BIEXCITON LUMINESCENCE IN CuCl AND CuBr

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ABSTRACT

When CuCl and CuBr are excited in their band to band absorption, biexcitons are generated from carriers and excitons. They are characterized by a Boltzmann distribution function with a temperature higher than that of the sample. They decay radiatively from their ground state to exciton-polariton states. Broad emission bands are observed.

When biexcitons are directly created by a resonant two-photon absorption in their ground state, they may form a Bose-Einstein condensate. When they recombine radiatively, sharp emission bands are indeed observed on the high energy edge of the broad emission bands.

Additional emission lines have been observed on the low energy side of the free exciton emission in CuCl and CuBr, under high excitation intensities at low temperatures. They have been previously attributed to the radiative decay of biexcitons from their ground state to the ground states of excitons.[1,2] As will be shown, different emission spectra are obtained when the biexcitons are generated from the population of carriers and excitons, or created directly.

I. GENERATION OF BIEXCITONS FROM THE POPULATION OF CARRIERS AND EXCITONS

When the crystals are excited in their band to band absorption by an intense ultraviolet light, (1 MW Lambda Physik Nitrogen laser, 3.677 eV) a large number of free carriers are created. They thermalized rapidly and form excitons.[3] Biexcitons are then generated from this large pool of excitons.

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The spectrum obtained for CuCl at 4.2 K under an excitation intensity of 8×10^{21} UV photons/cm^2 sec is drawn in solid line in Fig. 1.

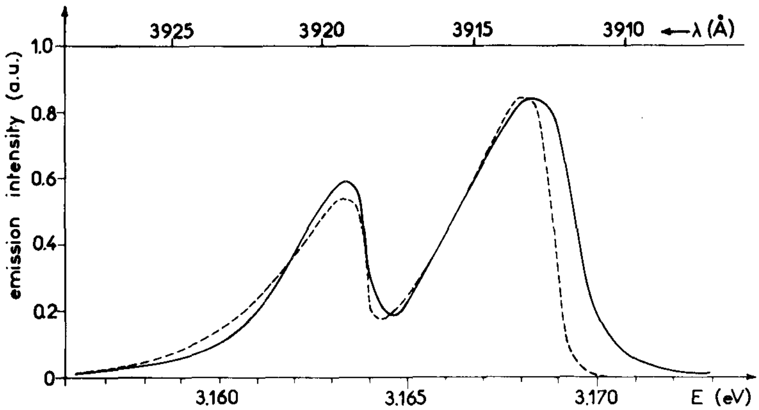

Fig. 1. Experimental luminescence spectrum of CuCl (solid line) under strong excitation (8×10^{21} photons/cm^2 sec) in its band to band absorption at 4.2 K.
Theoretical curve (dashed line) with T = 18 K and E_M^b = 28 meV.

Two broad emission bands called B_T (3.168 eV) and B_L (3.164 eV) are observed. Their line shape has been calculated assuming transitions from the biexciton ground state Γ_1[4] to the longitudinal Γ_5 exciton and the corresponding upper and lower polaritons.[5] The transition towards the lower Γ_2 exciton level is forbidden.

The biexcitons are assumed to be thermalized in their ground state and characterized by a Boltzmann distribution function with a temperature T.* Their binding energy E_M^b is defined relatively to the energy of the lowest Γ_2 exciton state. These two quantities have been used as adjustable parameters in order to fit best theoretical and experimental spectra.

The calculated curve, corresponding to the experimental spectrum given in Fig. 1, is drawn in dashed line in the same figure. The values

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* Souma et al.[6] had previously shown that the B_L band could be characterized by a Boltzmann function.

of the parameters are T = 18 K and E_M^b = 28 meV.

An increasing discrepancy exists between the calculated curve and the experimental spectrum at higher excitation intensities. In the experimental spectrum, the B_T line broadens more and more, while the B_L line remains almost unchanged. The discrepancy is certainly due to simplifying assumptions made in our calculations. However, the experimental intensities ratio of B_T and B_L remains equal to two for all excitation intensities, corresponding to the statistical creation of one longitudinal exciton for two transverse excitons in the radiative decay of biexcitons.

When we excite high quality single crystals of CuBr in their band to band absorption, three broad emission bands are observed. Their peaks are approximatively at 2.945 eV for the B_t band at 2.940 eV and 2.929 eV for the B_T and B_L bands[7] respectively. The spectrum obtained at an excitation intensity of 6×10^{22} UV photons/cm^2 sec at 1.6 K is drawn in Fig. 2.

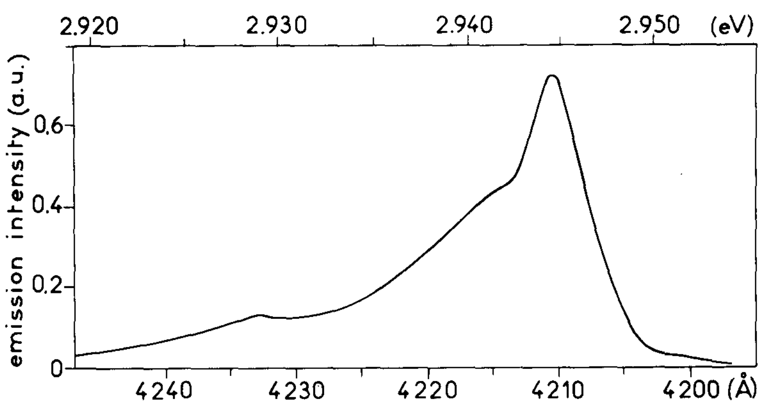

Fig.2. Experimental luminescence spectrum of CuBr under strong excitation (6×10^{22} photons/cm^2 sec) in its band to band absorption at 1.7 K.

We know from Comte's theoretical investigation[8] that there are three possible symmetries Γ_1, Γ_3 and Γ_5 for the most stable states of the biexciton corresponding to an envelope function which is symmetric under electron and hole permutations. These three states are not split by the electron-hole exchange interaction. Therefore, it we assume that these states remain degenerate, the observed emission can be simply explained by the radiative decay of the biexcitons.

The B_t line may be due to the allowed transitions from the biexciton ground state to the degenerate Γ_3, Γ_4 lower exciton state in CuBr. The binding energy of the biexciton in its ground state, defined relatively to the lower Γ_3, Γ_4 exciton state, is shown to be equal to 17 meV. The two other emission bands B_T and B_L can be related to the radiative decay of biexcitons from their ground state to the longitudinal Γ_5 exciton state and the corresponding lower polariton state, as in CuCl.

II. DIRECT GENERATION OF BIEXCITONS

The direct creation of biexcitons by a resonant two-photon absorption has been predicted theoretically by Hanamura[9)] and first observed by Gale and Mysyrowicz in CuCl.[10)] All biexcitons are then generated with the same translational momentum 2 $\vec{K}_o$, $\vec{K}_o$ being the wave-vector of the exciting photons.

In Fig. 3, are drawn the emission spectra of a cleaved single crystal of CuCl, excited at 1.7 K by a tunable dye laser [2×10^{-3} M/l Butyl PBD in toluene pumped by the Lambda Physik Nitrogen laser] emitting at 3890 Å (3.187 eV) with a spectral width of 2.5 meV. Two photons simultaneously absorbed directly create a biexciton in its Γ_1 ground state[11)] as it can be deduced from the known biexciton binding energy and as it has been observed by Ueta and his group in the two-photon excitation spectrum.[12)]

We have observed two narrow emission peaks as in ref.(12) showing an instrument limited linewidth of 0.6 meV on the high energy edge of the two broad emission bands B_T and B_L at 3909.4 Å (3.1713 eV) and

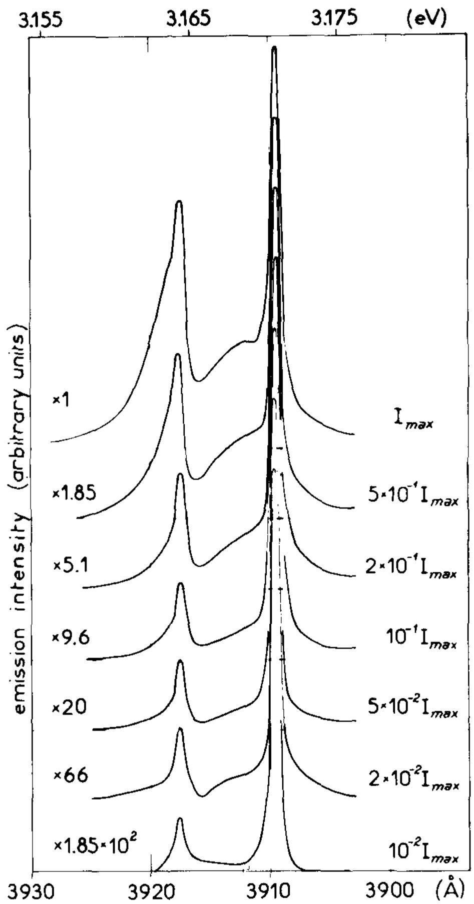

Fig.3. Experimental luminescence spectra of CuCl under two-photon excitation at 3.187 eV. The normalization factor for each spectrum is given on the left hand side of the figure.

3917.3 Å (3.165 eV) respectively. The first line is several times more intense than the second one.

The line intensities show a pronounced dependence on excitation intensity. At low excitation intensities, only the sharp lines are present. When the excitation intensity increases, the broad emission bands B_T and B_L appear and increase more rapidly than the sharp ones. They vary as the quadratic power of the excitation intensity as expected from a two-photon excitation, while the sharp lines vary linearly in this range of excitation, after a quadratic increase at low intensities

These sharp emission lines are also very sensitive to the temperature. They decrease and disappear very rapidly when the temperature increases ($T \simeq 20$ to 30 K).

The sharp lines have been attributed by Ueta *et al.*[12] to the radiative decay of biexcitons condensed in the $\vec{K} = 0$ or $2\,\vec{K}_0$ state as predicted by Hanamura.[9] These sharp lines cannot be related to any stimulated process, their study in function of the excitation intensity is not showing any exponential growth. They can neither be identified with known impurity emission lines.

Figure 4 shows the emission spectra of a cleaved single crystal of

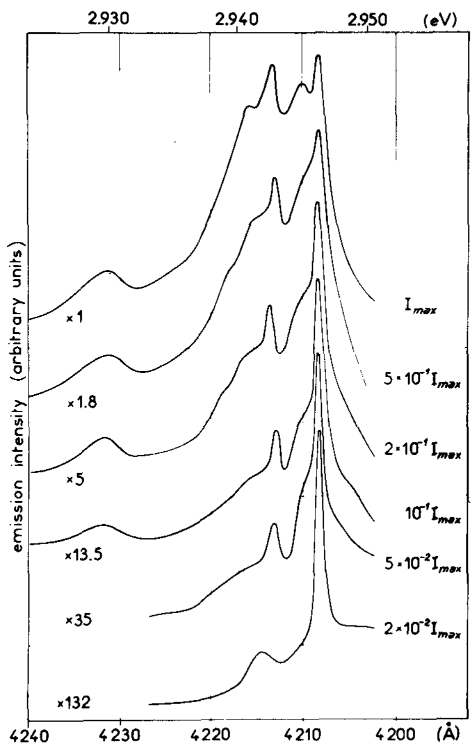

Fig.4. Experimental luminescence spectra of CuBr under two-photon excitation at 2.955 eV. The normalization factor for each spectrum is given on the left hand side of the figure.

CuBr at 1.7 K. In this case, the tunable dye laser [10^{-3} M/1 POPOP in Toluene pumped by the nitrogen laser] emits a 4196 Å (2.955 eV) light with a spectral width of 1.25 meV. This laser generates biexcitons in their ground state, by resonant two-photon absorption, as can be deduced from the value of their binding energy.

As in CuCl, two narrow lines are observed on the high energy edge of the B_t and B_T bands respectively at 4208.3 Å (2.946 eV) and 4213.5 Å (2.9424 eV). Ueta and his group have only observed a sharp line on the high energy edge of the third B_L line, which was not found in our experiments.[13)*]

The observation of these lines in CuBr at the spectral position expected from the radiative decay of biexcitons condensed in the $\vec{K} = 0$ or $2\ \vec{K}_o$ state is another argument in favour of Hanamura's interpretation.[9)]

III. CONCLUSION

We have shown that biexcitons decay radiatively from their ground state to exciton-polariton states. When biexcitons are generated from carriers and excitons, broad emission bands are observed, due to the large population of biexcitons in their ground state corresponding to temperature higher than that of the sample. When they are directly generated, sharp emission lines are observed on the high energy edge of the broad bands. They can be tentatively attributed to a Bose-Einstein condensation of biexcitons.

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* Nagasawa *et al.*[14)] have reported the observation of three sharp lines on the high energy edges of the B_L, B_T and B_t.

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