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Radiative recombination and self-trapping of excitons via biexciton states in RbI

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We have observed a luminescence band at 5.675 eV in RbI under dense excitation with a uv laser. The band is located 50 meV lower than the main peak of the free-exciton luminescence (FEL). The intensity of the band increases with an increase in the excitation intensity depending quadratically on the FEL intensity. The 5.675-eV band is assigned to luminescence of a biexciton leaving an exciton behind. The luminescence spectrum of self-trapped excitons changes with the appearance of the biexciton luminescence. The spectral change is explained by a model including formation and decomposition processes of biexcitons. [S0163-1829(96)51224-5]

Photoexcitation of a crystal at an energy slightly below the band gap generates bound electron-hole pairs called free excitons (FE's). FE's can be combined into bound FE-FE pairs called biexcitons. Biexcitons contribute to nonlinear phenomena through the third or higher order electric susceptibility, which phenomena have been extensively studied in semiconductors such as CuCl.[1] A theory of biexciton formation predicts that the lowest biexciton state is energetically lower than a two-exciton state irrespective of the ratio of the effective mass of an electron to that of a hole in the crystal.[1] Experimental studies on biexciton luminescence are extended in various materials accordingly, for example, in III-V compounds such as GaAs quantum wells[2] and in II-VI compounds such as CdS and CdSe.[3] In alkali halide crystals, which have a wider band gap than these compounds, strong electron-lattice interaction induces deformation of the lattice around a FE to make a self-trapped exciton (STE), and the luminescence of the FE (FEL) is hardly observed.[4] However, FEL is observed in alkali iodides such as RbI, KI, and NaI, under excitation in the $n=1$ exciton absorption region. Recently, it has been clarified experimentally that FEL in RbI originates from a spin-triplet state[5] and that the lifetime is as long as 1.2 ns at low temperatures.[6] The rather long lifetime of FE's offers a possibility to make biexcitons.

In order to search for the evidence of biexciton formation in alkali halide crystals, we measured luminescence spectra of FE's and STE's under dense excitation in the $n=1$ exciton absorption region in RbI. We have observed a new luminescence band at 5.675 eV, which is about 50 meV lower than that of FEL. The intensity of the band increases with increase in the excitation intensity depending quadratically on the FEL intensity. In addition to the appearance of the new luminescence band, a spectral change in STE luminescence has been found. These results will be explained by a simple model of exciton kinetics including the biexciton states.

A single crystal of RbI was obtained from the University of Utah. A cleaved specimen of $\sim 10\times10\times1$ mm^3 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. The second harmonic light of the output of coumarin 440 was used for excitation in the $n=1$ exciton absorption region. The linewidth of the light was less than 0.3 meV, and the pulse duration was about 15 ns. The peak density of the excitation light was ~ 100 kW/cm^2 and was attenuated by neutral-density filters. Luminescence from the sample was detected through a single-grating monochromator attached with a CCD multichannel detector cooled by liquid nitrogen for the measurement of FEL. A photomultiplier tube and a boxcar averager were used for the measurement of STE luminescence.

Figure 1 shows luminescence spectra of RbI measured under 5.861 eV excitation at 10 K. The peak due to FEL is seen at 5.727 eV in each spectrum. The excitation intensities were (a) ~ 0.3 kW/cm^2 and (b) ~ 50 kW/cm^2, respectively. Each spectrum is normalized at the peak. In Fig. 1(a) phonon side bands are seen on the low-energy side of the peak, and orthoexciton luminescence is seen on the high-energy side.[7] In Fig. 1(b) a band is seen at 5.675 eV, which is not distinguished in Fig. 1(a). The intensity of FEL (I_X) and that of the 5.675-eV band (I_{XX}) are shown by open squares and closed circles, respectively, as a function of the excitation

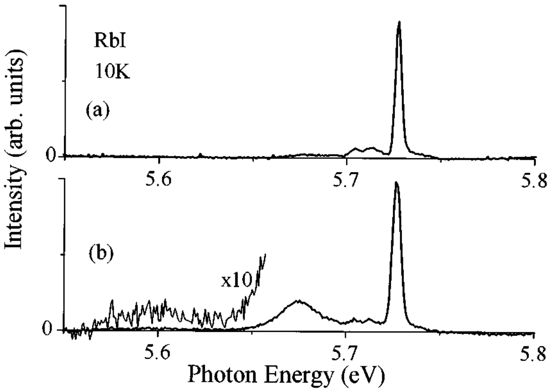

FIG. 1. Luminescence spectra of FE's in RbI under 5.861 eV excitation at 10 K. Excitation intensities are (a) ~ 0.3 kW/cm^2 and (b) ~ 50 kW/cm^2.

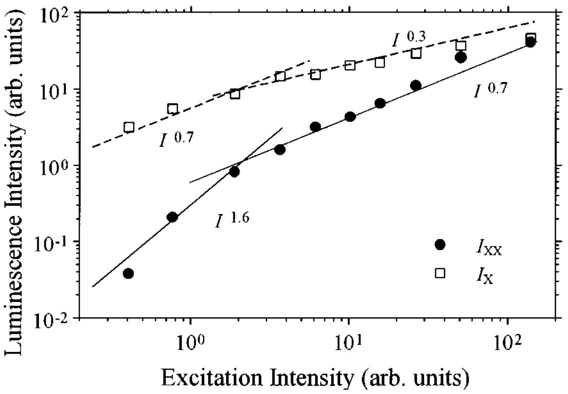

FIG. 2. The intensity of FEL (I_X) and that of the 5.675 eV luminescence (I_{XX}) are plotted as a function of excitation intensity (I) by open squares and closed circles, respectively.

intensity (I) in Fig. 2. We find that $I_X \propto I^{0.7}$ and $I_{XX} \propto I^{1.6}$ for low excitation intensities and $I_X \propto I^{0.3}$ and $I_{XX} \propto I^{0.7}$ for high excitation intensities, as shown by broken and solid lines. Namely, the intensity of the 5.675-eV band depends quadratically on the FEL intensity, which indicates an interaction between two excitons. It was reported that a perturbation by a STE lowers the energy of a FE.[8] However, the perturbed FE is not the origin of the 5.675-eV band since its absorption band locates at 5.61 eV, which is lower than 5.675 eV. A FE might be excited to an upper state due to collision with another FE, which gives some energy to the former FE to decay radiatively. However, this process is not the origin of the 5.675-eV luminescence since there are no upper states whose exceeding energy corresponds to the energy difference between FEL and the 5.675-eV band. Consequently, the biexciton is the most probable candidate for the origin of the 5.675-eV band. We attribute the 5.675-eV band to luminescence of a biexciton leaving an exciton behind.

Another luminescence band due to a biexciton leaving a longitudinal exciton behind is expected at 5.577 eV, since the value of longitudinal-transverse splitting of FE in RbI is 98 meV.[9] We find a band around 5.60 eV with a weak intensity as seen in the spectrum on an expanded scale in Fig. 1(b). The location of the band is slightly higher than the expected position. The band around 5.60 eV might possibly be a composite band of the biexciton luminescence and the luminescence of a FE perturbed by a STE. We tried to observe the biexciton luminescence by direct generation of biexcitons through two-photon excitation. However, the Urbach tale of one-photon absorption and strong Raman scattering resonant to a FE inhibited the detection of the biexciton luminescence.

The luminescence band attributed to the recombination of biexcitons is observed about 50 meV lower than FEL. The lowest state of FE in RbI is a paraexciton state with total angular momentum $J=2$. An orthoexciton state with $J=1$ locates 21 meV above the paraexciton state.[9] It has been clarified experimentally that the main peak of FEL in RbI is due to paraexcitons.[5] The exciton that is left behind by the radiative decomposition of a biexciton should be the orthoexciton since the lowest state of the biexciton has zero angular momentum.[1] Therefore, the binding energy of the biexciton is estimated at 30 meV, by taking the two-paraexciton state as the zero of energy. According to the theory of Hanamura on the binding energy of biexcitons,[1] the binding energy of 30 meV indicates that the ratio of the effective mass of an electron to that of a hole, denoted by σ, is 0.23. The reduced mass of an exciton in RbI was reported to be $0.32m_0$, where m_0 is the bare electron mass.[10] We have no more available data for the exciton masses in RbI. The total mass and the effective mass of an exciton in KI were estimated at $3.7m_0$ (Ref. 11) and $0.40m_0$,[12] respectively. Using these data of KI, which are expected not to differ so much from those of RbI, we can deduce the σ to be 0.11–0.25. This is not consistent to the theoretical prediction.

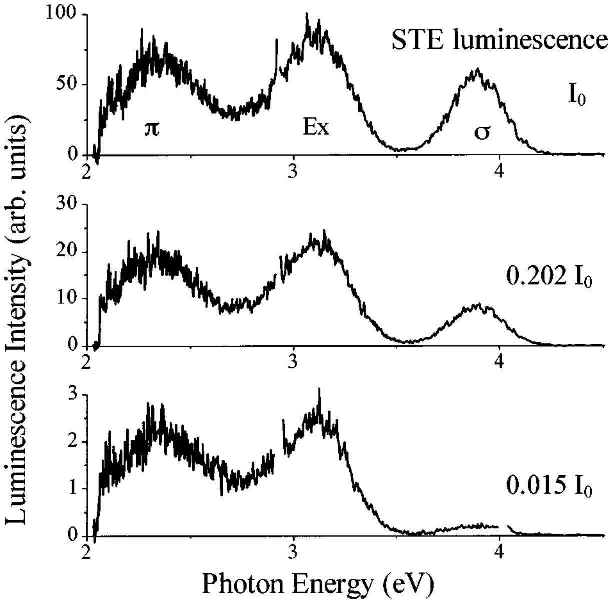

FIG. 3. STE luminescence spectra of RbI measured for different excitation intensities under 5.861 eV excitation at 10 K. The excitation intensity increases from the bottom to the top and relative values are written on the right.

In addition to the appearance of the biexciton luminescence, spectral change in STE luminescence is observed with increasing the excitation intensity as shown in Fig. 3. Relative intensities of the excitation light are indicated in the figure. Three luminescence bands are seen: the σ band at 3.9 eV, Ex band at 3.1 eV, and π band at 2.3 eV.[4,13] The σ band has a short decay time of the order of ns. It is accepted that the band originates from the singlet state of the on-center STE where the core of a STE (I_2^-) occupies the midpoint of the original positions of the two halogen ions.[4,14] The Ex and π bands have long decay times of the order of μs. The bands originate from the triplet state of STE's with the off-center configurations where I_2^- is displaced along the [110] direction of the crystal.[4,14] We have clarified in previous papers[7] that the intensity of the σ band relative to the sum of the intensities of Ex and π bands is proportional to the population of the orthoexciton relative to that of the paraexciton. That is, the σ band originates mainly from the orthoexciton and the Ex and π bands mainly from the paraexciton. We, therefore, hereafter refer to the σ band as the singlet STE luminescence and the Ex and π bands as the triplet STE luminescence. The intensity of the singlet STE luminescence is weak under excitation in the $n=1$ exciton absorption re-

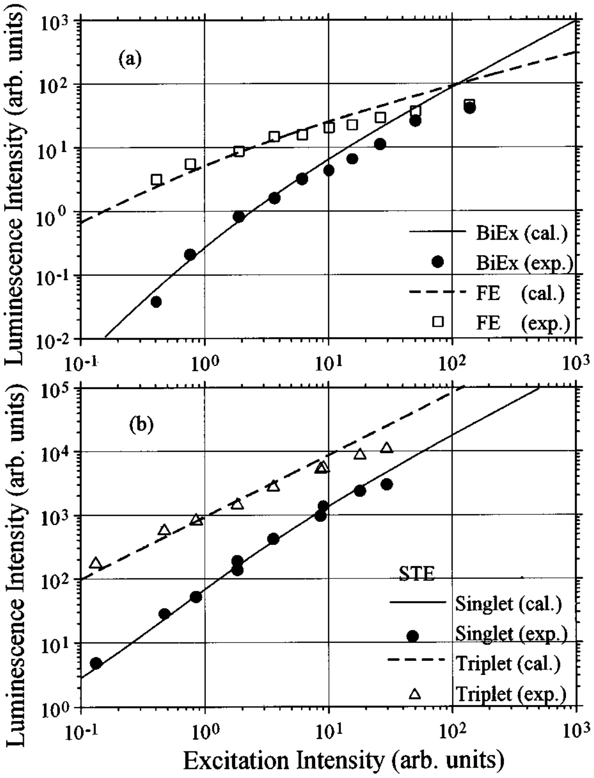

FIG. 4. The intensities of (a) FEL and biexciton luminescence, and (b) singlet and triplet luminescence of STE's as a function of excitation intensity. The experimental data (exp.) and calculated curves (cal.) are shown. (a): □, FE (exp.); ●, biexciton (exp.); dashed line, FE (cal.); solid line, biexciton (cal.). (b): △, triplet STE (exp.); ●, singlet STE (exp.); dashed line, triplet STE (cal.); solid line, singlet STE (cal.).

gion, which has been interpreted as the scattering of orthoexcitons to the paraexciton state.[7] As shown in Fig. 3 the intensity of the singlet luminescence is enhanced with the increase of the excitation intensity. The intensity of Ex band relative to that of π band remains constant. The intensities of the singlet and triplet luminescence of the STE's versus the excitation intensity are shown by closed circles and open triangles, respectively, in Fig. 4(b). When the excitation intensity is weak, the singlet luminescence is less than 0.02 of the total luminescence of STE.[7] With the increase of the excitation intensity the singlet luminescence increases superlinearly, whereas the triplet luminescence increases almost linearly. The total yield of the luminescence remains almost constant, which indicates that the rate of nonradiative processes is independent of the excitation intensity.

We focus our attention on the mechanism of the spectral change in STE luminescence. In semiconductors the dominant process of annihilation of a biexciton is known as $XX \rightarrow X + \hbar\omega$, where XX denotes a biexciton, X a free exciton, and $\hbar\omega$ an emitted photon leaving X behind.[1] We refer hereafter to this process as process (I). An orthoexciton is produced by process (I) as mentioned before. Since the orthoexciton prefers to relax into the on-center STE to induce the singlet STE luminescence, on-center STE's are expected to be generated efficiently through the formation of biexcitons and process (I). This seems a possible interpretation of the enhancement of the singlet luminescence. However, in the present result, the intensity of the biexciton luminescence is too weak to explain the increase of the singlet STE luminescence. It does not exceed the intensity of FEL, whose quantum yield is less than 0.01,[4] even under high-density excitation as shown in Fig. 2. The weak yield of the biexciton luminescence is not attributed exclusively to a reabsorption effect because the measured absorption coefficient at 5.68 eV (the energy of the biexciton luminescence) was about one-tenth of that at 5.86 eV (the excitation photon energy). Alternative process is, therefore, necessary in order to explain the enhancement of the singlet STE luminescence. Direct formation of two excitons out of a biexciton is energetically forbidden because of the binding energy of the biexciton. However, it may be possible to make a FE and a STE by tunneling through a two-exciton state: $XX \rightarrow X + \mathrm{STE}$. We refer hereafter to this process as process (II). Pairs of an on-center STE and an orthoexciton could be generated through process (II) under high-density excitation. This may explain both the enhancement of the singlet STE luminescence and the weakness of the biexciton luminescence.

We will now investigate the model on kinetics of FE's and biexcitons. Rate equations for the densities of the FE (n_X) and the biexciton (n_{XX}) are given by[15]

$$dn_X/dt = G(t) - n_X/\tau_X - n_X^2/(\tau_c n_c) + n_{XX}/\tau_{XX}$$

and

$$dn_{XX}/dt = n_X^2/(2\tau_c n_c) - n_{XX}/\tau_{XX},$$

where $G(t)$ denotes generation rate of FE's by the excitation light, τ_X and τ_{XX} are lifetimes of the FE and the biexciton, n_c is the characteristic density, and $1/\tau_c$ is the characteristic conversion rate from FE's to biexcitons when $n_X = n_c$. n_X is nearly equal to the density of the paraexciton because of the rapid scattering of orthoexcitons to the paraexciton state.[7] In the condition of the present experiment the pulse duration of the excitation light is long enough compared to τ_X, τ_{XX}, and τ_c. Then we consider the stationary case. We assume that η_r $(0 < \eta_r < 1)$ of excitons that annihilate due to the second term in the right-hand side of the first equation emit photons, η_{nr} $(0 < \eta_{nr} < 1)$ of excitons annihilate nonradiatively, and $(1 - \eta_r - \eta_{nr})$ of excitons are self-trapped. We also assume that ζ $(0 < \zeta < 1)$ of biexcitons that annihilate due to the last term of the second equation emit photons leaving an exciton behind, and $(1 - \zeta)$ of biexcitons break into a FE and a STE as expressed in process (II), ignoring nonradiative processes. The intensities of the luminescence of FE's and of biexcitons (I_X and I_{XX}) are expressed as $I_X = \eta_r n_X/\tau_X$ and $I_{XX} = \zeta n_{XX}/\tau_{XX}$, respectively. The intensities of the singlet and triplet luminescence of STE's (I_S and I_T), which originate from on-center and off-center STE's, are given by

$$I_S = (1 - \eta_r - \eta_{nr})\alpha n_X/\tau_X + (1 - \zeta)\beta n_{XX}/\tau_{XX}$$

and

$$I_T = (1 - \eta_r - \eta_{nr})(1 - \alpha) n_X/\tau_X + (1 - \zeta)(1 - \beta) n_{XX}/\tau_{XX},$$

where α and β are constants between 0 and 1. The last term of the second equation is the consequence of process (II):

pairs of an off-center STE and a paraexciton as well as those of an on-center STE and an orthoexciton are generated according to the selection rule.

The calculated intensities of FEL and biexciton luminescence are drawn by a broken curve and a solid curve, respectively, in Fig. 4(a), and those of singlet and triplet luminescence of STE's are drawn by solid and broken curves in Fig. 4(b). The scales of the calculated curves are adjusted to the experimental data shown by closed circles, open squares, and open triangles. We determined α to be 0.02 from the measurement under low-density excitation.[7] Since process (II) and self-trapping are the dominant processes of annihilation of biexcitons and FE's, respectively, $(1-\zeta)$ and $(1-\eta_r-\eta_{nr})$ are close to unity. Consequently, we fixed $(1-\zeta)/(1-\eta_r-\eta_{nr})$ at unity in the fitting procedure. Parameters ζ/η_r and β were fitted, and 0.14 and 0.20 were obtained, respectively. Figure 4 shows that our model reproduces the experimental results well. For the highest excitation intensities the calculated curves lie above the experimental data. We cannot exclude the possibility that the discrepancy is due to the rise of temperature and damage of the surface of the sample. We discuss briefly a possible modification of process (II). There might be a process where two STE's are directly generated out of a biexciton ($XX \rightarrow 2$STE). Adopting this process instead of process (II) induces some changes in the expressions of dn_X/dt, I_S, and I_T. However, no essential changes are induced in the fitting functions.

There exists another candidate to explain the enhancement of the singlet STE luminescence. It was reported that an off-center STE can be converted to an on-center STE by an irradiation of a light pulse with an energy in the absorption band of FE's perturbed by STE's (off-STE $+X\rightarrow on$-STE).[16] We tried a fitting procedure on this model, and found that the model does not explain the experimental result.

In conclusion, we have observed the luminescence band at 5.675 eV in RbI under dense excitation in the $n=1$ exciton absorption region. The band is assigned to recombination luminescence of biexcitons. The binding energy of the biexciton is estimated at 30 meV. Superlinear increase of the singlet luminescence of STE is observed accompanied by the appearance of the biexciton luminescence. A simple model on kinetics of FE's and biexcitons reproduces the experimental result concerning the intensities of FEL, biexciton luminescence, and STE luminescence consistently.

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