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Abstract. The dynamics of the formation of self-trapped excitons (STEs) and of Frenkel pairs have been studied in KCl and RbCl upon band-gap excitation by femtosecond laser pulses. The relaxation process of photogenerated electron–hole e–h pairs is found to comprise two distinct stages with different natures. The Frenkel pair consisting of an F and an H centre is formed in the first stage which terminates within a few picoseconds after excitation, while the STE with the off-centre configuration is formed only at the second stage which follows the first stage and lasts over 20 ps at low temperatures. The relaxation pathways of e–h pairs and their temperature-dependent changes are examined and discussed on the basis of the experimental results and their analysis in terms of a rate-equation model.

1. Introduction

The lattice relaxation of holes, excitons and free electron–hole e–h pairs in alkali halide crystals has been studied extensively as a typical example of relaxation processes of elementary excitations in solids with a strong electron–phonon interaction [1, 2]. Self-trapping of holes or of excitons has been well documented, and the structural and electronic properties of the self-trapped holes (STHs) and the self-trapped excitons (STEs) have been determined in detail [2]. In contrast with the hole which takes only one stable relaxed configuration, known as the V_K centre, in the form of an X_2^- molecular ion (X denotes a halogen atom) occupying two adjacent halogen sites [3], excitons or e–h pairs have been shown to relax into several different configurations. These include not only the three distinct structures of STEs, which are often classified as types I, II and III [4], but also the Frenkel pair consisting of an F centre, an electron trapped at a halogen vacancy, and an H centre, an interstitial halogen atom in the form of X_2^- molecular ion occupying a single halogen site. The Frenkel pair is called hereafter the F–H pair.

Extensive studies on the structures of the STEs in alkali halides by means of resonance Raman spectroscopy [5, 6] and optical spectroscopy for absorption [7, 8] and luminescence [4] have shown clearly that the hole component, the X_2^- molecular ion, of type I STE maintains almost the same vibrational and electronic properties as those of the V_K centre, and that the electron is bound with a diffused orbital around the hole. Therefore, the type I STE has the structure of the V_K centre which traps an electron and is usually referred to as the on-centre STE [2, 9]. On the other hand, the type III STE is essentially the nearest-neighbour pair of an F centre and an H centre [6], showing a large displacement of the X_2^- molecular ion from the V_K-centre site along a $\langle 110 \rangle$ direction. This configuration is referred

to as the off-centre STE [2]. The type II STE, which is an exception, is presumed to have a configuration intermediate between the two. The formation of the off-centre configuration of the STE has been attributed to the strong interplay between electron–phonon and hole–phonon interactions, and the interplay is now regarded as the primary origin of the formation of lattice defects of F–H pairs [1, 2].

In some alkali halide crystals, two or three configurations of STEs can coexist, while only one type of STE (type I or type III) is formed in others [2]. Also, the yields of STEs with the respective configurations and of the F–H pairs have been shown to change strongly depending on the kind of crystal [10, 11]. These material-dependent changes in the structures and in their yields of the relaxed configurations of e–h pairs, which are the direct consequences of the characteristics in the relaxation of e–h pairs, are still far from well understood, although a phenomenological classification has been proposed [4]. Therefore, in order to understand the microscopic origin of these material-dependent changes, it is highly desired to study the dynamics of the relaxation process of e–h pairs more extensively for crystals which show typical features in these changes.

By applying the femtosecond time-resolved spectroscopy technique, Shibata *et al* [12]. have studied the relaxation process of e–h pairs in KBr and found that the process is classified into two distinct stages which have different natures. In the initial stage of the relaxation within 5–6 ps after excitation, the first stage, the complex consisting of an electron and the localized hole which is still on the way to relaxation into the V_K-centre configuration, or the relaxing hole, is generated, and the decay of the complex results in the fast formation of F–H pairs and on-centre STEs. The second stage of the relaxation, which follows the first stage and last over 100 ps at low temperatures, has been shown to be the off-centre relaxation of the on-centre STE into both the F–H pairs and the off-centre STEs. Thus, the on-centre STE is formed in the first stage, while the off-centre STE is generated only in the second stage. The F–H pairs are generated by two different processes in both the first and the second stages. Recent studies by Sugiyama *et al* [13] have shown that a similar relaxation process is the case in RbBr, too.

The two crystals KBr and RbBr used in the previous studies are typical examples in which both type I and type III STEs, as well as F–H pairs, are formed efficiently. Similar studies for other crystals which show different characteristic features are certainly needed for generalizing the relaxation processes of e–h pairs to a wider viewpoint, and for clarifying the origin of the material-dependent properties in generating several possible relaxed configurations of e–h pairs in alkali halides. In this paper, we report the results of the femtosecond time-resolved spectroscopy study of the relaxation of e–h pairs in KCl and RbCl in which only a type III STE has been observed within the three possible configurations of STEs.

2. Experimental details

Specimens of pure KCl and RbCl with a thickness of about 1.0 mm were obtained from crystal blocks purchased from Harshaw Chemical Co. 160 fs laser pulses, 804 nm in wavelength and 5 mJ in energy per pulse, were generated by a laser system comprising a mode-locked Ti:sapphire laser (Coherent, Mira 900F), a pulse stretcher–compressor (BMI SC400) and regenerative amplifier (BMI RA10) pumped with a *Q*-switched Nd:YAG laser (Spectra Physics GCR130). The third harmonics (268 nm), generated by two BBO crystals with a thickness of 0.5 mm, were used for generating e–h pairs by two-photon absorption, and the femtosecond white-light pulses generated in a H_2O 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 1.3 and 2.7 eV by analysing the spectra of the source beam and of the light transmitted through the specimen by a set of polychromators consisting of grating monochromators (Jobin–Yvon HR320) and photodiode array detectors (Princeton RY1024). The time delay of the probe pulse with respect to the incidence of the excitation pulse was controlled with an optical delay line. 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.
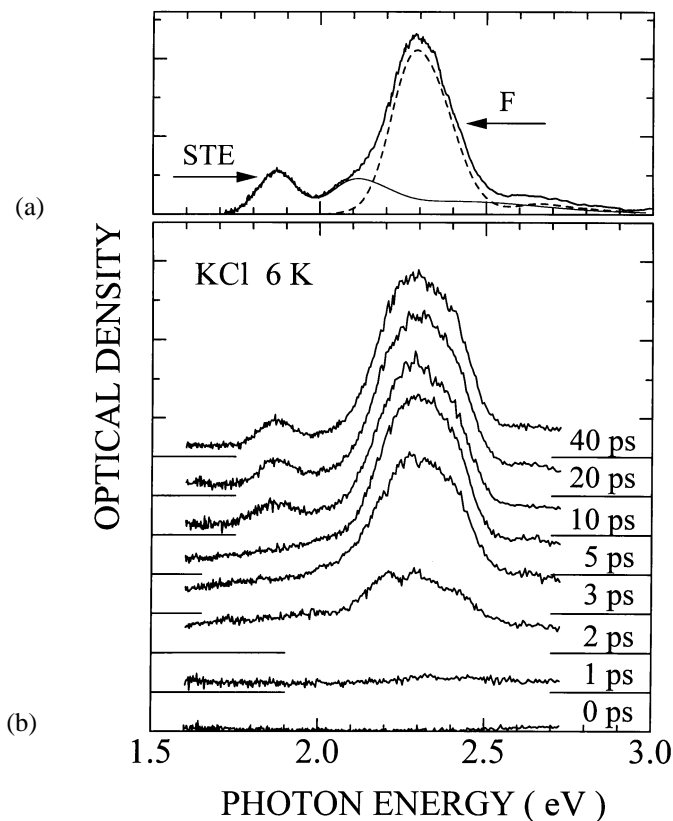

Figure 1. (a) The transient absorption spectrum measured at 1 μs after electron-pulse irradiation at 8 K; the absorption spectrum is decomposed into the STE band (thin solid curve) and the F band (broken curve). (b) Time series of optical absorption spectra in KCl at 6 K; the probe pulse delay is given for each curve.

3. Experimental results

Figure 1 shows the time-resolved optical absorption spectra of KCl at 6 K after irradiation with a femtosecond laser pulse. The delay t_d of the probe pulse with respect to the excitation pulse is indicated for each curve in figure 1(b). In the figure 1(a) are shown for comparison the absorption band due to the off-centre STE, the STE band and the F band for KCl at 8 K

generated by electron-pulse irradiation. The off-centre STE has two prominent absorption bands at 1.85 and 2.12 eV [14], while the F band shows a peak at 2.30 eV. The spectra before 1.2 ps are characterized by a broad band extending over the whole photon energy range of the present detection system. This broad absorption band seen in the initial step of the relaxation is called hereafter the B band. The F band at 2.30 eV is generated after 2 ps. On the other hand, the STE band at 1.85 eV is detected only after 7 ps. The absorption at 5 ps in this photon energy range still shows a broad band extending to a much lower energy range, while the STE band is clearly seen in the 10 ps spectrum. The result that the off-centre STE is generated only in the later stage of relaxation at 7–10 ps after excitation indicates that some intermediate states which act as the precursor of the off-centre STE are generated in the earlier stage of relaxation. After 25 ps, the absorption spectra induced remain almost unchanged until 150 ps.
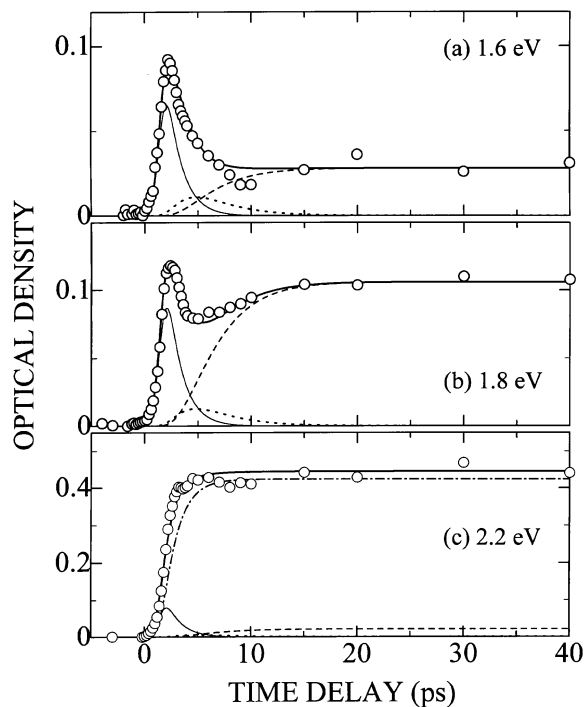

Figure 2. Optical density changes at (a) 1.6 eV, (b) 1.8 eV and (c) 2.2 eV in KCl at 6 K as functions of delay after two-photon band-to-band excitation. The solid curves pertaining to data points are the results of analysis using a rate-equation model (see the text). In (a), (b) and (c), the thin solid and dotted curves show the temporal evolution of the B band and the absorption band due to intermediate state I, respectively. In (a) and (b), the broken curve shows the temporal evolution of the STE band, and in (c) the chain and dotted curves show the two components of the growth of the F band.

In figures 2(a), 2(b) and 2(c), we show the temporal evolution of the optical absorption measured for KCl at 1.6 eV, 1.8 eV and 2.2 eV, respectively. In the figure, the solid, dotted, broken and chain curves represent the results of analysis based on a rate-equation model, the details of which will be given later. The optical absorption at 1.6 eV, at which neither STEs nor F centres make a significant contribution to the absorption strength, monitors mainly the temporal evolution of the B absorption band. It reaches a maximum at about

2 ps after excitation and decays within 10 ps. The long-lasting stable component is ascribed to the small overlap of the STE absorption band. On the other hand, the optical absorption at 2.2 eV is mostly due to the F band as evidenced by the spectra in figure 1. It is clear that the growth of the F band is completed within 5 ps. In contrast with the fast growth of the F band, the growth of the STE band monitored at 1.8 eV exhibits only slow growth which lasts over 20 ps; the apparent fast growth at 1.8 eV is primarily due to the B band as evidenced by the time-resolved spectra shown in figure 1.
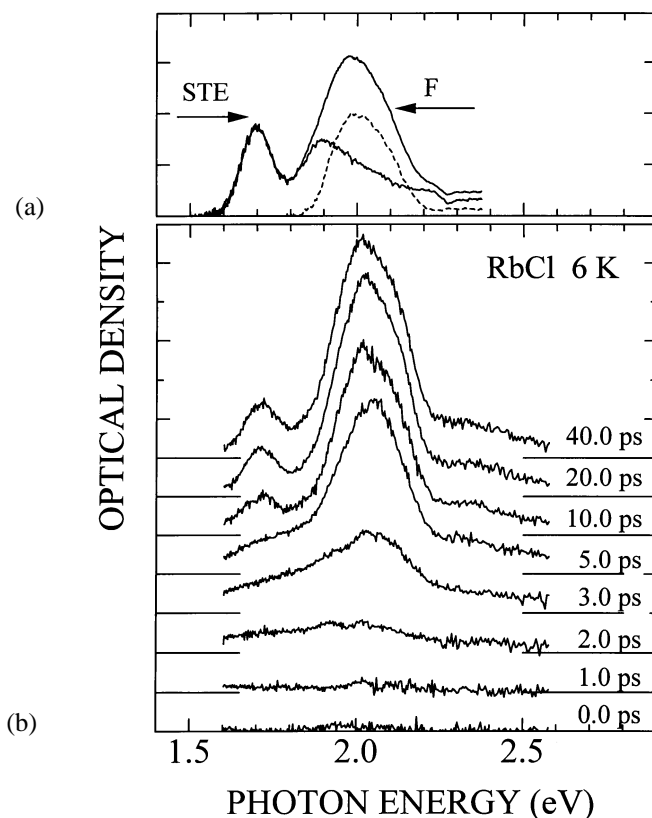

Figure 3. (a) The transient absorption spectrum measured at 1 μs after electron-pulse irradiation at 8 K; The absorption spectrum is decomposed into the STE band (thin solid curve) and the F band (broken curve). (b) Time series of optical absorption spectra for RbCl at 6 K; the probe pulse delay is given for each curve.

Figure 3 shows the time-resolved optical absorption spectra for RbCl at 6 K after irradiation with a femtosecond laser pulse. The delay t_d of the probe pulse with respect to the excitation pulse is indicated for each curve in figure 3(b). In figure 3(a) are shown for comparison the STE band and F band for RbCl at 8 K generated by electron-pulse irradiation. The STE band is characterized by two well resolved two peaks at 1.70 and 1.89 eV [14], while the F band shows a peak at 2.05 eV. Similarly to the case of KCl, the spectra before 2 ps are characterized by a broad band extending over the whole photon-energy range. The F band at 2.05 eV is detected after 3 ps, while the peak of the STE band at 1.70 eV is seen only after 10 ps. Thus, the off-centre STE is formed only in the

later stage of relaxation of e–h pairs in RbCl, similarly to the case in KCl. The absorption spectra induced remain almost unchanged after 25 ps until 150 ps.

In figures 4(a), 4(b) and 4(c), we show the temporal evolution of the optical absorption measured for RbCl at 1.6 eV, 1.7 eV and 2.0 eV, respectively. In these figures, the solid, dotted, broken and chain curves represent the results of analysis based on the rate-equation model. The optical absorption at 2.0 eV, which monitors the changes in the F-centre concentration, shows fast growth, while the STE band, monitored at 1.7 eV, exhibits only slow growth which lasts over 20 ps, similarly to the case for KCl. The fast-growth component at 1.7 eV is ascribed to the B band as seen in the time-resolved spectra shown in figure 3. In the temporal evolution of the optical density at 1.6 eV at which the STE absorption contributes less strongly than at 1.7 eV, fast growth associated with a partial decay of the absorption can be seen. However, the decay time of the absorption appears to be a little longer than for KCl (see figure 2(a)).
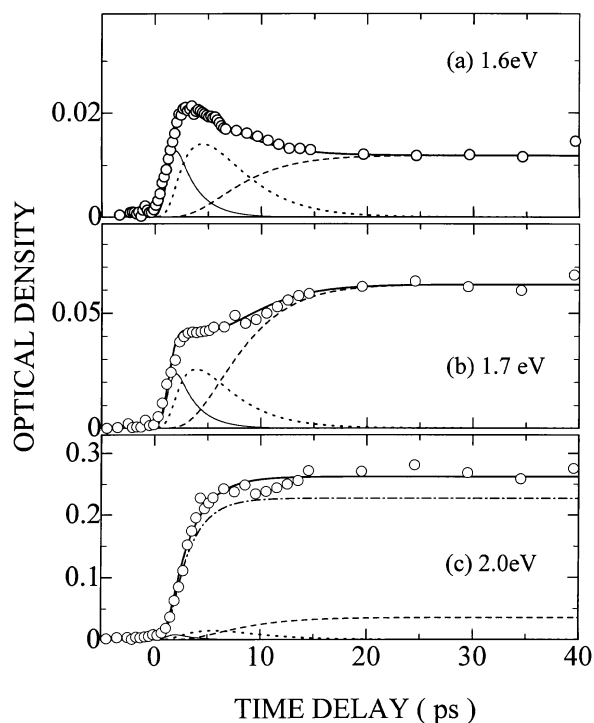

Figure 4. Optical density changes at (a) 1.6 eV, (b) 1.7 eV and (c) 2.0 eV in RbCl at 6 K as functions of delay after two-photon band-to-band excitation. The solid curves pertaining to data points are the results of analysis using a rate-equation model (see the text). In (a), (b) and (c), the thin solid and dotted curves show the temporal volution of the B band and the absorption band due to intermediate state I, respectively. In (a) and (b), the broken curve shows the temporal evolution of the STE band, and in (c) the chain and dotted curves show the two components of the growth of the F band.

In order to examine the effects of temperature on the relaxation process of e–h pairs in KCl and RbCl, we carried out similar time-resolved optical absorption measurements in the wide temperature range 6–300 K. At temperatures higher than 80 K, we could not resolve the STE absorption band clearly because of significant broadening of the intense
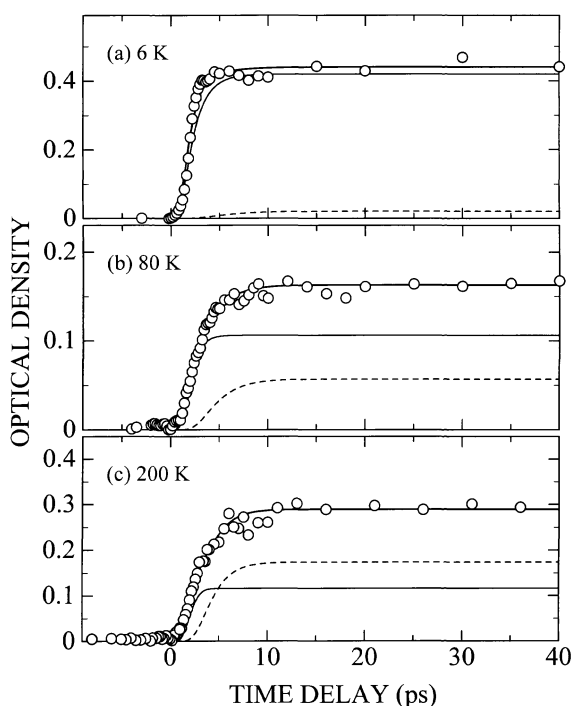
Figure 5. Optical density changes at 2.2 eV in KCl at (a) 6, (b) 80 and (c) 200 K as functions of delay after two-photon band-to-band excitation. The solid curves are the results of analysis using a rate-equation model (see the text). The two components of the fast and slow growth of the F band, resolved by the analysis, are shown by thin solid and broken curves, respectively.

F-absorption band. Therefore, temporal evolution of the F band is mainly described. In figures 5 and 6, we show the temperature-dependent changes in temporal evolution of the F band measured at 2.2 eV in KCl and at 2.0 eV in RbCl, respectively. The results at 6 K, which have already been shown in figures 2 and 4, are presented again to emphasize the features of temperature-dependent changes in temporal evolution. In these chloride crystals, it appears that the growth of the F centres is characterized by a single rise time at any temperature; the F band grows monotonically until a maximum value. Interestingly, the rise time apparently becomes 'longer' at higher temperatures, in particular for RbCl. The temperature-dependent changes in the kinetics of the F-centre formation will be discussed in detail later.

4. Discussion

4.1. Qualitative features of the relaxation process of the e–h pair in KCl and RbCl

From the results shown in figures 1 and 2 for KCl and in figures 3 and 4 for RbCl, we can distinguish between two distinct stages of the relaxation process of e–h pairs in these chloride crystals at 6 K. These are the first stage which terminates within 6 ps after excitation and the second stage which follows the former and lasts over 20 ps at 6 K. The first stage is characterized by the formation and annihilation of the B band and by the fast growth of the F band, and the second stage by the formation of the off-centre STE. The fact that
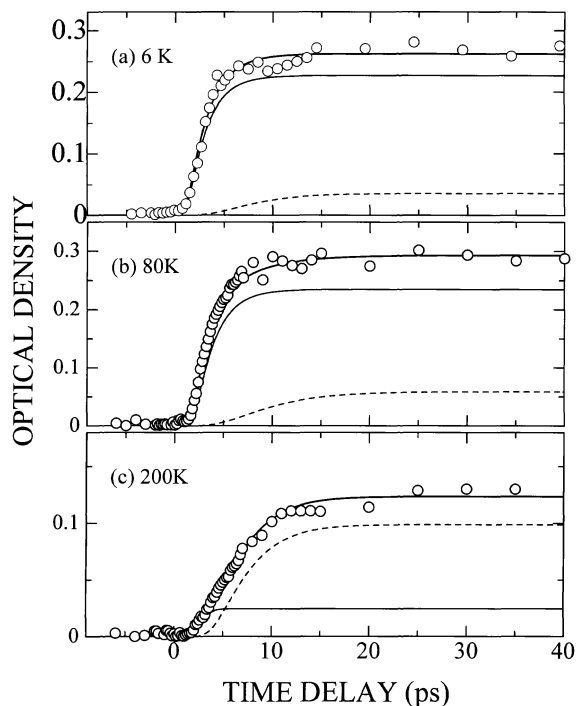
Figure 6. Optical density changes at 2.05 eV in RbCl at (a) 6, (b) 80 and (c) 200 K as functions of delay after two-photon band-to-band excitation. The solid curves are the results of analysis using a rate-equation model (see the text). The two components of the fast and slow growth of the F band, resolved by the analysis, are shown by thin solid and broken curves, respectively.

the off-centre STE is formed only in the second stage implies that an intermediate state which is the precursor of the off-centre STE is generated in the first stage; the intermediate state is tentatively called hereafter state I. The results shown in figures 5 and 6 show the other feature of the relaxation process of e–h pairs in these crystals; the growth of the F band becomes slower at higher temperatures. This feature indicates that relaxation pathways and/or the rates which govern the formation of F–H pairs change with changing temperature. In order to gain deeper insight into the relaxation process in these chloride crystals, below we briefly summarize the results for bromide crystals obtained previously and compare the features with those of KCl and RbCl obtained in the present study.

By using a similar femtosecond time-resolved spectroscopy technique, Shibata *et al* and Sugiyama *et al* have studied the relaxation processes of holes and e–h pairs in KBr and RbBr. One of their important findings is that the F–H pairs are formed through two different processes; the fast process which takes place within 5 ps after excitation, and the slow process which follows the former and lasts over 100 ps at low temperatures. The off-centre STEs are formed after only 5 ps in parallel to the slow process of the F-centre formation. From the comparative study of the hole relaxation in this crystal using a specimen doped with an effective electron-trapping impurity, it has been shown that the hole relaxation into the V_K centre takes place via a precursor state with a time delay of about 10 ps even at 273 K. For the precursor, or the transient hole state, a broad absorption band has been detected extending over the whole photon energy range from 1.4 to 2.9 eV,

and this is called the B band. The decay of the B band eventually leads to the formation of the V_K band in KBr doped with electron-trapping impurities. The broad absorption band, the features of which are essentially the same as the B band in doped crystals, has been observed also for pure KBr as the primary product of the relaxation of e–h pairs, and it has been shown that the decay of this broad band is associated with the fast formation of F–H pairs. From these results, Shibata *et al* have suggested that the fast process of F–H pair formation is due to the interaction of electrons with the transient localized hole states, or the relaxing holes, which are undergoing relaxation into the V_K-centre configuration. Also, careful examination of the spectral changes has shown that the slow process of the F–H pair formation, which is associated with the formation of off-centre STEs, is due to the off-centre relaxation of the on-centre STEs which are formed in parallel to the fast process of the F–H pair formation. Thus, for KBr and RbBr, the relaxation process of e–h pairs has been divided into the following two stages. The first stage is essentially the relaxation of a complex consisting of an electron and a relaxing hole through which the F–H pairs and the on-centre STEs are formed, and the second stage is the off-centre relaxation of the on-centre STE formed in the first stage.
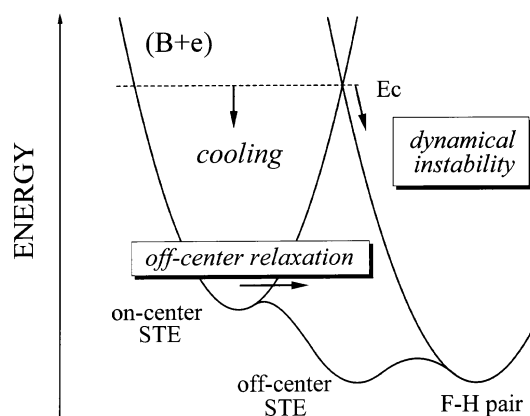

Figure 7. The schematic configuration coordinate diagram showing the model of relaxation pathways of e–h pairs in KBr and RbBr. (B + e) stands for the state comprising an electron and a relaxing hole. The arrows show possible relaxation routes. (After [13].)

These characteristics of the relaxation process of e–h pairs in KBr and RbBr can be described schematically by the model shown in figure 7 in which relaxation pathways are portrayed in terms of the configuration coordinate diagram [13]. 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). Since the detailed properties of the relaxing holes have not been obtained yet [15], the (B + e) state has just been assigned to vibrationally excited states of the on-centre STE. This assignment has been based partly on the result that the relaxing holes showing the B band are eventually converted into the V_K centres in the hole relaxation process. At a certain step of the relaxation of (B + e), the dynamical instability is induced to decompose the complex into the F–H pair. This process corresponds to the fast formation of F–H pairs. Competitively, the on-centre STE is generated through the vibrational relaxation, or the cooling transition, of (B + e). The off-centre relaxation of the on-centre STE formed in the first stage then follows to form F–H pairs and the off-centre STE in the second stage of the relaxation.

The model shown in figure 7 involves a few important consequences. The first is that the relative yield of the F–H pairs formed by the two different processes can be a function of the temperature. As shown theoretically [16], the rate of the cooling transition is enhanced with increasing temperature, which changes the branching ratio between the cooling transition and the dynamical instability. Experimentally, it has been certainly observed that the yield of F–H pairs by the fast process which is the dominant component at low temperatures is replaced by the yield by the slow process due to the off-centre relaxation of the on-centre STE at higher temperatures. The second consequence is that the rate of the off-centre relaxation, which characterizes the formation time of the F–H pairs in the second stage, changes with changing temperature because of the presence of the barrier. The results and the analysis for KBr and RbBr have shown that the rate is certainly enhanced at higher temperatures.

When we compare the characteristic features of the experimental results for KCl and RbCl obtained in this study with those for KBr and RbBr described above, one apparent difference is evident; the F-centre formation in chlorides does not show a well distinguished two-mode growth which has been clearly observed in bromides, particularly at low temperatures. However, except for this difference, we find several similarities, such as the formation of the B band as the primary product of the relaxation of e–h pairs, the fast formation of F–H pairs at 6 K in the first stage, and generation of the off-centre STEs only in the second stage. Therefore, here we adopt, as a primary working hypothesis, the model of relaxation pathways proposed for bromide crystals for analysing results for KCl and RbCl quantitatively. Accordingly, the intermediate state I is assumed to be the on-centre STE in chlorides. The quantities thus evaluated will be used to check critically the validity of applying this relaxation scheme to KCl and RbCl. Discussions to emphasize the characteristic features seen for chloride crystals follow, based on the results and their analysis.

4.2. Analysis of the temporal evolution in terms of a rate-equation model

A system of rate equations has been formulated on the basis of the relaxation-model scheme shown in figure 7, for analysing temporal evolution of optical absorption in KBr and RbBr. Since the details of the rate-equation model have been described elsewhere [13], here we briefly summarize a few features of the model.

One of the features of the rate-equation model is the introduction of a generation function of the (B + e) state for simulating the relaxation process of holes leading to the formation of the B band. As discussed in detail by Sugiyama *et al* it is presumed that the relaxation process of holes is composed of a few distinct but unresolved steps, and that the time which is needed for an optically generated hole to be localized at a certain lattice site with a certain degree of relaxation is delayed with respect to the incidence of the excitation pulse and is also distributed significantly. As 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, a generation function $g(t)$ of (B + e), given by a Gaussian of the form of

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

was then introduced. The function is characterized by the overall delay t_0 and the distribution with a half-width of $w/\sqrt{4\ln 2}$.

The other feature in the rate-equation model is the assumption that, among many of the substates of (B + e) with different degrees of relaxation, only the state which satisfies some conditions can induce the dynamical instability to generate F–H pairs. Consequently, many substates which are located below this 'reactive' state do not contribute to the F–H pair formation, although they still give rise to the B-band absorption. This assumption has been simulated by the rate equation by introducing two different levels for (B + e). At the level (B + e)$_h$, the dynamical transfer to the F–H pair with the rate k_h^F and the vibrational relaxation with the rate k_h^v towards lower states takes place competitively. The lower level (B + e)$_l$ has relaxation pathways only to the on-centre STE with the rate k_l^v. The on-centre STE formed from (B + e)$_l$ has two relaxation pathways to the off-centre STE with the rate k_l^S and to the F–H pair with the rate k_l^F. It has been shown for KBr and RbBr that the assumption which is simulated by introducing the two levels of (B + e) is essential for describing the temporal evolution of the respective states and their temperature-dependent changes [13].

By applying the same system of rate equations as used for bromide crystals, the concentrations at (B + e)$_h$, (B + e)$_l$, the on-centre STE, the off-centre STE and the F–H pair were calculated numerically as functions of delay after excitation, using a fourth-order Runge–Kutta algorithm, to obtain the fitting to the temporal evolution of optical densities at typical photon energies. In the fitting procedure, the same values of the parameters t_0 and w were used for a given specimen at any photon energy. The solid curves shown in figures 2, 4, 5 and 6 represent the calculated results of the best fit. In figures 2 and 4, the thin solid and dotted curves show temporal evolution of the B band due to (B + e) and state I, respectively. The components of F bands induced by the fast and slow processes are shown by chain and broken curves in figures 2(c) and 4(c), and by solid and broken curves in figures 5 and 6, respectively. It is evident that our analysis in terms of the rate-equation model reproduces reasonably the temporal evolution of optical densities at several photon energies. Some important quantities obtained by best-fit analysis are given in table 1, in which corresponding values for bromide crystals are given.

Table 1. The low-temperature tunnelling time $1/k_0$ and the activation energy E_a in the formation process of the F centre in the second stage in KCl, RbCl, KBr and RbBr. The ratio γ of the yield of F centres in the second stage relative to that in the first stage at 6 K is also given.

Crystal	$1/k_0$ (ps)	E_a (meV)	γ
KCl	7.1	5.8	< 0.1
RbCl	8.2	6.2	0.16
KBr	24.3	20	0.79
RbBr	33.3	28	0.39

4.3. Quantitative feature of relaxation process of e–h pairs in KCl and RbCl

Here we first examine the validity of applying the relaxation scheme established for KBr and RbBr to the results for KCl and RbCl, based on the results obtained by the analysis. As described in section 4.1, some essential features of the results for chlorides are quite similar to those for bromides; these are the formation of the B band in the first stage, the major contribution of the fast process in the F–H pair formation at 6 K, and the formation of the off-centre STEs only in the second stage. Also, as seen in figures 2 and 4, the temporal evolution of F, STE and B bands at 6 K for KCl and RbCl are well described

by the rate-equation model. These may allow us to conclude that the relaxation scheme shown in figure 7 applies to KCl and RbCl, at least at low temperatures. However, before drawing a definite conclusion, we need to examine the following two points closely; these are concerned with the kinetics of the F-band growth and its temperature-dependent changes and with the assignment of the intermediate state I.

As pointed out previously, the growth of the F band in KCl and RbCl crystals appears to show a 'single-mode' growth in the whole temperature range from 6 to 300 K, instead of the clearly distinguished two-mode growth observed for KBr and RbBr. Also, the growth of the F band, when it is assumed to be characterized by a single rise time, becomes slower at higher temperatures. In view of the results of analysis by the rate-equation model, these features of the kinetics of the F-centre formation in chlorides can be interpreted consistently and successfully in the framework of the relaxation model shown in figure 7. As seen in table 1, analysis has given a time constant $1/k_0$ of 7–8 ps which characterizes the formation time of the F centre by the slow process in the second stage. The magnitude is much smaller than those in bromides, which makes it difficult to distinguish very clearly the two different growth processes of the F band. Also, as shown by the magnitude of γ in table 1, the yield of the F centres formed by the slow process at 6 K is much smaller than those for KBr and RbBr, which also contribute to the apparent single-mode growth of the F band at low temperatures. On the other hand, as seen in figures 5 and 6, the results of analysis shown by the thin solid and broken curves indicate that the yield of the F centre in the first stage is reduced, whereas that in the second stage is enhanced with increasing temperature. This change in the yield by the slow process relative to that by the fast process can be regarded as the main origin of why the apparent formation time of the F band becomes longer at higher temperatures. It should be emphasized here that this temperature-dependent change in the relative yield of the F–H pairs is one of the direct consequences of the model of the relaxation pathways of figure 7, as pointed out above; the rate of the cooling transition of $(B + e)$ leading to the on-centre STE is enhanced at higher temperatures to reduce the F-centre yield by the fast process. Also, the formation time of the F centres in the second stage becomes shorter at higher temperatures, similarly to the case in bromides. Therefore, the apparent difference between the kinetics of the F-centre formation in chlorides and in bromides can be interpreted consistently and satisfactorily by the relaxation-model scheme shown in figure 7.

The second point to be examined is concerned with the assignment of the state I which is a precursor of the off-centre STE formed in the second stage. In the case of KBr, a similar intermediate state has been identified to be the on-centre STE based on its spectroscopic features in the ultraviolet and infrared parts of the spectrum; the on-centre STE shows the V_K-band-like absorption in the ultraviolet region and a strong infrared band extending up to the visible region [8,13]. Unfortunately, the present range of detection could not allow us to measure the absorption above 2.7 eV. So, we lack crucial information to identify state I definitely. However, as seen in figures 1–4, it can be certainly concluded that state I shows a significant absorption in the photon energy range below 1.8 eV for both KCl and RbCl. This low-energy absorption is one of the important characteristics of the on-centre STE [8]. Also, as seen in figures 2 and 4, the results of analysis show that the absorption due to the intermediate state I is much more pronounced for RbCl than for KCl, and that the amount of the F centres as well as the off-centre STEs formed at the second stage is much higher for RbCl than for KCl at 6 K. These results are consistent with the assignment that state I in chlorides is the on-centre STE. Therefore, it may be concluded, although tentatively, that on-centre STEs are formed in the first stage and they are converted into F–H pairs and the off-centre STEs in the second stage in KCl and RbCl. Thus, we can conclude that the

relaxation pathways of e–h pairs in KCl and RbCl are essentially the same as those in KBr and RbBr and that the main difference lies in the magnitudes of the rates which characterize the respective steps of the relaxation. Below we discuss the quantitative values for these chloride crystals, comparing with those for KBr and RbBr, in order to obtain some insight into the material-dependent properties.

Because of the difference between the excitation pulse width used in this study and those used for KBr and RbBr, comparison of the quantitative values of parameters characterizing the relaxation in the first stage may not be very meaningful. So, we focus our attention mainly on the relaxation in the second stage which takes place at longer t_d where the difference in the pulse duration may be neglected. The second stage of the relaxation of e–h pairs has been concluded to be the off-centre relaxation of the on-centre STE into the F–H pair and the off-centred STE. The analysis shows that the relaxation is characterized by a single time constant $\tau_I (= k_I^S + k_I^F)$, which depends on temperature and also on the kind of crystal. τ_I which remains constant at low temperatures becomes shorter with increasing temperature as seen in figures 5 and 6. This temperature dependence of τ_I is found to be well fitted by the classical formula of the non-radiative transition probability:

$$\frac{1}{\tau_I} = k_0 + \nu \exp\left(\frac{-E}{k_B T}\right) \tag{2}$$

where k_0 is the rate of low-temperature tunnelling, k_B is the Boltzmann constant, and ν and E are the frequency factor and activation energy, respectively, of the thermally activated process. The best-fit parameters are given in table 1, together with those for KBr and RbBr obtained in the previous study [13].

As clearly seen in the table, there exists a large difference between the low-temperature tunnelling time (inverse of k_0) and the barrier height in the off-centre relaxation in chlorides and bromides; the k_0-values for chlorides are much larger than those for bromides, and the barrier heights for chlorides are much lower than for bromides. These magnitudes of parameters which govern the rate of the off-centre relaxation make the relaxation rate much faster for chlorides than for bromides. On the other hand, we show in the table the ratio γ of the yield of the F centre formed in the second stage relative to that in the first stage at the lowest temperature in the four crystals. As seen in the rate equations, this ratio reflects the efficiency of the cooling transition relative to the dynamical instability; it is an important factor in populating the on-centre STE. As seen in the table, the value for chlorides is much smaller than that for bromides, indicating the smaller yield of the cooling transition for chlorides than for bromides. Although the microscopic origin of this material dependence in the ratio is not evidently clear at this moment, this factor certainly has an effect of governing the population of the on-centre STE. These two characteristics of the magnitudes of τ_I and γ for KCl and RbCl described above, both of which reduce the population of the on-centre STE, are reasonably related to the lack of the luminescence from the on-centre STE in these crystals.

5. Summary

In this paper, we have studied the dynamics of the relaxation of e–h pairs in KCl and RbCl in which the luminescence (the σ luminescence) due to radiative decay of the on-centre STE is missing. On the basis of the results and their analysis, it has been shown that the relaxation pathways of e–h pairs can be distinguished in the two different stages. In the first stage, the F–H pairs and the intermediate state I which has been tentatively identified to be the on-centre STE are formed, and in the second stage the off-centre STEs

and F–H pairs are formed. Thus, the pathways of the relaxation of e–h pairs in these chloride crystals are shown to be essentially the same as those in KBr and RbBr in which both type-I and type-III STEs are formed efficiently. Quantitative values obtained by the analysis in terms of the rate-equation model has shown that the population yield of the on-centre STE should be smaller in chlorides because of the less efficient yield of the cooling transition rate, and because of the higher off-centre relaxation rate enhanced by the smaller barrier height and larger low-temperature tunnelling rate. Thus, important features of the relaxation of e–h pairs in crystals where type-I luminescence is missing have been provided. The theoretical consideration of these features based on the fundamental properties of these crystals is an interesting future problem for generalizing the material-dependent properties in the relaxation process of e–h pairs in alkali halides.

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