Exciton relaxation in KBr and CaF$_2$ at low temperature: molecular dynamics study

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We report here recent study of molecular dynamics simulation of exciton relaxation in several ionic crystals at low temperature. Both the lowest energy spin triplet and some of the low lying hole excited states are allowed to relax in view of studying the radiation defect formation channels. The previously used semi-classical program has been modified to implement the solution of Newton's equations with 0.48 fs time step. The relaxation of an exciton localized on a single site (as $Br^0 + e$, or $F^0 + e$, respectively) is studied at 10 K in KBr and in CaF$_2$. In KBr the triplet self-trapped exciton leads to separated Frenkel pair in about 1–2 ps, followed by slow oscillation of the hole center along the $\langle 110 \rangle$ axis. The defect pair created is separated by about 10 Å (third nearest neighbor). In CaF$_2$, the relaxation reaches the geometry of the nearest Frenkel pair, with the hole center oriented along a $\langle 111 \rangle$ axis in about 0.3 ps at 10 K. However, at 80 K the system can undergo further relaxation into a slightly more distant defect pairs. When the hole is excited to higher levels, the molecule bond of the hole center undergoes violent oscillations. In KBr, the hole center is found to form in the second nearest neighbor position within about 0.5 ps. The species formed are, however, different from the well known primary radiation defects. Similar process is also observed in CaF$_2$.

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1. Introduction

In ionic halides under study in this paper, the top valence band originates from the halogen *p*-orbital and is narrow (about 1 eV). The conduction bands are broad and originate from several excited orbitals of both ions. The hole is quickly self-trapped in the form of a molecule ion X_2^-, and is stable at low temperature. When an exciton is created, it is also self-trapped. The nature of the self-trapped exciton (STE) in these ionic halides has been of great interest in part because of its role in the radiation defect creation process [1]. The low-temperature dynamic *F* center production is now understood to be the result of strong axial relaxation of the STE in alkali halides of NaCl structure. This has been demonstrated by both static calculations of the STE structure as well as by recent molecular dynamics (MD) studies. As for the alkaline earth fluorides (AEF), the early magnetic resonance data clearly showed that the STE itself is a close *F−H* pair [2], with the hole center oriented along a $\langle 111 \rangle$ axis.

There has been an ongoing debate about the possible role of the hole excitation in the defect process. Experiments have indicated that in the AEF stable Frenkel pairs (well separated pairs) are created when the STE is excited in the hole absorption band [3]. A recent paper [4] suggested similar process leading to even faster creation of Frenkel pairs in NaCl-type crystals than by the dynamic channel.

In this paper we present results recently obtained on the possible channels of defect creation as a result of exciton relaxation in ionic halides of two different lattice structures: KBr and CaF$_2$. We first compare the relaxation of the lowest energy spin triplet STE state in the two materials, and discuss the similarities and differences. The dynamic relaxation of the triplet STE in KBr and NaBr at 10 K has recently been published [5]. In this work, a system of a hole and excited electron is allowed to relax for about 3 ps. The main results obtained are as follows. The localization of the excited electron at an anion site drives the relaxation process, resulting in the fast formation of interstitial-vacancy pair in the anion sublattice (respectively known as the *H* center and the *F* center). The spin

triplet STE in KBr leads to spatially separated Frenkel defect pair in about 1−2 ps, followed by slow oscillation of the hole center along the (110) axis. The defect pair created is separated by about 10 A (third n.n.). In CaF_2, the situation is qualitatively different due to the different lattice structure and the coordination of atoms. The relaxation reaches the geometry of the nearest Frenkel defect pair, with the hole center oriented along a (111) axis in about 0.3 ps at 10 K and 0.2 ps at 80 K. However, at 80 K the system can undergo further relaxation into a slightly more distant defect pairs, reoriented by about 70°.

We then present results of relaxation when the exciton is in one of the low-lying hole excited states. In particular when the hole is excited to higher level the violent oscillations do appear of the molecule bond of the hole center. In KBr, it is found that a set of three defects are formed: an *F* center at an anion vacancy; a V_k center (occupying two adjacent anion sites) at the second nearest neighbor site from the anion vacancy; an *I* center (an interstitial Br ion close to the *F* center). Depending on the rate of energy dissipation employed in the MD simulation this process takes place very fast, within about 0.5 ps. The species formed are, therefore, different from the well known primary radiation defects (a pair of Frenkel defects). Similar process takes place in CaF_2 resulting in the creation of three above defects. These results are compared with experimental data.

2. Method

The method is based on a semi-classical approach of excited defect study in insulating crystals [6], which has recently been modified for MD simulation [5]. The details are given in Refs. 5, 6. At the beginning the perfect lattice in the ground state is equilibrated at the specified temperature. In the present work the number of atoms included in the MD simulation varies between about 110 and 180 depending on the system studied. This cluster is embedded in an infinite lattice. The role of hole excited states in the exciton relaxation is examined by keeping the hole in several molecular obitals (MO): σ_u (...222221), π_g {(...222212) and (...222122)}, and π_u {(...221222) and (...212222)}. The σ_u MO is the bonding, the π_g MO a nonbonding and the π_u MO an antibonding states. Excess electronic energy of about 1−2 eV becomes available when the hole is in an antibonding MO. To prevent an excessive temperature rise associated with the small size of the MD cluster, a fixed rate of kinetic energy dissipation is implemented in the program. We found it reasonable to reduce the kinetic energy of all atoms by a factor of 0.85 every 5 time steps (designated as 0.85/5) for the lowest triplet STE state, by 0.55/3

for the excited hole states. As will be shown below, the rate does not have an influence on the final range of the defect pair separation, but will have an influence on the time scale of onset of the final relaxation product.

3. Results

3.1. STE relaxation in KBr

As a reference we present in Fig. 1 the relaxation of the triplet STE at 10 K obtained previously [5]. A Frenkel-type free exciton (a Br^0 with an electron in a diffuse orbital around it in an otherwise perfect lattice) is allowed to relax. The time evolution of the x coordinate of the five Br atoms as well as the position (the x coordinate) of the center of gravity of the hole charge are shown. The main points are: the Br atom nearest to the electron at (000) moves off-center well before the hole center (the Br molecule ion) forms; the hole center continues to move ahead jumping from the first to the second and then to the third nearest neighbor position in about 2 ps. What is noteworthy is that even before a well-formed hole center is established the electron seems to be in an *F* center-like state, within about 0.5 ps. In fact, it is the transformation of the excited electron into an *F* center which is driving the entire process of off-center relaxation.

We present here two hole excited states: (...212), a π_g state, and (...21222), a π_u state. The time evolu-
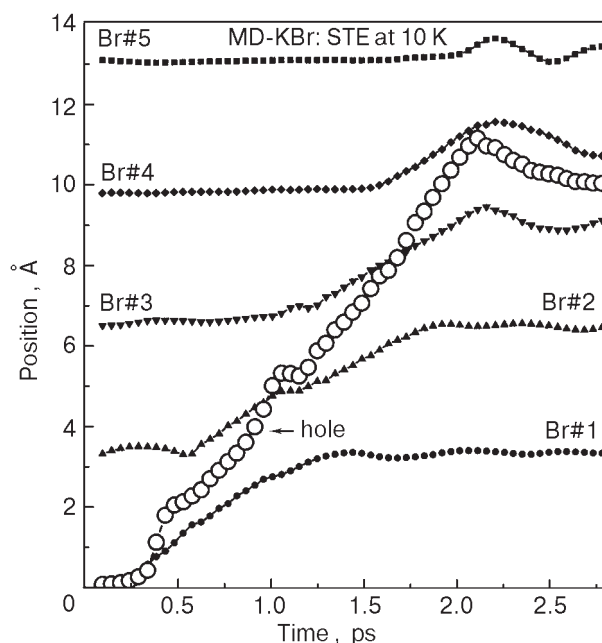

Fig. 1. MD results of exciton relaxation in KBr (at 10 K), with the hole in the lowest energy σ_u MO. Positions of the five Br atoms and the hole charge distribution (the x coordinates on the (110) plane in Å) as functions of time are shown.
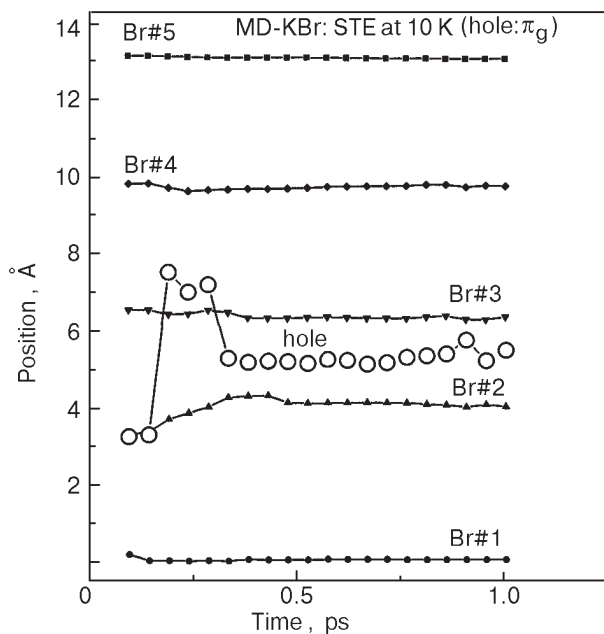
Fig. 2. MD results of exciton relaxation, with the hole in the π_g MO. The dissipation used: 0.75/3.

Fig. 3. A schematic diagram showing the end products of exciton relaxation. With the hole in the σ_u MO, a *H* center is created at the fourth anion site. With the hole kept at an excited π_g MO, a V_k center is formed by the second and third Br atoms. The solid circles are Br atoms along the (110) axis. The dumbbell suggests a hole center shared between two Br atoms. The larger grey circle represents the excited electron, the *F* center.

tion of the Br atoms relaxations is shown for the π_g state in Fig. 2. It is obtained with 0.75/3. The hole is kept in the π_g MO throughout the time shown. The main point is that initially the hole jumps around until it fixes between the Br atoms at (110) and (220). The bond forms at around 0.5 ps. With faster dissipation 0.55/3 the hole center forms at the same geometry, but more slowly: after about 1.5 ps and remains there for the duration of our study. The hole center thus formed is, however, more like a V_k center (a Br$_2^-$ occupying two anion sites) than an *H* center (a Br$_2^-$ occupying one anion site).

With the π_u state we observe similar result. A stable hole center forms at around 0.4 ps independent of the dissipation rate. Although the hole center forms quite early at the second n.n. position from the electron localized at an anion vacancy, there is no further diffusion toward more distant position in all of our studies. It should be noted that the created hole center is an *H* center in the case of the lowest energy STE, but is a V_k center when the hole is in an excited state. As a result of this difference, the Br atom originally at (000) lingers around the *F* center and therefore becomes an *I* center (interstitial anion), instead of moving to the next site (110) as it does in Fig. 1. Figure 3 illustrates the difference of the two types of relaxation in a more schematic way.

3.2. STE relaxation in CaF$_2$

The situation in the fluorites is different from that in the halides of NaCl structure because of the difference of lattice structure. The self-trapped hole is of
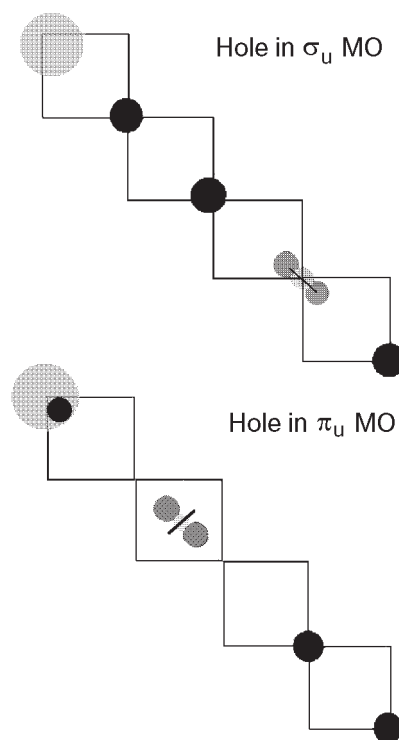
the molecular form, F$_2^-$, as in the NaCl lattice. However, it is oriented along a (100) axis. In 1975 [2] it was determined from optically detected ESR study that the STE is made of a pair of *F* center on a fluoride ion site and *H* center oriented along the (111) direction. It was not possible to identify from ESR alone which of the four possible orientations it actually was occupying. From analysis of the zero-field splitting parameter *D*, the actual orientation was identified [7]. This geometry is shown in Fig. 4,*b*. The present MD results were obtained at 10 and 80 K. As the relaxation in CaF$_2$ lattice involves both axial translation as well as rotations, it is not possible to draw the time evolution of the principal F ions as was done for KBr. Instead, we illustrate the final geometry of the centers in a schematic way in Fig. 4. At 10 and 80 K, the final relaxed structure is reached in about 0,2–0.3 ps. This is to be compared with 0.69 ps reported in Ref. 8 at room temperature. The geometry shown in Fig. 4,*b* is precisely the same as deduced in Ref. 7.

a

b

c

a

b

c
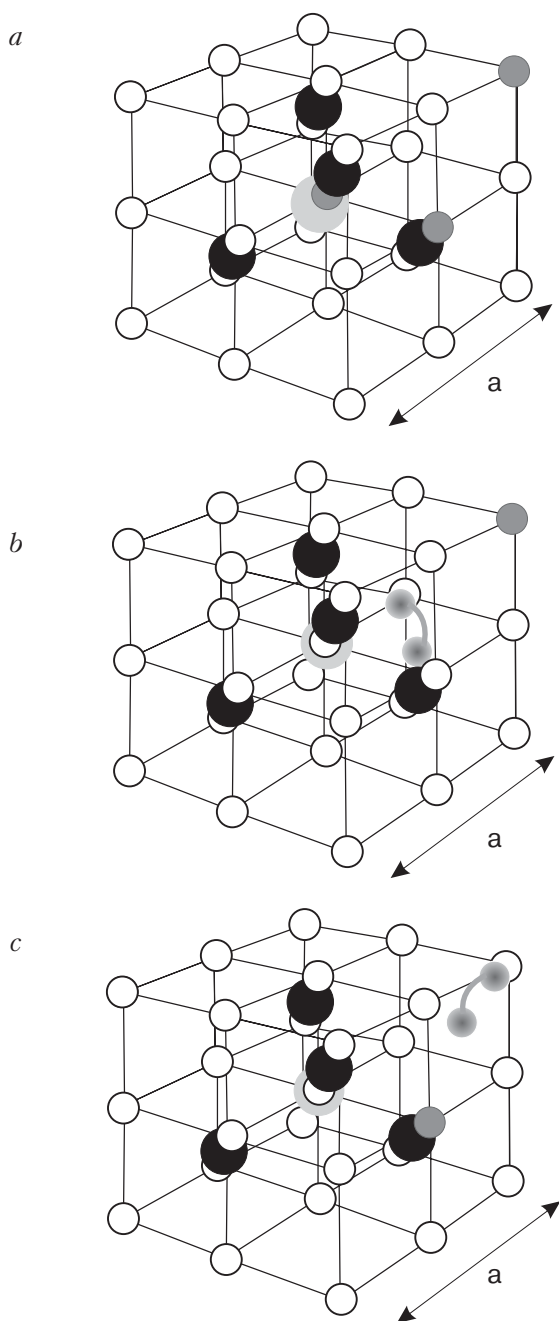
Fig. 4. A view of the CaF$_2$ lattice. The larger solid circles represent Ca atoms, while the smaller open circles are F atoms. A dumbbell represents the hole center. (*a*) The set of three grey F atoms are those taking part in the hole center bonds. (*b*) The relaxed STE nearest *F–H* pair formed after 0.2–0.3 ps at respectively 80 and 10 K. (*c*) After further relaxation the hole center is seen to migrate to a more distant site at 80 K.

We also observed that at 80 K the hole center can undergo further bond changes into a larger electron-hole separation. This is shown in Fig. 4,*c*. The dividing temperature seems to be around 40 K. Starting from a slightly different set of F atoms to represent the hole center, it was possible to induce migration of
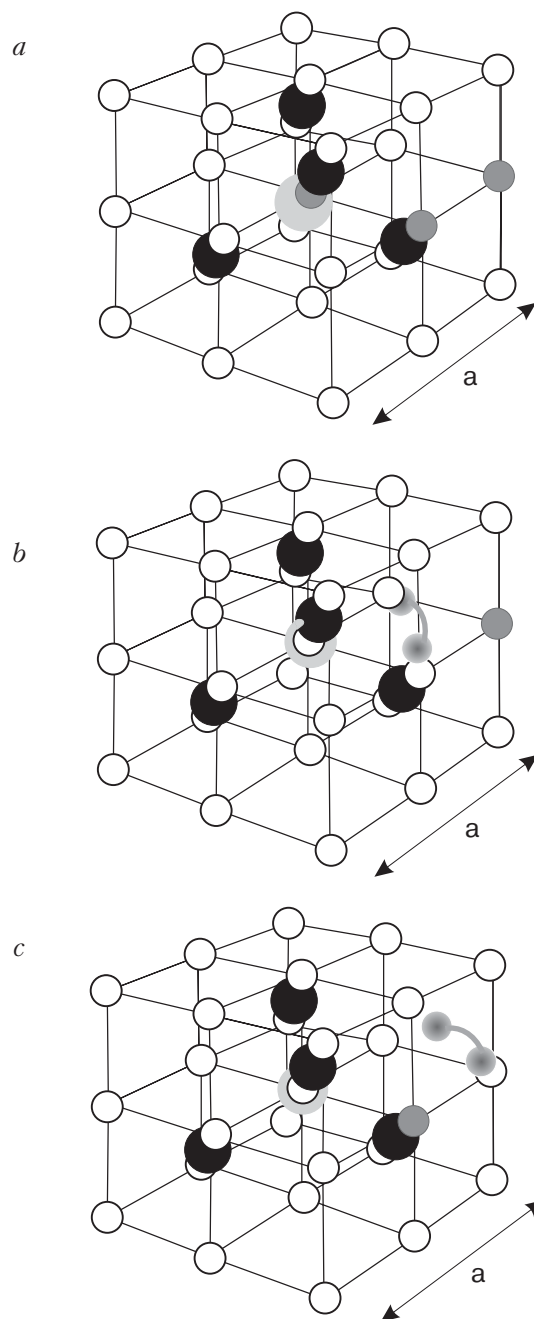
Fig. 5. Similar to Fig. 4, with a different set of F atoms taking part in the hole localization.

the hole center to a different configuration relative to the *F* center, shown in Fig. 5.

We have studied the effect of hole excitation on the STE relaxation in CaF$_2$, similar to what we did in KBr. Two different starting states have been studied. In the first, an unrelaxed Frenkel-type exciton with a cluster of four F atoms is allowed to relax at 80 K. The MO at which the hole was kept excited was π_u (2…1222). Within about 50 fs the hole center formed away from the *F* center as shown in Fig. 6. The resulting system consists of a *F* center (an electron at
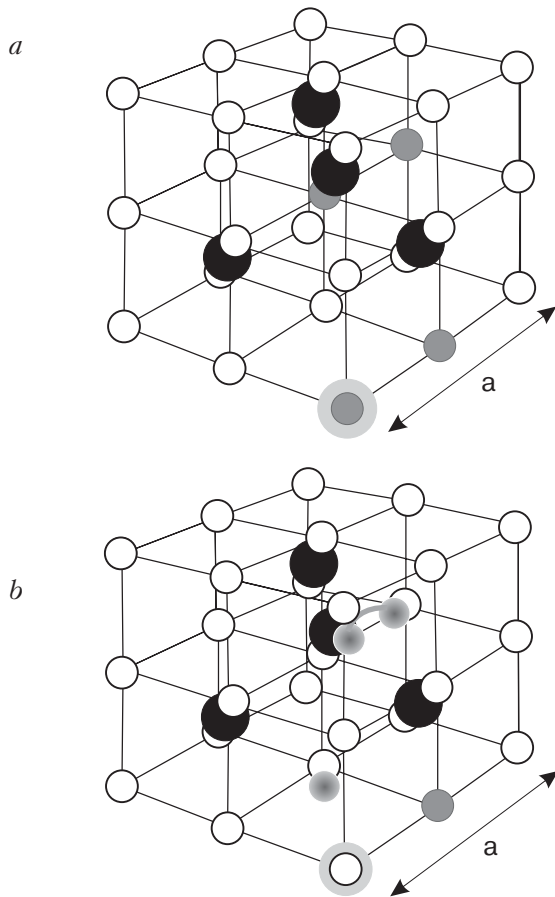
Fig. 6. Relaxation of the exciton in CaF$_2$ at 80 K with the hole staying at the π_u MO state. (*a*) The set of four grey F atoms are those taking part in the hole center bonds. (*b*) The final relaxed defects reached after about 50 fs. The centers are respectively an *F* center (large grey circle), an *I* center (inside an unoccupied cube) and a V_k center (represented by a dumbbell).

(000)), an *I* center (F$^-$ at (0.5,0.5,0.5)), and a V_k center formed between the F atoms at (111) and (211). In the second case, the relaxed STE shown in Fig. 4,*b* served as the starting point and the hole was then brought to the same π_u (2..1222) MO. Again within about 50 fs after the hole excitation, the same set of defects as above was formed. We have studied also other sets of F atoms with several different hole excited states. Generally, a similar set of defects was created. We found that under excitation of hole center, similar defect sets are created in both KBr and CaF$_2$ despite the difference in the lattice structure. In the fluorites the formation of the *I* center was more clear than in KBr, due to the presence of unoccupied body center of the elementary cubes. The production of these centers in CaF$_2$ [9] have been reported and therefore lend support to our work.

4. Discussion

The results of molecular dynamics study obtained for the lowest energy triplet STE confirm the earlier static calculations for both KBr and CaF$_2$. It, however, gives the time scale the relaxation takes to reach the equilibrium starting from a localized Frenkel-type exciton. The study of the hole excited STE relaxation produced quite novel results in both materials. The main motivation of the present work was to examine the possible channels of *F*−*H* pair creation from excited hole states as has been recently discussed [4]. The study of higher excited states is intrinsically more complicated due to the crowding of many states, of both electron and hole excitation. Also their lifetimes are expected to be quite shorter than that of the triplet state which is typically between ms and μs. In [4], the authors argued that this excited hole-mediated channel would be faster than the dynamic channel. Indeed according to the present study, the hole excited state produces a second nearest neighbor hole center (a V_k center) within about 0.5 ps, compared with the dynamic channel taking about 1.25 ps (creating an *H* center). There are, however, several aspects which present difficulties. First, in the «direct» channel the hole center produced is not an *H* center, but a V_k center. Second, the electron localized on the anion site has a Br$^-$ very close by (refer to Figs. 2, 3 above), with its energy raised upward as a result. Both are attributable to the excited hole jumping to a distant site and forming a Br$_2^-$ center, rather than undergoing a sequence of bond switching as does the triplet state STE shown in Fig. 1.

It is to be noted that the monitoring of fast species creation is done by observing the rise of absorption of the prove light corresponding to the *F* center or the STE. From Fig. 1 it appears that a relatively well formed *F* center appears as soon as the first Br atom has reached the site of the next anion site taking barely 1 ps. It is therefore possible that the primitive *F* center shows up as early as this fast. The off-center STE may appear at some later time. Because the off-center STE and a well separated *F*−*H* pair are on the same adiabatic energy surface, it is not immediately clear where the two species part in Fig. 1. In the ODMR study of correlated *F*−*H* pair in KBr at 4 K, Meise et al. [10] have reported that stable pairs are mostly in the fourth nearest neighbors. It is therefore reasonable to argue that the nascent *F* center appears earlier than the STE by maybe about 1 ps in the dynamic channel. More studies are needed. It would be interesting to conduct experiment monitoring the onset of the hole center absorption, thereby distinguishing the *H* center from the V_k center which seem to separate the dynamic channel from the «direct» chan-

nel. In both KBr and CaF_2 the resulting defects are rather similar under hole excitation. They can be identified as an *F* center, an interstitial anion (known as *I* center) and a V_k center. Such combination of defects has been reported in AEF [9]. This has not been reported in alkali halides of NaCl lattice.

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