

## TWO-PHOTON GENERATION OF EXCITONIC MOLECULES IN CuCl AND CuBr

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### ABSTRACT

Radiative recombination of excitonic molecules in CuCl and CuBr is reviewed. The emission consists of  $M_L$  and  $M_T$  bands in CuCl and of  $M_L$ ,  $M_T$  and  $M_F$  bands in CuBr. These bands correspond to the recoil of an exciton into the longitudinal, transverse and triplet states, respectively. When excitonic molecules are generated indirectly by the excitation of crystals into the band-to-band region, the line shape of the bands is explained by considering that excitonic molecules are in Maxwell-Boltzmann distribution. Excitonic molecules are found to be generated directly by the giant two-photon absorption. In this case, extremely sharp emission lines appear at the high energy edges of each M band, which are attributed to the Bose condensation of excitonic molecules. The two-photon resonance Raman scattering is discussed in connection with the emission from the Bose condensed state.

### I. INTRODUCTION

#### 1.1 Excitonic Molecule

There are two main interaction products between excitons in highly excited semiconductors; an excitonic molecule and electron-hole metallic phase. The former is found in cuprous halides and probably in CdS and CdSe and the latter in Ge and Si. The Wannier exciton is analogous to the hydrogen atom so that excitonic molecules have been expected to be formed since 1958 by Lampert<sup>1)</sup> and Moskaleiko.<sup>2)</sup> From the theoretical work<sup>3)</sup> dealing the binding energy of the excitonic molecule, it was considered to be unstable in crystals having the electron and hole effective mass ratio,  $M_e/M_h$ , ranging between 0.2 and 0.4. Therefore, experimental work to find the excitonic molecule was directed to crystals such as CuCl having  $M_e/M_h < 0.2$  and Ge or Si in which  $M_e/M_h > 0.7$ .

In 1966, Haynes<sup>4)</sup> found a superlinear emission band at 1.08 eV in Si and considered it as the radiative annihilation of an excitonic molecule with leaving a free electron and hole pair behind. In Ge, a similar emission band was later found at 0.708 eV.<sup>5)</sup> These emission bands are now attributed to the electron-hole drops, other than the excitonic molecules.

In CuCl crystals, a new emission band was found by ruby laser excitation and it was assigned as due to the excitonic molecule by Grun *et al.*<sup>6)</sup> and by Goto *et al.*<sup>7)</sup>, because the emission intensity increased in proportion to the square of the excitation density and the energy separation of the emission band from the free exciton band,  $\sim 40$  meV, was reasonable for the binding energy of the excitonic molecule expected from the theoretical work. Here an excitonic molecule was assumed to be annihilated radiatively with an exciton left behind.

In highly excited states, a number of elementary interactions between exciton-exciton and exciton-free charge carriers lead to superlinear emissions, the photon energies of which depend on the interaction mechanisms. Therefore, the observation of the square dependence of emission intensity upon excitation power and the energy position of the emission band are not enough to decide uniquely the elementary processes responsible for the emissions.

The first reliable proof of the existence of excitonic molecules was given by Souma *et al.*<sup>8)</sup> in zone refined CuCl through the line shape analysis of a new superlinear emission band, called M band, which appeared when the crystal was illuminated by a giant ruby laser at 4.2 K. A similar emission band attributed to excitonic molecules has been found also in CuBr.<sup>9)</sup> After theoretical work concerning the binding energy of an excitonic molecule by Akimoto and Hanamura<sup>10)</sup> which showed that the excitonic molecule could be formed in crystals, having any values of  $M_e/M_h$ , new emission bands similar to the asymmetric M band in CuCl and CuBr, were found by Shionoya's group successively in

CdS,<sup>11)</sup> CdSe<sup>12)</sup> and ZnO,<sup>13)</sup> and they were attributed to the radiative annihilation of excitonic molecules. On the other hand, a somewhat different assignment has been made by another group that they are attributed to the stimulation of acoustic side bands of bound excitons.<sup>14)</sup> However, the experiment on the stress effect in CdS, carried out by Segawa and Namba,<sup>15)</sup> seems to give a confirmation of the molecule. The complex band structure, anisotropy of electron and hole masses, some difficulty of purification and small binding energies make the exciton molecule emission complex in II-VI compounds. Different exciton complexes found in different groups might have their emission bands in nearly the same energy positions.

## 1.2 Bose Condensation of Excitons and Excitonic Molecules

The boson-like nature of excitons and excitonic molecules has been the basis for the discussions<sup>16)</sup> on how their statistics manifests themselves in the phase change at low temperature. The first experimental report on a narrow emission line showing the Bose condensation of excitons has been done by Akopyan *et al.*<sup>17)</sup> in CdSe excited by the second harmonics of a neodymium laser at 4.2K. The conclusion of the Bose condensation was based on the consideration that excitons in CdSe are repulsive to each other and satisfy the necessary conditions for the Bose condensation. However as described above, excitons are attractive to form excitonic molecules. Thus, the Bose condensation of single excitons in CdSe becomes to be unexpected. In fact, the narrow line reported by Akopyan *et al.* has not been observed by other researchers. Czaja and Schwerdtfeger<sup>18)</sup> are the second reporter of the Bose condensation of indirect excitons in AgBr at 1.6 K. They found a narrow emission line near  $K=0$  in the TA phonon-assisted exciton band. Together with the very low threshold temperature for the appearance of the emission line, the Bose condensation has been concluded.<sup>19)</sup>

On the Bose condensation of excitonic molecules, Kuroda *et al.*<sup>20)</sup>

reported an emission line on the high energy edge of the emission band of the excitonic molecule in CdSe, and attributed it to the Bose condensation of the excitonic molecule at  $K=0$ . However, Johnston and Shaklee<sup>21)</sup> have claimed on the conclusion of Kuroda *et al.*, and assigned the narrow emission to a bound exciton complex involving a neutral donor. Thus, the Bose condensation of excitonic molecules has not been clarified yet. In the experiments above mentioned, crystals were excited into their band-to-band region and excitonic molecules are formed secondarily through the interactions between excitons generated by the recombination of hot electrons and holes. Therefore, the temperature of the excitonic molecules will not be low enough to condense as confirmed by Souma *et al.*<sup>8)</sup>

Hanamura<sup>22)</sup> has recently shown theoretically that excitonic molecules can be generated directly by the giant two-photon excitation with using photons, of which energy is given by

$$h\nu = E_{\text{ex}} - \frac{1}{2} E_{\text{m}}^{\text{b}} \quad (1)$$

where  $E_{\text{ex}}$  stands for the exciton energy and  $E_{\text{m}}^{\text{b}}$  the binding energy of an excitonic molecule. Furthermore, the Bose condensed molecules are expected to be created coherently with using a laser excitation. Hanamura has further shown that the absorption coefficient for the two-photon generation of excitonic molecule given by (1) depends on the photon density, and it amounts to the order of  $\sim 10^5/\text{cm}$  with using the photon density, of  $10^{15}$  photons/ $\text{cm}^2$ . Gale and Mycyrowicz<sup>23)</sup> have confirmed the two-photon generation of excitonic molecules in CuCl by observing that the absorption coefficient for the two-photon absorption increases rapidly, when the incident photon energy approaches that given by (1) and the extrapolated absorption coefficient at the peak will be the same as that for the one-photon absorption in the exciton band,  $\sim 10^5/\text{cm}$ , with photon density of  $10^{17}/\text{cm}^2$ .

We could confirm also the efficient generation of the excitonic

molecules by the two-photon excitation in CuCl as well as in CuBr. Moreover, the emission band has been found to show extremely sharp lines at the high energy edges of the  $M_L$  and  $M_T$  bands, which is considered to show the Bose condensation of the excitonic molecule at  $K \sim 0$ .

In this paper, we present experimental results in cuprous halides carried out in our laboratory on the emission bands originating from excitonic molecules in their thermal equilibrium and Bose condensed states.

## II. EXPERIMENTAL RESULTS AND DISCUSSIONS

### 2.1 Emission of Excitonic Molecules of Maxwell Distribution in CuCl and CuBr Crystals near 4.2 K

Cuprous halides have the zincblende crystal structure, and an exciton consists of a  $\Gamma_6$  electron and a  $\Gamma_7$  or  $\Gamma_8$  hole. The exciton absorption bands<sup>24,25)</sup> in CuCl and CuBr crystals, called  $Z_3$  and  $Z_{1,2}$ , are well separated from the continuous band due to the band-to-band transition, and thus the binding energy of the exciton is rather large, 190meV for CuCl and ~120meV for CuBr.

The M band due to the excitonic molecule was found<sup>8)</sup> to have an asymmetric line shape as mentioned before, and this was explained to reflect the Maxwell-Boltzmann distribution of the kinetic energy of excitonic molecule. The line shape was expressed by

$$I(E) \propto E^{1/2} \exp(-E/kT), \quad (2)$$

where  $E$  is measured towards the low photon energy side. The emission is concluded to arise from the transitions between energy levels of excitonic molecule and single exciton as shown in Fig.1. Namely, an excitonic molecule is concluded to be annihilated radiatively with leaving an exciton behind. From the energy separation of the peak from the high energy edge, which is equal to  $1/2kT$ , the temperature of

the excitonic molecule was shown to be 26 K which was higher than the lattice temperature in Souma's experimental condition; the crystal was illuminated by a Giant Ruby laser with  $\sim 50 \text{ MW/cm}^2$ . By assuming the above conclusion of the M-emission mechanism correct, the binding energy of the molecule is determined from the energy separation between the free exciton band and the high energy edge of the M band to be 34 meV in  $\text{CuCl}$ <sup>8)</sup> and 26 meV in  $\text{CuBr}$ .<sup>9)</sup>

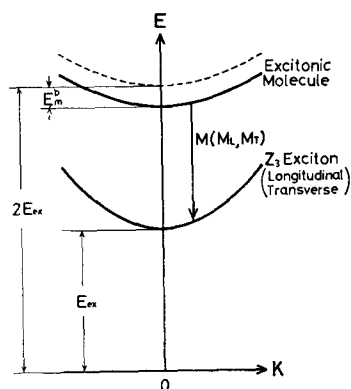


Fig.1. Schematic representation of energy levels of exciton and excitonic molecule.

The remaining exciton can be in either longitudinal or transverse states. With reflecting this fact, the M band was found by Koda's group<sup>26)</sup> to consist of two bands, called  $M_L$  and  $M_T$  bands. The energy separation between them was in fact equal to that of the L-T splitting of the exciton, being 5.4 meV.<sup>27)</sup> The longitudinal state is singlet and the transverse state is doubly degenerate, so that the  $M_T$  intensity must be twice as much as the  $M_L$  intensity. However, as shown in Fig. 2, the intensity ratio is a function of excitation density, and with increasing excitation density, the  $M_L$  band becomes much stronger than the  $M_T$  band. Grun *et al.*<sup>28)</sup> have shown the intensity ratio of 2 is observed in a wide range of excitation density. For the dependence of the  $M_L$  and  $M_T$  band-intensities upon excitation density, an opinion has been proposed that the two M bands come from the different rotational levels of the molecule.<sup>29)</sup>

In  $\text{CuBr}$ , the M band was previously found to consist of two bands,  $M_1$  and  $M_2$ , and they were previously assigned as the recoil of an excitor into the transverse and triplet states,<sup>9)</sup> respectively. However in a

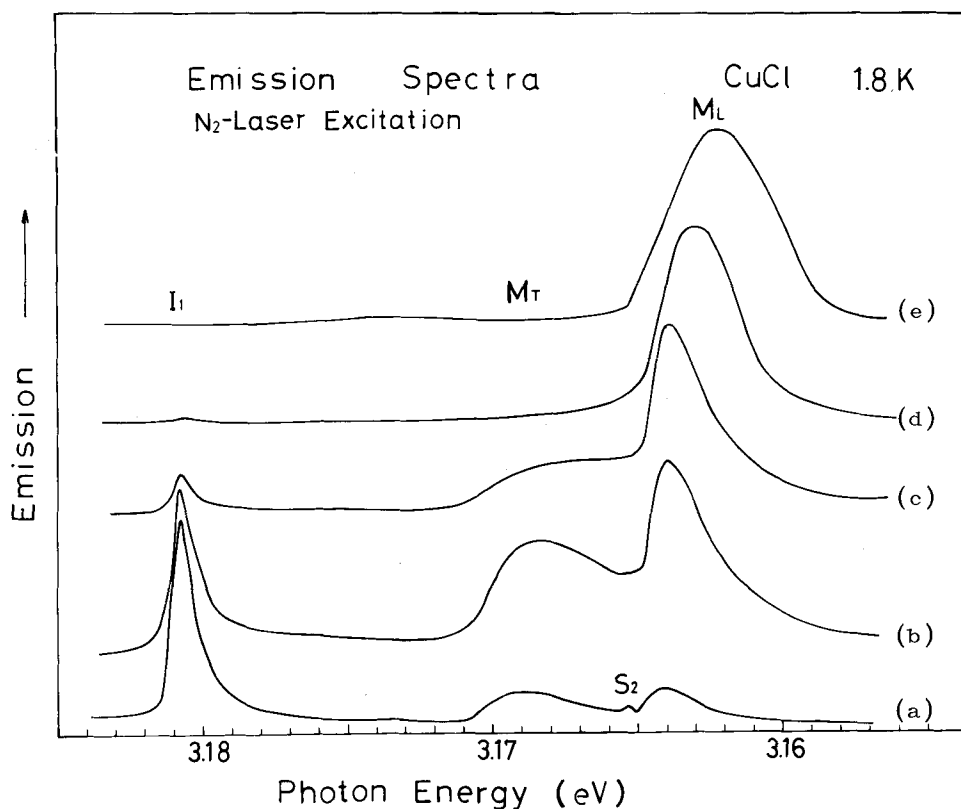


Fig.2. The variation of emission spectrum of excitonic molecule with the power of exciting  $N_2$ -laser in CuCl. Excitation intensity increases from (a) toward (e).

recent work, they have been clearly assigned to the  $M_L$  and  $M_T$  as in CuCl, because the energy separation between two bands coincides also with the L-T splitting of the exciton, 11.2 meV, which is determined from the Kramers-Kronig analysis of a reflection spectrum. Therefore, the two bands in CuCl are considered to be due to the recoil of an exciton into the L and T states, rather than to be attributed to the rotational structure.

## 2.2 Line Shape of the M Band

Figure 3 shows a typical M emission spectrum of CuCl<sup>30)</sup> excited into the band-to-band region with using a  $N_2$  laser. The spectrum is

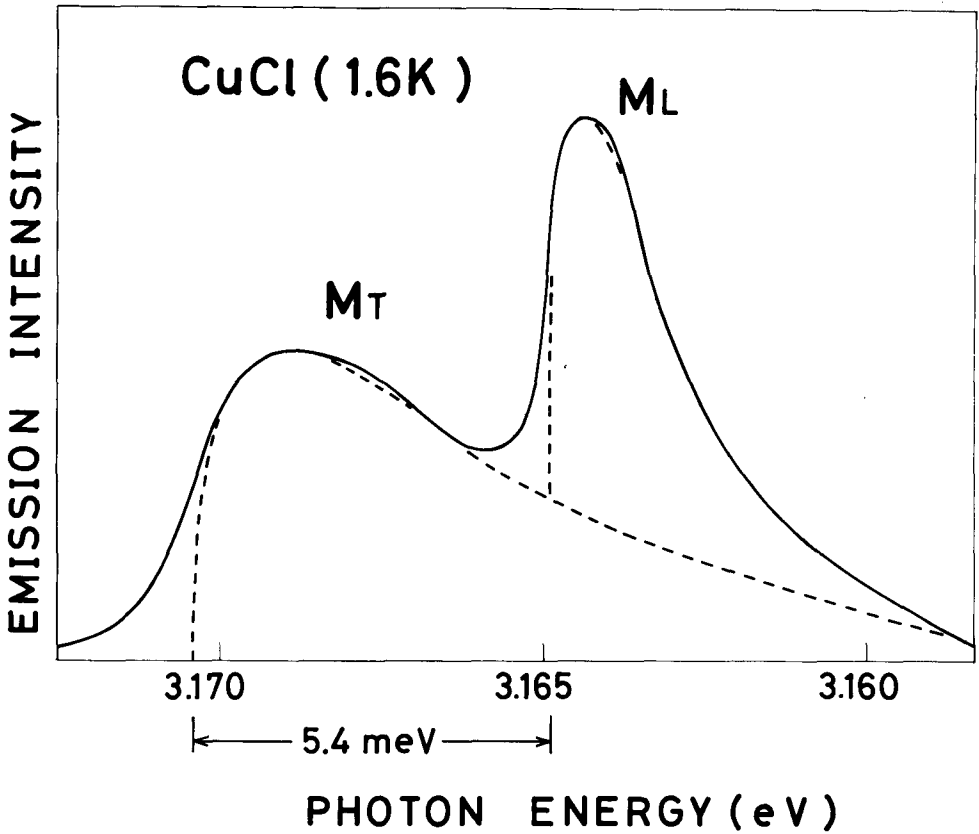


Fig.3. Line shape of the  $M_L$  and  $M_T$  emission bands of excitonic molecule in CuCl in the case of the excitation into the band-to-band region with a  $N_2$  laser.

the same as (b) in Fig.2 showing two bands,  $M_L$  and  $M_T$ , in the case of relatively weak laser excitation. The line shapes are found to be fitted to the formula (2). The high energy edges of the both bands, corresponding to  $E=0$ , are determined to be,

$$3.1647 \text{ eV } (M_L) \text{ and } 3.1700 \text{ eV } (M_T) \text{ in CuCl.} \quad (3)$$

The energy difference of these edges, 5.3 meV, is in agreement with the L-T splitting of the exciton, 5.4 meV.<sup>27)</sup> In CuBr crystal, the M band was found to have another band,  $M_F$ , in addition to the  $M_L$  and  $M_T$  bands and it was assigned as due to the recoil of an exciton



into the triplet state. By a similar procedure the high energy edges were determined to be,

$$2.930 \text{ eV } (M_L) \text{ and } 2.941 \text{ eV } (M_T) \text{ in CuBr.} \quad (4)$$

The energy difference of these edges, 11 meV, is also in agreement with the L-T splitting of the exciton. For the  $M_T$  band, the determination was not clear because of the superposition of an unknown emission band. The high energy edges of the bands correspond to the transitions from the state  $K=0$  of the excitonic molecule as described before.

With increasing the  $N_2$  laser power, the  $M_L$  band becomes much stronger than the  $M_T$  in both cases of CuCl and CuBr, and has a symmetric line shape with broader band width. The line shape was expected to be Lorentzian which is due to the collisions between excitonic molecules.<sup>31)</sup> If the gain saturation of the emission, which was found by Shaklee *et al.*,<sup>32)</sup> was taken into account, the  $M_L$  band shape would be more complicated than the simple Lorentzian.

### 2.3 Excitation Spectra of the $M_L$ and $M_T$ Bands

With using a frequency tunable dye laser, excitation spectra of the  $M_L$  band in CuCl and CuBr were measured<sup>33,34)</sup> near the high energy edges of the bands as shown by upper curves in Fig.4. Sharp excitation peaks are observed at 3.187 eV and at 2.954 eV in CuCl and CuBr, respectively. The photon energies of these peaks are almost exactly the same as those expected from the formula (1) by adopting known values:

$$E_x = 3.204 \text{ eV and } E_m^b = 34 \text{ meV for CuCl and}$$

$$E_x = 2.967 \text{ eV and } E_m^b = 26 \text{ meV for CuBr.}$$

Thus, the excitonic molecule was found to be generated effectively by the two-photon absorption. The excitation spectrum for the  $M_T$  band in CuCl was found to show a sharp peak at exactly the same photon energy

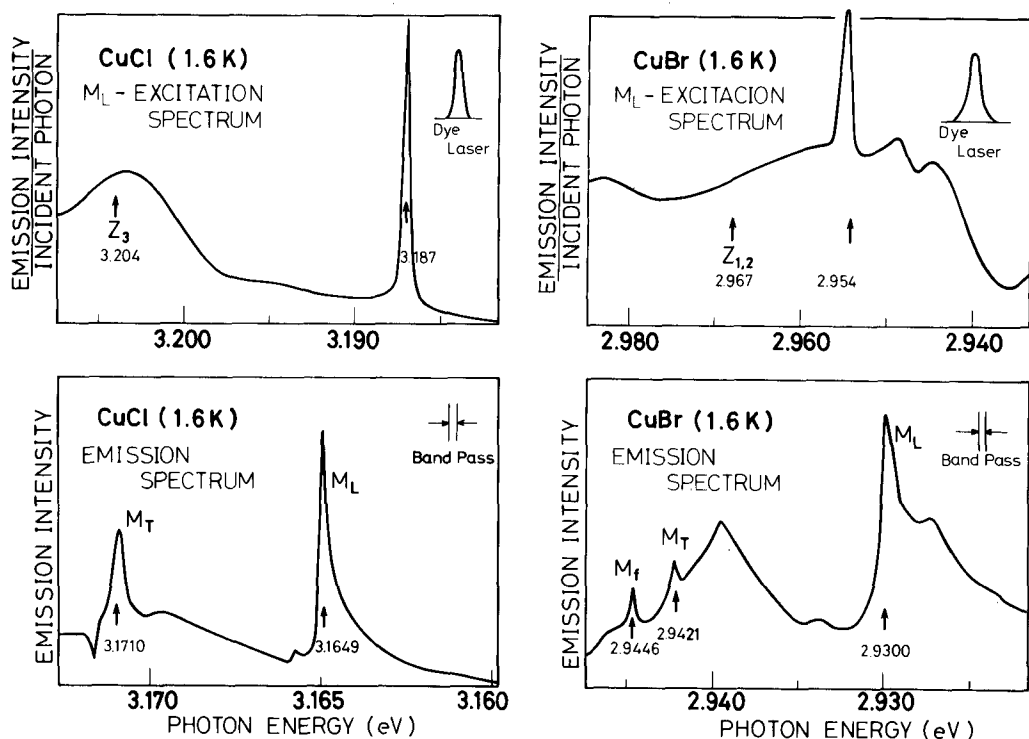


Fig.4. Upper curves: Excitation spectra of the  $M_L$  emission due to excitonic molecule in CuCl and CuBr, indicating two-photon excitation peaks. Lower curves: Emission spectra of CuCl and CuBr excited into their two-photon excitation peaks in the upper curves, showing a sharp line at the high energy edge of the  $M_L$  band.

as in the  $M_L$  band, namely at 3.187 eV as shown by Fig.5 in ref. (30).

Gale and Mycyrowicz<sup>35)</sup> measured firstly the excitation spectra for  $M_L$  and  $M_T$  bands in CuCl, and found the same peak at 3.187 eV for the  $M_L$  bands and a different peak at 3.199 eV for the  $M_T$  band. In our case, the initial states responsible for both  $M_L$  and  $M_T$  bands can be reached with using the same photon energy, 3.187 eV, but in the case of Gale and Mycyrowicz the situation is somewhat different. In their case, the initial state for the  $M_T$  band should be different from that for the  $M_L$  band. Other emission bands due to bound excitons appeared in their M band region, so that the identification of the  $M_T$  band seemed to be

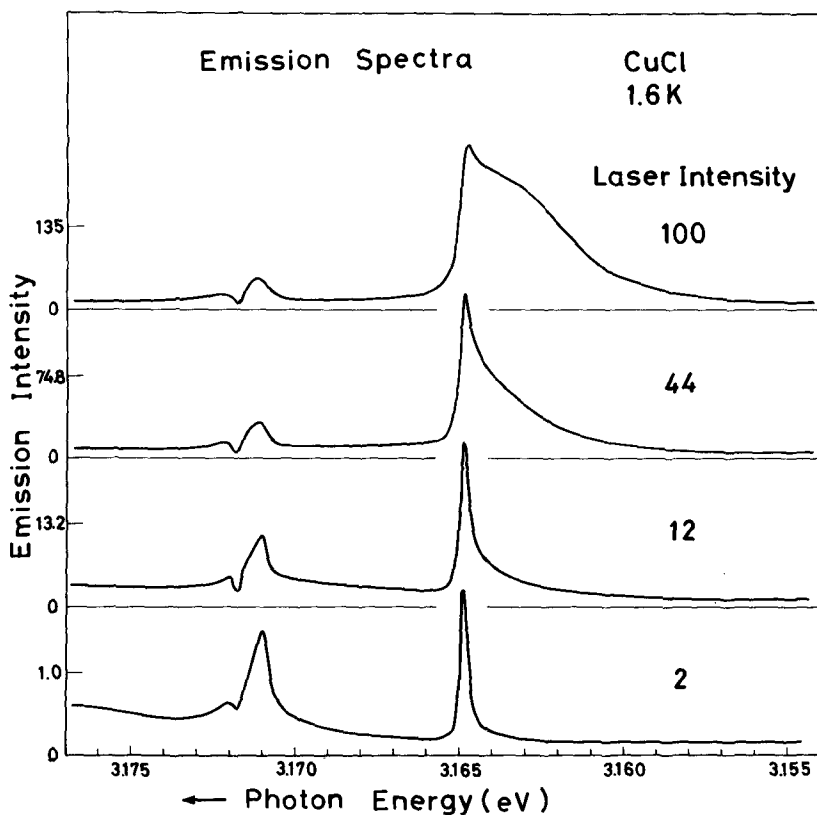


Fig.5. Variation of emission intensities of the sharp line and its side band of the Bose condensed excitonic molecules, with respect to the excitation power.

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#### 2.4 Emission Spectra of Excitonic Molecules Directly Generated and the Bose Condensation of Excitonic Molecules<sup>30,34)</sup>

When CuCl and CuBr crystals are excited into the sharp peaks in the excitation spectra, very sharp emission bands are observed in each  $M_L$ ,  $M_T$  and  $M_F$  band regions as shown by lower curves in Fig.4. The photon energies of these emission bands are:

$$\begin{aligned}
 &3.1649 \text{ eV}(M_L) \text{ and } 3.1710 \text{ eV}(M_T) && \text{for CuCl,} \\
 &2.9300 \text{ eV}(M_L), 2.9421 \text{ eV}(M_T) \text{ and } 2.9446 \text{ eV}(M_F) && \text{for CuBr.}
 \end{aligned}
 \tag{5}$$

Comparing (5) with (3) and (4), one can see that the sharp emissions of CuCl and CuBr in the  $M_L$  band region coincide in energy exactly with those of the high energy edge of the  $M_L$  band of Maxwell distribution, but the one at  $M_T$  band region is located at an about 1meV higher energy position of the edge of the  $M_T$  band. The same applies to the sharp emission line in the  $M_f$  band because its energy separation from that in the  $M_T$  band, 2.5 meV, is almost equal to the energy difference between the transverse and triplet exciton bands, 2.7 meV, determined from the reflection spectrum. A dip observed at the high energy side of the sharp emission band of  $M_T$  is due to a bound exciton.<sup>36)</sup>

With increasing excitation density, a broad side band comes out at the low energy side of the sharp emission line in CuCl as shown in Fig. 5. With a further increase of excitation intensity, the relative intensity of the sharp emission against the side band decreases and the peak of the side band shifts to the low energy side. With the highest excitation density of our laser ( $\sim 50 \text{ kW/cm}^2$ ), the peak separation from the sharp emission line amounts to  $\sim 3 \text{ meV}$  as seen in curve a) of Fig. 6. The shape of the side band can not be expressed by the formula (2) as shown by a dotted curve. For comparison, the emission spectrum excited into the  $Z_3$  exciton band was shown by curve b). In this case, the line shape is well expressed by (2). Thus, the emission spectrum of the excitonic molecule, directly generated by the giant two-photon excitation, consists of a sharp line and a side band which originates from the non-thermalized excitonic molecules. From the very sharpness of the line together with its energy corresponding to the transition from the  $K=0$  state of the excitonic molecule, the Bose condensation of the molecules at  $K\sim 0$  has been concluded. By the simple theory,<sup>37)</sup> the relative concentration of Bose condensed particles  $N_0$  with respect to the total one,  $N$ , is expressed by,

$$\frac{N_0}{N} = 1 - \frac{8}{3\sqrt{\pi}} a^{3/2} \left(\frac{N}{V}\right)^{1/2},$$

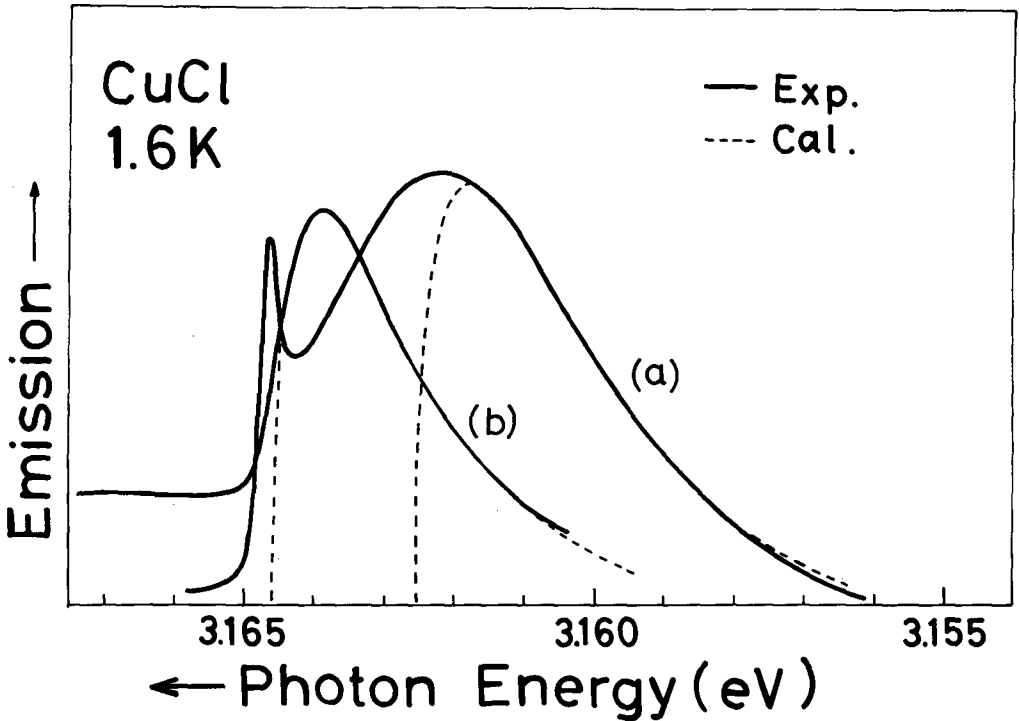


Fig.6. Comparison of  $M_L$  emission bands in different generation processes of excitonic molecules in CuCl; a) the direct formation through the two-photon excitation, and b) indirect generation through the band-to-band excitation.

where  $V$  stands for the crystal volume and  $a$  is the scattering amplitude expressing the interaction between particles. If we consider that the intensities of the sharp emission line and its side band are proportional to  $N_0$  and  $N-N_0$ , respectively, the decrease of sharp emission line with respect to the side band with increasing laser intensity is explained qualitatively by the theory.

Qualitative temperature dependence of the emission spectra is shown in Fig. 7. With increasing temperature, the sharp peak decreases its intensity and disappears at  $\sim 25$  K. However, if one makes the excitation density increase at this stage, the sharp peak becomes to appear again. This fact shows that there is a certain critical temperature for the appearance of the sharp emission line and it depends

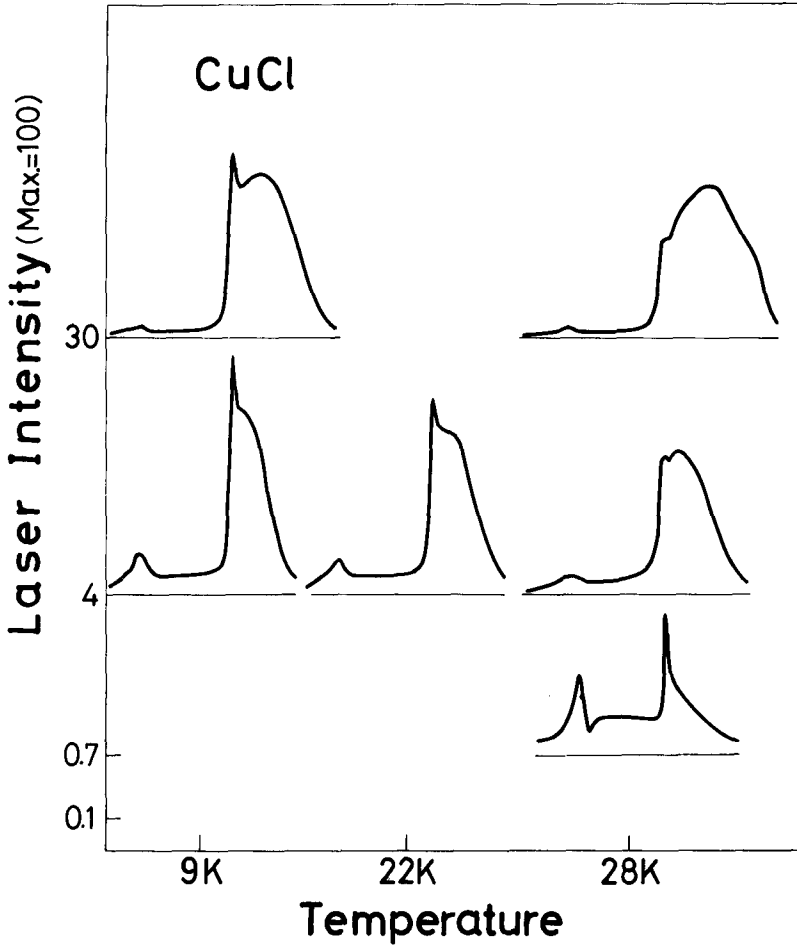


Fig.7. Variation of the  $M_L$  emission with respect to the temperature and excitation power changes.

on excitation density. These facts are also explained by the Bose condensation which shows that the critical temperature for the condensation increases in proportion to the particle concentration with

$$T_c \propto \left(\frac{N}{V}\right)^{2/3}.$$

Further, the concentration  $N_0$  is shown to decrease with the increase of  $T$  in a range  $0 < T < T_c$  by,

$$\frac{N_0}{N} = \left\{ 1 - \left( \frac{T}{T_c} \right)^{3/2} \right\},$$

if the excitonic molecule is treated as an ideal boson gas. Thus, the excitation density and temperature dependence of the intensities of the sharp line and side band are qualitatively explained by the Bose condensation. Therefore, it is considered that the majority of the excitonic molecules, generated by the two-photon absorption, condense at the state  $K=0$  and decay radiatively from there. The side band is considered by Hanamura<sup>16)</sup> to arise from the collective motion of condensed molecules.

By considering the polariton nature of the transverse exciton, it is found that the photon energy of the emission from the  $K=0$  state of the excitonic molecule to the transverse exciton ought to deviate much from the high energy edge of the  $M_T$  band. However, from the  $K = 2K_0$  state, the observed deviation of 1 meV is reasonable, where  $K_0$  is the wave number of a photon given by (1). Thus the excitonic molecules are considered to condense at  $K = 2K_0$ .

To distinguish the emission line from the Bose-condensed state from the one due to bound exciton complexes, the study of the Zeeman splitting is most important. At the present stage of experiment, the magnetic field effect was studied for only  $\text{CuCl}$ .<sup>30)</sup> No splitting and no shift of the 3.1649 eV emission line in the  $M_L$  band were found in a magnetic field of 60 kG. The splitting of the 3.1700 eV band in the  $M_T$  band region was not clear because of a little broader width of it and of the superposition of a bound exciton line, responsible for the dip above mentioned, which split into four components. No splitting of the 3.1649 eV emission is in agreement with the assignment that the emission is due to the transition from the Bose condensed state of the excitonic molecule to the longitudinal exciton state and is not due to bound exciton complexes.

## 2.5 Two-Photon Absorption Spectrum for the Generation of Excitonic Molecules

In connection with the relaxation of the excitonic molecules to the Bose-condensed state, and also with the resonant Raman scattering, which is described later, we have to know the detailed line shape of the two-photon absorption spectrum for the generation of excitonic molecules. As mentioned before, the absorption cross-section depends on the power of the exciting laser light. We could obtain the profile of the absorption spectrum as shown in Fig. 8, with using a dye laser of a moderate intensity having the photon density of  $\sim 10^{15}/\text{cm}^2$ . The used dye laser has the 0.25 meV half-width which is narrowest in our case. The absorption peak is located at 3.1870 eV as a matter of

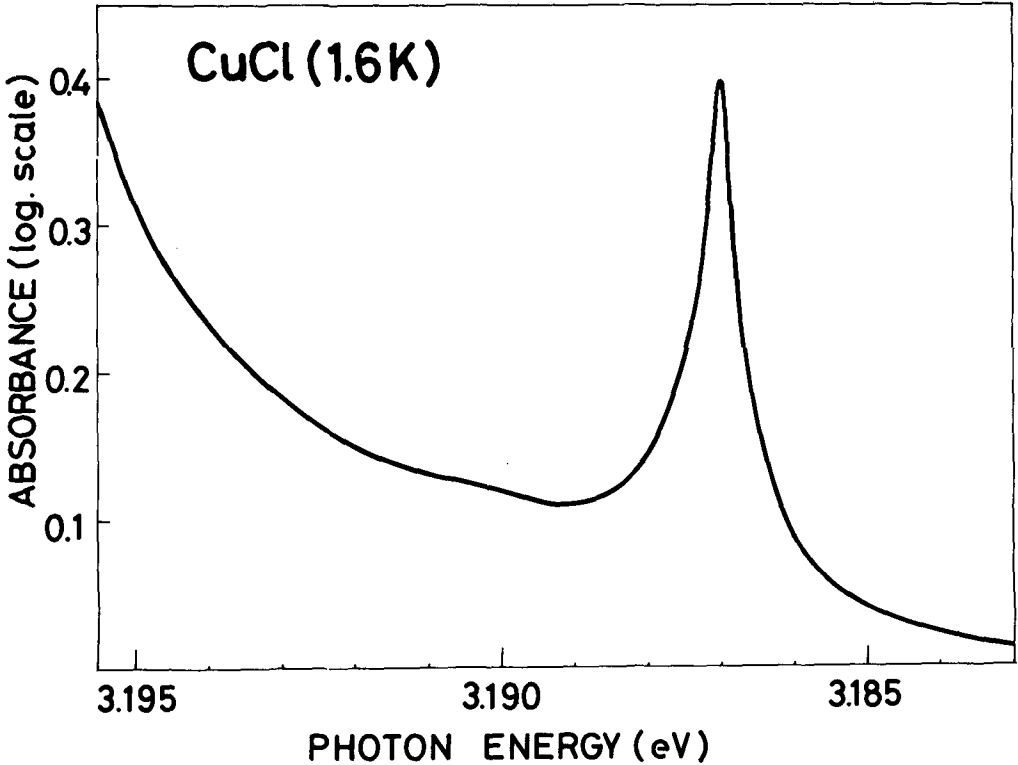


Fig.8. Two-photon absorption spectrum for the generation of excitonic molecule in CuCl, measured with a dye laser of 0.25 meV half width.



course and its absorption coefficient amounts to  $\sim 10^3/\text{cm}$ .

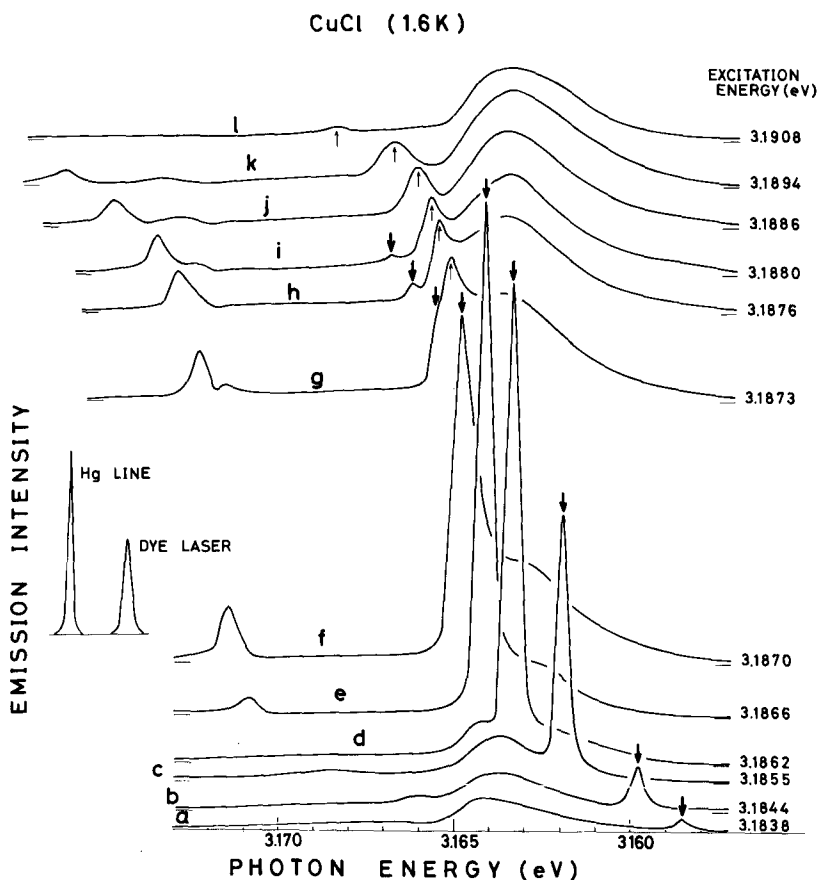


Fig.9. Two-photon resonance Raman spectrum of CuCl with using a dye-laser of 0.25 meV half width.

## 2.6 Two-Photon Resonance Raman Scattering

In regard to a question that the present sharp emission line, which we considered as being due to the Bose-condensed excitonic molecules, might be due to the two-photon resonance Raman scattering, emission spectra were studied in CuCl with shifting the energy of the dye laser. In the present case of the Raman process, the excitonic molecule and exciton are the intermediate and final states, respec-

tively. Figure 9 shows the Raman spectra measured with using a dye laser of 0.25 meV half-width. The photon energy of the excitation laser was shifted in a range from 3.184 eV to 3.191 eV which covers the absorption spectrum in Fig. 8. When the energy of the dye laser

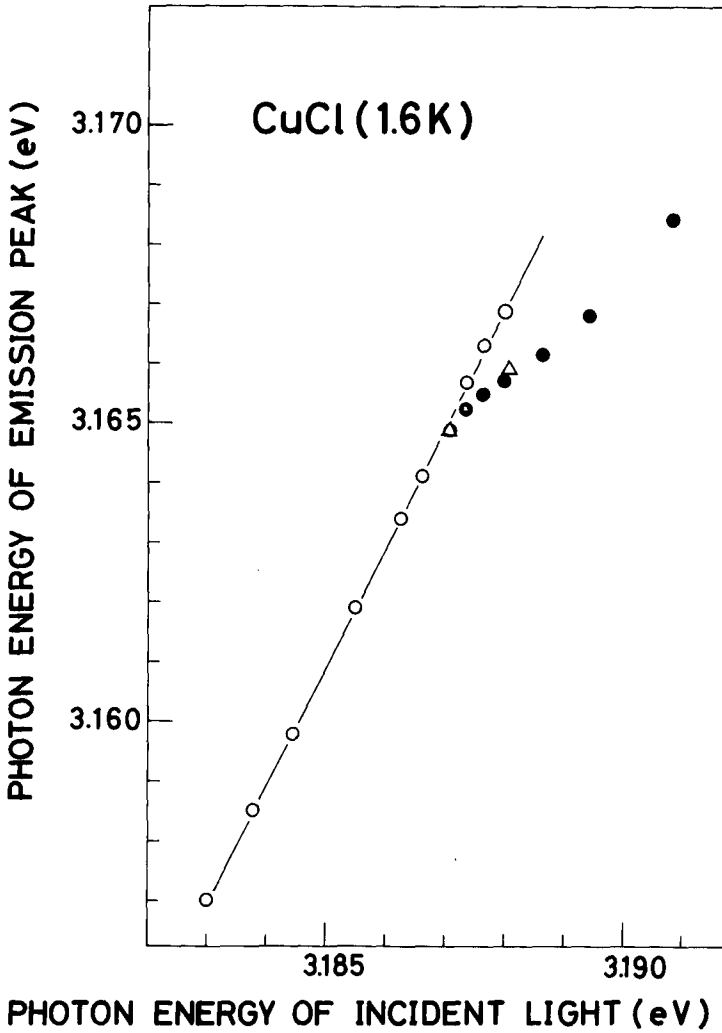


Fig.10. Shift of the Raman and emission peaks in Fig.9 versus the shift of the dye-laser energy. Data marked by  $\Delta$  was obtained with using two photons,  $\hbar\omega_1 + \hbar\omega_2$  having a small energy difference.

approaches 3.1870 eV, sharp peaks, marked by thick arrows, are much enhanced, and at the off-resonance in the high energy side from 3.1870 eV, the peak intensity decreases very rapidly. The energy of the sharp peaks was plotted by open circles with respect to that of the exciting dye laser in Fig. 10. With the shift of the exciting light,  $\Delta\nu$ , the peak is found to shift by  $2\Delta\nu$ , indicating that these peaks are the two-photon Raman bands.

The highest intensity of the Raman band occurs at  $3.1642 \pm 0.0001$  eV with the excitation at  $3.1866 \pm 0.0001$  eV. Namely, it does not occur with the excitation at the two-photon absorption peak, but does so at a little lower energy position by 0.4 meV.

As seen in curves from g) to k), another bands marked by thin arrows are observed when the excitation energy is larger than 3.1870 eV. The shift of these bands deviates from the straight line in Fig. 10 as shown by closed circles. A broad band, of which the peak is located at  $\sim 3.1635$  eV, is found in all curves, and becomes to predominate with the increase of the excitation energy. The line shape of this band seems to be expressed by the formula (2), so that it is considered to originate from the one-photon excitation in the exciton absorption tail which overlaps with the two-photon absorption spectrum as seen in Fig. 8. The Raman bands have  $\sim 0.45$  meV half-width, which is a little broader than that of the dye laser. This fact is also valid when the dye laser band width is broadened to 0.45 meV as shown previously.<sup>34)</sup>

Small bands which appeared near the 3.172 eV ( $M_T$  band) region were previously attributed to the emission from the Bose condensed excitonic molecules with recoiling transverse excitons. These peaks are also found to shift by  $2\Delta\nu$  with respect to that,  $\Delta\nu$ , of the excitation laser energy. Thus, the bands are attributed to the two-photon resonance Raman scattering having the transverse exciton as the final state.

When the band width of the dye laser is broadened to 2 meV in

such a way that it covers the whole region of the excitation spectrum for the generation of excitonic molecules as shown in Fig. 11 a), the emission spectra show a sharp peak at 3.165 eV and a little broader one at 3.171 eV in common, and two-photon resonance Raman peaks which shift by  $2\Delta\nu$  were not observed as seen in figure b) as reported in ref. (34). Curves 1-5) are the spectra with the excitation of the laser at respectively numbered regions in a). It is emphasized that the band width of the 3.165 eV emission is narrower than 0.15 meV, that is nearly the same as the band pass of the detecting monochromator. Further, the peak positions of two bands at 3.165 eV and at 3.171 eV do not change with the shift of exciting laser light.

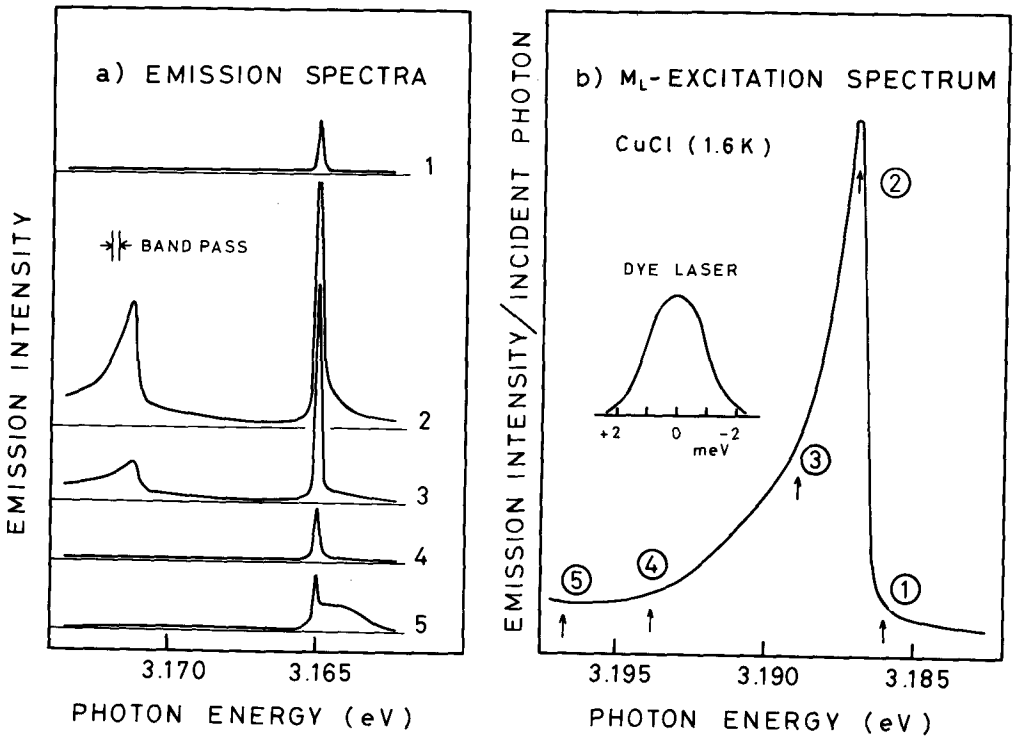


Fig.11. a): Two-photon excitation spectrum for the generation of excitonic molecule, measured with a dye-laser of 2 meV half width.

b): Emission spectra excited at the two-photon absorption region in a) with a dye laser of 2 meV half width.

A problem becomes very stimulating whether or not the distinction is possible between the resonance Raman scattering due to the one-step process and the luminescence due to the two-step process of the absorption and subsequent emission of photons. An approach to this problem has been proposed by Kubo *et al.*<sup>38)</sup> By the theory, the scattered spectrum consists of Raman and luminescence parts and the luminescence part remains when the band width of the excitation dye laser is much wider than the modulation of excitonic molecule as discussed by Hanamura<sup>39)</sup> in connection with our results shown in Fig. 11.

The extreme narrowness of the 3.165 eV emission band and no shift of this band as well as the one at 3.171 eV with respect to the shift of the excitation light energy, shown in Fig. 11, are not in contradiction to the consideration of the Bose condensation of excitonic molecules.

When the crystal is strongly excited by the two-photon process with using a wide band dye laser of 3.187 eV energy, the generated molecules give rise to the Bose condensation. On the other hand, the weaker excitation with narrow band laser brings about the Raman scattering, and the sharp emission from the condensed state is not observed. From these facts, the critical density of the excitonic molecules is shown to be necessary for the Bose condensation in the present case as well. If we could use a more intense dye laser, both the two-photon resonance Raman and the emission from the Bose condensed state might be expected to be observed simultaneously even in the case of making the laser band width narrow. The emission bands marked by thin arrows in Fig. 9, which are enhanced only when the crystal is excited above 3.187 eV, might be the luminescence from the unrelaxed states of excitonic molecules. It is probable that such an emission and also the one from the Bose condensed state are considered to be hidden in the Raman peak at 3.165 eV.

For making the Bose condensation of excitonic molecules and dis-

inction between Raman and luminescence clearer, the studies with using an intense dye laser of tunable band width and time resolved spectroscopy of the sharp line and its side band are indispensable. The precise determination of the laser intensity on the sample is also very important.

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