

## BIEXCITONS IN CuCl

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### ABSTRACT

The experimental evidence for the existence of the biexciton in CuCl is discussed. It relies on the analysis of the luminescence of strongly excited crystals, on the two-photon absorption and excitation spectrum. In the second part, measurement of the biexciton lifetime at 4.2°K is reported.

The study of strongly excited crystals has become a subject of increasing interest during the last few years. If a high density of electron-hole pairs is generated, new collective excitation states appear in the system. The simplest such collective excitation is represented by the biexciton, an excitonic molecule composed of two electron-hole pairs bound by direct Coulomb and exchange interaction. This quasiparticle has been reported in a large number of crystals. In this paper, some of the experimental evidence for the existence of biexcitons in CuCl is discussed.

The first kind of evidence relies on the appearance of a new emission, located on the low energy side of the free exciton luminescence in pure CuCl crystals subject to an intense irradiation with UV laser light. At 4.2°K, this new emission consists of four lines, which are observed in a large variety of samples, provided the excitation rate is important enough (see Fig. 1). The origin of the lines B and C at 25567 cm<sup>-1</sup> and 25522 cm<sup>-1</sup> has been attributed to the presence of biexcitons in the crystal.<sup>1)</sup> The main argument for this interpretation relies on the particular intensity dependence of these lines upon excitation intensity. In a large range of excitation, the lines show a quadratic

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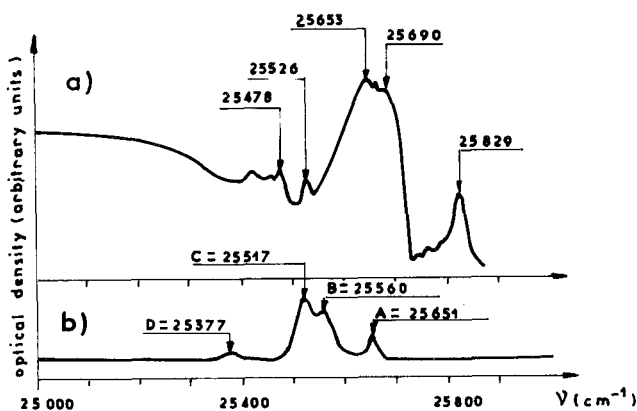


Fig.1. Microdensitometer trace of CuCl luminescence at 4.2°K when excited  
 a) by a low intensity light source  
 b) by the high intensity light from a UV laser ( $\hbar\omega = 288000 \text{ cm}^{-1}$ ).

dependence until they become linear, at higher input intensities. The free exciton decay line, in contrast, remains linear in the whole excitation range. Such a behaviour may be understood if one assumes that the new luminescence results from the radiative decay of biexcitons into photons and free excitons. The biexcitons are formed because of the high density of hot free carriers generated by incident light absorption so that the quadratic dependence is observed since two photons are required to produce a single molecule. The linear law at higher input intensities is due to the fact that a free exciton is generated in the decay process. A detailed analysis of the kinetics has been given by Knox *et al.*<sup>2)</sup>

The position of the lines yields a value for the binding energy of the molecule which is in good agreement with the calculations.<sup>3,4)</sup> The large value  $E_B = 275 \text{ cm}^{-1}$  (comparable to the exciton binding energy in many II-VI compounds) is due to the important admixture of d-like orbitals in the upper valence band (80%),<sup>5)</sup> resulting in a very small electron-to-hole effective mass ratio (0.02) for the quasi-particle, which has thus a strong similarity with the hydrogen molecule.

A confirmation for the above interpretation has been given by Ueta *et al.* from an analysis of the luminescence line shape.<sup>6)</sup> It was found

that the band-to-band two-photon excited luminescence line shape could be fitted with a model in which the initial biexciton population had a Maxwell velocity distribution, as expected for a gas of free particles in interaction with the lattice. The effective temperature of the biexciton gas was found to be significantly higher than the lattice temperature.

More recently, Koda and Suga have analysed the luminescence of strongly excited mixed CuCl-CuBr crystals.<sup>7)</sup> From the fact that the splitting between lines B and C varied as a function of composition in the same way as the splitting between the longitudinal and transverse  $\Gamma_5$  exciton, they assigned the two lines to a transition from the same biexciton level to the transverse and longitudinal branch of the exciton-like polariton.

It must be noted that this set of results, although convincing, does not constitute a definite proof for the existence of biexcitons in CuCl. This can be best seen from the example of Si and Ge, where the existence of excitonic molecules was first inferred from a similar kind of experimental evidence,<sup>8,9)</sup> until the concept of electron-hole drops was proposed<sup>10)</sup> and further experiments showed that the observed emission was related to the presence of metallic drops in these materials.<sup>11)</sup>

A different type of evidence may be obtained from the study of the absorption spectrum of the biexciton. Such an approach has been proposed first by Hanamura.<sup>12)</sup> It provides a powerful method of investigation because here one measures directly the biexciton resonance energy, in contrast with the previous method which relies on the analysis of a decay process. As noted by Hanamura, the two-photon transition rate from the ground state to the molecular state exceeds by several orders of magnitude the usual two-photon band-to-band transition rate in the same spectral region and takes exceptionally large values of the order  $10^4 \text{ cm}^{-1} \text{ MW}^{-1}$ . There are two reasons for this giant non-

linear absorption coefficient; first, the proximity of the exciton state from the single photon energy, at  $E_{\text{exc}} = \hbar\omega + E_B/2$  which acts as a quasi-resonant intermediate state; secondly, the particular (two-electron) type of transition further enhances the non-linear response of the medium.

A direct measurement of the two-photon absorption coefficient has been performed, in a limited spectral range, around  $2\hbar\omega = E_M = 2E_{\text{exc}} - E_B$  in CuCl by Gale and Mysyrowicz.<sup>13)</sup> This can be done by measuring the transmitted intensity of a parallel propagating intense monochromatic light beam through the sample as a function of input intensity. In presence of linear loss  $\alpha$  and non-linear loss  $\delta I_0$ , the transmission law reads:

$$I/I_0 = \exp(-\alpha \ell) / [1 + \alpha^{-1} \delta I_0 \{1 - \exp(-\alpha \ell)\} ] \quad (1)$$

A plot of  $I/I_0$  versus  $I_0$ , the incident intensity, directly yields  $\alpha$  and  $\delta$ , the two-photon transition cross-section. In agreement with the theoretical predictions, a strong and sudden increase of  $\delta$  was measured in the expected region from values  $\leq 10^{-49} \text{ cm}^4 \text{ sec}$  typical of band-to-band transitions in solids, up to  $\delta = 10^{-44} \text{ cm}^4 \text{ sec}$  at  $214 \text{ cm}^{-1}$  below the  $\Gamma_5$  exciton line. Unfortunately, this kind of measurement could not be performed at higher frequencies, close to the exciton resonance, because of the rapidly increasing linear and non-linear losses, which prevented any significant amount of light to be transmitted through the sample, so that no independent measurement of the biexciton internal energy  $E_M$  could be obtained by this method. A complete two-photon absorption spectrum, extending over an entire line profile, would be very useful. The interpretation of such a spectrum will suffer from two complications; first, one must consider the influence of a resonant enhancement in the intermediate state, whenever the incident photon energy coincides with a real level of the crystal. Such levels exist close to the exciton, they are due to donor impurities. Even if the

number of centers is small ( $10^{17}$ ), it can increase the two-photon transition rate considerably and thus distort the true biexciton absorption spectrum. Secondly, a structure in reflectivity has been observed around  $\hbar\omega = 2E_{exc}$  by Cardona<sup>14)</sup> at room and nitrogen temperature. It arises from an anomaly in the joint density-of-states due to the second conduction band. In a non-centrosymmetric crystal like CuCl, this structure can also be observed in the two-photon absorption spectrum. Its contribution to the measured spectrum must be evaluated; this may require more linear absorption or reflection data, especially at liquid helium temperature.

Another method of investigation, related to the previous one, consists in measuring the biexciton excitation spectrum. Whenever the incident photon energy of the intense light source equals a half the biexciton energy, one expects an increase of the characteristic molecular luminescence, because a large number of molecules is directly created by giant two-photon absorption. Hence, by monitoring the output intensity as a function of input frequency (with constant input intensity) one can get informations upon the biexciton resonance energy. Such a method of investigation has the advantage of a great sensitivity but requires caution in the interpretation. The excitation spectrum does not reproduce directly the two-photon absorption spectrum, but is affected by the competition between linear and non-linear attenuation of the light beam in the medium. Further, the spectrum shape depends upon the experimental conditions. In particular, the detection geometry is crucial since the penetration depth of the beam in the sample varies considerably with  $\alpha$  and  $\delta I$ .

The total molecular luminescence excited by two-photon absorption is of the form:

$$I_M = c \int_0^{\ell} I^2(x) dx, \quad (2)$$

where  $\ell$  is the sample thickness.

For a parallel propagating beam  $I(x)$  is given by eq.(1)

Integration of (2) yields:

$$I_M = c I_0 \left\{ \frac{(1 + \varepsilon) \{1 - \exp(-\alpha l)\}}{1 + \varepsilon \{1 - \exp(-\alpha l)\}} - \frac{1}{\varepsilon} \ln [1 + \varepsilon \{1 - \exp(-\alpha l)\}] \right\}. \quad (3)$$

Thus, the output luminescence is a complicated function of  $\varepsilon$ , the ratio between two-photon and linear absorption and only in special conditions will it have a quadratic law dependence upon  $I_0$ . For example, in the case of important linear loss ( $\alpha l > 1$ ) eq.(3) reduces to

$$I_M = c I_0 \left\{ 1 - \frac{1}{\varepsilon} \ln(1 + \varepsilon) \right\} \quad (4)$$

and  $I_M$  is insensitive to variations of the two-photon absorption coefficient, resulting in a broadening of the resonances. This behaviour reflects the fact that all incident photons are absorbed in the medium.

The molecular excitation spectrum of CuCl at 4.2°K and 77°K has been measured by Gale and Mysyrowicz.<sup>13,15)</sup> (see Figs. 2 and 3). In this experiment, a backward geometry was used and care was taken that the luminescence from the whole sample depth was collected. In this way, the molecular excitation could be compared, through eq.(3) with the direct measurement of  $\delta$  performed in the same spectral range. Excellent agreement was found between both methods. (see Fig. 2). The behaviour of lines B and C is consistent with the interpretation of these lines given earlier. They exhibit a peak in the excitation spectrum at the expected frequency  $\hbar\omega = E_M/2$ . (the relative intensity of these two lines, however, changes with input frequency, with a maximum for the ratio C/B at  $\hbar\omega = 25815 \text{ cm}^{-1}$ , the energy of the forbidden  $\Gamma_2$  exciton, a fact presently not understood). As expected from eq.(3), the intensity dependence of the lines upon  $I_0$  varies between a quadratic and a linear law. The highest slope is observed at the lower excitation frequencies, becoming close to one near the excitation spectrum peak and remaining there at higher frequencies. Further the

Fig.2. Two-photon excitation spectrum of CuCl at 77°K plotted in function of the difference between the  $\Gamma_5$  exciton frequency and that of the incident light. The open circles are obtained from the direct measurement of  $\delta$ . The input intensity is 100 kW.

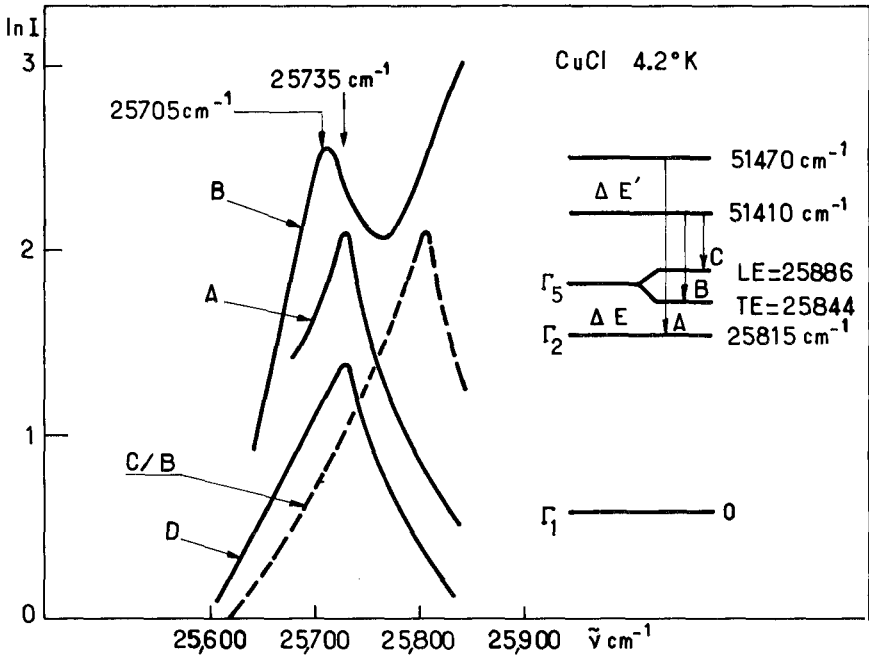
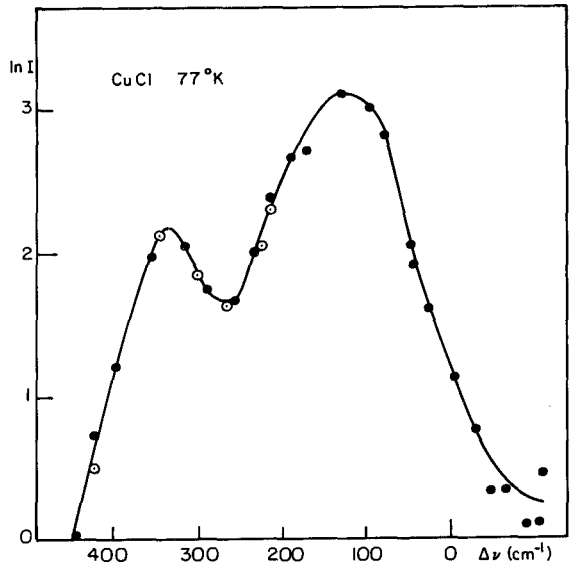


Fig.3. Two-photon excitation spectrum of the various emission lines of CuCl at 4.2°K plotted in function of input light frequency. The input intensity is 100 kW. Curve C/B gives the ratio of the intensities of lines C and B.

width of the lines is smaller at the peak of the excitation spectrum where  $2 \hbar\omega = E_M$  (see Fig. 4); this results from the fact that here cold biexcitons (with a wave vector  $2 k_0$  ( $k_0$  = incident photon wave vector)) are directly created. In that case the thermalisation of the

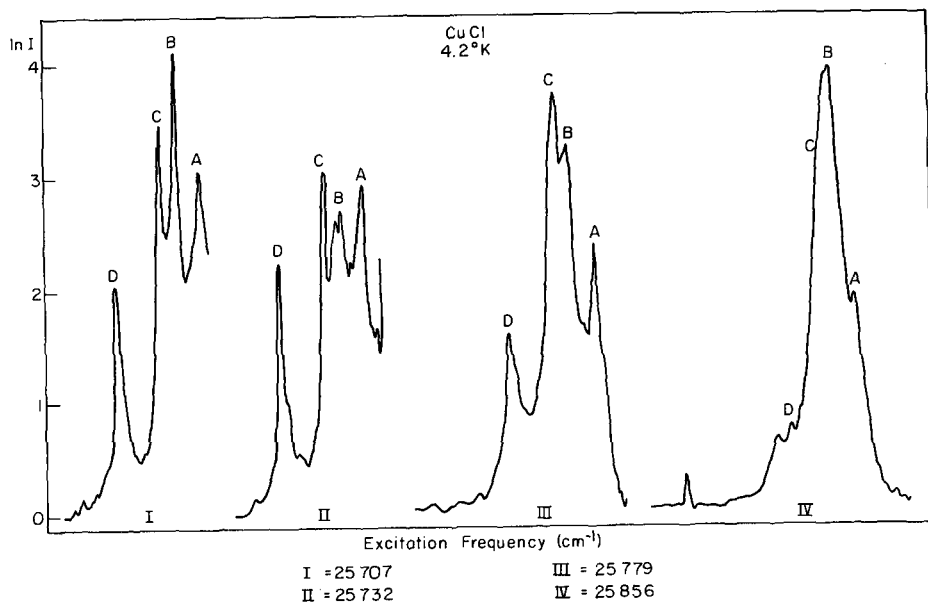


Fig.4. Luminescence spectrum of CuCl at 4.2°K, for different input frequencies. The input intensity is approximatively equal in each case  $\approx 100$  kW. Curve I corresponds to resonant two-photon excitation of biexcitons. In curve IV, the input photon energy is resonant with the  $\Gamma_5$  free exciton.

particles with respect to the lattice involves an interaction with acoustic phonons and occurs in a time comparable with the lifetime of the particles. Therefore, the thermalisation process is incomplete and the decaying biexcitons have an effective temperature lower than the lattice temperature. Therefore, the molecular emission will be narrow, since the biexciton and exciton bands are flat, due to the large mass of the particles ( $m_B = 2m_{exc} \approx 40 m_0$ ;  $m_0$  = free electron mass). By contrast, at higher input frequencies, an excess energy is delivered to the system, which must be dissipated locally, leading to a higher effective temperature for the gas of biexcitons as deduced from the



lineshape analysis.<sup>6)</sup> Collisions with other particles present in that case (excitons, free carriers) also contribute to the broadening of the lines.

A different explanation of the observed narrowing at resonant two-photon excitation, in terms of the occurrence of a Bose-Einstein condensation of biexcitons has been proposed by Ueta *et al.* (see this volume).

Other features observed in the excitation spectrum cannot be explained simply. The broad new emission appeared at 77°K, as well as lines A and D at 4.2°K, shows a peak of the excitation spectrum at a different, higher input photon energy. This has been attributed to the presence of an excited molecular state, 60 cm<sup>-1</sup> above the lowest free biexciton state.<sup>15)</sup> According to Bassani *et al.*<sup>16)</sup> a state of symmetry  $\Gamma_4$ , corresponding to the first rotational level of the orthomolecule of hydrogen, is stable in a compound like CuCl. However, the two-photon transition from the ground state  $\Gamma_1$  to a state of symmetry  $\Gamma_4$  with a single light beam is forbidden in first approximation, so that the direct creation of biexcitons in the excited state  $\Gamma_4$  appears unlikely.

In the last part of this paper, the luminescence obtained with intense, picosecond pulse excitation is described and a measurement of the biexciton lifetime is reported.<sup>17)</sup> The experimental set-up is shown in Fig. 5. A pulse, of duration 25 ps is switched out from a single transverse mode (TEM<sub>00</sub>) mode locked ruby laser pulse train and after subsequent amplification to a final energy of up to 10 mJ illuminates the sample held at liquid helium temperature. The luminescence is detected in the backward geometry. The microdensitometer trace of a typical emission spectrum, obtained in a single shot exposure is shown in Fig. 6. It differs from that obtained when the same sample is irradiated with a nanosecond UV pulse (see same figure) in that only two of the four characteristic lines are seen, while a new emission peak E appears at 25455 cm<sup>-1</sup>.

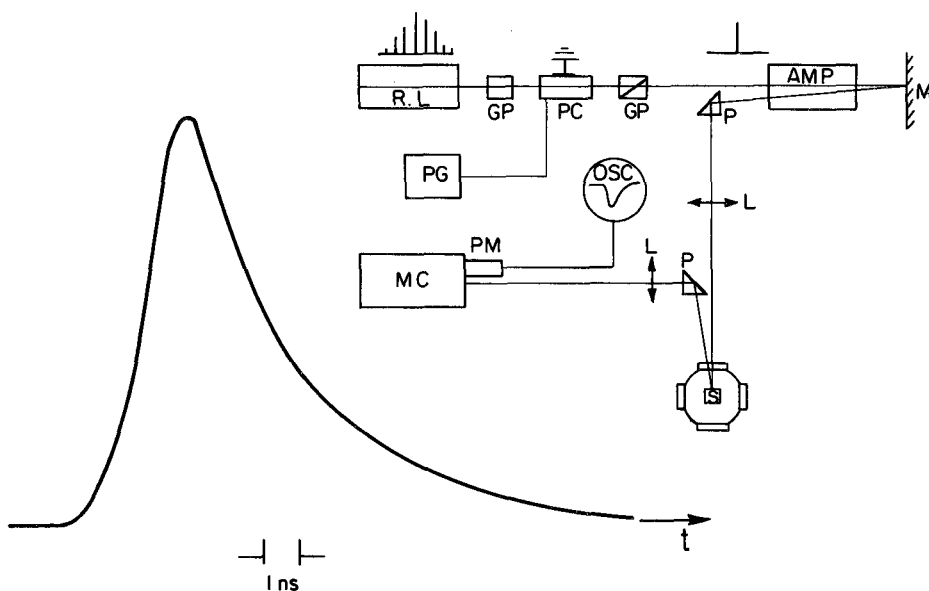


Fig.5. Time resolved luminescence at  $25510 \text{ cm}^{-1}$  from picosecond - excited CuCl at  $4.2^\circ\text{K}$ .

Experimental set-up (inset)

- R.L - Mode-locked ruby laser
- G.P - Glan-Thompson polarising prism
- P.C - Pockel's cell
- AMP - Ruby amplifier
- M - Mirror
- P - Prism
- PG - Pulse generator
- L - Lens
- S - CuCl sample at  $4.2^\circ\text{K}$  or  $77^\circ\text{K}$
- MC - Monochromator
- P.M - Photomultiplier.

The disappearance of lines A and B can be explained by considering the particular conditions of excitation in this case: The generation of one electron-hole pair requires the absorption of two red photons. Since the two-photon absorption coefficient in this spectral region ( $2h\nu = 28800 \text{ cm}^{-1}$ ) is small, of the order  $0.1 \text{ cm}^{-1} \text{ MW}^{-1}$ , excitation occurs in the volume of the sample.

After fast thermalisation of the hot free carriers, a relatively low density of excitons ( $10^{16} \text{ cm}^{-3}$ ) is formed; the total, instantaneous number of excitons is large, however, since the exciting pulse is short

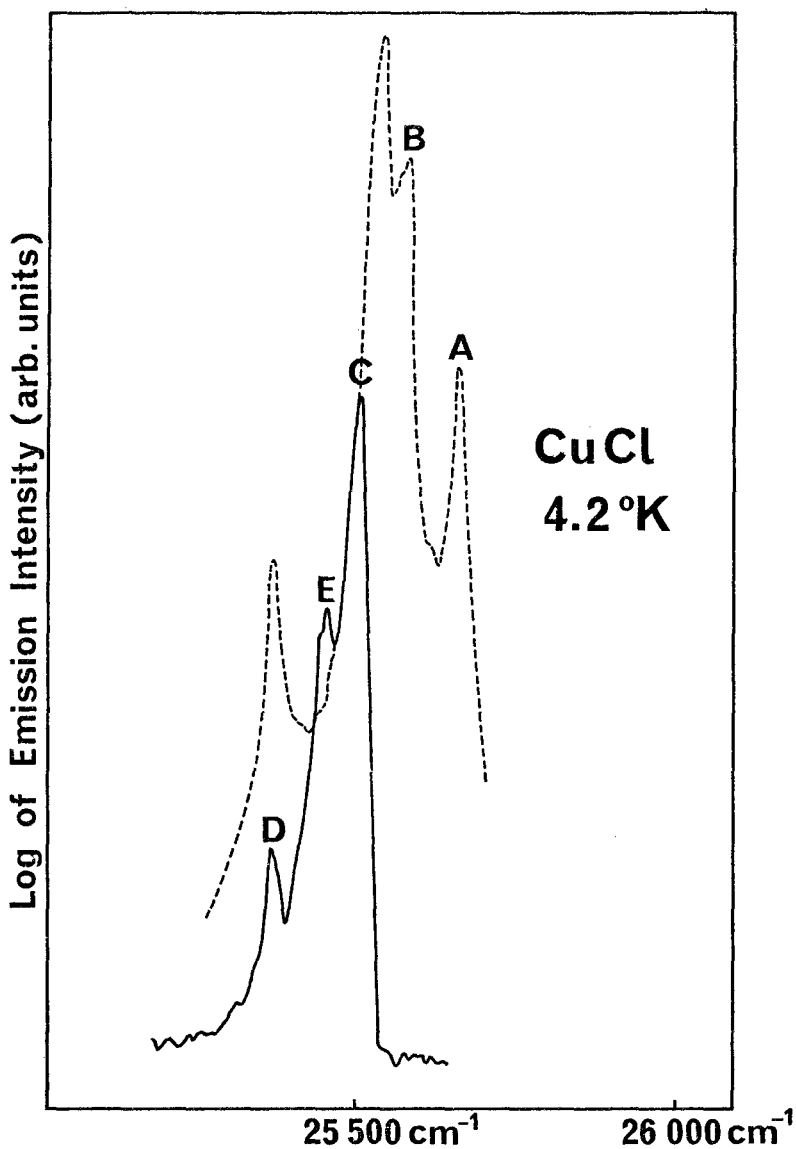


Fig.6. Solid line; Microdensitometer trace of CuCl luminescence at 4.2°K excited by single ruby picosecond pulse.  
Dotted line; Luminescence from the same sample excited by a ns UV pulse at 25780  $\text{cm}^{-1}$ .

compared to the lifetime of excitons. Of these, only a small fraction will couple into molecules ( $10^{-3}$ ) because of the large mean separation between the particles. In such a situation, where the decaying biex-

citons are surrounded by a large number of excitons, part of the volume emission will experience reabsorption before reaching the sample surface and being detected. This reabsorption occurs because the reverse process takes place, in which photons are destroyed in the vicinity of existing excitons, to create biexcitons. This process has a very large probability, as shown by Golovin and Rashba.<sup>18)</sup> It occurs for line B, but not C, indicating that only the lower lying transverse branch of the exciton-like polariton is substantially populated from the relaxation of the free carriers. Reabsorption of line A takes place because of the appreciable linear losses at this frequency. There are two reasons which render the molecular emission predominant, even if the number of biexcitons is small compared to that of the excitons: First, all biexcitons can participate in the decay, independent of their initial momentum while conserving both energy and momentum; by contrast, only optical excitons, with a k-vector of the order  $kc = \omega$  can recombine. Secondly, the transition has a giant oscillator strength, as mentioned before.<sup>18)</sup>

The decay time of line C has been measured<sup>17)</sup> using a fast photomultiplier and a wide-band oscilloscope. A decay time of  $3 \pm 1$  ns has been found at  $4.2^\circ\text{K}$ . This value is in agreement with the prediction of Golovin and Rashba.<sup>18)</sup> At  $77^\circ\text{K}$ , no significant deviation from an instrument limited pulse could be seen, indicating a biexciton lifetime inferior to 0.5 ns at this temperature.

In conclusion, even if no single experiment at the present time proves in a totally irrefutable way the existence of the excitonic molecule in  $\text{CuCl}$ , a series of different results render its presence highly plausible.

It is a pleasure to acknowledge many fruitful discussions with Dr. G. M. Gale.

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