Parity-broken and -unbroken self-trapped excitons in alkali halides

Ken-ichi Kan'no,[a] Tamao Matsumoto[a] and Yosuke Kayanuma[b]

[a]*Department of Physics, Kyoto University, Sakyo, Kyoto 606, Japan*
[c]*Collage of Engineering, University of Osaka Prefecture, Sakai 593, Japan*

Abstract: We review updated understandings of the electronic and atomic structures, relaxation dynamics and spin-multiplicity of self-trapped excitons (STEs) in alkali halide crystals, on the bases of recent experimental results of the STE luminescence. It is pointed out that seemingly complicated diversity in the features of STE luminescence and F-H pair formation can be explained from an unified viewpoint. That is, depending upon the kinds of crystals there can arise the *"adiabatic instability"*, which results in multiple local minima on the adiabatic potential energy surfaces (APES's) for the singlet and triplet STE states of the lowest orbital energy. A simple phenomenological model is proposed, which indicates that the electron-hole spin interaction plays an essential role in correlation with the electron-lattice and hole-lattice interactions. The shape of the APES's, the configuration dependence of the electron-hole exchange energy, relaxation dynamics and the structure of STEs are discussed in relation to the bi-stability of parity-broken and -unbroken STEs.

INTRODUCTION

In these several years, relaxation dynamics of excitons in wide-gap ionic crystals has been a subject of extensive studies with respective to so-called *"adiabatic instability"*, which results in the symmetry breaking of the self-trapped exciton (STE) state. As reviewed in the recent monograph by Song and Williams (ref.1), alkali halides are the most attractive materials for which various kinds of studies on the exciton self-trapping and photo-induced phenomena have been carried out experimentally and theoretically over three decades. Nowadays, it has been generally accepted that the adiabatic instability brings great influence on radiative and non-radiative decay processes, and plays an essential role in the formation mechanism of Frenkel defect pairs. A simple explanation for the instability is a pseudo Jahn-Teller s-p mixing by odd parity distortion modes. The idea of this kind of instability was firstly proposed by Toyozawa (ref.2), in relation to the formation mechanism of F-H defect pairs, and has been extensively developed to the idea of so-called "off-center STE" by Song and his coworkers (refs.3-5). In 1990, a key to open a new stage of investigations was discovered in the STE luminescence by Kyoto group (refs.6-8) collaborating with Kayanuma (ref. 9).

In the present article, we review updated understandings of what happens in alkali halide crystals and how it proceeds immediately after the excitons or electron-hole pairs optically created come to attain energetically more stable situation. One can find a key parameter to understand seemingly complicated diversity in the features of STE luminescence and F-H pair formation in correct way. A general picture to reasonably be imagined is that depending upon the kinds of crystals there can appear multiple local minima on the adiabatic potential energy surfaces (APES's) for the singlet and triplet STE states of the lowest orbital energy. As schematically shown in Fig.1, the STE configuration in which an electron and a hole are both localized on the same center of symmetry (*on-center type*) is, in many cases of alkali halides, rather unstable against odd-parity lattice distortion modes, resulting in spontaneous transformation into the asymmetric configuration of a spatially dissociated electron-hole pair (*off-center type*), or further into the nearest-neighbor (nn) F-H pair. A simple phenomenological model is also proposed: The shape of the APES's, the configuration dependence of the electron-hole exchange energy and relaxation dynamics are discussed in relation to the bi-
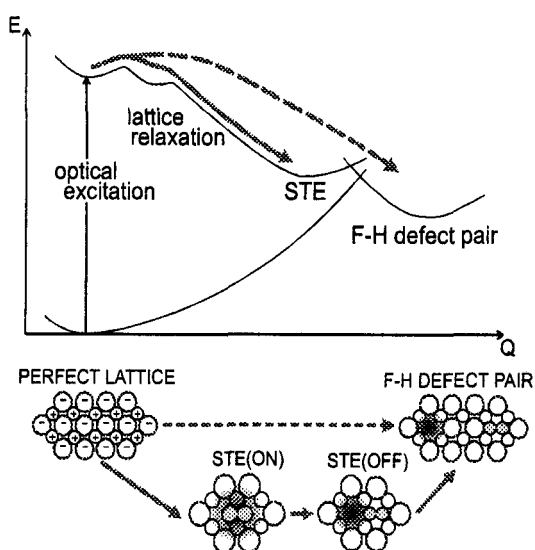

Fig.1 Schematic drawing of exciton self-trapping processes in alkali halide crystals.

stability of parity-broken and -unbroken STEs. It will be stressed that the electron-lattice interaction, hole-lattice interaction and electron-hole spin interaction cooperatively or competitively play essential roles during exciton self-trapping.

MATERIAL DEPENDENCE OF THE STE LUMINESCENCE SPECTRA

In 1964 Kabler (ref.10) proved that the host-dependent broad luminescence bands found in alkali halides at low temperature are the result of electrons recombining radiatively with self-trapped holes (V_K centers). The luminescence bands were found to be polarized either parallel (σ) or perpendicular (π) to the principal molecular axis of the aligned V_K centers. Kabler and Patterson (1967, ref.11) showed that the σ-polarized short-lived bands arise from radiative decay of singlet states and the π-polarized, long-lived bands arise from triplet states. One might reasonably expect to find that optical spectra of alkali halide families would be replicated almost unchanged, or be shifted gradually from one crystal to the other in some orderly way. This is really the case, for example, in the fundamental absorption spectra of the evaporated thin films, indicating that elementary excitation itself is in regular order with respect to a different combination of the anion and cation of host crystals (ref.12). The reality of the situation of the STE luminescence is not so simple, however: The first is concerned with the variety in the number of STE bands appearing in particular crystals. As seen in Fig.2 where emission and excitation spectra of the STE luminescence in nine crystals, (Na, K, Rb) x (Cl, Br, I) are summarized, the π-band (hatched) appears in all the crystals while the σ-band is observed only in five crystals. That is, the σ-band is apparently missing in KCl, RbCl, NaBr and NaI. Moreover, RbI looks like a peculiar crystal, where one can see three intrinsic emission bands. Why does only one band or else more appear in a particular crystal ? Another point not to be overlooked is concerned with the spectral range where the emission bands appear. Usually, the π emission band is located in the visible part. The Stokes shift relative to the free exciton is dramatic, being at least half the band gap in most cases, and reaching more than 5 eV in KCl and RbCl, for example. But in both NaBr and NaI the π band is located in the ultraviolet part with a rather small Stokes-shift. How can the variety in the magnitude of the Stokes-shift be adequately understood ? In fact, reasons or rules for many of the variations were not obvious in about 20 yr. of inspection. One suspects, therefore, that the bands among which one should look for orderly trends are not grouped along the obvious lines of σ and π, or singlet and triplet.
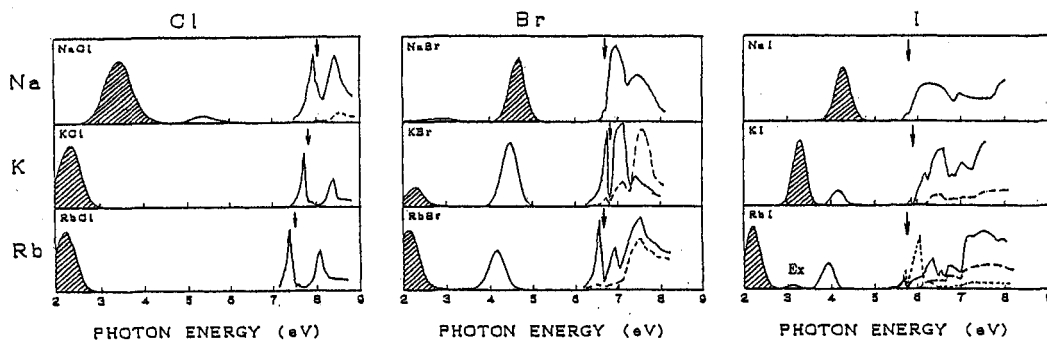

Fig. 2   STE luminescence spectra in nine alkali halides, (Na, K, Rb) x (Cl, Br, I), with predominantly triplet bands shaded and predominantly singlet bands not shaded. Excitation spectra are shown in the right hand side with arrows indicating the lowest exciton absorption peak. (after K.Kan'no et al., ref. 6) .

Studies on mixed crystals of alkali halides identified both the key parameter and the proper groupings of bands to render the variation in band positions quite logical. Kan'no and coworkers (ref.6) reasoned that if one wants to know how luminescence bands change from one alkali halide to the next, then it should be illuminating to gradually change one pure crystal to the next through progressive alloying, and watch how the luminescence bands evolve. One has the choice of changing the alkali while keeping constant halide, or of changing the halide while keeping constant alkali, with different aspects probed in each case. The experiments suggested three categories of STE emission bands in the nine alkali halides (Na, K, Rb) x (Cl, Br, I), designated mainly according to spectral position and the way peaks evolve through the mixed crystal series. These categories are called types I, II, and III, in order of increasing Stokes shift energy. For typical example of the experiments, we mention the results of NaBr-KBr mixtures in the following.

In the system $Na_{1-x}K_xBr$ with x taken from 0 to 1.0, one observes STEs always involving the Br_2^- molecular ion, as its surroundings and the average lattice constant of the crystal are gradually changed. The STE spectra and decay curves are shown in Fig. 3. For $x = 0$, the crystal is NaBr, and the band at 4.6 eV is the familiar triplet π luminescence with a lifetime of 490 ns, shown as the shaded part of the decay curve. Actually, these data show something new even for pure NaBr. That is the weak 1.5 ns decay component, which has the same spectral distribution as the π band (ref.8). The surprise in Fig. 3 is that as the potassium fraction x increases, the triplet π band of NaBr turns smoothly and continuously into the singlet σ band of KBr ! This is seen both in the spectra and the decay curves. The triplet π band of KBr

at 2.28 eV appears at $x = 0.6$, without any significant precedent in the NaBr spectrum. The 2.8 eV band at intermediate compositions is associated with the sodium impurity-perturbed STE in KBr. Using $Na_{1-x}K_xI$ mixtures, the bands in NaI and KI were confirmed to be related in a very similar way (ref.13). Experiments changing the halogen along the $KBr_{1-x}I_x$ system further clarified that the triplet π band in KI has no counterpart in KBr, even in this case where the singlet σ band of KI simply corresponds to the singlet of KBr (ref.14). That is, the triplet π bands in both crystals must be classified into different categories from each other.

It is not surprising, then, that one has been unable to perceive clear trends of the π band from one crystal to the next, or of the σ band from one crystal to the next. These are evidently not the primary distinguishing-categories, since one polarization or spin state can turn into the other at corresponding energies across alloy diagrams such as Fig. 3. It appears that there must be something more fundamental distinguishing the ultraviolet bands in NaBr and KBr from the green band in KBr, for example. Since "singlet vs. triplet" and "σ vs. π" do not seem to be suitable category names when discussing such trends versus crystal, the ultraviolet bands with small Stokes shift, whether singlet or triplet, were simply assigned to "type I". Only KCl and RbCl do not exhibit type I bands. Band correspondences within the mixed crystal series showed that the π-polarized band called Ex in RbI certainly and the π band in NaCl probably, as well as the π band in KI belong to type II, whereas the π bands in all other crystals except NaBr and NaI are type III. Hence, the 4.6 eV π-band in NaBr and the 2.28 eV π-band in KBr turns out to be types I and III under new nomenclature, respectively.

Essentially the same situation has been also confirmed in the luminescence spectra of impurity-associated excitons; bromine or iodine monomer and dimer impurity emission bands in alkali chloride and bromide crystals. Actually the first indication of

Fig.3 (A) Luminescence spectra of $Na_{1-x}K_xBr$ mixed crystals at 10 K, excited by 7.7 eV photons. (B) Decay profiles of the uv band under pulsed excitation with 7.7 eV synchrotron radiation (after Kan'no *et al.*, ref. 6).

Fig.4. Luminescence spectra of STE's in NaI, KI and RbI (left), and those of iodine associated monomer excitons in NaBr:I, KBr:I and RbBr:I (right). (after Kan'no *et al.*, ref. 16)

different families in triplet luminescence bands was found in KBr:I (ref.15) and KCl:Br (refs.7) by Tanaka *et al.* A typical example is seen in the spectra due to iodine monomers in alkali bromides, i.e., NaBr:I, KBr:I and RbBr:I (ref.16). This is the analogue of the STE luminescence in NaI, KI and RbI. As shown in Fig.4, one, two and three emission bands, all arising from relaxed excitons with hetero-nuclear halogen core (BrI)ˉ, are located at corresponding energies to the STE bands in the three iodides. Emission bands in 17 different systems except the iodine monomer system in NaCl:I were classified into the same categories, types I, II and III, based on the spectral evolution and band correspondences within the mixed crystal series. (NaCl:I is exceptional because the single band in this system belongs to another category called "NE emission", which originates from the relaxed exciton state of one-center type (ref.17)).

Since all STE luminescent states, including the cases of impurity-associated excitons, have been shown to involve halogen pair relaxation of the "V_K" type, there must be some additional degree of relaxation to differentiate the various categories of bands and account for the substantial energy differences between them. Before finding the three categories, Song and Chen (ref.18) had pointed out the correlation that exists between π band energy and the degree of off-center relaxation. Song *et al.* (ref.19), Kan'no *et al.* (ref.6) and Kayanuma (ref.9) proposed that the degree of off-center relaxation provides the basis for the observed trends and resulting categories. Since the type I emission is observed for crystals with larger halide ions, in which off-center motion of the halogen molecular ion core is more constrained, it was attributed to on-center STEs with the $V_K + e$ configuration as in Kabler's original model (refs.6,9), or to the STEs situ-
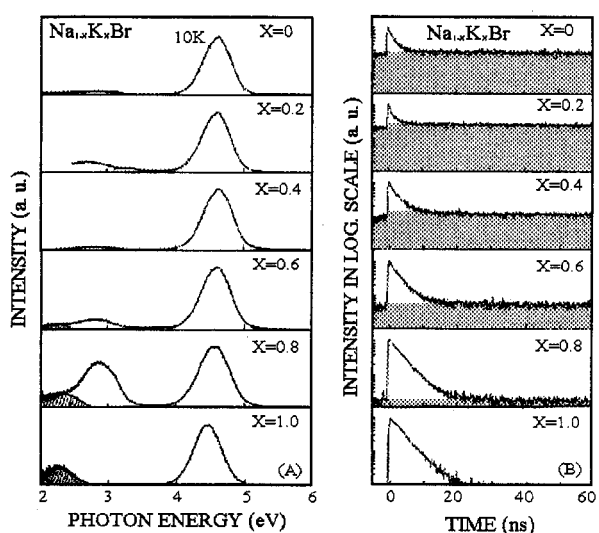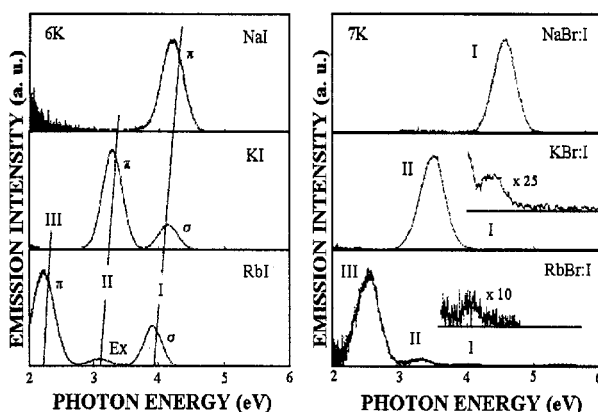
ating "nearly on center"(ref.20). Because of the extreme Stokes shift of the type III bands, there must be substantial additional lattice relaxation in addition to the V_K distortion. Thus type III was attributed to off-center STEs with configuration close to the nn F-H pair. Type II is then an intermediate degree of off-center relaxation.

ORDERLINESS OF THREE TYPES AGAINST RABIN-KLICK PARAMETER

Stokes shift energies

As shown by Song *et al.*(ref.19) and Kan'no *et al.*(ref.6), the degree of off-center relaxation in the STE correlates with the Rabin-Klick parameter S/D (ref.21). The parameter S is defined as the separation of two adjacent halide ions along a <110> row minus twice the halide-ion radius, i.e. the "excess space" measured between hard spheres placed at the ion positions. D is the diameter of the halogen atom. The ratio S/D was originally proposed as a geometric measure of space available for the insertion of an interstitial halogen atom to form an H center, or in the present context, space for the STE to relax off-center. The S/D is a suitable parameter convenient for neat pigeonholing of not only the intrinsic STE bands but also impurity associated exciton luminescence, as described below. We present a new diagram in Fig. 5, as an extension of plotting the ratio of Stokes shift to the 1s exciton energy against S/D for the 15 STE bands in the 9 alkali halides (ref.6). It includes 24 additional data points from impurity associated bands due to monomer and dimer
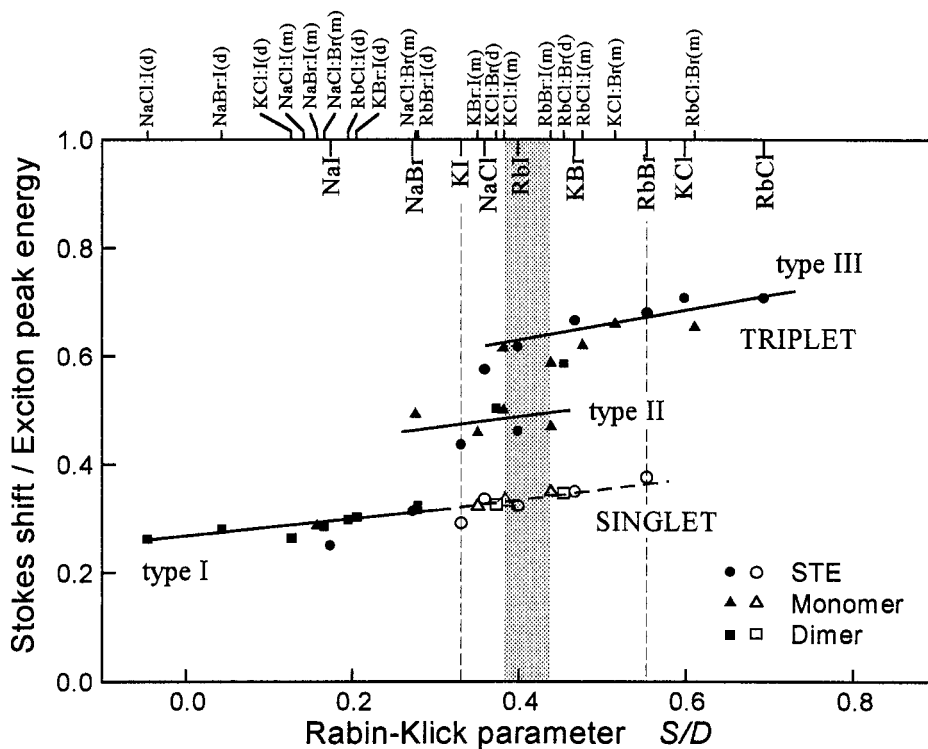

Fig. 5 Plot of Stokes shift of STE luminescence bands in nine alkali halides, and of monomer (designated by m) and dimer (designated by d) luminescence due to halogen impurity associated excitons, normalized by the energy of the lowest exciton absorption peak. (see text)

excitons. The S/D, which was originally defined as the measure against the crystal structure, is redefined to scale every individual geometry to be situated by intrinsic and impurity-associated STEs as follows: For the intrinsic STEs of X_2^- core in alkali (M^+) halide (X^-) crystal, S and D are given by $S = (a/\sqrt{2}) - 2r_X$ and $D = D_X$, according to the original definition. Here a is the lattice constant of the host crystal A^+X^-, r_X the halide-ion radius and D_X the diameter of halogen atom. As for the $A^+X^-:Y^-$ crystal containing foreign halogen ions Y^-, we define effective values of S and D by $S = (a/\sqrt{2}) - (r_X + r_Y)$ and $D = D_X$ for the impurity monomer exciton of $(XY)^-$ core, whereas by $S = (a/\sqrt{2}) - 2r_Y$ and $D = D_Y$ for the impurity dimer exciton of Y_2^- core. In Fig.5 the abscissa is effective S/D thus defined. The ordinate is the Stokes-shift energy normalized by the energy of the lowest absorption peak, so that it may be the direct measure for the lattice relaxation energy. Predominantly π bands of STEs, monomers and dimers are shown by filled circles, triangles and squares respectively, and predominantly σ bands of the corresponding excitons are shown by open symbols. The order that emerges on this plot is astonishing. The π emission starts as type I (on-center, or nearly so), and then around

$S/D = 0.3$ makes the transition progressively through type II (moderately off-center), finally to type III (nn F-H configuration) in crystals with large S/D. The main portion of the singlet STE population never gets to the type II or type III off-center configurations, suggesting that the singlet spin state is stabilized in the type I configuration, even though the singlet-triplet splitting is known to be small. It is also noteworthy that the three types do coexist in the systems of $0.38 < S/D < 0.45$; i.e. the STE in RbI and the iodine monomers in KCl:I and RbBr:I.

Two step transitions in the ordinate against increasing S/D are exactly correlated with the evolution from type I to type II and further type III. This clearly indicates that in addition to the V_K-type lattice relaxation, at least two distinctive distortion modes are concerned with stabilizing off-center configurations, in agreement with theoretical anticipation of Q_2 and Q_2' distortions (ref.19). In the present model, the singlet STE luminescence arises from the same orbital state as the triplet luminescence, but subtle spin interactions may make one of the lattice configurations I, II, or III more favored than another. It is perhaps not the stability of the singlet at the type I configuration that is remarkable and that causes the type I STEs to be predominantly singlets, but rather the instability of the triplet STE at the type I configuration, which goes downhill into the more off-center potential minima. This is just the adiabatic instability discussed by Toyozawa (ref.2), Song and coworker (refs.3,4), Williams *et al.*(ref.5) and by Kayanuma (ref.9). Overlaid with the conventional Rabin-Klick diagram for F center production at 4.2 K (ref.21), one can see that when the lattice becomes favorable for F-center production at low temperature, the type III configuration is favored by the STE. One may conclude from the trends that if the lattice is open enough to allow large off-center relaxation of the STE, then any barriers to further separation of the F-H pair are also likely to be small.

Triplet lifetimes

In addition to the above-mentioned diversity of the luminescence bands, their lifetimes also vary in ways that are not obvious upon inspection. The lifetime τ_π of the lowest triplet $^3\Sigma_u^+$ state is given by $\tau_\pi^{-1} = C\,E_\pi^3\,b^2\,|\langle^1\Pi_u|\,r\,|\,^1\Sigma_g^+\rangle|^2$. Here, C is a numerical constant, E_π the π emission band energy and b the mixing parameter of a higher singlet $^1\Pi_u$ state into the $^3\Sigma_u^+$ state by the halogen spin-orbit interaction. In the perturbation limit, b is approximated by λ/Δ_{STE}, where λ and Δ_{STE} are the spin-orbit coupling constant of the halogen atom and the energy separation between $^1\Pi_u$ and $^3\Sigma_u^+$, respectively. The lifetime of the π emission had been known to be shorter in heavier halides (ref.11). This was satisfactorily accounted for in terms of the larger spin-orbit interaction in heavier halides. However, the lifetime exhibits anomalous variation even within a given halide family. For example, the lifetime of the type I π band in NaBr is 490 ns, which is two order of magnitude shorter than 130 μs of the type III π band in KBr. Obviously, such difference in lifetimes comes partly from the appreciable difference in emission band energies between types I and III bands. The difference between E_π's in NaBr (4.6 eV) and KBr (2.3 eV), however, only accounts for the difference by one order of magnitude. A large
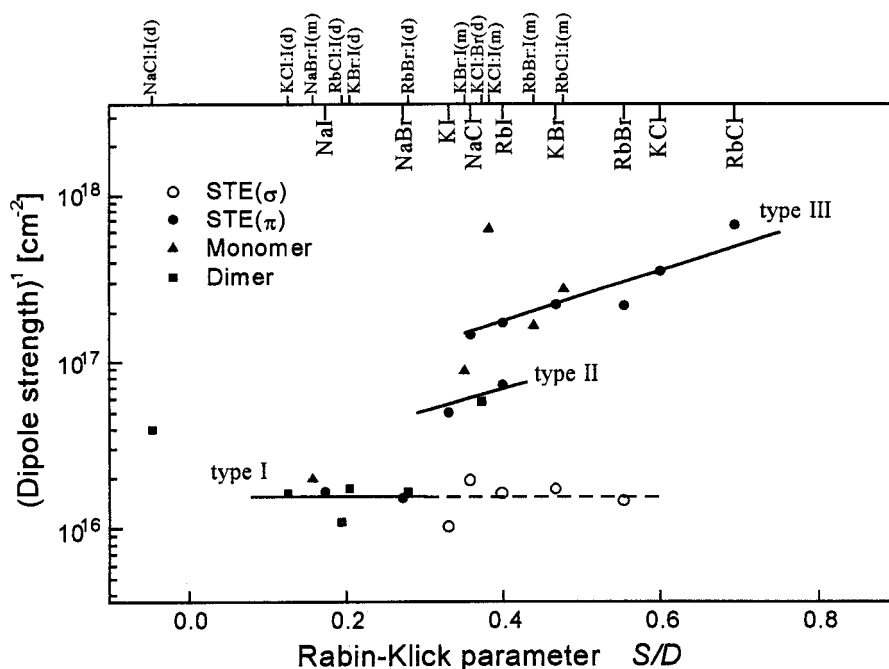

Fig.6. Plot of inverse of dipole strength of STE luminescence and monomer (m) and dimer (d) impurity exciton luminescence vs. Rabin-Klick parameter S/D. (see text)

difference over one order of magnitude still remains unexplainable, and it must come from either variation in the energy separation Δ_{STE} and/or the transition dipole strength $d \equiv |\langle {}^1\Pi_u | r | {}^1\Sigma_g^+ \rangle|^2$.

Kawata *et al.* (ref.22) suggested the possibility that Δ_{STE} is appreciably smaller in the type I STE than in the type III STE, by assuming $\Delta_{STE} \approx \Delta_{VK}$ for type I on-center STEs while $\Delta_{STE} \approx \Delta_H$ for type III off-center STEs. Here, Δ_{VK} and Δ_H are the energy splitting between ${}^2\Pi_u$ and ${}^2\Sigma_u$ in the V_K and H centers, respectively. A trend of $\Delta_{VK} < \Delta_H$ was reasonably expected from the observed difference in g-shifts between V_K and H center EPR spectra, leading to the conjecture that Δ_{STE} is larger in off-center STEs than in on-center STEs. On the one hand, Song and Chen (ref.18) derived the relation in which d reasonably correlates with the off-center relaxation coordinate Q_2, under the simplification that the variation in Δ_{STE} is negligible. In Fig. 6, we also present an interesting trend found in the experimentally determined d values against S/D: The ordinate d'^{-1} stands for the inverse of the transition dipole strength implicitly including a correction factor $\varepsilon \equiv (\Delta_{VK} / \Delta_{STE})^2$. That is, $d'^{-1} \equiv (\varepsilon d)^{-1} = \tau_\pi C E_\pi^3 (\lambda/\Delta_{VK})^2$. The data points (closed symbols) were obtained, therefore, independent of uncertainty in evaluating Δ_{STE}. For comparison, data points for the dipole strength, $d_s \equiv |\langle {}^1\Sigma_u | r | {}^1\Sigma_g^+ \rangle|^2$, directly evaluated from the singlet σ luminescence lifetime are also plotted by open symbols. The order that emerges on this figure is impressive, too. There is an astonishing resemblance between Figs. 5 and 6, except difference in scaling the ordinates (linear scale in Fig. 5 versus log-scale in Fig. 6). This result offers strong indication that the manner of electron-hole overlap vary in essentials from one type to the other of luminescent states. It is also noteworthy that the magnitude of the closed symbols of type I bands coincide with that of the open ones.

PARITY-BROKEN AND -UNBROKEN STEs

All mentioned above leads us to the context that three types of the STE luminescence arise at different local minima on the APES of the lowest orbital energy, on which another local minimum can also occur as the F-H defect pair state. Such conjecture (ref.6,9) of bi-stability or multi-stability for the parity-broken (i.e., off-center) and -unbroken (on-center STEs have been partly reproduced by recent theoretical investigations (refs.20,23,24), and evidenced by several extensive experiments in these several years; i.e., dilation effect (ref.25), time-resolved luminescence spectroscopes using synchrotron radiation (ref.26) or ns laser pulses (ref.27), streak-camera observation of STE evolution in ps time range (ref.28), resonant Raman scattering (ref.29), transient IR spectroscopy (ref.30), pump-probe fs spectroscopy (ref.31), and so on. These works have already been reviewed in some details (ref.1). In the following, we briefly mention only the most recent result of optically detected magnetic resonance (ODMR) due to triplet STEs in NaBr (ref.32).

In Fig. 7 is shown the ODMR spectrum due to [110]-oriented STEs in NaBr, which was time-resolved by using a novel combination of detecting emission decays and applying pulsed X-band microwave (ref.32). For comparison, the well-known X-band ODMR spectrum by Marron *et al.* (ref.33) is reproduced in the upper part of the figure. An ODMR spectrum in RbBr was also reported, which is very similar to the one in KBr. One can intuitively see that the NaBr spectrum is surprisingly different from the other. It comes from remarkable difference in the magnitude of zero-field splitting energy D. This is one of the direct evidences that the type I STE in NaBr is most probably situated in the on-center (or nearly on-center) configuration distinct from the off-center type III configuration in KBr and RbBr. It should be noted that the ODMR spectra are quite compatible with the previous analysis of lifetime experiments by Kawata *et al.*(ref.22). The D values estimated by the triplet-

Fig.7. X-band ODMR spectra due to triplet STEs in NaBr and KBr (after Kan'no et al., ref.32).

lifetime analyses have been received with some doubt (ref.1), because the analysis might depend strongly on the mechanism of relaxation assumed between the sublevels. However, for the case of NaBr it may safely be said to be evidenced by the ODMR study. Unambiguously, 0.2 meV should be accepted as a correct D value in NaBr. Interestingly enough, this value is one order of magnitude *larger* than that in KBr (0.03 meV). The zero-field splitting D is composed in general of contributions from spin-orbit and spin-spin interactions: $D = D_{SO} + D_{SS}$. In NaBr, D_{SS} is negligible relative to D_{SO}. To the extent that $D \sim D_{SO}$, D is given by $D = \lambda^2 J / 4(\Delta_{STE})^2$, here λ is a spin-orbit coupling constant, Δ_{STE} the energy of higher Π_u-like states, and J the spin-exchange interaction (ref.1). Both J and Δ_{STE} may depend sensitively upon the degree of the off-center shift of the V_K core. As will be discussed later, J is not likely to differ so much between the on- and off-center configurations, though it is expected to attain a maximum value somewhere at an intermediate shift. We suppose, therefore, that the large difference in D's of the two bromides comes mainly from appreciable difference in Δ_{STE} between the type I and type III configurations, as mentioned in the preceding section.
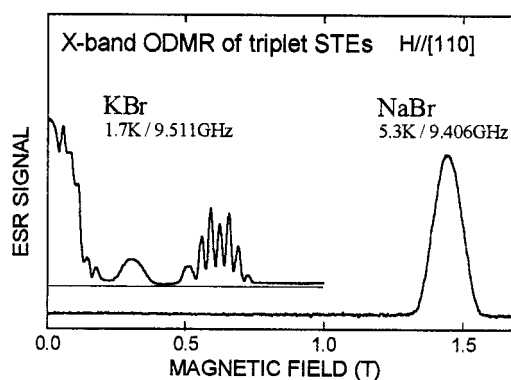
RELAXATION PATHWAY ON APES

One of the recent topics extensively studied is to see how the shapes of the APES's are, how the population is fed into each minimum, and how it decays from there. As already mentioned, the on- or off-center STE is solely realized for $S/D < 0.3$ or $S/D > 0.6$, respectively. This must be the simple case that a doubly-degenerated minimum is located at the on- or off-center position on the APES's of the singlet-triplet STE pair. However, in crystals with an intermediate S/D value, such as NaCl, KI, RbI, KBr, RbBr, the on- and off-center STEs must coexist, because their STE luminescence spectra exhibit multiple bands of types I and II (and/or) III. Interestingly, the type I STEs in these crystals preferentially decay from the singlet state to emit the predominantly σ-polarized luminescence, whereas the type II or III STEs decay exclusively from the triplet state to emits the π-luminescence. This suggests that the adiabatic instability and the spin multiplicity of excitons are closely correlated to each other, via the relaxation dynamics.

Kayanuma (ref.9) had already discussed how the different excitation spectra for σ- and π-luminescence can come about through population dynamics within the off-center model. An interesting point is the fact that the type I band is hardly stimulated in the spectral range of the $n=1$ free exciton (FE) where the triplet π-band of type II or III is stimulated more efficiently. Matsumoto et al. (ref. 26) have measured the excitation spectra of types I, II and III STE luminescence in 7 alkali halides using time resolution to distinguish singlet and triplet components of the type-I luminescence, and correcting for both reflectivity and surface dead-layer effects. It was concluded that excitons created in the $n = 2$ and higher states can readily relax to on-center type-I (singlet and triplet) STEs, as well as type II or III. Between the $n = 1$ and $n = 2$ exciton peaks, the yield of type-I luminescence is small *irrespective to its triplet component or singlet component*, suggesting that the smallest Bohr radios of the $n = 1$ exciton is essential to trigger very unstable situation toward off-center relaxation. They discussed an overall model of relaxation dynamics, which explains their experiments in a consistent way, by taking the following two points into account: 1) The remarkable contrast in features of excitation spectra between above and below the $n=2$ FE means that relaxation pathways from the $n=1$ FEs must be different from those from the $n=2$ FEs and from free electron-hole pairs. 2) Recent works (refs.34,35) have shown that the $n = 1$ free exciton scatters quickly to the triplet state within intraband relaxation. Essence of their relaxation model is summarized as follows (refs.26,36):

Relaxation proceeds in two dimensional coordinate space of Q_1 and Q_2, here Q_1 stands for the V_K-type on-center relaxation and Q_2 for the off-center relaxation toward the nn FH pair configuration. Figure 8 shows schematic plots of the sections of APES along three characteristic axes in the Q_1- Q_2 space, (a):Q_{on}, (b): Q_{off} and (c): Q_{on-off}. As shown in (d), the Q_{on} axis is the Q_1 axis, while the Q_{off} and Q_{on-off} axes are represented by linear combinations of the Q_1 and Q_2. As for the excitation above E_g, relaxation will proceed toward the Q_{on} direction because of the steepest gradient, as indicated by the solid arrow in Fig. 8(a). After cascade relaxation within the on-center configuration, a dominant part of the triplet component further relaxes into the off-center minimum along the path shown in (c). The singlet component, however, may stay in the on-center minimum unable to overcome the barrier because the barrier to off-center relaxation in the singlet state must be larger than in the triplet state as mentioned in the next section, giving rise to the fast component of the type I band. When the $n=2$ FEs are initially created, some part, x, is scattered into the $n=1$ FE state (indicated by a small wavy arrow) but the rest may relax along a path similar to that for the band-to-band excitation. As for the excitation into the $n=1$ FE, singlet FEs are efficiently scattered into the triplet FE state. Finally, major part will be self-trapped preferentially into the off-center configuration, owing to the steepest gradient along Q_{off} axis, as shown by broken arrows in (b).
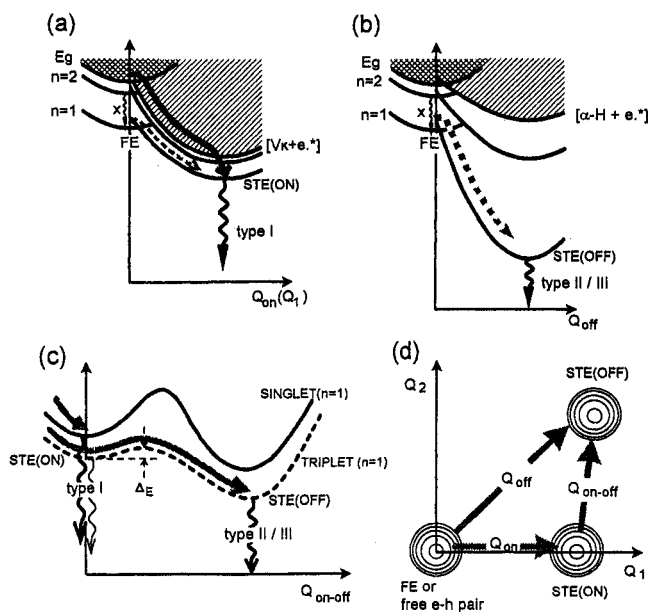
Fig.8. Schematic plots of three sections of APES's on which relaxation proceeds after photo-excitation, from FEs or free electron-hole pairs to the on-center and off-center STE states (after T.Matsumoto et al., ref. 25).

CORRELATION BETWEEN SPIN STATES AND STE STRUCTURES

In this section, we discuss the physical basis of the parity-broken and -unbroken STEs, especially concerning the problem why and how both STEs can coexist in many alkali halides. The key is most probably the electron-hole spin correlation depending upon the off-center lattice relaxation modes (refs.6,9). Recently Matsumoto *et al.* (ref.36) demonstrated a remarkable variation of exchange splitting energy along the relaxation path Q_2 from the on-center configuration to the off-center configuration, by simulating the singlet APES and the triplet APES. It naturally explains the basic features of how the σ-luminescence from the singlet appears exclusively at the on-center configuration while the π-luminescence from the triplet arises dominantly at the off-center configuration (shown in Fig. 8(c)).

In the following, we treat the same problem, but with a different way. We describe a pseudo-potential for the electron phenomenologically by a linear combination of one long range Coulombic potential and two short range Gaussian well potentials. In the on-center configuration, although the hole is represented by the halogen molecule ion X_2^-; the electron is in reality attracted by a pair of half-anion vacancies, each of which contains $e/2$ of charge. At the center of this region of attractive potential there is a fairly large space occupied by X_2^-, whose pseudo-potential is repulsive. For the on-center configuration, therefore, we describe the pseudo-potential for the electron by superposition of two Gaussian well potentials, which are positioned at half-anion vacancies and a Coulombic potential placed at the center of them to represent a long-range part of the potential. The width of one Gaussian well was assumed to increase and that of the other well to decrease both linearly with the increase of the off-center shift, while depths of both wells were set constant independent of the off-center shift. The long range part of the potential (Coulomb potential) moves in the opposite direction to that of the halogen molecule ion. At the nn F-H configuration, where the halogen molecule ion is positioned at one halogen ion site and a halogen vacancy is left, superposition of the Coulomb potential and the expanded Gaussian well represent a potential similar to that for an F-center like electron. Following parameters estimated from experimental results were used in the calculation; $\varepsilon = 3.4$, $m^*/m = 0.4$, $V = 0.35$ Ry and $W_{off} = 1$, where ε is dielectric constant, m^* the effective electron mass, V the depth of Gaussian wells and W_{off} the width of the expanded Gaussian well at the nn F-H configuration. The wave function for the electron was approximated by linear combination of two Gaussian functions whose peak positions and widths were fitting parameters. At each arbitrary off-center shift, binding energy of the electron was calculated by a variational method, by adjusting the electron wave function to make the total energy minimum. The exchange energy was then calculated using the wave function obtained for the electron and a linear combination of two p-type functions for the hole (ref.4) whose central position shifts in accordance with the off-center shift.
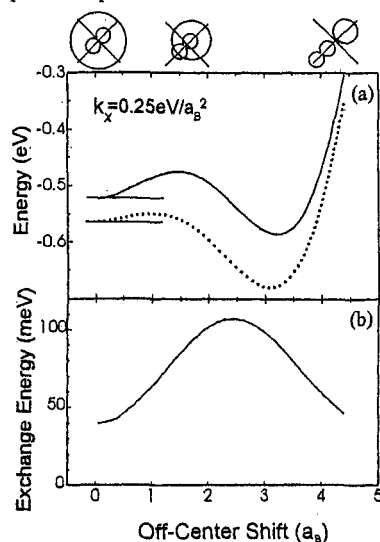

Fig. 9 (a) Calculated APES's for singlet (solid curve) and triplet (broken curve) STEs; (b) Calculated exchange energy. (see text)

The calculated binding energy of the electron is small and changes little as far as the off-center shift is small, while, as the off-center shift exceeds a critical value, $1 \sim 2$ a_B, the binding energy begins to drop. It is due to the fact that a Gaussian well with its depth fixed has bound states only when its width exceeds a critical value. Thus when the Gaussian well is not wide enough to have any bound state, the electron is trapped mainly by the long range Coulomb potential whose binding energy scarcely depends on the off-center shift, while when the width of the expanded well exceeds a critical value, the electron begins to be trapped by the well whose binding energy depends on the off-center shift through its width. If an elastic energy, $k_x^2/2$, is added, due to the combination of sudden drop of the binding energy at a critical off-center shift and quadratic increase of the elastic energy, the resultant triplet APES has two minima at the on- and off-center configurations (broken curve in Fig. 9(a)). In Fig. 9(b), the calculated exchange energy is shown against the off-center shift. It is about 40 meV at the on- and off-center configurations, in good agreement with reported values determined experimentally (ref. 8). In between, it takes a maximum of more than 100 meV.

Both at the on- (V_K+e) and off-center (nn F-H) configurations, overlap of the electron wavefunction and the hole wavefunction is small: For the on-center configuration, the electron wavefunction is very de-localized while the hole one is compact. For the nn F-H configuration, both wavefunctions are compact and sufficiently separated from each other. Somewhere at an intermediate separation, the exchange energy attain a maximum value because there should be the situation that the electron wavefunction becomes fairly compact but the electron-hole separation is not so large. Solid curve in Fig. 9(a) is the APES for the singlet STE, which was obtained by shifting the triplet APES by the exchange

energy. A potential barrier intervening between the on- and off-center configurations is much larger for the singlet than for the triplet because of the increase in the exchange energy around there. Thus the present model calculation has also demonstrated the conjecture that the exchange interaction of electron-hole pair plays an important role for realizing that the σ bands appears at the on-center position even then the π band appears from the off-center position (refs.6, 9).

INSCRIPTION

This paper is dedicated to the death in Kyoto on August 7, 1996, from complications following the main artery detachment, of Dr. Yoshio Nakai, Professor Emeritus of Kyoto University. Some part reviewed in this article is a memorial to his experienced supervising over a long span of years (1967 - 1990) in the laboratory of solid state spectroscopy, Department of Physics, Kyoto University.

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