

Free-exciton luminescence in alkali iodides under external magnetic fields at low temperatures

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Spectroscopic properties of the free-exciton luminescence in RbI and KI under applied external magnetic fields of up to 6 T have been studied between 1.2 and 4.2 K. It is found that the resonance line in RbI is redshifted, while that in KI splits into blueshifted and redshifted components under a magnetic field. These spectral changes are in accordance with the Zeeman shift of the lowest spin-triplet state of the exciton. It is found also that the resonance peak grows and shifts to higher energy upon warming a sample from 1.2 to 4.2 K. The results are explained in terms of the polariton model in which the spin-triplet exciton state acts as an effective bottleneck.

I. INTRODUCTION

Excitons in alkali halides have been a subject of extensive studies of solid-state spectroscopy.¹⁻⁷ In particular, formation of the self-trapped state and its coexistence with the free-exciton state⁸⁻¹⁰ are unique features of excitons observed in iodides, which have attracted much attention in view of the relaxation of the elementary excitation in solids.¹¹

Optically created excitons are first placed on the dispersion curve of the exciton polariton^{12,13} at points having finite values of the translational wave vector k . Then they are relaxed to states with smaller k values through successive scattering by phonons. This energy dissipation, or relaxation in momentum space, of excitons in many semiconductors has been described satisfactorily in terms of the polariton model.^{14,15} On the other hand, in solids, where exciton-phonon coupling is strong enough, excitons are self-trapped spontaneously by deforming the lattice around them, resulting in the formation of the self-trapped excitons (STE's).¹¹ This self-trapping is relaxation in real space, and the STE thus formed emits Stokes-shifted luminescence. Therefore, the excitons in alkali halides are subjected to two types of relaxation: one in momentum space, intraband relaxation; and the other in real space, lattice relaxation.

The electronic structure of the excitons in alkali halides has been studied extensively theoretically.^{1,16,17} Recent three-photon spectroscopic studies of the excitons have produced a precise experimental determination of the polariton structures in several alkali halides.²⁻⁴ These results have provided a fundamental basis for studies of the relaxation processes of excitons in momentum space.

On the other hand, recent studies of the STE have shown clearly that there exist three distinct relaxed configurations, each of which is characterized by the Stokes shift (S_1) of the luminescence band¹⁸ or by the ab-

sorption energy (E_a) of the electron transition from the initial state of the luminescence to a higher excited state.¹⁹ One configuration (type I) shows the smallest S_1 and lowest E_a , the second (type III) shows the largest S_1 and highest E_a , and the third (type II) is an intermediate between the former two. In materials where both type I and type III (and/or type II) are formed, the STE of type I is at a spin-singlet state which emits σ -polarized luminescence (σ luminescence), whereas the STE of type III (and/or type II) is at a spin-triplet state which emits π -polarized luminescence (π luminescence).⁶

The self-trapping processes of free excitons have been studied experimentally by measuring the excitation spectrum of the STE luminescence.^{10,20-23} An important feature is that, upon generating the lowest ($n=1$) exciton, π luminescence but not σ luminescence is emitted. It has also been shown that both emission bands are produced efficiently when excitation occurs in higher ($n \geq 2$) exciton bands lying near the band gap. This anomalous behavior of the excitation spectrum of the STE luminescence, which is originated from characteristic features of the intraband relaxation and/or lattice relaxation of the excitons, indicates that the internal structure of free excitons plays an important role in the relaxation process from the exciton-polariton state to the self-trapped state. Although several arguments have attempted to explain this anomaly,^{22,23} no clear model has been presented.

The intraband relaxation of excitons in alkali halides has been studied extensively by Nishimura *et al.*⁹ They concluded that the optically generated exciton in the $n=1$ singlet state is relaxed to the band bottom through phonon scattering while keeping its spin-singlet character, and then it is subjected to self-trapping and radiative recombination. According to them, the free-exciton luminescence (FEL) arises from the radiative decay of the singlet free excitons. On the other hand, Itoh²⁴ has shown that the peak energy of the FEL in thin crystals of KI and RbI agrees with that of the triplet-exciton absorption which is partially allowed by the internal stress act-

ing in the thin crystals. He examined further the relation between the crystal thickness and the peak energy of the FEL, and suggested that the FEL in the bulk sample originates from the triplet state of the free excitons. Thus even the identification of the initial state of the FEL is still controversial, and the details of the intraband relaxation of excitons in alkali halides are far from being well understood.

The purpose of the present study is to clarify the electronic nature of the initial state of the FEL in RbI and KI by studying the effects of external magnetic field on the FEL. (A brief description of the results of RbI has been given elsewhere.²⁵) The peak shift of the resonance line of the FEL achieved by applying a magnetic field is clearly observed. The shift follows exactly the Zeeman shift of the lowest level of the triplet exciton observed by Beerwerth and co-workers.^{2,3} The result reveals conclusively that the FEL in RbI and KI arises from the spin-triplet state. It is also found that the resonance peak of the FEL grows and shifts to higher energy upon warming a sample from 1.2 to 4.2 K. This feature is explained satisfactorily by the polariton model in which the spin-triplet state acts as an effective bottleneck. Based on these results, intraband relaxation and lattice relaxation of the excitons are discussed.

II. EXPERIMENT

Specimens with a size of $5 \times 10 \times 1$ mm³, cleaved from a crystal block purchased from the University of Utah, were set inside the sample chamber of a magneto-optical cryostat (Oxford, SM-4) capable of applying a magnetic field (B), of which the strength at the sample position was up to 6 T. The specimen in the sample chamber was immersed in liquid helium, and the temperature of the sample was controlled by changing the chamber pressure and was measured with a Pt resistor. A $\langle 100 \rangle$ crystal axis of the specimen was oriented nearly (within 2°) along the magnetic-field direction, and the specimen was excited by monochromatic UV light propagating parallel to the magnetic-field direction. The UV light from a 150-W D₂ lamp was dispersed through a monochromator (Jobin/Yvon, H-20) with a band pass of 1 nm, and then focused by a CaF₂ lens on the sample surface. Luminescence emitted along the direction perpendicular to the magnetic-field direction was analyzed by a grating monochromator (Jobin/Yvon, HR-320) and detected with a multichannel detector (Princeton, IRY1024). A grating with 4960 grooves/mm was used to achieve high spectral resolution. This detection system allowed us to determine precisely the relative shift of the peak position of a luminescence line induced by applying a magnetic field or by changing temperature. Wavelength correction of the detection system was made carefully by measuring several lines of a Hg lamp placed at the sample position. The absolute accuracy of the wavelength thus determined was within an error of ± 0.08 Å, which corresponds to an energy of ± 0.2 meV in the wavelength range concerned. The errors in the peak energies of luminescence lines described below are not of this absolute accuracy, but of the

relative one which was mainly incorporated into the data-analyzing process.

III. RESULTS

Figure 1 shows luminescence spectra near the $n=1$ exciton absorption edge in RbI at 1.2 K. Excitation was made with 5.99-eV photons, of which the energy corresponds to the high-energy side of the $n=1$ exciton resonance. Curves (a), (b), and (c) were taken for $B=0$, 2.4, and 5.6 T. For $B=0$, a sharp luminescence line appears at 5.7266 eV ± 0.1 meV, which has been identified as the resonance line of the FEL. The observed half-width (full width at half maximum) is 1.4 meV. This line is followed by three or more sidebands, the energy spacing of which is approximately equal to the LO-phonon energy (13.1 meV). No other luminescence lines were detected on the high-energy side of the 5.7266-eV line. The intensity of the resonance line increases by applying a magnetic field, and its peak shifts to lower energy. On the other hand, the phonon sidebands are less enhanced in intensity, but show low-energy shifts as the resonance lines.

In Fig. 2, the spectral shapes of the resonance lines at $B=0$ and $B=5.6$ T are depicted in an expanded scale to examine the field-induced change. In the first place, it is clear that the peak energy is redshifted by about 0.8 meV at $B=5.6$ T. Together with the shift, it appears that the spectral shape becomes asymmetric, with a tail extending toward the high-energy side. Vertical lines in the figure indicate the energy levels of the triplet-exciton states determined by the three-photon magnetoabsorption studies.³ The field-induced change in the line shape and its correlation to the triplet-exciton levels are discussed later.

Similar measurements under excitation with 6.14-eV photons at 1.2 K were carried out for KI. At zero magnetic field, the spectrum shows a sharp resonance line at 5.8277 eV ± 0.1 meV. This line is accompanied by phonon sidebands with a spacing close to the LO-phonon energy of 17.6 meV. When the magnetic field is applied, the

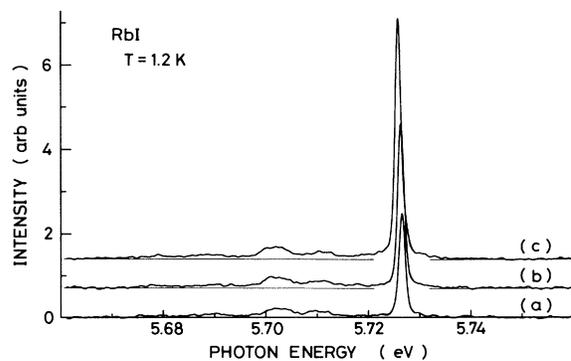


FIG. 1. Luminescence spectra of RbI observed in the edge region of the first ($n=1$) exciton absorption band at 1.2 K: curves (a), (b), and (c) were obtained under external magnetic fields of $B=0$, 2.4, and 5.6 T, respectively. The excitation was made with UV photons at 5.99 eV.

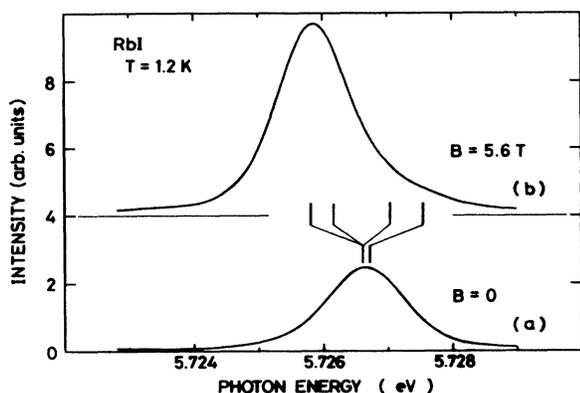


FIG. 2. The spectral change of the resonance line of the free-exciton luminescence in RbI obtained by applying magnetic field; curve (a) is for $B=0$ and (b) for $B=5.6$ T. The excitation was made at 1.2 K with 5.99-eV photons. Vertical lines show the energy levels of the $J=2$ exciton state determined by three-photon magnetoabsorption spectroscopy (Ref. 3).

intensity is enhanced as in the case of RbI, but with a smaller enhancement ratio; the intensity at $B=5.6$ T is about 140% of that at $B=0$. The change in the shape of the resonance line shows features somewhat different from those in RbI. In Fig. 3, we show the spectral shape of the resonance lines measured at $B=0$ and $B=5.6$ T. At $B=0$, the line is nearly symmetric with a half-width of 1.5 meV, while at $B=5.6$ T the resonance line splits into at least two components, lying on the high- and low-energy sides of the peak at $B=0$. As a result, the linewidth is broadened significantly. As for the low-energy peak, it is shifted by an amount of about 0.8 meV, similarly to the case of RbI. The vertical lines in Fig. 3 are the energy levels of the triplet-exciton states in KI which have been determined at $B=0$ and $B=5.6$ T by three-photon magnetoabsorption spectroscopy.²

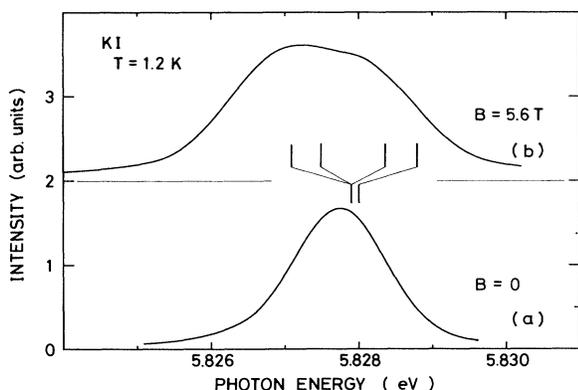


FIG. 3. The spectral change of the resonance line of the free-exciton luminescence in KI obtained by applying magnetic field; curve (a) is for $B=0$ and (b) for $B=5.6$ T. The excitation was made at 1.2 K with 6.14-eV photons. Vertical lines show the energy levels of the $J=2$ exciton state determined by three-photon magnetoabsorption spectroscopy (Ref. 2).

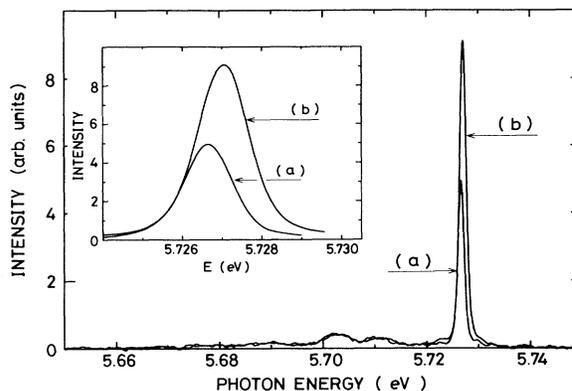


FIG. 4. The spectra of the free-exciton luminescence in RbI measured at (a) 1.2 K and (b) 4.2 K. The excitation was made with 5.99-eV photons in the absence of external magnetic fields. The inset shows the line shape of the resonance line in an expanded scale.

When the temperature of the specimen is raised from 1.2 K, which is the lowest temperature we could achieve in this study, the spectral shape of the resonance line shows characteristic changes. In Fig. 4, the luminescence spectra in RbI measured at 1.2 and 4.2 K are compared. With increasing temperature, the resonance line becomes intense and the peak energy shifts to the high-energy side, as clearly seen in the inset of the figure, in which the resonance lines are presented in an expanded scale. On the other hand, no corresponding change of the phonon sidebands is found. The magnitude of the blueshift of the peak energy is about 0.4 meV. Furthermore, it is noted that the low-energy parts of the peaks at 1.2 and 4.2 K agree with one another; it appears that only the high-energy side gains strength. Similar changes were also found in KI; the magnitude of the blueshift is approximately 0.2 meV in this case.

The external magnetic-field effects on the FEL were also examined at 4.2 K. In RbI, the peak energy of the resonance line was shifted to a lower energy by the same amount (0.8 meV) as that at 1.2 K. In KI, the width of the resonance line was broadened approximately by the same amount as that at 1.2 K, although the splitting of the resonance line was less clear at 4.2 K. The luminescence intensity was also enhanced at 4.2 K in RbI and KI, but with a smaller enhancement ratio than that at 1.2 K. Thus features of the effects of a magnetic field on the luminescence line shape at 4.2 K are essentially the same as those at 1.2 K.

IV. DISCUSSION

As described in the previous section, the spectroscopic feature as well as the intensity of the FEL in RbI and KI changes remarkably with applied external magnetic field and with varying temperature. This indicates that the initial state of the luminescence is perturbation sensitive. In order to discuss the results obtained in the present study, we first summarize the main results regarding the electronic structure of the exciton in alkali halides.

A. The electronic structure of the exciton in alkali halides

The exciton with the lowest energy in alkali halides is located at the Γ point of the Brillouin zone, and its wave function is expressed in terms of the s -like conduction band consisting of alkali orbitals and the p -like valence band consisting of halogen orbitals.¹⁶ The conduction band is of Γ_6^+ symmetry, with the angular momentum $j_c = \frac{1}{2}$. Because of the spin-orbit interaction, the valence band splits into an uppermost band of Γ_8^- ($j_v = \frac{3}{2}$) and a lower band of Γ_6^- ($j_v = \frac{1}{2}$) symmetry. The total angular momentum J of the exciton can be derived from the coupling of the valence- and conduction-band j values. Since we are interested only in the lowest excitons, we get $J = 1$ (Γ_4^-) and $J = 2$ (Γ_3^-, Γ_5^-) from $j_c = \frac{1}{2}$ and $j_v = \frac{3}{2}$ states. These exciton states of $J = 1$ and $J = 2$ are further split by the exchange interaction, as studied by Onodera and Toyozawa.¹⁶ The $J = 1$ state is a singlet-triplet mixed state and hence dipole active; it couples strongly with photon fields. The $J = 2$ state, which lies below the $J = 1$ state, is a pure spin-triplet state and is dipole inactive. However, if the selection rules are relaxed by any perturbation, the $J = 2$ state becomes mixed with the dipole-active $J = 1$ state, and consequently is incorporated into the optical processes.¹⁷

The mixing and splitting of the exciton states induced by magnetic field have been studied by means of three-photon magnetoabsorption spectroscopy for RbI and KI by Beerwerth and co-workers.^{2,3} They resolved clearly the $M = \pm 1, \pm 2$ components of the $J = 2$ state: the $M = -1, -2$ levels shift down, while the $M = +1, +2$ levels shift up in energy from the zero-field value. Based on these results, they derived the resonance energies of the spin-triplet excitons to be $E_r = 5.7266$ eV for RbI and $E_r = 5.8279$ eV for KI.

B. The change in the line shape of the resonance luminescence induced by magnetic fields

From results of the present study, the resonance lines of the FEL are found to appear at 5.7266 eV in RbI and 5.8277 eV in KI for zero magnetic field at 1.2 K. These are in excellent agreement with the values of E_r obtained by Beerwerth and co-workers.^{2,3} In RbI, the resonance line is shifted to the low-energy side under the magnetic field, as is clearly seen in Fig. 2, where energy levels of the $J = 2$ exciton state determined by three-photon spectroscopy for $B = 0$ and $B = 5.6$ T are also shown for comparison. It is clear that the peak energy of the resonance line is almost identical to the energy of the lowest ($M = -2$) Zeeman-split level. We have confirmed²⁵ that a plot of the resonance peak energy as a function of magnetic-field strength is in accordance with the Zeeman shift of the lowest $M = -2$ level of the triplet-exciton absorption. In KI, a single line at zero field splits into two components; one shifts to lower energy and the other to higher energy, as seen in Fig. 3. The observed zero-field energy of the resonance line in KI is lower by 0.2 meV than the value of E_r derived in Ref. 2. At this moment, we cannot say whether this difference is due to a real effect or comes from the error in determining the wave-

length of the detection systems. However, it is clear that the amounts of the relative shift of the peak energy of the resonance line induced by applying a magnetic field are in good agreement with the Zeeman shift of the $J = 2$ exciton state. Thus we conclude that the initial state of the FEL in both RbI and KI is the pure spin-triplet $J = 2$ state.

We note that the excitons emitting the resonance luminescence are not in thermal equilibrium among the Zeeman-split levels, particularly in KI; high-lying levels contribute significantly to the luminescence intensity. In RbI, a contribution from the lowest level of luminescence intensity overshadows those from high-lying levels, but the latter contributions, which are responsible for the high-energy tail, are still much larger than those predicted from the thermal-equilibrium distribution; the thermal energy $k_B T$ at 1.2 K (0.104 meV) is substantially smaller than the separation (1.7 meV) of the sublevels at $B = 5.6$ T. Thermalization will take place via emission or absorption of a single acoustic phonon within the exciton lifetime. At low temperatures, the rate of the downward conversion from high-lying levels to lower ones by acoustic-phonon processes has been shown to be proportional to temperature.²⁶ Because of this dependence, together with the low density of states for acoustic phonons having low frequencies, the rate of downward conversion is expected to be suppressed with decreasing temperature. Therefore, the thermalization within the Zeeman-split levels will not be achieved at low temperature; the lifetime of the exciton is shorter than the relaxation time.

Magnetoabsorption study has shown that the qualitative and quantitative features of the Zeeman splitting of the $J = 2$ exciton levels are very similar for KI and RbI.^{2,3} However, as seen in Figs. 2 and 3, the emission from high-lying levels is more pronounced in KI than in RbI. We interpret this difference to be caused by the shorter lifetime of excitons in KI. Since the quantum yield of the FEL is much less than unity in both specimens,⁹ the yield is proportional to the exciton lifetime, which is governed by the deexcitation processes rather than the radiative annihilation. It has been shown that the yield of the FEL in KI is smaller than that in RbI,¹⁰ which is consistent with our interpretation.

C. A polariton model for the luminescent process of the free exciton

As shown in Fig. 4, the spectral shape as well as the intensity of the resonance line changes significantly with varying temperature. These changes reflect the structure of the polariton-dispersion curve and the relaxation dynamics on it. In order to examine the dynamics, we need to introduce a polariton model in which the mixing of the $J = 1$ and 2 states is taken into account; such models have been proposed for CuBr (Ref. 27) and alkali halides.²⁴ Based on the experimental results of Ref. 4, a plausible dispersion curve of the exciton polariton in alkali halides is depicted schematically in Fig. 5. The resonance energies of the transverselike $J = 1$ and 2 states are denoted as E_T and E_l , respectively. According to recent experiments,^{4,28} the longitudinal-transverse splitting

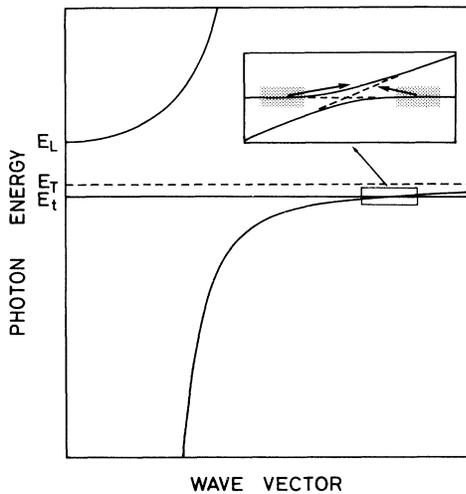


FIG. 5. Schematic polariton-dispersion curves in the vicinity of the $n = 1$ exciton in alkali halides. The resonance energies of the longitudinal exciton and the transverselike $J = 1$ and 2 exciton states are denoted as E_L , E_T , and E_i , respectively. The inset shows the bottleneck region of the lowest branch in an expanded scale. The polaritons are accumulated around the shaded areas. Possible acoustic-phonon absorption processes are indicated by arrows.

$\Delta_{LT} = E_L - E_T$ is about 100 meV for KI and RbI, and the exchange splitting $\Delta_{ex} = (\frac{3}{2})(E_T - E_i)$ is 20–29 meV for KI and 26–33 meV for RbI. The uppermost curve is the usual upper branch of the $J = 1$ exciton polaritons. The lowest curve is the polariton branch associated with the $J = 1$ state, and is expected to cross the $J = 2$ exciton state. This crossing may result in a repulsion of the dispersion curves, as shown in the inset of Fig. 5.

When polaritons are created at energies above E_T , they interact with phonons and are scattered on the transverselike $J = 1$ exciton branch. Under subsequent scattering by phonons, they fall further down along the dispersion curve and are finally relaxed to the bottleneck region (the shaded areas in the inset), where they have a character of the spin-triplet exciton state. The rate α of the polariton accumulation in this bottleneck region is certainly affected by the mixing of $J = 1$ and 2 states at finite- k region. At very low temperature (1.2 K), the polaritons existing in the bottleneck region have two channels of radiative decay processes; one is the direct conversion into external photons at the crystal boundaries (rate k_r), and the other is scattering into the low-lying photon-like branch by emitting LO phonons (rate k_s). When the polaritons are converted into external photons after the second process, the sideband luminescence is emitted. Under magnetic field, rates α and k_r will increase as a result of the field-induced mixing between $J = 1$ and 2 states. On the other hand, k_s is supposed to not depend sensitively on the magnetic field. Therefore, it is expected that the enhancement of the intensity of the resonance line is more pronounced than that of the sidebands. This is indeed observed, as shown in Fig. 1.

When the temperature is raised from 1.2 K, an additional scattering process by acoustic-phonon absorption will be activated. In this process, the polaritons are excited, as shown by the arrows in the inset of Fig. 5, into the dispersion curve slightly above the bottleneck region, in which the excitonic nature of the polaritons changes from tripletlike to singletlike. Thus the polaritons become more strongly coupled to photon fields; the conversion rate into photons is enhanced with increasing temperature. Accordingly, the resonance line gains strength on the high-energy side, which leads to the blueshift of the peak energy accompanied by an increase in intensity. The difference of $k_B T$ between 1.2 and 4.2 K is estimated to be 0.26 meV. This value is close to the observed peak shift (0.2–0.4 meV), supporting our interpretation described above. On the other hand, the sample-temperature rise does not give any effects for the LO-phonon scattering rate k_s , since $\hbar\omega_{LO}/k_B \gg 5$ K. It is, therefore, expected that the resonance line grows with the shifting of its peak energy to the high-energy side, while the phonon sidebands remain almost unchanged, which is a feature seen in Fig. 4.

D. The role of the intraband relaxation in the formation process of the STE's

As described in the Introduction, the excitation spectra for the STE luminescence show an anomalous feature in that the singlet STE luminescence (the type-I band) is not excited when $n = 1$ excitons are generated. This anomaly was regarded as evidence that the initial state of the σ luminescence is the STE with an electron excited to the totally symmetric second-excited level.²⁹ However, recent understanding of the configuration of STE's has given an alternative assignment of the σ -luminescent state; its electronic level is the lowest, as the initial state of the π luminescence, but with a different atomic configuration.³⁰ Irrespective of the model for the σ -luminescent STE, the results and conclusions drawn in this study provide new light for the understanding of the anomaly.

As shown already, $n = 1$ excitons generated in the $J = 1$ state are relaxed to the lowest triplet $J = 2$ levels where radiative recombination giving rise to the FEL takes place. A recent excitation-spectroscopic study of the FEL by Kishigami-Tsujibayashi, Toyoda, and Hayashi,³¹ using narrow UV-laser light, has shown that the population of the $J = 2$ exciton state increases with an increasing degree of off-resonance in E_T in the energy range between E_T and E_L . Their result has confirmed that the conversion from $J = 1$ to $J = 2$ states occurs certainly during intraband relaxation of the exciton. In the present study, no luminescence lines could be detected on the high-energy side of the resonance line by excitation with UV photons of energy below the $n = 2$ exciton resonance. Therefore, the resonance line due to the radiative decay of the $J = 2$ triplet exciton is the highest-energy luminescence under ordinary UV excitation. The singlet free-exciton luminescence, if any, is extremely weak.

It has been shown that formation of the $n = 1$ exciton produces almost exclusively the triplet STE (π) lumines-

cence.²² We presume that the singlet free excitons generated by photoexcitation are exclusively converted to $J=2$ triplet excitons during intraband relaxation. Moreover, we presume that the spin multiplicity is maintained in the process of self-trapping of excitons. These presumptions can explain the absence of singlet FEL and σ luminescence following formation of $n=1$ singlet free excitons.³²

The above model is certainly still hypothetical; the fraction of the triplet free excitons populated during intraband relaxation has not yet been determined, and the conservation of the spin multiplicity during lattice relaxation has not yet been proven. Further studies of the relaxation of excitons are needed in order to yield critical

information based upon which we can clarify the origin of the anomaly seen in the excitation spectra of the STE luminescence in alkali halides.

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