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Lattice relaxation of highly excited self-trapped excitons in CaF_2

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We have investigated relaxation in the lattice of CaF_2 at 80 K, caused by the electronic excitation of self-trapped excitons. We employed sequential excitation: first an electron pulse to create self-trapped excitons, and second a laser pulse addressed to the electron or the hole. Hole excitation gives rise to stable *F* centers; these are not generated in significant numbers by an electron pulse alone. Excitation of the electron produces only the transient species, which are also generated by irradiation with an electron pulse.

I. INTRODUCTION

It is well established that lattice defects are formed by electronic excitation in certain types of inorganic insulators, as a result of the adiabatic instability of self-trapped excitons. A typical example is defect formation in alkali halides, in which an exciton is self-trapped within about 1 ps and subsequently removed by one of the following deexcitation channels: (a) deexcitation to the ground state by radiative or nonradiative recombination through its lowest state, and (2) conversion to a pair comprised of a vacancy (an *F* center) and an interstitial (an *H* center) pair.[1–3] Processes similar to those in alkali halides are considered to be the cause of defect formation in some other insulators, such as alkaline-earth fluorides[4,5] and even in amorphous SiO_2.[6] The defect-formation processes described above are induced by individual excitation events; we refer to them as single-exciton process.

There are a few series of phenomena which are considered to be induced by electronic excitation but cannot yet be accounted for by single-exciton processes. One such series is comprised of the structure changes along heavy-ion tracks in insulators, including quartz, CaF_2, and several minerals.[7] Chemical etching attacks material at these tracks much more rapidly than in the undamaged region. Recent observation of pre-etching tracks by Duraud *et al.*[8] for SiO_2 indicates that there is amorphous transformation at the tracks. Similar amorphous transformation has been observed upon irradiation of SiO_2 with an intense electron beam in an electron microscope.[9] It seems certain that electronic excitation is essential to track formation, but the mechanism is not yet clear. Earlier, Fleisher, Price, and Walker[7] suggested that the electric field generated by nonuniform charge distribution along the tracks causes dielectric breakdown and hence produces defects. This model cannot explain certain experimental findings.[10]

Laser damage defines another series of phenomena which cannot be explained by single-exciton processes. Many insulating materials, including alkali halides, alkaline-earth fluoride, and quartz, may be damaged by laser irradiation for photon energies well below the band gap. This phenomenon has also been attributed to dielectric breakdown induced by a strong electric field of an intense laser beam.[11] Deficiencies of the model were pointed out as long as a decade ago,[12,13] but as yet no definite conclusion has been drawn.

Track formation and laser damage are similar in that each is due to electronic excitation but cannot be attributed to single-exciton processes. The correlation of these two phenomena is not yet established. Unfortunately, both of these observations are macroscopic and our characterization of them is phenomenological. Some efforts have been made to observe the predamage stage,[8] but microscopic information on the defects or local disorder causing these phenomena cannot be obtained by simply measuring the effects of irradiation either with a laser beam or with heavy ions.

An approach to make clear the mechanism of the effects of electronic excitation in heavy-ion tracks and under laser irradiation is to consider the well-characterized microscopic processes which are known to occur under the given conditions. The results may be used for qualitative and quantitative analyses of the effects of heavy-ion irradiation and laser irradiation. Because of the relatively long lifetime of a self-trapped exciton and because of the extensive lattice relaxation associated with a self-trapped exciton, it may define a site for the localization of electronic excitation in solids, particularly for further excitation. It follows that, in solids in which excitons can be self-trapped, higher excited states of self-trapped excitons are generated, either by heavy-ion or laser irradiation. The former may support this because of the high spatial density of excitation[10] and the latter because of the large photon flux.[14,15]

Since an exciton is a two-particle system in solids, there are three modes of highly excited states: electron-excited states, hole-excited states,[16] and bulk-excited states localized by a self-trapped exciton.[17] Studies of the processes that follow electron excitation of self-trapped excitons in alkali halides were first carried out by Williams[18] and subsequently extended by several authors.[19–23] These studies have shown that excitation of the electron of a self-trapped exciton induces defect formation in alkali halides. Processes that follow the hole excitation have been studied recently by Tanimura *et al.* for

NaCl,[24] RbI,[25] and KI.[24] It has been shown that the hole-excited states of the self-trapped excitons can be converted efficiently to the electron-excited states and, hence, the effects of hole excitation do not differ from the effects of electron excitation in alkali halides. The efficient conversion from the hole-excited states to the electron-excited states has been ascribed to the Auger transition, arising from strong interaction between the electron- and hole-excited states. It is an open question whether the Auger transition is an efficient channel for the deexcitation of highly excited self-trapped excitons in other materials.

Among other simple ionic crystals which may support analogous processes, the alkaline-earth fluorides are of particular interest; because of the resisting damage, they have proved quite useful for laser windows. Like the alkali halides, however, they are susceptible to damage by sufficiently intense beams, even for photon energy less than the band-gap energy.[26,27] In view of this extensive use, it is of importance to understand the mechanism of laser damage.

Another interesting aspect of the alkaline-earth fluorides is the difference in the atomic structure of the self-trapped excitons from that in alkali halides. According to the studies of optically detected magnetic resonance, a self-trapped exciton in CaF_2, SrF_2, and BaF_2 is the closest possible pair of an *F* center and an *H* center (a F_2^- molecular ion on a F lattice point with a $\langle 111 \rangle$ orientation).[5,28] Measurements of the transient optical absorption induced by an electron pulse have indicated that the products are a composite.[5] An optical-absorption band due to the electron transition from the lowest 1*s* orbital to 2*p* orbitals and another broad band due to the hole transitions from the σ_g orbital to the antibonding σ_u orbital to the F_2^- molecular ion has been assigned. Further details of the nature of the component bands are not yet clear.

The purpose of the present paper is to show the nature of the transient optical absorption and the effects of electron and hole excitation of self-trapped excitons in CaF_2. We found that the transient optical-absorption change induced by an electron pulse is comprised of two components: one due to the self-trapped excitons and the other due to the *F* and *H* centers. We found also that both electron and hole excitation of the self-trapped excitons generate *F* centers; those generated by hole excitation are much more stable than those generated by electron excitation.

II. EXPERIMENTAL TECHNIQUES

The specimens were obtained from a crystal block of CaF_2, purchased from Harshaw Chemical Co. They were cut into a size $10 \times 6 \times 1$ mm^3. The 6×10 mm^2 surfaces were polished and the 6×1 mm^2 surfaces were cleaved (111) planes. A specimen was attached to a cold finger of a cryostat having three quartz windows and an aluminum window and placed in the optical path of an apparatus for measurements of transient optical absorption induced by irradiation with an electron pulse.

For generation of the self-trapped excitons, a specimen was bombarded with an electron pulse generated with a Febetron. The electron beam was incident on a 10×6 mm^2 surface. For further excitation of the self-trapped excitons generated by the electron pulses, either XeCl excimer-laser (Lambda Physik EMG201MSC) pulse (308 nm) or a Xe-lamp-pumped dye-laser (Phase R, DL2100A) pulse (475 nm) was directed to the opposite surface of the specimen, within the lifetime of the self-trapped excitons. The former is to excite the hole of a self-trapped exciton to the antibonding state of the F_2^- molecular ion and the latter is to excite the electron of a self-trapped exciton from the lowest 1*s* orbital to higher 2*p* orbitals. The probe light for optical-absorption measurements, either from a Xe flash lamp having a duration of 0.9 μs a continuous mercury-xenon lamp, was incident on a 6×1 mm^2 surface.

For transient optical-absorption studies we obtained either the time-averaged optical-absorption spectra using a pulsed probe-light beam and a multichannel spectrometer or the time change of the optical absorption at a fixed wavelength. The multichannel spectrometer consists of a flat-field grating monochromator (Jobin Yvón UFS-200) and a multichannel optical detector (Princeton Instruments D/SIDA). Optical-absorption spectra were determined by dividing the output spectral distribution by the spectral distribution of the light intensity determined by the same system. By changing the time delay of the flash lamp with respect to the electron pulse, we determined the optical-absorption spectra at several delay times. The use of an intense flash lamp enabled us to obtain optical-absorption spectra in the presence of relatively intense intrinsic luminescence. In order to obtain the transient optical-absorption change at a fixed wavelength, induced by an electron pulse and by a subsequent laser pulse, we used the experimental equipment described in Ref. 23. In this case the optical-absorption change was detected by a photomultiplier, placed after a monochromator, and recorded by an oscilloscope.

III. EXPERIMENTAL RESULTS

In order to make clear further details of the transient optical-absorption spectra of CaF_2 induced by an electron pulse, the time-resolved spectra were measured at 77 K. In Fig. 1 we show the decay curves of the optical-absorption change induced by irradiation with an electron pulse, measured at 3.40 eV (365 nm) [Fig. 1(a)] and 2.76 eV (450 nm) [Fig. 1(b)]. The latter photon energy corresponds to the peak of an absorption band due to the self-trapped exciton and the former is close to the peak (3.28 eV) of the *F* band. The decay curve measured at 2.76 eV is exponential, and the decay time is found to be 38.2 μs. This value agrees with the lifetime of a self-trapped exciton obtained by Williams *et al.* at 80 K. On the other hand, the decay curve measured at 3.40 eV includes another component which decays much faster than the self-trapped excitons. Subtracting the 38.2-μs component from the observed data, we obtained the dashed curve in Fig. 1(a). The resulting decay curve cannot be expressed as a single exponential function, but is fitted well by the sum of two such components; the decay

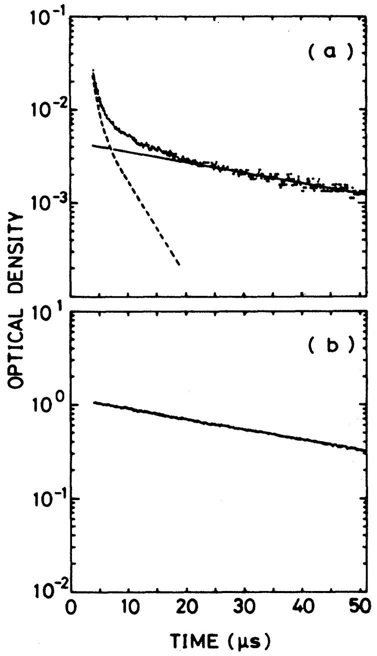

FIG. 1. The decay curves of the optical-absorption change of CaF_2 induced by irradiation with an electron pulse, measured with probing light of (a) 3.40 eV (365 nm) and (b) 2.76 eV (450 nm) at 80 K. Each dot represents one datum. The solid line shows the component of 38.2 μs and the dashed curve shows the difference between the data and the solid line.

times are 4.2 and 0.42 μs. We call these components component II.

The time-resolved optical-absorption spectra are shown in Fig. 2. Figure 2(a) shows the spectrum probed by a pulsed beam from a flash lamp incident at a delay time of 10 μs after excitation with a pulsed electron beam. Since the pulse duration (0.9 μs) is smaller than the delay, the spectrum can be regarded as that at a delay time of 10 μs. Since component II is annihilated substantially in 10 μs [see Fig. 1(a)], the spectrum shown in Fig. 2(a) exhibits a kinetic component decaying with a time constant of 38.2 μs; this is assigned to the self-trapped excitons. We refer to this component as component I or simply as self-trapped excitons. The spectral features are essentially the same as those obtained by Williams *et al.*[5] at 10 K, except that a dip around 3.4 eV is much sharper. The low-energy band has been ascribed to the electron transition and the high-energy band to the hole transition.

The spectrum measured with a pulsed Xe-lamp beam delayed by 0.5 μs may include component II [of Fig. 1(a)] as well as that due to self-trapped excitons. Since the fraction of the self-trapped excitons that decays before 2 μs is negligible, we subtracted the spectrum measured 2 μs after an electron pulse from that measured 0.5 μs after an electron pulse to obtain the optical-absorption spectrum due to component II. The difference, representing the optical-absorption spectrum of component II, is shown in Fig. 2(b). The spectrum consists of two broad bands peaking at 3.21 and around 4 eV. For a comparison, the optical-absorption spectrum of CaF_2 after continuous electron irradiation at 80 K is shown in Fig. 2(c).[29] The low-energy peak in Fig. 2(c) is the *F* band, and the high-energy peak may be attributed to *H* centers. Clearly, the peak of the low-energy band in Fig. 2(b) is close to the *F*-band peak. For a given electron pulse the ratio of the peak of component-II optical absorption to the low-energy self-trapped–exciton peak was found to be 0.15 at 80 K.

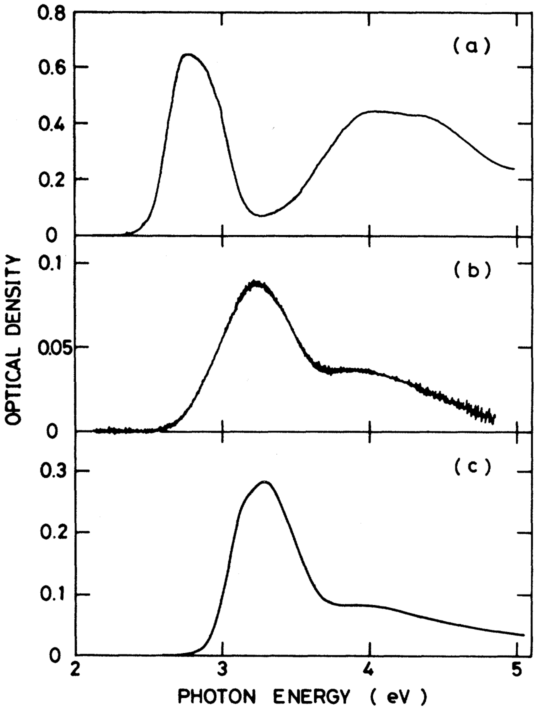

FIG. 2. Time-resolved optical-absorption spectra of CaF_2 after irradiation with an electron pulse: (a) 10 μs after irradiation, (b) the difference between the optical absorption 0.5 and 2 μs after irradiation with an electron pulse, and (c) the spectrum produced by continuous irradiation with electron beams at 80 K.

We now describe the optical-absorption change induced by irradiation with a laser pulse of 2.61 eV of a specimen which is populated with self-trapped excitons. According to the assignment by Williams *et al.*, a laser pulse of this photon energy induces electron excitation of self-trapped excitons. Irradiation with a laser pulse was carried out with a delay longer than 10 μs, where component II is not included. Figure 3 shows the oscilloscope traces of the optical-absorption change induced by sequential irradiation of an electron pulse and a 2.61-eV laser pulse, probed at 2.84 and 3.40 eV; at the former photon energy the optical-absorption band due to the self-trapped excitons dominates, and at the latter photon energy component II dominates. It is clear that photoexcitation of the self-trapped excitons annihilates them and enhances component II. The laser-induced decrease in optical absorption due to the self-trapped excitons and the laser-induced increase of component II were found to

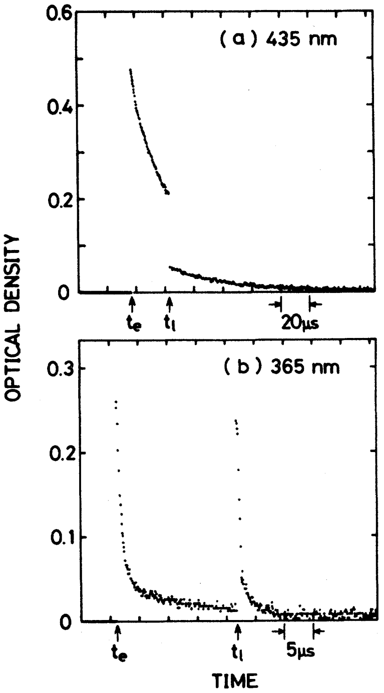

FIG. 3. Oscilloscope traces of the optical-absorption changes in CaF_2 induced by sequential irradiation with an electron pulse at t_e and with a 2.61-eV (475 nm) dye-laser pulse at t_l. The optical absorption is probed at (a) 2.85 eV (435 nm) and (b) 3.40 eV (365 nm).

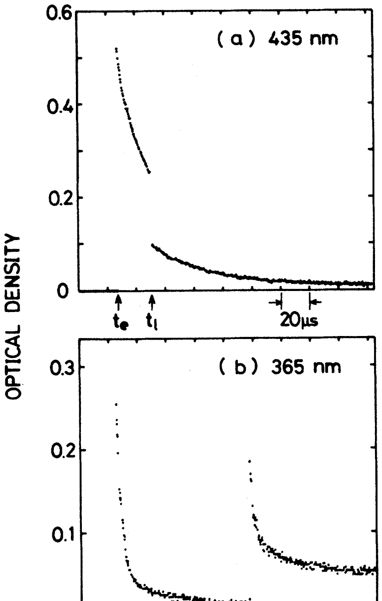

FIG. 4. Oscilloscope traces of the optical-absorption changes in CaF_2 induced by sequential irradiation with an electron pulse at t_e and a 4.03-eV (308 nm) excimer-laser pulse at t_l. The optical absorption is probed at (a) 2.85 eV (435 nm) and (b) 3.40 eV (365 nm).

be proportional to each other, indicating that the latter is produced from the former. We also found that the decay characteristics of component II produced by a laser pulse and an electron pulse agree with each other.

Figure 4 exhibits oscilloscope traces of the optical-absorption change induced by sequential irradiation with an electron pulse and a laser pulse of 4.03 eV, proved at (a) 2.84 eV and (b) 3.40 eV corresponding to data for 2.61-eV excitation in Fig. 3. A laser pulse of this photon energy induces hole excitation of the self-trapped excitons. Compared with Fig. 3, we note a remarkable difference in the optical-absorption change measured at 3.40 eV. In this case, besides formation of component II, there is a component that remains stable at least for a few hundred μs. We refer to this component as component III. The height of component III, the value 15 μs after the laser pulse, as a function of the monitoring photon energy is shown in Fig. 5. It is clear that component III is due to the *F* centers. Figure 6, which shows the correlation between the increment (ΔN_F) of component III and the decrement (ΔN_{STE}) of optical absorption due to the self-trapped excitons, clearly indicates that component III is generated by the hole excitation of the self-trapped excitons.

Even though both components II and III have a peak near the *F*-band maximum, their stabilities differ considerably. The higher stability can be ascribed to a larger *F*-*H* pair separation. Since the specimens are subjected to irradiation with light directly from the mercury-xenon lamp during measurements of transient absorption, we were unable to determine the stability of the *F* centers of this component in the dark; under irradiation with a mercury-xenon lamp, component III was annihilated within a few minutes. However, we found that irradia-

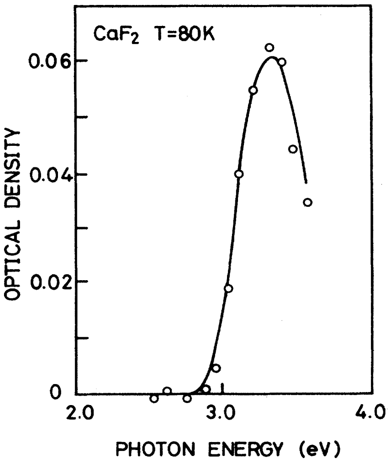

FIG. 5. The spectrum of the stable component of the optical-absorption change, generated by sequential irradiation of CaF_2 with an electron pulse and a 4.03-eV excimer-laser pulse at 80 K. The amount of the optical-absorption change 10 μs after the laser pulse is plotted.

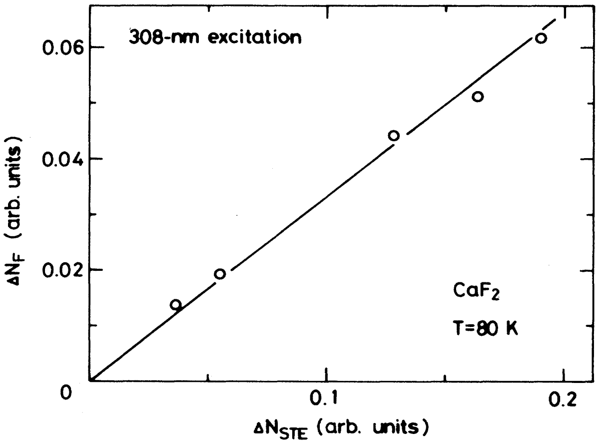

FIG. 6. The relation between the laser-induced increment (ΔN_F) of the stable component of the optical-absorption change probed at 3.40 eV and the laser-induced decrement (ΔN_{STE}) of the optical-absorption change, probed at 2.84 eV, due to the self-trapped excitons of CaF_2, induced by irradiation with a 308-nm excimer-laser pulse.

tion with an electron pulse alone generates component III after the combined electron and 4.03-eV laser-pulse irradiation. Therefore it appears that the *F* centers giving rise to component III are bleached, leaving halogen vacancies which are converted to *F* centers by trapping electrons by the next electron-pulse irradiation. Thus we consider that the *F* centers generated by hole excitation of the self-trapped excitons are relatively stable and we refer to them as stable *F* centers.

IV. DISCUSSION

Study of the transient optical-absorption change induced by irradiation of CaF_2 with an electron pulse indicates the generation of at least two components: component I due to the self-trapped excitons, and component II. Both components I and II have two major optical-absorption bands: one in the visible region and the other in the ultraviolet region. Furthermore, the excitation of the electron associated with a self-trapped exciton converts component I into component II. Existence of two components of similar nature has been observed in SrF_2.[30] For SrF_2, component I was also ascribed to self-trapped excitons. In Table I we show the peak positions of the optical-absorption bands and the decay times for these two components in CaF_2 and SrF_2. For both of these crystals, the yield of the self-trapped excitons by irradiation with an electron pulse is larger than that of component II.

Since component II is generated by electron excitation of self-trapped excitons, it has been assigned to be an *F-H* pair having another configuration.[30,31] Naturally we consider that the optical transition energy of the electron of a self-trapped exciton or an *F-H* pair differs from that of the *F* band because of the presence of the *H* center in its proximity. Therefore if components I and II are due to *F-H* pairs with different separation, the distant pair should have an optical transition energy closer to the *F* band and a longer lifetime. This ordering holds for SrF_2 but not for CaF_2. At present, no conclusion can be derived for this apparent conflict. One may argue that the lifetime depends more strongly on the orientation of the molecular ion, although the peak energy of the *F* band may be a smooth function of the separation. Thus the molecular orientation of the *F-H* pairs at the next-nearest neighbors in CaF_2 may be in favor of rapid recombination.

The results of the present investigation indicate very clearly that optical hole excitation of the self-trapped excitons in CaF_2 creates the stable *F* centers, while electron excitation exclusively generates component II or the *F-H* pairs of another configuration. It follows that the effects of excitation of the hole differ remarkably from the effect of excitation of the electron. Since the hole-excited state reached by optical absorption at the ultraviolet region is the antibonding state of the F_2^- molecular ion, one of the fluorine atoms is considered to be ejected from the lattice point, resulting in formation of a distant *F-H* pair. We note that excitation of the electron, which does not contribute to the bonding, can produce only a small change in the structure of the *F-H* pair.

The results that the distant *F-H* pairs are generated by hole excitation of the self-trapped excitons suggests that the radiation effects under dense electronic excitation or under laser irradiation may possibly differ from radiation

TABLE I. Two major transient components in the optical-absorption change induced by irradiation with an electron pulse in CaF_2 and SrF_2.

	CaF_2[a]				SrF_2[b]		
Components	Peak energy (eV)		Decay time (μs)		Peak energy (eV)		Decay time (μs)
I (self-trapped excitons)	2.75	4.0	38.2		2.34	4.13	59
II	3.21	4.0	0.42	4.2	2.7	3.35	7700
F band	3.30				2.80		

[a] Measured at 80 K.

[b] Reference 30; measured at 6 K.

effects under conventional ionizing radiation. Hole-excited states of the self-trapped exciton will be certainly generated under intense laser irradiation with photon energies near 350 nm. It is also plausible that under dense electronic excitation, as in heavy-ion tracks, a hole-excited self-trapped exciton may be generated by interaction of two excitation events. Thus the present results may give a clue to the mechanism of radiation effects in heavy-ion tracks and by laser irradiation.

The present results have also some significance on the mechanism of defect creation in an alkaline-earth fluoride under conventional irradiation. Irradiation with an electron pulse generates self-trapped excitons but almost no stable *F* centers, unless self-trapped excitons are reexcited. It is known, however, that continuous irradiation with ionizing particles produces stable *F* centers and *H* centers at an efficiency of about 10^{-2} of that to produce self-trapped excitons.[32] The mechanism of the formation of the stable defects is not yet clear. Because of a large linear energy deposition density of low-energy secondary electrons, the probability that two consecutive excitations occur along the tracks of low-energy electrons is relatively high and evaluated to be about 10^{-2} of a single excitation.[33,34] Thus it is plausible that the stable defects are generated only by interaction between two excitation events, as originally suggested by Klick in a somewhat different concept.[35]

The effects of hole excitation of the self-trapped excitons in CaF_2, found in the present paper, are remarkably different from those in NaCl. In NaCl the effects of hole excitation have been found to be very similar to those of electron excitation, in regard to generation of the singlet luminescence and reorientation of the self-trapped excitons.[24] Therefore it was concluded that the Auger process converts the hole-excited state of the self-trapped exciton to a pair comprised of a free electron and a self-trapped hole, with the hole at the ground state. In CaF_2 it is likely that, because of the open-spaced lattice structure, excitation to the antibonding state separates an *F* atom to a distance from which no recovery occurs at low temperatures. It may be also the case that the Auger-transition probability is low because of a small overlap in the energy between the hole-excited state and the state comprising a V_k center and a free electron.

In conclusion, we have shown clearly that hole excitation of self-trapped excitons in CaF_2 creates stable *F* centers. Thus the present experimental result has demonstrated that a highly excited self-trapped exciton has an instability toward conversion to a stable *F-H* pair. The excitation of the hole of a self-trapped exciton may occur at a high rate under intense midgap laser irradiation and in heavy-ion tracks.

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