of pure KBr and of NaBr and KBr doped with an electron trapping impurity of NO_2^- were excited with the third harmonics of a Ti:sapphire laser (photon energy of about 8 eV) at 80 K, and time-resolved absorption was measured with white light generated by the 80-fs fundamental beam of the laser. The details of experimental apparatus and techniques were described elsewhere.[7] An important point specific for present measurements is the stability of V_K centers in NaBr and KBr at 80 K. Because of that, it is not possible to make averaging by repeated irradiation of several pulses on the same spot in order to obtain data with better signal-to-noise ratios; photoexcitation of V_K centers formed by the preceding pulses produces significant artifacts in the spectra. Therefore, in the present measurements, each absorption spectrum was taken for a single shot at a virgin spot of a specimen. Similar single-shot measurements were also made on pure KBr. We note that very similar spectra on these samples have been obtained in this laboratory also using different laser systems and detection methods, demonstrating the reproducibility of the results.
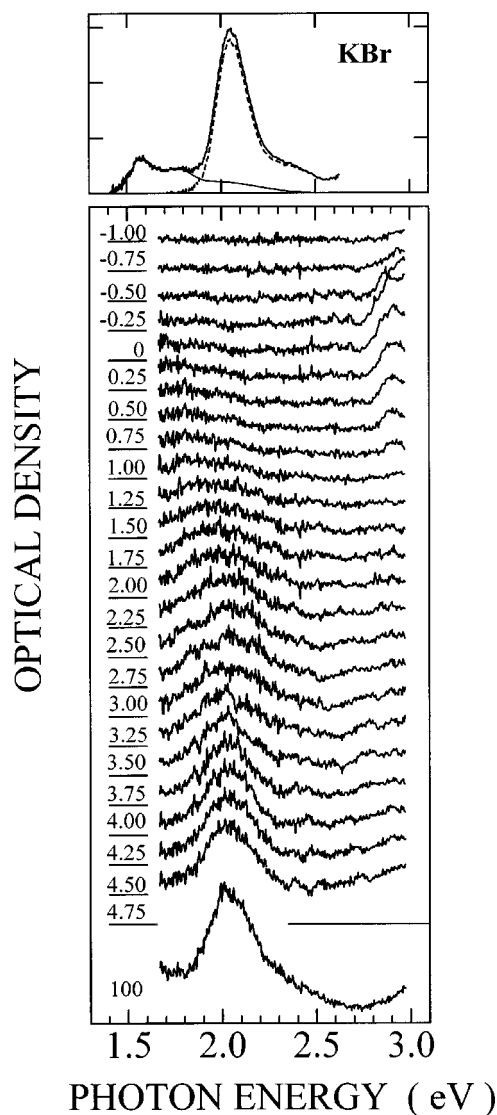

FIG. 4. Time series of optical absorption spectra for pure KBr at 80 K. The number on the left-hand side of each spectra shows the time delay in picoseconds. The top panel shows the transient absorption spectrum in pure KBr measured at 1 μs after an electron pulse irradiation at 8 K. The latter spectrum is decomposed into the STE band (thin solid curve) and the F band (broken curve).

A. Experimental spectra

In Fig. 4 we present the time-resolved absorption spectra of KBr irradiated with femtosecond laser pulses. In the top panel of Fig. 4, the absorption band due to the F center and the bands due to the lowest triplet STE in KBr at 8 K generated by a nanosecond electron pulse are shown for comparison. Since the initial process of the relaxation is our main interest here, the spectra during 4.5 ps after excitation are shown with a time interval of 250 fs. The horizontal short lines in the figure represent the zero levels of the absorption. A stepwise absorption band above 2.8 eV in the spectra corresponding to the time delay of the probe pulse from -1.0 to $+1.0$ ps with respect to the excitation pulse is due to the two-photon cross-correlated absorption of pump and probe pulses discussed by Thoma, Yochum, and Williams.[8]

For the sake of discussion, we divide the spectra presented in Fig. 4 into the two photon-energy regions: 1.5–2.5

eV and 2.5–3.0 eV. In the first region, starting from a time delay of less than 1 ps, one can clearly see the development of a broad absorption band. Its intensity increases with time and the maximum shifts from approximately 1.8 eV at 1 ps to 2.0 eV at 4.5 ps. It has an approximately Gaussian form and gradually becomes sharper. After a time delay of 4.5 ps, the F absorption band is clearly seen. In the second energy region, from 2.5 to 3.0 eV, a broad featureless band can be seen starting from about 1.5 ps. It then evolves in such a way that only a tail of the absorption band peaked at an energy that is higher than 3 eV is detected at time delays longer than 2.5 ps after excitation. This tail is very similar to the optical absorption of the V_K center in this energy region, but the origin of the band is discussed below.

The spectra at 4.5 ps after excitation are representative of the products of the first stage of the relaxation in KBr. At longer delays of 100 ps, which correspond to the end of the second stage of relaxation, the sharp F-center band and the tail characteristic of the H-center absorption band are clearly seen in the spectrum. The broad shoulder below 1.7 eV in the 100-ps spectrum is the optical absorption of the lowest triplet STE.

For differentiating the relaxation processes of electrons and holes and for revealing their interplay during the relaxation, the time-resolved spectra were also measured for KBr and NaBr doped with NO_2^- under the same excitation conditions; hole relaxation is the dominating process in these doped specimens. The results are shown in Figs. 5 and 6; in the top panels the V_K-center absorption bands at 80 K are shown for comparison. In Fig. 5, similar to the case of pure KBr, the band due to the two-photon correlated absorption is seen in the spectra at the delay times less than 1.0 ps. Except for this contribution, we see the broad absorption band extending over the whole photon-energy range. The band shows a peak at 2 eV in the spectrum at a time delay of 0.75 ps and converges, as time proceeds, to the V_K bands peaked at 1.7 and 3.2 eV, although only the tail of the 3.2-eV band is detectable. The important feature of these spectra is that the absorption tail characteristic of the V_K center is detectable only starting from around 3 ps after excitation. In the spectrum corresponding to the delay of 4 ps, one can see the tail due to the V_K absorption more clearly, but it is still associated with significant broadening and there is an additional absorption contribution in the range from 2 to 2.5 eV. This can be interpreted such that the lattice relaxation to form the V_K center is not completed even at 4 ps after excitation. The absorption band due to completely relaxed V_K center is generated only at 10 ps after excitation in KBr.

In contrast to KBr, the formation of the V_K center in NaBr is a much faster process, as revealed by temporal evolution of absorption spectra after femtosecond-pulse excitation of NaBr:NO_2^- shown in Fig. 6. The absorption band characteristic of the V_K center is already detectable in this specimen at 0.5 ps after excitation. Although the initial bands show some broadened features, the band shape measured at a time delay of 10 ps is essentially the same as that measured at 1.0 ps. This suggests that almost completely relaxed V_K centers are formed in NaBr already at 1.0 ps after the excitation. The significant difference in the hole relaxation time to form the V_K center between NaBr and KBr found in this work may
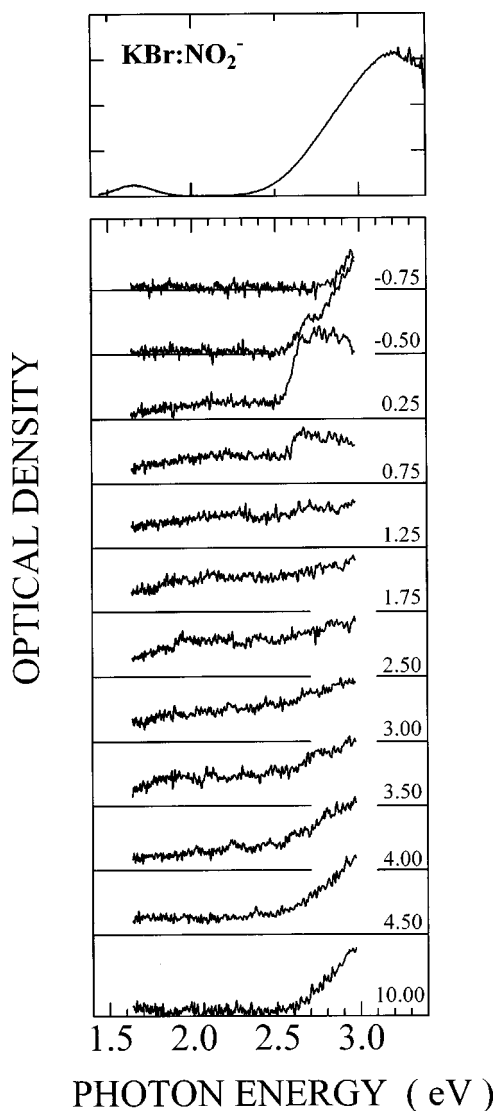

FIG. 5. Time series of optical absorption spectra for KBr:NO_2^- at 80 K. The number on the right-hand side of each spectra shows the time delay in picoseconds. The top panel shows the stationary absorption spectrum of the V_K center.

have important implications for the relaxation of electron-hole pairs in pure specimens, which are discussed below.

Similarities between spectra corresponding to time delays longer than 3 ps in Figs. 4 and 5 suggest that in the case of undoped samples they are also due to the V_K centers. We could not detect any optical absorption of stable V_K centers in the pure specimen, indicating that the concentration of electron-trapping impurities is below the detection level of our experiment. Therefore, the V_K-like tail of the optical absorption in this specimen can be attributed to the temporal existence of the V_K centers that still have not trapped electrons, and to the on-center STE in which the hole component is almost the same as the V_K center.[41]

The femtosecond pulse creates about 2.1×10^{17} cm^{-3} electron-hole pairs in the bulk of KBr. The optical absorption shown in Fig. 4 decays almost completely within 1 s, which implies that very close defect pairs are mostly formed. Finally, we note that previous analysis of the time evolution of the optical absorption on the same samples has
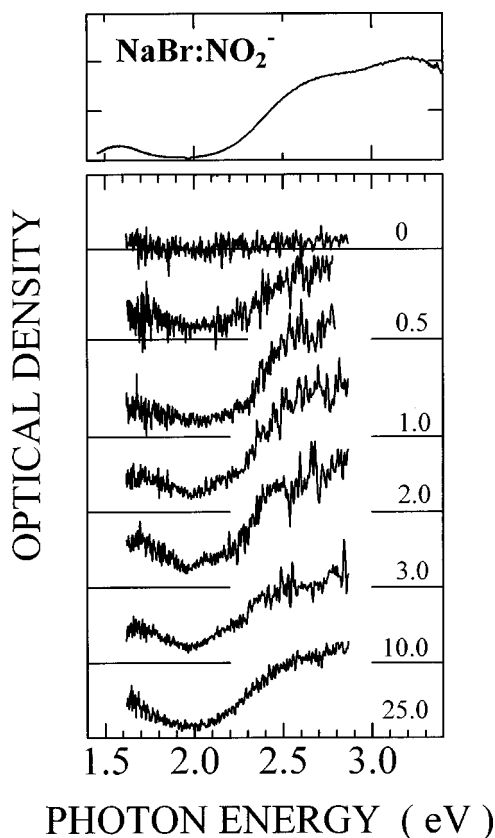
FIG. 6. Time series of optical absorption spectra for NaBr:NO$_2^-$ at 80 K. The number on the right-hand side of each spectra shows the time delay in picoseconds. The top panel shows the stationary absorption spectrum of the V_K center.

demonstrated[5] that at 6 K approximately half of all F centers that survive until 100 ps after excitation are formed by the fast mechanism.

On the basis of these data it has been suggested[5] that, since the V_K center spectrum develops significantly later than the F-center band appears in the spectrum, the fast F-center formation is promoted by the interaction of electrons with the holes that still are in the process of their vibrational relaxation. A preliminary theoretical analysis of this model has been published in Ref. 42. A more detailed argument is presented below.

B. Theoretical model

As has been demonstrated by Petite $et\ al.$,[12] the number of electrons excited across the band gap in KBr that remain delocalized in the conduction band decays exponentially for about 4 ps at 10 K before all of them recombine with holes to produce excitons or F-H pairs. Holes are known to self-trap in alkali halides forming V_K centers; however, the results shown in Fig. 5 demonstrate that formation of the completely relaxed V_K-center state may take up to 10 ps, although the first signs of the V_K-center absorption appear at 3–4 ps. Therefore it seems clear that at time delays less than 3 ps electrons interact with holes that still are in the process of relaxation. The mechanism of the hole relaxation is basically unknown. Due to thermal fluctuations it can start directly from a one- or two-center state and then cool down into the V_K-center configuration. There can be more delocalized ini-

tial states too; however, in alkali halides the lattice polarization will eventually favor only the one- or two-center states.[43,44] Only these states can be treated in the cluster model, and we start our discussion from considering some initial relaxation of a two-center hole state.

In the two-center initial state the hole is shared by the two nearest-neighbor Br ions situated close to their lattice sites. However, we have found[42] that if the distance R between the two Br ions carrying the hole is larger than a critical value R_C of about 3.65 Å, the energy of the two-center hole state is higher than that of the ''one-center'' relaxed state. The latter corresponds to a preferable localization of the hole on one Br ion with a adiabatically adjusted lattice relaxation. The value of R_C is by about 0.55 Å longer than the equilibrium distance in the V_K center. Therefore, at the Br-Br distances longer than R_C any asymmetric lattice distortion polarizes the system towards the one-center hole state. This results from the interplay between the lattice polarization that favors the charge localization and the chemical bonding between the Br^0 and the surrounding Br ions, which is weak at long distances, as discussed in Ref. 44. The one-center polarized hole state is unstable with respect to shortening the distance R with any of the twelve nearest-neighbor Br ions. However, the resulting adiabatic potential of the hole transformation into the two-center state along R is very soft, which implies that this transformation is largely diffusive,[45] i.e., the system makes many random walks along the reaction path. These results are similar to those obtained for a combination reaction $I^- + I \rightarrow I_2^-$ in solutions (see, for example, Refs. 26 and 27).

The hole redistribution by two ions at $R \approx R_C$ is accompanied by the symmetry change and significant reorganization of the lattice distortion. This cannot be accomplished immediately due to the crystal resistance, which can be expressed in terms of the polarization force, F_{pol}, exerted by the polarized lattice on the internuclear coordinate R between the two Br ions forming the V_K center. This force has its maximum close to R_C where the lattice reorganization from the one-center into the two-center hole state is the strongest (see also Refs. 26–28).

Based on these theoretical results, part of the holes in KBr during the relaxation pass through a period of preferably one-center localization before they transform into a two-center state and undergo cooling relaxation to form the V_K centers. To be able to compare the theoretical predictions with experimental results, we have calculated optical transition energies for a number of configurations of localized holes. The optical absorption of Br$_2^-$ depends very strongly on R (Ref. 46). At R corresponding to small departure from the ideal one-center hole state, the calculated optical absorption predicts several strong bands in the energy range between 2.6 and 3.5 eV and a weak band at about 2.1 eV. These bands are due to the electron transitions from the occupied electronic states delocalized by surrounding lattice anions to the unoccupied hole state.[44] As the distortion increases towards formation of the two-center state with one of the nearest anions, the calculations show the enhancement of the optical absorption first at about 2.7 eV, which then shifts to about 1.9–2.3 eV. The latter is associated with hole transfer to the nearest Br$^-$ ion forming the bond. This transition is analogous to the optical polaron transfer discussed in Ref.

47. The diffusion of the system along R leads to a large variety of Br-Br separations existing at the same time (due to fluctuations of the surrounding lattice), which should be accompanied by a strong broadening of the red band. Therefore it is expected that the relaxing holes should show optical absorption ranging from 1.9 to 3.5 eV. Because of the finite temporal width of the excitation pulse and due to fluctuations in the localization process, the relaxing holes should show significantly broadened absorption bands. Taking into account these effects, the theoretical prediction of the hole relaxation process discussed above is totally consistent with the features in the time-resolved absorption spectra before 3.0 ps seen in Fig. 4.

Next we modeled the interaction of an electron with the relaxing hole in the ground electronic state and calculated the adiabatic transformation of a triplet exciton into a next-nearest-neighbor F-H pair using the technique described above. The important feature of the one-center and then of the two-center hole states (when R is smaller R_C) is that the adiabatic potential is very soft with respect to the simultaneous displacement of the two bromine ions forming the bond along the $\langle 110 \rangle$ axis. The electron was added to the one-center hole state, and its wave function was described by five Gaussians with their positions and exponents optimized at each point of the exciton adiabatic potential. Both the hole instability towards formation of the two-center state and its displacement along the $\langle 110 \rangle$ axis are enhanced by the interaction with the electron. The calculated energy of the ground state of the exciton that corresponds to the electron trapped initially by the relaxing hole with $R \geqslant R_C$, dependent on atomic configuration, is about 1.0–1.2 eV higher than that of the relaxed exciton state (configuration A in Fig. 2). The barrier for the off-center exciton transformation into the nearest F-H pair was found to be about 0.28 eV. Analysis of the forces acting on ions during the relaxation shows that they drive the downhill relaxation and formation of the F-H pair because the initial hole configuration is already favorable for this process. We believe that large excess energy provides high probability to overcome the separation barrier. Thus our results confirm that fast formation of the F-H pairs can proceed on the ground-state potential energy surface.

These results point towards a possible explanation of the time evolution of the electron-hole pair into the F-H pair reflected in the spectra in Fig. 4. We suggest that the outcome of each individual electron-hole interaction process that takes place during the first several picoseconds after crystal excitation depends on the degree of the hole relaxation into the V_K-center state. Just after the electron-hole pair excitation, most of the electrons are in the conduction band and holes are in their initial stages of relaxation. As our results demonstrate, these holes are more likely to be polarized towards the one-center state and experience also the displacement vibrations. The interaction of electrons with these holes will lead to formation of off-center STE and their transformation into the nearest and NN F-H pairs. Nearest F-H pairs are formed first and then separate into the NN F-H pairs. The number of NN F-H pairs is initially smaller also because of the possibility of the non-radiative transition into the crystal ground state from the nearest F-H state.

This model can explain the significant peak shift of the optical absorption in the 2-eV region at time delays of 0.75–1.5 ps. The red part of the spectrum can be due to the nearest pairs and the higher-energy part due to the NN F-H pairs. The shift of about 0.1 eV agrees with our prediction of the optical absorption shift for the nearest and NN F-H pair (see Table II).

As the time delay after excitation increases, a larger number of electrons are interacting with holes, but also a larger number of holes have already relaxed closer to their final V_K-center state. This can partly explain the V_K-like tail in the blue part of the spectra that appears after about 3.5 ps. We suggest that the electrons that interact with holes that are close to their symmetric relaxed state are more likely to form on-center triplet STE's. This can explain the persistent V_K-like tail in the blue part of the spectra at longer times. Transformation of these excitons into the triplet off-center form and the F-H pairs can be responsible for the slow growth of F centers, which still takes place even after 100 ps.

The idea that the mechanism of F-H pair formation could be related to the speed of hole relaxation is supported by the time-resolved spectra of the V_K-center formation in NaBr:NO$_2^-$ presented in Fig. 6, which demonstrates the very fast formation of V_K centers in this crystal. This correlates with a very small yield of stable F-center formation and a high yield of σ exciton luminescence characteristic of on-center $V_K + e$ type excitons in NaBr.[3] Our time-resolved measurements on the undoped NaBr samples, made using the same excitation conditions as for the undoped KBr, could not detect any F centers either. Therefore we conclude that the yield of F-H pair formation in NaBr is smaller by several orders of magnitudes than that in KBr.

The described model also suggests why the effectiveness of the fast mechanism of F-H pair formation decreases as the temperature increases.[5] As has been demonstrated in Ref. 12, at 300 K the electrons survive longer in the conduction band and are trapped by weaker traps. In this context, the "trap" depth means the electron binding energy either in the STE or in the F center, which is larger. As has been suggested in Ref. 12, during 20 ps more F centers are formed at low temperature, which agrees with the results of this study. Certainly this results from the interplay of several factors, one of them being the faster hole relaxation at higher temperatures, which leads to creation of STE's but not F-H pairs.

V. DISCUSSION

In this paper we have presented a consistent and comprehensive set of calculations of the STE and Frenkel defects in KBr and applied these results in order to model a possible mechanism of exciton self-trapping and the "fast" mechanism of F-center creation in KBr in conjunction with the results of time-resolved optical spectroscopy.

The main new theoretical results of this work can be summarized as follows. Our embedded cluster Hartree-Fock calculations predict (see Figs. 2 and 3) (i) the off-center configuration of the STE to be about 0.25 eV lower than the nearest separated F-H pair, (ii) the Franck-Condon crossing between the adiabatic potential of the triplet STE and the crystal ground state in KBr to happen at the F-H separation exceeding the nearest F-H pair, (iii) the separated α-I pair to have about 1.3 eV lower energy than the F-H pair, (iv) the fast process of the F-H pair formation in KBr, prior to the

V_K-center formation takes place in the ground electronic state of the relaxing exciton. This process is driven by the interaction of the relaxing hole with an electron. Experimentally, we demonstrate that the hole relaxation time to form the V_K center is about 1 ps in NaBr and 10 ps in KBr. The theoretical modeling and the results of time-resolved spectroscopy of hole and exciton self-trapping in NaBr and KBr allow us to arrive to a more general conclusion that the speed of hole relaxation could be one of the crucial factors that determine the mechanism and effectiveness of F-H pair formation in alkali halides.

Our calculations demonstrate a satisfactory and, in some cases, even good agreement between the theoretical results and the experimental data for a broad number of spectroscopic properties of the STE and the Frenkel defects in KBr. However, besides some quantitative discrepancies, there is one qualitative feature characteristic of all Hartree-Fock calculations of the STE in alkali halides. It concerns the strong polarization of the hole component of the STE, which contradicts the EPR data,[48,49] which suggest an equivalent hole distribution between the two Br ions. This most probably results from the electron correlation unaccounted for in our calculations. The results[24] for the STE in NaCl demonstrate that this could be the case, although no direct proof has been found. Indirectly, we can see this effect also in a much better agreement with experiment of the optical excitation energy of the STE with respect to that for the F center, which can be explained by the small effective charge of the Br ion closest to the vacancy [see Fig. 2(A)].

In a more general sense, the fact that the electron correlation is not properly included can result in the fact that the role of the lattice polarization is overemphasized in some of our calculations. Polarization strongly favors polarized solutions that increase the polarization energy. This could also affect the results concerning the polarization of Br_2^- in the lattice when modeling the hole relaxation process. Although the effect of hole polarization is physically transparent and has also been obtained in modeling the time evolution of the

relaxation of X_2^- molecules in solutions,[27,28] the details have not yet been finalized. For instance, our critical separation R_C could be underestimated.

Another side of the electron correlation effect concerns the on-center STE (see Fig. 1). As has been discussed in our previous publications,[22,24] the UHF method fails to reproduce correctly the symmetrical solutions in the on-center STE. Therefore our calculations can add no details to the proposed formation of the on-center triple STE as the first stage of the slow mechanism of the F-center formation.

The admitted failure of the Hartree-Fock method to treat delocalized states and the feasible size of quantum clusters essentially confine our approach to the states that are already well localized on the atomic scale. Therefore it requires some assumptions regarding the initial localization of exciton and hole, which could not be tested in this work. Nevertheless, further analysis of lattice vibrations and thermal fluctuations, similar to that presented in Ref. 50, should allow us to get deeper insight into the initial stages of hole and exciton trapping in insulators and to understand why, for instance, V_K centers in NaBr relax much faster than in KBr. We view these results as a useful step towards further assessment of the accuracy of modeling of excited states in crystals and building up potential energy surfaces that could be used for simulating dynamical processes using, e.g., wave-packet propagation methods.

[1] *Defect Processes Induced by Electronic Excitation of Insulators*, edited by N. Itoh (World Scientific, Singapore, 1989), p. 278.

[2] C. B. Lushchik and A. Ch. Lushchik, *Decay of Electronic Excitations with Defect Formation in Solids* (Nauka, Moscow, 1989), p. 262.

[3] K. S. Song and R. T. Williams, *Self-Trapped Excitons* (Springer-Verlag, Berlin, 1993), p. 404.

[4] T. Shibata, S. Iwai, T. Tokizaki, K. Tanimura, A. Nakamura, and N. Itoh, Phys. Rev. B **49**, 13 255 (1994).

[5] T. Sugiyama, H. Fujiwara, T. Suzuki, and K. Tanimura, Phys. Rev. B **54**, 15 109 (1996).

[6] S. Iwai, T. Tokizaki, A. Nakamura, K. Tanimura, N. Itoh, and A. Shluger, Phys. Rev. Lett. **76**, 1691 (1996).

[7] H. Fujiwara, T. Suzuki, and K. Tanimura, J. Phys.: Condens. Matter **9**, 923 (1997).

[8] E. D. Thoma, H. M. Yochum, and R. T. Williams, Phys. Rev. B **56**, 8001 (1997).

[9] W. Meise, U. Rogulis, F. K. Koschnick, K. S. Song, and J. M. Spaeth, J. Phys.: Condens. Matter **6**, 1815 (1994).

[10] *Physics of Color Centers*, edited by W. B. Fowler (Academic, New York, 1968), p. 656.

[11] A. M. Stoneham, *Theory of Defects in Solids* (Clarendon, Oxford, 1975).

[12] G. Petite, P. Daguzan, S. Guizard, and P. Martin, Mater. Sci. Forum **239–241**, 555 (1997).

[13] R. N. Barnett, U. Landman, C. L. Cleveland, and J. Jortner, J. Chem. Phys. **88**, 4429 (1988).

[14] R. N. Barnett, U. Landman, and A. Nitzan, J. Chem. Phys. **89**, 2242 (1988).

[15] R. N. Barnett, U. Landman, and A. Nitzan, J. Chem. Phys. **91**, 5567 (1989).

[16] E. Neria, A. Nitzan, R. N. Barnett, and U. Landman, Phys. Rev. Lett. **67**, 1011 (1991).

[17] C. H. Leung, G. Brunet, and K. S. Song, J. Phys. C **18**, 4459 (1985).

[18] R. C. Baetzold and K. S. Song, J. Phys.: Condens. Matter **3**, 2499 (1991).

[19] K. S. Song and R. C. Baetzold, Phys. Rev. B **46**, 1960 (1992).

[20] R. C. Baetzold and K. S. Song, Phys. Rev. B **47**, 1199 (1993).

[21] A. L. Shluger, N. Itoh, V. E. Puchin, and E. N. Heifets, Phys. Rev. B **44**, 1499 (1991).

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

[23] A. L. Shluger, A. H. Harker, V. E. Puchin, N. Itoh, and C. R. A. Catlow, Modell. Simul. Mater. Sci. Eng. **1**, 673 (1993).

[24] V. E. Puchin, A. L. Shluger, and N. Itoh, Phys. Rev. B **52**, 6254 (1995).

[25] G. H. Peslherbe, R. Bianco, J. T. Hynes, and B. M. Ladanyi, J. Chem. Soc., Faraday Trans. **93**, 977 (1997).

[26] B. J. Gertner, K. Ando, R. Bianco, and J. T. Hynes, Chem. Phys. **183**, 309 (1994).

[27] I. Benjamin, P. F. Barbara, B. J. Gertner, and J. T. Hynes, J. Phys. Chem. **99**, 7557 (1995).

[28] P. K. Walhout, J. C. Alfano, K. A. M. Thakur, and P. F. Barbara, J. Phys. Chem. **99**, 7568 (1995).

[29] N. Dalaney, J. Faeder, and R. Parson, J. Chem. Phys. **111**, 651 (1999).

[30] A. Sanov, T. Sanford, S. Nandi, and W. C. Lineberger, J. Chem. Phys. **111**, 664 (1999).

[31] J. H. Harding, A. H. Harker, P. B. Keegstra, R. Pandey, J. M. Vail, and C. Woodward, Physica B **131**, 151 (1985).

[32] J. M. Vail, J. Phys. Chem. Solids **51**, 589 (1990).

[33] J. M. Vail, R. Pandey, and A. B. Kunz, Rev. Solid State Sci. **5**, 241 (1991).

[34] B. G. Dick and A. W. Overhauser, Phys. Rev. **112**, 90 (1958).

[35] These techniques have been reviewed in a special issue edited by C. R. A. Catlow and A. M. Stoneham, J. Chem. Soc. Faraday. Trans. 2 **85** (1989).

[36] M. J. Norget (unpublished).

[37] C. R. A. Catlow, K. M. Diller, and M. J. Norgett, J. Phys. C **10**, 1395 (1977).

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

[39] K. Tanimura and N. Itoh, J. Phys. Chem. Solids **45**, 323 (1984).

[40] Y. Kayanuma, in *Defect Processes Induced by Electronic Excitation of Insulators* (Ref. 1), p. 13.

[41] T. Suzuki, K. Tanimura, and N. Itoh, Phys. Rev. B **49**, 7233 (1994).

[42] A. L. Shluger and K. Tanimura, J. Lumin. **76&77**, 591 (1998).

[43] I. G. Lang, Zh. Eksp. Teor. Fiz **45**, 2152 (1977) [Sov. Phys. JETP **72**, 1130 (1977)].

[44] A. L. Shluger and J. D. Gale, Phys. Rev. B **54**, 962 (1996).

[45] A. L. Harris, J. K. Brown, and C. B. Harris, Annu. Rev. Phys. Chem. **39**, 341 (1988).

[46] W. R. Wadt and P. J. Hay, J. Chem. Phys. **82**, 284 (1985).

[47] I. G. Austin, J. Phys. C **5**, 1687 (1972).

[48] M. J. Marrone, F. W. Patten, and M. N. Kabler, Phys. Rev. Lett. **31**, 467 (1973).

[49] A. Wasiela, G. Ascarelli, and Y. M. d'Aubigne, Phys. Rev. Lett. **31**, 993 (1973).

[50] A. L. Shluger, J. L. Gavartin, M. A. Szymanski, and A. M. Stoneham, Nucl. Instrum Methods B (to be published).