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Transient absorption due to self-trapped excitons in NaBr and NaI

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Optical transient absorption due to self-trapped excitons (STE's) in both NaBr and NaI crystals has been investigated. Both crystals exhibited optical absorption in a region below 1 eV, peaks of which might be located below 0.23 eV, due to the electronic transitions in the STE. The absorption bands due to the hole transitions appeared at 1.6 and 3.2 eV in NaBr, and at 1.4 and 3.0 eV in NaI, which were very close to those due to the V_k centers. Absorption bands at 3.2 eV in NaBr decayed with two components, the intensity of which reflected the initial population in the triplet sublevels. These results strongly suggest the "on-center" configuration of the STE in NaBr and NaI.

I. INTRODUCTION

The excitonic relaxation process in alkali halide crystals is one of the most attractive paradigms of strong exciton-phonon interaction and its succeeding defect formation process in solids. The relaxed state of the exciton in alkali halide crystals is well known as a self-trapped exciton (STE). A traditional model of the STE proposed by Kabler[1] is the so-called "on-center" type, which consists of a halogen molecule ion ($X_2{}^-$) and an electron trapped by it. Although this model explains various experimental results, it has been difficult to understand the spectral position of the transient absorption bands due to electronic transitions (called "electronic transition bands" hereafter) in the STE.[2–8] Recently, however, this problem was solved by the "off-center" STE model.[8–11] In this model, the configuration of the STE is primarily equivalent to the nearest-neighbor *F-H* pair and the electronic state should resemble that of the *F* center. In fact, the transient absorption spectra of the STE in alkali halides except NaBr and NaI exhibited the electronic transition bands near the *F* bands.[6] On the other hand, electronic transition bands in NaBr and NaI have never been reported except for an incomplete tail down to 0.5 eV in NaBr.[6] Recently, we found an electronic transition band due to the STE localized at an iodine dimer ($I_2{}^{2-*}$) in KCl:I at 0.36 eV and suggested the on-center configuration of the STE.[12] Also, recent systematic study of photoluminescence properties[13,14] suggested that the STE in NaBr and NaI may be classified as the on-center type. Thus the search for the electronic transition bands of the STE in NaBr and NaI is very interesting and important for the study of the STE configuration, and its succeeding relaxation process.

II. EXPERIMENT

Nominally pure single crystals of NaBr and NaI grown at the University of Utah were excited by a two-photon absorption process with a KrF excimer laser ($2h\nu$=10.0 eV, pulse duration =22 ns). To measure the transient absorption spectra, a Xe flash lamp (pulse duration ~6 μs) was used as a probe light source. The probe light was passed through the sample perpendicularly to the excitation light beam and detected through a grating monochromator followed by a photomultiplier tube in the visible region ($2.0 \leq h\nu \leq 4.0$ eV), by a Ge photodiode in the near-infrared region ($1.0 \leq h\nu \leq 2.5$ eV), or by an InSb photodetector in the infrared region ($0.23 \leq h\nu \leq 1.1$ eV). Time-resolved signals from the detectors were recorded by a digital storage oscilloscope.

III. RESULTS

Figure 1 shows the transient absorption spectra of NaBr immediately after the excitation at 8 K. The spectra exhibited intense absorption below 1 eV, the peak of which may be below 0.23 eV, and rather weak bands around 1.6 and 3.2 eV. The absorption decayed with two components of τ_f=0.45±0.01 μs (open circles) and $\tau_s \gg 10$ μs (solid circles), although the faster component could not be observed in the spectral region below 1 eV because of insufficient transient response of the InSb photodetector. The decay time (τ_f) of the faster component

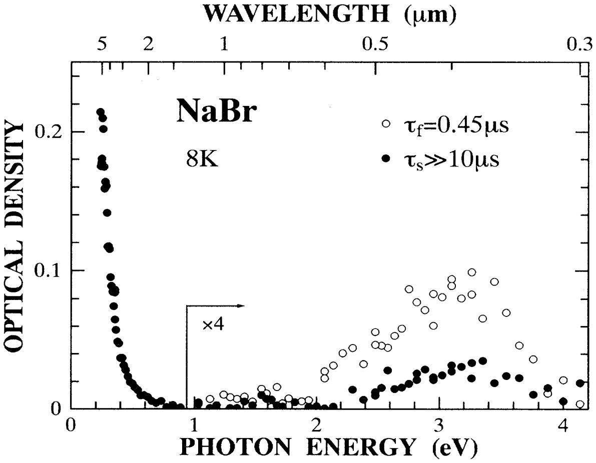

FIG. 1. Transient absorption spectra of the self-trapped exciton in a NaBr crystal at 8 K. Open circles indicate the spectrum for the faster decay component (τ_f=0.45 μs), and solid circles for the slower one ($\tau_s \gg 10$ μs).

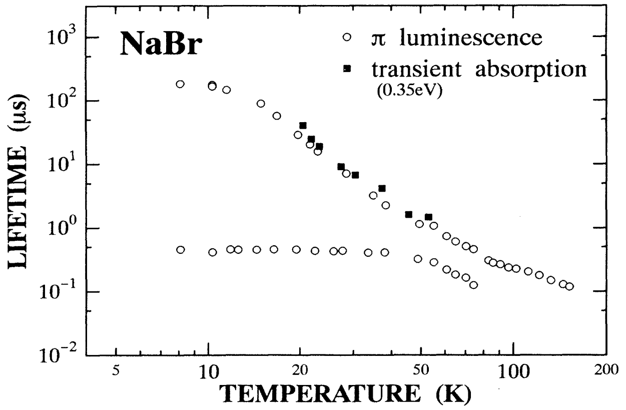

FIG. 2. Temperature dependence of the decay time of the transient absorption at 0.35 eV (solid squares) and that of triplet luminescence (open circles) due to the self-trapped exciton in NaBr.

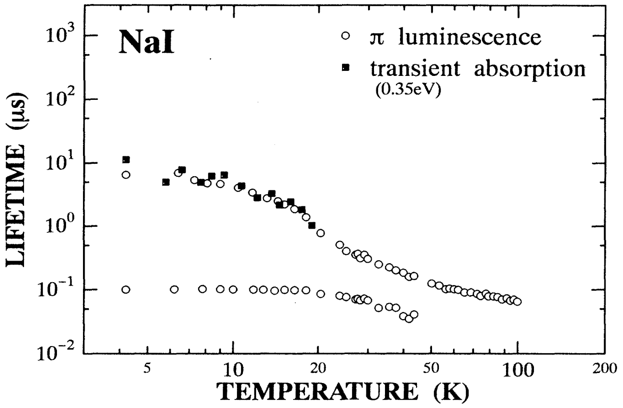

FIG. 4. Temperature dependence of the decay time of the transient absorption at 0.35 eV (solid squares) and that of triplet luminescence (open circles) due to the self-trapped exciton in NaI.

coincided with that of triplet (π) luminescence of the STE,[15] indicating the same initial state for the present transient absorption as that for triplet luminescence. The measurable range of the slower decay time was limited to a range below several tens of microseconds by the pulse duration of the probe light. To confirm the consistency of the decay time (τ_s) of the absorption below 1 eV with that of triplet luminescence, we measured the temperature dependence of τ_s in comparison with that of triplet luminescence. As shown in Fig. 2, the absorption decay time (τ_s, solid squares) coincided with that of triplet luminescence (open circles). Thus it is certain that the initial state for the transient absorption is the same as that for triplet luminescence. Furthermore, the ratio of the optical density (3:1) between the fast (open circles) and slow (solid circles) components in Fig. 1 was almost the same as the ratio of the time-integrated intensity of the two decay components of triplet luminescence. This result also implies that the initial state of both the transient absorption and triplet luminescence are the same.

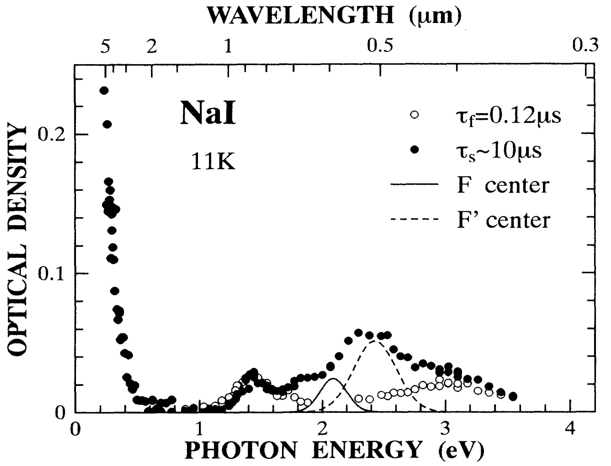

FIG. 3. Transient absorption spectra of the self-trapped exciton in a NaI crystal at 11 K. Open circles indicate the spectrum for the faster decay component (τ_f=0.12 μs), and solid circles for the slower one (τ_s~10 μs). Solid and broken lines indicate the absorption bands due to F and F' centers (Ref. 16), respectively.

Figure 3 shows the transient absorption spectra of NaI immediately after the excitation at 11 K. Similar to the case of NaBr, the spectra exhibited an intense absorption below 1 eV, the peak of which may be below 0.23 eV, and several bands around 1.4–3.2 eV. The absorption decayed with two components of τ_f=0.12±0.01 μs and τ_s~10 μs. In the spectrum of the slower component (τ_s), the bands around 2.1 and 2.5 eV might be due to transiently formed F and F' centers, the absorption bands of which were indicated by the solid and broken lines.[16] After subtraction of the F and F' bands, the spectra of the two decay components exhibited almost the same shape above 1 eV, with bands around 1.4 and 3.0 eV. The ratio of the optical density between the two decay components above 1 eV was about 1:1, which disagreed with that observed for triplet luminescence (2:1). The origin of the discrepancy is not clear at present, but may be due to the experimental inaccuracy in determining the absorption intensity which decays as fast as 0.1 μs. The decay time (τ_f) of the fast component coincided with that of triplet luminescence of the STE.[17] As shown in Fig. 4, temperature dependence of the decay time (τ_s) for the absorption below 1 eV was also consistent with that of triplet luminescence.

IV. DISCUSSION

The transient absorption spectra due to the STE in NaBr (Fig. 1) and NaI (Fig. 3) both exhibited distinct absorption below 1 eV. The coincidence of decay times between this absorption and triplet luminescence clearly indicates that the absorption is attributed to the triplet STE. Although the peak position is out of our measurable range, the band due to this absorption must be located in an extremely lower energy region than the electronic transition bands in other alkali halide crystals.[6,7] For instance, bands in NaCl, KBr, and KI appear above 1 eV as listed in Table I. This difference probably originates

TABLE I. Peak positions of the electronic transition bands in the self-trapped excitons.

Crystal	Peak position (eV)
NaBr	<0.23
NaI	<0.23
NaCl [a]	2.0
KBr [a]	1.6
KI [a]	1.1

[a] From Ref. 6.

from different configurations of their STE, i.e., the on-center type in NaBr and NaI while the off-center or the intermediate type in NaCl, KBr, and KI. The calculations based on the on-center model[2–5,8] predict that the transition energy from the $1s$ state to the $2p(b_{3u})$ state falls in the infrared region (0.1–1.1 eV). Thus the absorption below 1 eV in NaBr and NaI is tentatively attributed to the $1s(a_{1g})\rightarrow 2p(b_{3u})$ transition, although the absorption might also include the transitions to $2p(b_{1u}, b_{2u})$ and other higher states. It is noteworthy that the electronic transition bands of NaBr and NaI are in a lower energy region than that of localized STE ($I_2{}^{2-*}$) in KCl:I.[12]

The bands around 1.6 and 3.2 eV in NaBr, and those around 1.4 and 3.0 eV in NaI, are attributed to the hole transitions ($\pi_g\leftarrow\sigma_u$ and $\sigma_g\leftarrow\sigma_u$, respectively) in the STE because of their peak positions which almost coincide with those for the V_k centers (Table II). We call these bands "hole transition bands" hereafter. Since the V_k centers are the on-center type in the configuration of the halogen molecule ($X_2{}^-$), the coincidence of the peak positions also suggests the on-center-type STE in these crystals. On the other hand, the hole transition bands ($\sigma_g\leftarrow\sigma_u$) of the off-center-type STE in KCl, KBr, and so on, rather shift to the higher energy side than the V_k bands, because of the decreased interatomic distance between two halogens caused by the off-center configuration of the STE.[12]

The hole transition bands exhibited two decay components (τ_f and τ_s), which were consistent with those of triplet luminescence of the STE. The intensity ratio of the two decay components reflects the initial population distributed in the sublevels of the triplet STE, as described below. Following to the model proposed to understand the decay time of triplet luminescence,[20–23] the population in the triplet sublevels (A_u, B_{2u}, and B_{3u}) should obey the following equations:

$$dN_A(t)/dt = -(\tau_{rA}^{-1} + W_A)N_A(t) + W_B N_B(t), \tag{1a}$$

$$dN_B(t)/dt = -(\tau_{rB}^{-1} + W_B)N_B(t) + W_A N_A(t), \tag{1b}$$

where $N_A(t)$ and $N_B(t)$ are the population in A_u and $B_{2,3u}$, τ_{rA}^{-1} (~ 0) and τ_{rB}^{-1} are the radiative transition rate from A_u and $B_{2,3u}$ to the ground state, and W_A and W_B are the nonradiative transition rate between A_u and $B_{2,3u}$. In this model, B_{2u} and B_{3u} levels were treated as a quasi-doubly-degenerate level denoted by $B_{2,3u}$. At low temperature, provided $\tau_{rA}^{-1}\ll\tau_{rB}^{-1}$ and $W_{A(B)}\ll\tau_{rB}^{-1}$, Eqs. (1a) and (1b) have a set of solutions,

$$N_A(t) \sim N_A(0)\exp(-t/\tau_s), \tag{2a}$$

$$N_B(t) \sim N_B(0)\exp(-t/\tau_f), \tag{2b}$$

where $\tau_s^{-1} = \tau_{rA}^{-1} + W_A$ and $\tau_f^{-1} = \tau_{rB}^{-1}$. Thus the transient absorption from the triplet state to higher excited states decays with the two components. The ratio of the two components at $t=0$ should be the same as the population ratio $N_B(0)/N_A(0)$, provided that the transition oscillator strength is independent of the initial state. Similarly, luminescence intensity decays with the two components, and the time-integrated intensity of the two components should have the same ratio as $N_B(0)/N_A(0)$. If the population was distributed uniformly among the three sublevels, the ratio should be 2:1 reflecting the degeneracy of the $B_{2,3u}$ and A_u states. In fact, the ratio was observed to be almost 2:1 in the STE localized at an iodine dimer in KCl:I.[24] However, in the case of NaBr, the ratio was 3:1 not only in absorption but also in luminescence. This fact suggests the lack of uniformity of the initial population distribution in NaBr, although the results for NaI are still ambiguous. Considering the fact that the ratio of the luminescence intensity tends to be greater than 2 in other alkali halide crystals,[25] it seems that the distribution tends toward the $B_{2,3u}$ state. This lack of uniformity might be interpreted as a spin-conservation effect through the relaxation process from the singlet free exciton, or the electron-hole pair, to the triplet STE.

In conclusion, the transient absorption spectra of NaBr and NaI both exhibited the electronic transition bands in the lower-energy region below 1 eV, and the hole transition bands which are very close to their V_k bands. The transient absorption decayed with two components, the decay time of which coincided with that of triplet luminescence, indicating that the transient absorption originated from the triplet STE. In addition, the intensity ratio of the two components reflected the initial population distributed in the sublevels of the triplet STE. These results strongly suggest the on-center configuration for the STE in NaBr and NaI. We note that the transient absorption spectra of the STE sensitively reflect the configuration of the STE, and that the electronic states of the on-center-type STE are much different from those of the off-center type.

TABLE II. Peak positions of the hole transition bands in the self-trapped excitons, compared with those of the V_k bands.

Crystal	$\pi_g\leftarrow\sigma_u$ (eV)	$\sigma_g\leftarrow\sigma_u$ (eV)
NaBr (STE)	1.6	3.2
NaI (STE)	1.4	3.0
NaBr (V_k)[a]	1.58	3.22
NaI (V_k)[b]	1.41	2.87

[a] From Ref. 18.
[b] From Ref. 19.

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[1] M. N. Kabler, Phys. Rev. **136**, A1296 (1964).

[2] A. M. Stoneham, J. Phys. C **7**, 2476 (1974).

[3] K. S. Song, A. M. Stoneham, and A. H. Harker, J. Phys. C **8**, 1125 (1975).

[4] A. H. Harker, S. B. Lyon, and A. Wasiela, Solid State Commun. **21**, 1053 (1977).

[5] N. Itoh, A. M. Stoneham, and A. H. Harker, J. Phys. C **10**, 4197 (1977).

[6] R. T. Williams and M. N. Kabler, Phys. Rev. B **9**, 1897 (1974).

[7] R. T. Williams, M. N. Kabler, and I. Schneider, J. Phys. C **11**, 2009 (1978).

[8] K. S. Song and C. H. Leung, J. Phys. Condens. Matter **1**, 8425 (1989).

[9] C. H. Leung, G. Brunet, and K. S. Song, J. Phys. C **18**, 4459 (1985).

[10] *Atomic Processes Induced by Electronic Excitation in Nonmetallic Solids*, edited by W. B. Fowler and N. Itoh (World Scientific, Singapore, 1990), Chap. IV [Rev. Solid State Sci. **4**, 357 (1990)].

[11] R. T. Williams and K. S. Song, J. Phys. Chem. Solids **51**, 679 (1990).

[12] S. Hirota, K. Edamatsu, and M. Hirai, Phys. Rev. Lett. **67**, 3283 (1991).

[13] K. Kan'no, K. Tanaka, and T. Hayashi, Rev. Solid State Sci. **4**, 383 (1990).

[14] M. Itoh, S. Hashimono, N. Ohno, and K. Kan'no, J. Phys. Soc. Jpn. **60**, 61 (1991).

[15] Decay time of triplet luminescence of NaBr had two components of $\tau_f=0.45$ μs and $\tau_s=190$ μs at 8 K. The spectra of the two components exhibited the same peak position (4.61 eV) and the same half-width (0.41 eV).

[16] G. Baldacchini, D. S. Pan, and F. Lüty, Phys. Rev. B **24**, 2174 (1981).

[17] Decay time of triplet luminescence of NaI had two components of $\tau_f=0.11$ μs and $\tau_s=3.8$ μs at 11 K. The spectra of the two components exhibited the same peak position (4.24 eV) and the same half-width (0.35 eV).

[18] C. J. Delbecq, W. Hayes, and P. H. Yuster, Phys. Rev. **121**, 1043 (1961).

[19] R. B. Murray and F. J. Keller, Phys. Rev. **153**, 993 (1967).

[20] J. U. Fischbach, D. Frölich, and M. N. Kabler, J. Lumin. **6**, 29 (1973).

[21] T. Yoshinari and M. Hirai, J. Phys. Soc. Jpn. **39**, 1498 (1975).

[22] T. Karasawa and M. Hirai, J. Phys. Soc. Jpn. **40**, 128 (1976).

[23] T. Mukai, K. Kan'no, and Y. Nakai, J. Phys. Soc. Jpn. **58**, 1838 (1989).

[24] S. Hirota, Master thesis, Tohoku University, 1991 (in Japanese).

[25] H. Ishikawa, Master thesis, Tohoku University, 1990 (in Japanese).