

## Rapid Communications

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### Resonant luminescence spectra of excitons and their excitation-energy dependence in KI and RbI

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A weak luminescence band is observed on the high-energy side of the main band of exciton resonant luminescence in KI and RbI. It supports the identification that the main band originates from the triplet exciton state. The luminescence spectra show significant dependence on excitation energy in the  $n=1$  exciton absorption region. The relaxation process to self-trapped exciton states is discussed.

#### I. INTRODUCTION

Resonant luminescence of excitons in alkali halides was first observed by Kuusmann, Liblik, and Lushchik with electron-beam excitation.<sup>1</sup> The luminescence was also observed by X-ray irradiation and UV light excitation.<sup>2-4</sup> The observation of the resonant luminescence is restricted to iodide compounds, while the luminescence of the self-trapped excitons (STE) is observed in every alkali halide. The coexistence of free-exciton (FE) luminescence and STE luminescence indicates that at least in alkali iodides the FE state is retained as a metastable one, and is separated from the STE states by an adiabatic potential barrier. The barrier height was estimated from the temperature dependence of the intensity of the FE luminescence by several authors.<sup>5</sup>

There is a controversy about the spin multiplicity of the FE state which causes the main band of the exciton resonant luminescence. Itoh<sup>6</sup> assigned the resonant emission of KI and RbI to the emission from the triplet state on the basis of experimental studies on thin crystals which are dilationally strained. Fröhlich and co-workers<sup>7,8</sup> revealed using the three-photon absorption technique that there is a spin-triplet state at the same energy position as the main band of the FE luminescence spectra in KI and RbI. On the other hand, Nishimura,<sup>9</sup> by analysis of the phonon sidebands, attributed the main band of the FE luminescence to emission from the singlet state.

STE luminescence in many alkali halides consists of  $\sigma$  and  $\pi$  emission bands.<sup>10</sup> In KI and RbI the  $\sigma$  band has a short decay time on the order of ns, and is the emission of a singlet state of the STE, while the  $\pi$  band is the triplet emission having the long decay time on the order of  $\mu$ s. The large difference in the Stokes shift of the two bands has recently been attributed not to the difference in the corresponding electronic states but to the different relaxed

configurations of the STE.<sup>10</sup> That is, the  $\sigma$  and the  $\pi$  bands are the emission of the lowest state of an STE in "on-center" and "off-center" configurations,<sup>11</sup> respectively. The intensity ratio of the two bands has a significant dependence on the excitation photon energy: The  $\sigma$  band is very weak upon excitation in the  $n=1$  exciton absorption band. This fact tells us that the population distribution in the singlet and the triplet states of the STE is correlated with the states initially created by photoexcitation, though further interpretation has not been established yet.

In the present study we examine the resonant exciton luminescence spectra of KI and RbI under narrow-band UV excitation in the  $n=1$  exciton absorption region. A structure is observed on the high-energy side of the main band of FE luminescence in both crystals. We assign it to the orthoexciton luminescence and the main band to the paraexciton one. The orthoexciton state has a total angular momentum of  $F=1$  and the paraexciton state of  $F=2$ .<sup>7</sup> When the excitation energy is changed in the  $n=1$  exciton absorption region, significant change is observed in the resonant luminescence spectrum as well as in the STE luminescence spectrum. The relaxation and self-trapping processes of the FE will be discussed.

#### II. EXPERIMENTAL PROCEDURES

Single crystals of KI and RbI were obtained from the University of Utah. A sample obtained from Harshaw Chemical Company was also measured. A cleaved specimen of  $\sim 10 \times 10 \times 1$  mm<sup>3</sup> was mounted on a sample holder attached to a cryogenic refrigerator and was kept at 10 K. The sample was irradiated with an excimer laser pumped dye laser (LAMBDA PHYSIK EMG103MSC and FL3002) of the Laser Facility of Osaka Dental Uni-

versity. The second and the third harmonic lights of the output of coumarin 440 and rhodamine-B dyes, respectively, were used for excitation in the  $n=1$  exciton absorption region. The linewidth of the light was less than 0.3 meV. The luminescence from the sample was detected through a single monochromator (JOBIN YVON HR640), with a photomultiplier (HAMAMATSU R928 or R166UH) and a boxcar averager (Stanford Research Systems SR250).

### III. RESULTS AND DISCUSSION

Figure 1 shows the resonant luminescence spectrum of excitons in KI at 10 K. The excitation energy is 5.961 eV, which is higher than the longitudinal exciton energy ( $E_L=5.946$  eV). The main peak is located at 5.829 eV, and phonon sidebands appear on the low-energy side of the main band. On the high-energy side, a weak structure is observed. The peak height of this structure is about  $\frac{1}{30}$  of that of the main band at this excitation energy, and is comparable to that of the phonon sidebands on the low-energy side. The intensity of the high-energy structure is dependent on the excitation photon energy. It is most significant when the excitation energy is around 5.96 eV. We observed essentially the same spectra on samples from a different source. The structure on the high-energy side was observed also under excitation with UV light from a deuterium lamp filtered with a single path monochromator, which ensures that the structure is not specific to the high-density excitation by the laser. A similar spectrum is obtained in RbI as shown in Fig. 2. The intensity of the high-energy structure relative to that of the main band is weaker than in KI. The energy positions of the main peak and the high-energy structure are in good agreement with the values of  $E_P$  ( $=5.8279$  eV for KI and 5.7266 eV for RbI) and  $E_T$  ( $=5.847$  eV for KI and 5.748 eV for RbI) following Fröhlich *et al.*,<sup>8</sup> where  $E_P$  and  $E_T$  correspond to the energy of paraexciton and orthoexciton states, respec-

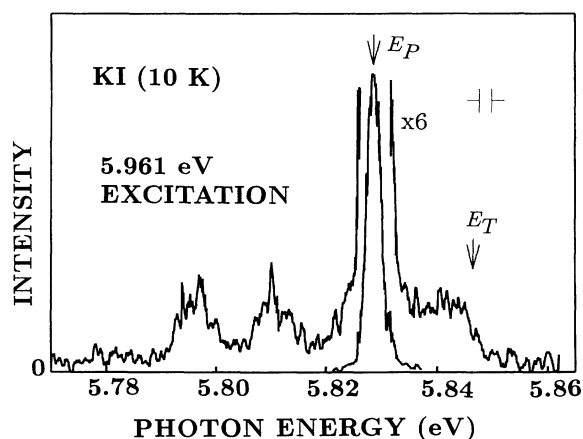


FIG. 1. Resonant luminescence spectrum of excitons in KI at 10 K.  $E_P$  and  $E_T$  represent paraexciton and orthoexciton energies following Fröhlich *et al.* (Ref. 8). Excitation photon energy is 5.961 eV which is higher than the longitudinal exciton energy ( $E_L=5.946$  eV).

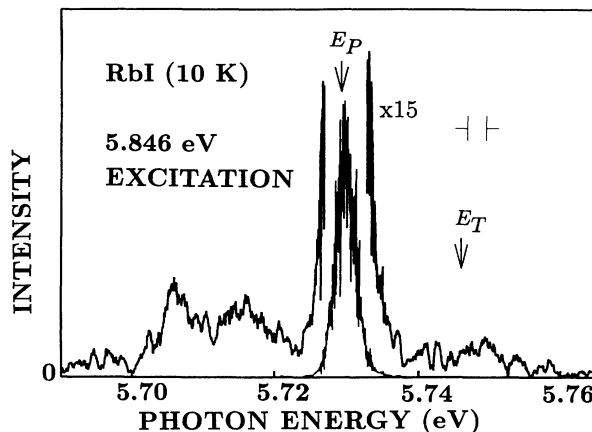


FIG. 2. Resonant luminescence spectrum of excitons in RbI at 10 K.  $E_P$  and  $E_T$  represent paraexciton and orthoexciton energies following Fröhlich *et al.* (Ref. 8). Excitation photon energy is 5.846 eV, which is nearly equal to  $E_L$ .

tively. The energy positions of  $E_P$  and  $E_T$  are indicated in Figs. 1 and 2 by the arrows. Because of their energy positions we conclude that the main band of the resonant luminescence spectrum originates from the paraexciton state and the weak structure from the orthoexciton state. Recently, Tanimura and Itoh<sup>12</sup> observed the energy shift of the main peak in RbI under applied magnetic field and clarified its triplet nature.

When the excitation energy is lowered below  $E_L$ , the emission spectrum on the high-energy side of the main band changes distinctly. Some of the luminescence spectra of KI measured at various excitation energies are shown in Fig. 3. Similar spectra were obtained in the case of RbI. The excitation energy positions are indicated by arrows in the figure. Each spectrum is normalized to its main peak. The peak of the high-energy emission band is located below the excitation energy in each case by an amount  $n\hbar\omega_{LO}$  ( $n=2$  or 3), as indicated by bars with scales of  $\hbar\omega_{LO}$ , where  $\hbar\omega_{LO}$  is the LO phonon energy of 16 meV. Hence the bands are considered to be Raman-like hot luminescence originating from excitons in the course of relaxation. The Raman-like hot luminescence is ascribed to radiative escape of exciton polaritons through the crystal surface. Since the polariton is a strongly coupled state of a photon and an exciton, the participating exciton should be the singlet one. Therefore, the intensity ratio of the main luminescence band at 5.829 eV and the hot luminescence would reflect the population ratio of the singlet and the triplet components of the FE. The ratio is plotted versus excitation photon energy in Fig. 4 by the solid circles. When the excitation energy is higher than 5.93 eV, the intensity of the orthoexciton luminescence relative to that of the main band is taken as the ratio.

The transition probability for the paraexciton should be very small because of its pure triplet nature at  $k=0$ . In fact, its optical absorption cannot be detected by conventional transmission measurements. However, most of the FE luminescence comes from the paraexciton state for excitation above  $\sim 5.9$  eV. Itoh has given an explanation<sup>6</sup> that free excitons are relaxed on the  $F=1$  polariton

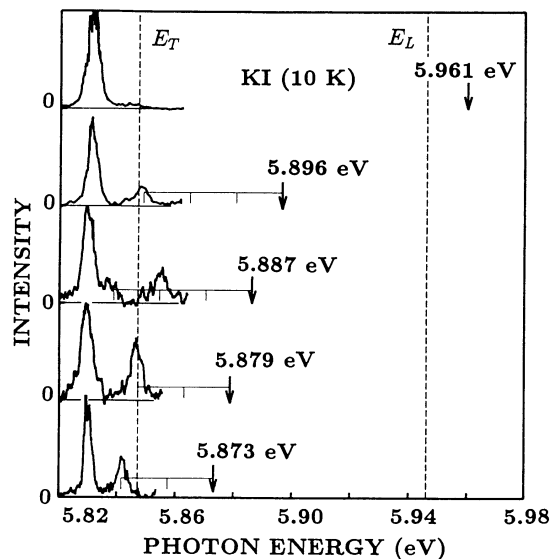


FIG. 3. FE luminescence spectra of KI at 10 K measured for various excitation photon energies, which are indicated by arrows. The bar drawn below each arrow shows the scale of  $\hbar\omega_{LO}$ , where  $\hbar\omega_{LO}$  is the LO phonon energy of 16 meV. Each spectrum is normalized to the main peak. The dashed lines with  $E_T$  and  $E_L$  denote orthoexciton and longitudinal exciton energies.

branch and the branch is connected to the triplet exciton ( $F=2$ ) state near the  $\Gamma$  point with a finite  $k$ . The polaritons are, hence, concentrated on the paraexciton state. They can radiate as a light emission by virtue of the symmetry-breaking effect<sup>13,14</sup> due to the finite wave vector. However, if the relaxation from orthoexcitons to paraexcitons occurs exclusively near the  $\Gamma$  point, the excitation energy dependence of the singlet-triplet ratio observed in the present study cannot be explained, since the radiative decay rate of each state does not depend on the excitation energy. Transition between states with large  $k$  should be considered. When the excitation photon energy is raised, the chance of a spin transition may increase during the long relaxation pathway.

The luminescence yield of  $\sigma$  emission, which is the singlet luminescence of STE in KI and RbI, is much depressed when the excitation energy is in the  $n=1$  exciton absorption region. This is called the “ $n=1$  anomaly.”<sup>15</sup> Because of this, it has been widely accepted that the initial state of the  $\sigma$  emission is an excited singlet STE state, not the lowest singlet one. However, in spite of its weakness, the  $\sigma$  luminescence is observable even with excitation in the  $n=1$  exciton absorption region. We measured the intensity of the  $\sigma$  emission relative to that of the triplet STE emission<sup>16</sup> as a function of the excitation photon energy. The ratio between STE emission bands is

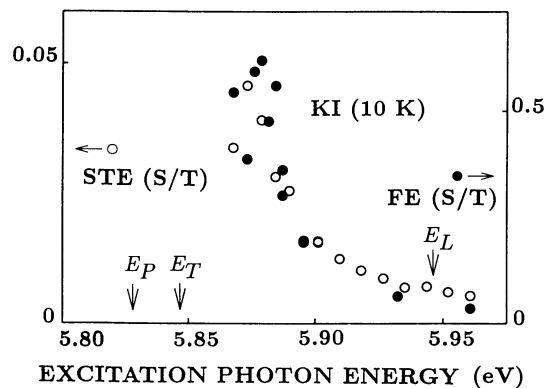


FIG. 4. Solid circles: The intensity ratio of the hot luminescence band to the main luminescence band of FE in KI at 10 K as a function of the excitation photon energy. Open circles: The intensity ratio of  $\sigma$  band (the singlet STE emission) to the triplet STE emission.  $E_P$ ,  $E_T$ , and  $E_L$  represent paraexciton, orthoexciton, and longitudinal exciton energies.

plotted in Fig. 4 by the open circles. It shows a dependence similar to that in the case of the FE depicted by solid circles. This fact suggests that the population ratio of the spin-singlet STE and the triplet STE is governed by a relaxation process in the FE band. When the excitation photon energy is raised in the  $n=1$  FE band, the relaxation of FEs into the paraexciton state much increases, and this may give rise to the reduction of the singlet component even in the STE states. For further increase in the excitation energy from 5.95 eV toward the  $n=2$  exciton energy, the intensity ratio of the singlet STE emission ( $\sigma$  band) to the triplet STE emission remains as low as  $6 \times 10^{-3}$ , while the ratio increases steeply to about  $1 \times 10^{-1}$  around the  $n=2$  exciton energy [6.186 eV (Ref. 9)]. Rapid self-trapping of excitons or holes may contribute to the increase in the intensity of the  $\sigma$  band, which is an alternative process of relaxation in the  $n=1$  FE band.

#### IV. SUMMARY

In conclusion, we observed a weak structure on the high-energy side of the main band of the resonant luminescence of excitons in KI and RbI, and assign it to orthoexciton luminescence. The main band is caused by the paraexciton state. When the excitation energy is lowered below  $E_L$  in KI, the population of the singlet component of the FE is increased. The relative intensity of the  $\sigma$  band to the  $\pi$  band of STE is also increased in the same way. This fact suggests that the population ratio of the spin-singlet STE and the triplet STE is determined by the relaxation process of the FE.

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