Femtosecond time-resolved spectroscopy of the formation of self-trapped excitons in CaF$_2$

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Self-trapped excitons (STE's) in CaF$_2$ are formed via two distinct processes after band-gap excitation by femtosecond light pulses at low temperatures; the fast process terminates within a few ps after excitation, and the slow process that follows the former lasts over 20 ps. The fast formation of STE's is associated with the decay of the precursor, which shows a broad absorption in visible region. The relaxation pathways of electron-hole pairs are discussed based on the experimental results and their analysis in terms of a rate-equation model.

I. INTRODUCTION

The lattice relaxation of holes, excitons, and free electron-hole (e-h) pairs has been known as a typical phenomena of relaxation processes of elementary excitations in solids with strong electron-phonon interaction.[1] Extensive studies of the relaxation processes in alkali halides have shown that excitons or (e-h) pairs relax into several different configurations, showing a strong contrast to the hole that takes only one stable relaxed configuration known as the V_K center.[2,3] The formation of several relaxed configurations of excitons has been attributed to the strong interplay between electron-phonon and hole-phonon interaction. The interplay is now regarded as the primary origin of the formation of lattice defects of the Frenkel pair, (F-H) pair, consisting of an F center, an electron trapped at a halogen vacancy, and an H center, an interstitial halogen atom in the form of halogen-molecular ion occupying a single halogen site. Microscopic understanding of the relaxation process of e-h pairs in alkali halides has been achieved by recent studies by means of femtosecond spectroscopy studies.[4–8]

CaF$_2$ and other fluorite crystals are other well-known examples where holes and excitons are self-trapped. Experimental and theoretical studies have revealed the structure of the STE that consists of a F$_2^-$ (F denotes a fluorine atom) molecular ion oriented along the ⟨111⟩ direction with a neighboring F center.[9,10] Since the self-trapped hole (STH), or the V_K center, has the configuration that is a F$_2^-$ molecular ion oriented along the ⟨100⟩ direction,[11] strong interplay between the electron-phonon and hole-phonon interaction is evident also in these crystals; translational and rotational motions of the F$_2^-$ molecular ion have been assumed upon recombination of the STH with an electron to reach this STE configuration. How these displacements takes place after e-h recombination is an interesting problem for understanding microscopic origin of the strong electron-phonon interaction that leads to the Stokes shift as large as 7 eV. Also, the basic knowledge of the primary process provides a sound basis for understanding several laser-induced effects in this practically important wide-gap material. Although a few studies have been done for clarifying the relaxation process of (e-h) pairs in fluoride crystals,[12,13] the dynamics of forming STE's has not yet been well resolved.

In this paper, I present the results of femtosecond time-resolved spectroscopy of the formation of STE's in CaF$_2$ at low temperatures. A transient state that acts as the precursor of the STE is detected, and the two-step process of STE formation is revealed. These features are discussed referring to the relaxation process of e-h pairs in alkali halides studied previously.

II. EXPERIMENT

Specimens of a thickness of about 1.0 mm of pure CaF$_2$ were obtained from crystal blocks purchased from Harshaw Chemical Co. 120-fs laser pulses, 804 nm in wavelength and 5 mJ in energy/pulse, were generated by a laser system comprising a mode-locked Tr.saphire laser (Coherent, Mira 900F) and a regenerative amplifier pumped with a Q-switched Nd:YAG (yttrium aluminum garnet) laser (BMI, Alpha-10). The third harmonics (268 nm) generated by two BBO crystals with their thickness of 0.3 mm were used for generating (e-h) pairs by multiphoton absorption, and the femtosecond white-light pulses generated in a H$_2$O cell by the fundamental beam were employed for probing optical absorption. The temporal width of the 268-nm pulses was estimated to be 350 fs. The optical absorption spectra were obtained in a range between 1.7 to 2.9 eV. An optical delay line controlled time delay of the probe pulse with respect to the incidence of the excitation pulse. The absorption spectra measured for respective lengths of the optical-delay line were used to obtain the time-resolved absorption spectra at time delays in the range from −10 to 150 ps by correcting the effects of the group-velocity dispersion of the white-light pulse.

III. RESULTS

Figure 1 shows the time-resolved optical absorption spectra in CaF$_2$ at 6 K after irradiation with a femtosecond laser pulse. The delay of the probe pulse with respect to the excitation pulse is indicated at each panel. In the top panel is shown, for comparison, the absorption band due to the STE in CaF$_2$ at 8 K generated by irradiation with a 1-MeV electron pulse and measured 2 μs after irradiation. The band peaked at 2.75 eV has been assigned to the electron transition of the STE.[14] As seen in the spectra at time delay later than 5 ps, the STE-absorption band is certainly induced by our fs-laser pulses. Since the optical band gap in CaF$_2$ is 12.1 eV,[15] three-photon absorption (and/or four-photon absorp-
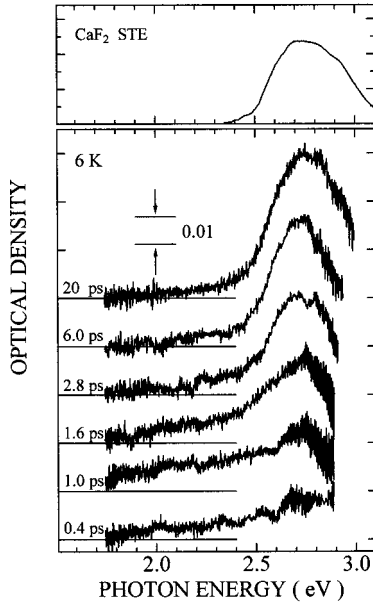
FIG. 1. Time series of optical absorption spectra in CaF$_2$ at 6 K; the probe pulse delay is given in each spectrum. The top panel shows the optical absorption spectrum due to STE measured at 1 μs after 1-MeV electron-pulse irradiation at 8 K.

FIG. 2. Optical density changes at (a) 2.2 eV and (b) 2.75 eV in CaF$_2$ at 6 K as a function of delay after fs-laser excitation. The curves in the figure are the results of analysis by using a rate-equation model (see the text); the broken, thin solid, and chain-dot curves represent temporal changes of the B band, the STE band formed at the first stage, and that formed at the second stage of relaxation, respectively. The best-fit parameters are the following: $t_0 = 0.4$ ps, $w = 0.55$ ps, $\tau_B = 0.9$ ps, $k_{BI} = 3.3 \times 10^{11}$ s^{-1}, $k_{BS} = 7.7 \times 10^{11}$ s^{-1}, and $\tau_1 = 5.0$ ps (for the meaning of the symbols, see the text).

tion) of 4.6-eV photons can generate (e-h) pairs. Because of the higher-order optical processes, the amount of induced optical absorption is low; the largest value of optical density is less than 0.1. However, spectral features of induced absorption are clearly resolved in the present results.

A broad band extending over the whole photon-energy range of the present detection system characterizes the time-resolved spectra before 1 ps after excitation. This broad band, called hereafter the B band, increases till a maximum intensity at 1 ps after excitation, where the absorption-band peak at 2.75 eV starts to grow. The STE band is clearly resolved 2.8 ps after excitation and it continues to grow till about 30 ps after excitation. After 30 ps, the induced absorption spectra remains almost unchanged till 150 ps.

In Fig. 2 is shown the temporal evolution of the optical absorption measured at 2.2 and 2.75 eV, respectively. In the figure, curves represent the results of analysis based on a rate-equation model, the details of which will be given later. The optical absorption at 2.2 eV, at which STE's have little contribution to absorption strength, monitors mainly the temporal evolution of the B absorption band. It reaches a maximum at about 1 ps after excitation and decays within 5 ps. The long-lasting component is ascribed to the small overlap of the STE absorption band. Based on this temporal change at 2.2 eV, we can introduce the first stage of the relaxation of (e-h) pairs, which terminates within 5 ps after excitation. The formation and annihilation of the B band characterize this first stage. On the other hand, the optical absorption at 2.75 eV, which is mostly due to the STE band as evidenced by the spectra in Fig. 1, certainly growths within 5 ps, but with a noticeable persistent growth after 5 ps till 30 ps. This persistent growth of the STE band indicates that the process of forming STE's is not a single process and suggests
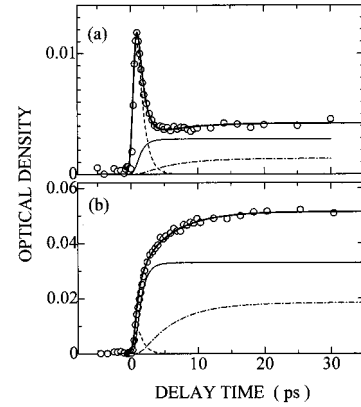
strongly the presence of the second stage of the relaxation of (e-h) pairs, which follows the first stage.

IV. DISCUSSION

The relaxation of (e-h) pairs in alkali halides has been characterized by the two-step relaxation in inducing structural change of forming (F-H) pairs and generating STE's. In the first stage of the relaxation, a complex consisting of an electron and the relaxing hole is formed; the complex is designated as ($B+e$), where B denotes the relaxing holes showing the B band. In specimens doped with electron-trapping impurities, where relaxation of holes can be detected by the optical absorption spectrum, the relaxing holes are eventually converted into the V_K centers within 10 ps.[4–8] In pure specimens, the dynamical instability is induced to decompose the complex into the (F-H) pair at a certain step of the relaxation of ($B+e$), leading to the fast formation of (F-H) pairs. Competitively, the on-center STE is generated through the cooling transition of ($B+e$), and the off-center relaxation of the on-center STE formed in the first stage then follows to form (F-H) pairs and the off-center STE in the second stage of the relaxation. The configuration-coordinate diagram portraying schematically the relaxation process, taken from Ref. 5, is shown in Fig. 3.

Comparing the features of the relaxation of (e-h) pairs in CaF$_2$ with those in alkali halides described above, we find significant similarities in the aspects of the formation and annihilation of the broad absorption band in the initial step of relaxation, and of the presence of the slow (or the second) stage of forming STE's. Based on the similarities, I use a system of rate equations formulated in the relaxation processes in alkali halides for analyzing temporal evolution of optical absorption in CaF$_2$. In the analysis, I treat the two

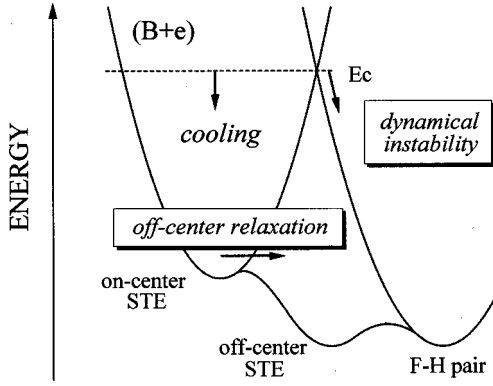FIG. 3. The schematic configuration co-ordinate diagram showing the model of relaxation pathways of $(e\text{-}h)$ pairs in alkali halides. $(B+e)$ stands for the state comprising an electron and a relaxing hole. Arrows show possible relaxation routes (from Ref. 5).

configurations of the off-center STE and $(F\text{-}H)$ pair in Fig. 3, which are distinctive in alkali halides, to be the same final product of $(e\text{-}h)$ relaxation in CaF_2. One reason for that comes from the fact that $(F\text{-}H)$ pairs are not formed in CaF_2 under ordinal excitation condition at low temperature. Furthermore, the configuration of STE's in CaF_2 can be regarded as the nearest-neighboring $(F\text{-}H)$ pairs. A critical discussion will be made later on states represented by the rate equations.

The system of rate equations, based on the relaxation model shown in Fig. 3, has included a generation function of the $(B+e)$ state for describing the relaxation process of holes. As discussed in detail by Sugiyama *et al.*,[5] the function is a phenomenological representation of the dephasing effects of the lattice relaxation at various lattice sites and of a convolution of the unresolved primary steps in the hole-relaxation process before forming localized hole states responsible for the B band. The function $g(t)$ is given by a Gaussian of the form of

$$ g(t)\exp\left\{-\frac{(t-t_0)^2}{w^2}\right\}, \qquad (1) $$

and it is characterized by the overall delay t_0 and the distribution with a half width of $w/\sqrt{4\ln 2}$. By using this $g(t)$, populations n_B of $(B+e)$, n_S of the STE, and n_I of the intermediate state, which is responsible for the second stage of the relaxation, are governed by the following equations:

$$ \frac{dn_B}{dt}=g(t)-\frac{1}{\tau_B}n_B, \qquad (2) $$

$$ \frac{dn_I}{dt}=k_{\mathrm{BI}}n_B-\frac{1}{\tau_I}n_I, \qquad (3) $$

$$ \frac{dn_S}{dt}=k_{\mathrm{BS}}n_B+k_{\mathrm{BS}}n_I, \qquad (4) $$

where τ_B and τ_I are the lifetimes of the $(B+e)$ and the intermediate states, and k_{BI} and k_{BS} are the transition rates

from $(B+e)$ to the intermediate state and to the STE, respectively. By using these rate equations, the concentrations of n_B, n_I, and n_S were calculated numerically as a function of delay after excitation, using a fourth-order Runge-Kutta algorithm, to get the fitting to the temporal evolution of optical densities at the two-photon energies. The curves shown in Fig. 2 represent the calculated results of the best fit. The broken curve is the temporal change of the B state, the thin solid curve is the component of STE's formed directly from the B state, and the chain curve represents the component of STE's formed via the intermediate state. The thick solid curve pertaining to the data points is the sum of these three components contributing to the optical density at a given photon energy. It is evident that the analysis in terms of the rate-equation model describes satisfactorily the temporal evolution of optical densities at different photon energies. When the intermediate state was omitted from the set of rate equations, by assuming the single step of the STE formation, which occurs as a result of the decay of the $(B+e)$ state, no reasonable fits with the same set of parameters were obtained for the temporal changes in optical density at different photon energies. Therefore, we can conclude here that the relaxation of $(e\text{-}h)$ pairs in CaF_2 includes two stages similar to the case in alkali halides.

The presence of the two stages of the STE formation revealed above could be ascribed to the two different processes of the recombination of photogenerated $(e\text{-}h)$ pairs, although an intermediate state formed after $(e\text{-}h)$ recombination has been assumed in the rate-equation model. However, previous interferometry studies of free electrons in wide-gap crystals have demonstrated that the decay of free electrons, or the localization can be described by a single-step process with a material- and density-dependent rate: no clearly resolved two-step recombination has been observed.[16] Furthermore, if a slow process of recombination of $(e\text{-}h)$ pairs, like uncorrelated pairs, is responsible for the second stage, then one may expect the B-band component that decays with the time-constant characteristic of the second stage, since $\tau_B < \tau_I$. However, we could not detect any such a component of the B band. Therefore, the introduction of the intermediate state formed after recombination of $(e\text{-}h)$ pairs may be more reasonable for explaining the second stage of the STE formation.

The above results and discussions have suggested that two transient species are involved in the formation process of STE's, these are the state responsible for the B band and an intermediate state responsible for the slow growth of STE's. In the case of alkali halides, the state responsible for the B band has been identified to be the relaxing hole, which is a localized hole on the way of relaxation into the V_K center. In CaF_2, the V_K center is also formed and the center shows a characteristic absorption band above 3 eV.[11] Therefore, the V_K center itself cannot be the state responsible for the B band. Although no detailed studied of hole relaxation have yet been made for CaF_2, it may not be unreasonable to assume that similar relaxing holes on the way of relaxation into V_K center are formed during the hole-relaxation process. Therefore, the relaxing hole trapping an electron can be a candidate of $(B+e)$, similar to the case in alkali halides.

Alternatively, one may ascribe the B band to the free-electron absorption. An interferometry study[16] for photogenerated free electrons in wide-gap insulators has shown that the lifetime of free electrons is the order of a few ps, which is almost the same as the lifetime of the B band. However, the B band reaches the maximum height only at 1 ps after excitation, showing a significant delay after excitation, while the rise of free-electron absorption is expected to be much faster. Thus, I tentatively ascribe the origin of the B band to the relaxing holes in CaF_2, although more detailed studies are certainly desired for definite conclusion.

The assignment of responsibility to the intermediate state responsible for the slow growth of STE's is more speculative, but I tentatively assume that the state is the ''on-center STE'' in CaF_2, in which the hole component of F_2^- is still oriented along a $\langle 100 \rangle$ direction with a trapped electron at a diffused orbital. Since the configuration of the STE in CaF_2 is achieved only through translational and rotational motion of the F_2^--molecular ion from the original V_K-center site, several possible intermediate configurations may be generated though temporarily. Previous time-resolved luminescence measurements have shown several components with lifetimes extending from a few tens ns to ms.[14] These components have been assigned to several morphologies resulting from possible combination between a neighboring F center and an interstitial F_2^- molecular ion.[14] However, the lifetime of the intermediate state responsible for the slow

growth of STE's is as short as 5 ps, so that these possible morphologies of the off-center STE's cannot be a candidate; the intermediate state may have the configuration before off-center displacement is induced. Therefore, the on-center STE in CaF_2, which has not identified yet, can be a possible candidate of the intermediate state that governs the slow stage of the STE formation.

In this paper, I have studied the dynamics of the relaxation of $(e\text{-}h)$ pairs in CaF_2. Based on the results and their analysis, it has been shown that STE's are formed through two distinctive stages. In the first stage, the state responsible for the B band acts as the precursor of STE's, and the state is tentatively assumed to be the relaxing hole. As the intermediate state that is responsible for the slow growth of STE's, a hypothetical entity of the on-center STE in CaF_2 crystals is proposed. More detailed measurements for a wider photon-energy region are certainly required to identify the intermediate configurations of $(e\text{-}h)$ pairs leading to STE's, and hence to clarify the relaxation process of this wide-gap insulator.

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