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Biexciton luminescence in CuCl microcrystallites

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Biexcitons in CuCl microcrystallites are investigated by recording their luminescence under high-laser-excitation conditions. The study of the line shape of the emission band attributed to biexciton-exciton transitions indicates an increase of the biexciton binding energy when the microcrystallite radius is decreased. In addition, the biexciton distribution established in microcrystallites is shown to be independent of the laser-excitation conditions, such as the laser intensity and frequency.

INTRODUCTION

Because of its simple band structure, direct-band-gap I-VII CuCl is a model semiconductor.[1] It presents a simple exciton series labeled Z_3. This exciton in its ground state of Γ_2 and Γ_5 symmetries has a binding energy of about 190 meV. Only the exciton of Γ_5 symmetry is dipole active. Furthermore, two excitons in the Z_3 ground state can couple together to give rise to another bound state: the excitonic molecule or biexciton. In its ground state of Γ_1 symmetry, the biexciton has a binding energy of 28 meV with respect to the continuum of two excitons of Γ_2 symmetry. The creation of biexcitons is allowed by two-photon absorption, the transition probability being very high because of a resonance enhancement and because of the large spatial extension of the biexciton wave function. Since biexcitons are quite stable with respect to perturbations, the optical properties of bulk CuCl can be well described by a three-level system which shows strong optical nonlinearities with interesting dynamical effects.[2,3]

Semiconductor microcrystallites or quantum dots have been extensively studied these recent years both experimentally[4-11] and theoretically.[12-17] This interest was first stimulated by the prediction of a possible increase of the optical nonlinearity due to confinement[15] or local-field effects.[17] Important excitonic nonlinearities have indeed been observed by pump-and-probe transmission measurements of CuCl-doped borosilicate glass.[10,11] However, they show up not because of the confinement and the thus modulated exciton wave functions, but rather because of the possibility they offer of working at the center of the excitonic resonance. Indeed, in this spectral region, due to the high exciton absorption, no light is transmitted through the bulk material and reflectance changes are only observed when using excitation intensities close to the damage threshold[18,19] of the material. In microcrystallite-doped samples, on the contrary, the exciton absorption presents an important bleaching at very low saturation intensities (beyond 1 MW/cm^2). These intensity values depend on the optical density of the sample studied and on the photon energy of the exciting pump beam.[10,20]

Concerning biexcitons,[21,22] two-photon absorption measurements have been performed with a pump-and-probe technique similar to the one which has been used in bulk material.[23,24] This technique, which has allowed us to reveal the biexciton structure and their dynamical properties in bulk samples, has been unsuccessful in CuCl microcrystallites up to now. More recently, luminescence measurements[25] have therefore been performed at liquid-He temperature.

As explained above, in CuCl, excitons and biexcitons have a large binding energy and Bohr radii of about 7 and 35 Å, respectively.[1] Therefore, when they are confined in large-radius microcrystallites ($\gtrsim 120$ Å), a straightforward approximation will be to consider excitons and biexcitons as good quasiparticles[12] whose kinetic energy is quantized due to the confinement. This situation is different from that of $CdS_{1-x}Se_x$ microcrystallites in which the Bohr radius of excitons is comparable to or even larger than the crystallite radius. In this case, electrons and holes should be considered as confined and their Coulomb interactions treated as perturbations.

EXPERIMENTAL SETUP

The experimental setup is similar to the one discussed in Ref. 11. Its configuration is schematically given in Fig. 1. A XeCl excimer laser (Lambda Physik EMG 100) pumps simultaneously two dye lasers and an amplifying dye cell containing BiBuQ in dioxane as active medium. In order to characterize spectroscopically our samples, we use a pump-and-probe technique. The pump laser of Hänsch configuration has a spectral width of less than 0.03 meV [full width at half maximum (FWHM)] and a pulse duration of about 16 ns. This laser beam passes through the amplifying cell and is focused, after a spatial filtering, onto the surface of the sample which is mounted strain free inside a cryostat (Oxford Instruments) at 3 K. The maximum intensity I_p^m obtained is 5 MW/cm^2. This intensity can be changed by a variable neutral density filter which does not deviate the pump laser beam.

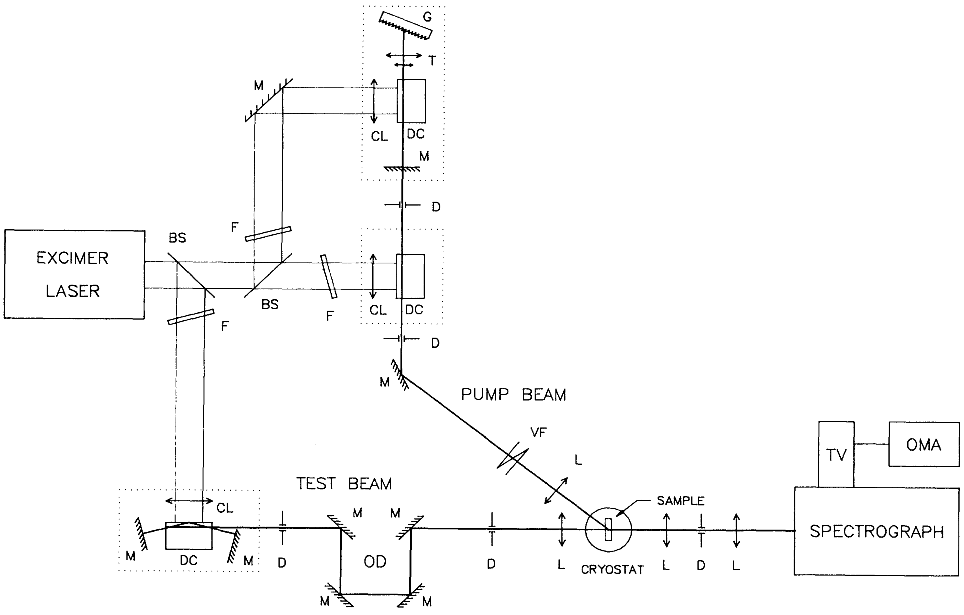

FIG. 1. Experimental setup: F, filters; CL, cylindric lens; BS, beam splitter; DC, dye cell; M, mirror; G, grating; D, diaphragm; L, lens; NF, neutral density filter; VF, variable neutral density filter; T, telescope.

The first samples studied consist of slabs of borosilicate glass doped by CuCl microcrystallites which have a radius larger than 120 Å. Samples with smaller microcrystallites will be considered later on. The preparation and linear optical properties of these CuCl-doped glasses have been discussed in detail in Ref. 11 and 20. Their emission is analyzed by a spectrometer and detected by an optical multichannel analyzer (BM Spektronik). This luminescence is either recorded in a forward-scattering configuration as indicated in Fig. 1, or in a backward configuration. The exciton luminescence clearly shows up only in the latter case. In order to test the stability of our experimental setup and to check that our samples are not damaged during their excitation, the linear and nonlinear transmission spectra of our samples were recorded before and after each series of luminescence studies. For this purpose, we have set up a quenched dye laser which was used as a test beam, as indicated in Fig. 1. It is excited by the excimer laser pulses. Its emission is spectrally broad (about 50 meV FWHM) and centered around the Z_3 exciton resonance of CuCl. Its pulses have a short duration (350 ps FWHM) and are well synchronized to the pump pulses. The maximum intensity of the test beam at its focus point on the surface of the sample is lower than 10 kW/cm^2. Great care is taken to realize its spatial coincidence with the pump beam. The test pulses arrive on the surface of the sample during the pump pulses, i.e., about 8 ns after the rising front. After being averaged over 50 laser shots, the overall spectral shape of the test beam is quite reproducible, showing less than 5% fluctuation over the whole spectral range. Comparing the spectral shape of the test beam when transmitted or not through the sample, allows us to determine the optical density of the sample. Figure 2(a) shows the linear optical density spectrum of the sample, i.e., without pump-beam excitation. It is important to notice that the microcrystallite radius in the first studied samples is so large that the exciton resonance is not shifted with respect to its bulk value. The inhomogeneous broadening of about 10 meV observed [Fig. 2(a)] is therefore not due to the size distribution of the microcrystallites but rather to a variation of the shape of the different crystallites or of the composition of the surrounding glass matrix,

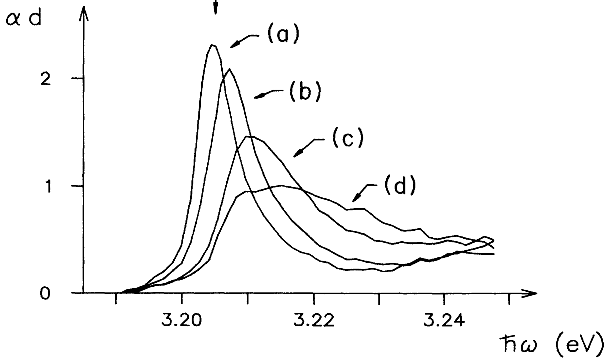

FIG. 2. $\alpha d = \ln(I_t^0/I_t^T)$ of microcrystallites of mean radius of 120 Å; immersed in liquid helium when excited by a pump pulse at the photon energy indicated by the arrow ($\hbar\omega_p = 3.2050$ eV). The excitation intensities I_p are (a) $I_p = 0$, (b) $I_p = 0.07$ MW/cm^2, (c) $I_p = 1.9$ MW/cm^2, (d) $I_p = 5$ MW/cm^2.

which may exercise fluctuating forces on the microcrystals.[10] Figures 2(b)–2(d) show the optical density spectra obtained for different intensities of the pump beam tuned to a fixed photon energy of $\hbar\omega_p = 3.205$ eV, close to the exciton resonance in CuCl.

As discussed in Ref. 10, due to the pump beam excitation, the optical density spectrum of CuCl microcrystallites is modified with respect to the linear transmission spectrum [Fig. 2(a)] when we increase the pump-beam intensity. We observe essentially a bleaching of the absorption below the photon energy of the pump beam and an increase at higher photon energy [Fig. 2(b)]. This behavior has been qualitatively well explained in the framework of a time-dependent Hartree-Fock theory as being due to exciton-exciton interactions.[26] These recordings of the transmission spectra of our samples assure us that they have not suffered during the luminescence experiments, as could easily be the case when the pump-beam intensities used are higher than 10 MW/cm^2.

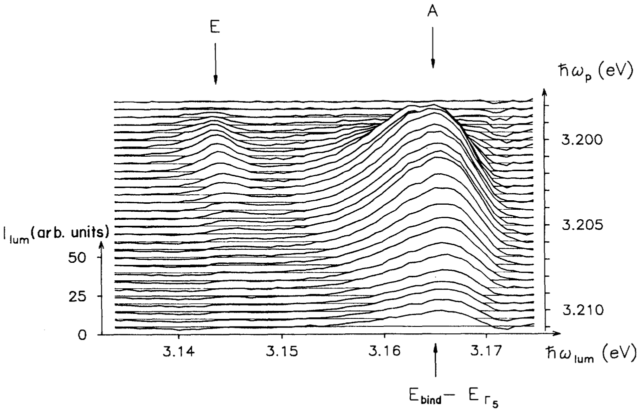

FIG. 4. Biexciton emission line A isolated from the luminescence spectra of Fig. 3 as explained in the text.

MICROCRYSTALLITE LUMINESCENCE

Figure 3 shows the luminescence spectra of the sample characterized in Fig. 2. The difference spectra correspond to different photon energies of the pump beam for a fixed intensity $I_p^M = 5$ MW/cm^2. The excitonic luminescence is not observed here because the measurements are performed in the forward configuration, the emitted light being reabsorbed during its propagation through the sample. However, in the spectral region below the excitonic resonance, several emission lines are observed.

The narrow line marked C is generally present in the luminescence spectra of bulk crystals. Therefore we can suppose that it has the same origin: the radiative decay of an exciton bound to a neutral center. We can also support the hypothesis of Certier, Wecker, and Nikitine,[27,28] that the neutral center we are concerned with is a copper vacancy, which gives a well-localized exciton. This would indeed explain why the photon energy of the corresponding emission lines does not vary with the mean radius of the microcrystallites as it would for extended impurity states. The line marked E is also observed in bulk material and is in the same way attributed to another impurity.

The line marked B can be tentatively attributed to a phonon replica of the exciton line. This luminescence band covers a spectral range between 25 and 35 meV below the excitonic resonance, which corresponds approximmately to the energy (26 meV) of LO phonons in bulk CuCl. We must notice that the phonon energy can be modified in microcrystallites and can vary with their radius. We can notice that no corresponding absorption line is observed at low temperature, when the phonon population is very low. In addition, one can see that the spectral position of the maximum of the B band depends, as the free-exciton line, on the mean radius of the microcrystallites. The line L is due to the Rayleigh-scattered light of the laser-beam excitation.

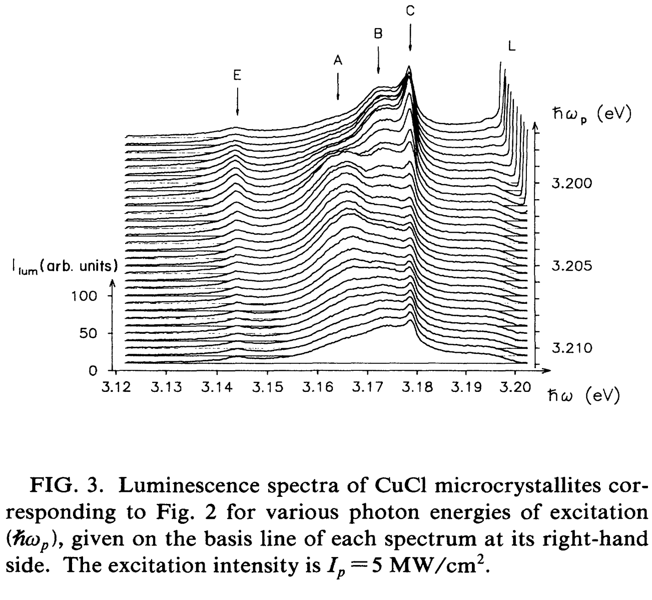

FIG. 3. Luminescence spectra of CuCl microcrystallites corresponding to Fig. 2 for various photon energies of excitation ($\hbar\omega_p$), given on the basis line of each spectrum at its right-hand side. The excitation intensity is $I_p = 5$ MW/cm^2.

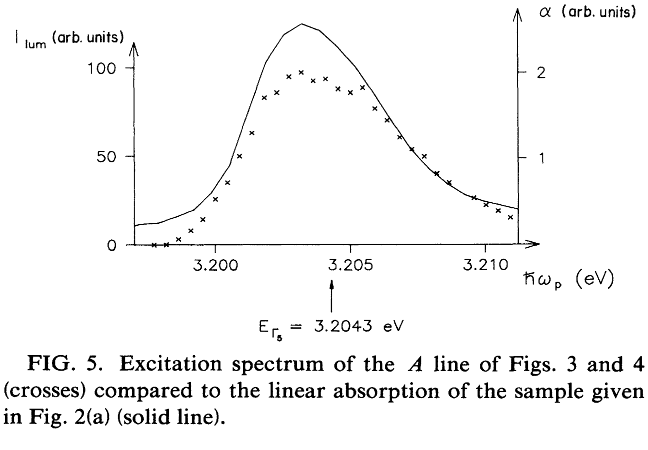

FIG. 5. Excitation spectrum of the A line of Figs. 3 and 4 (crosses) compared to the linear absorption of the sample given in Fig. 2(a) (solid line).

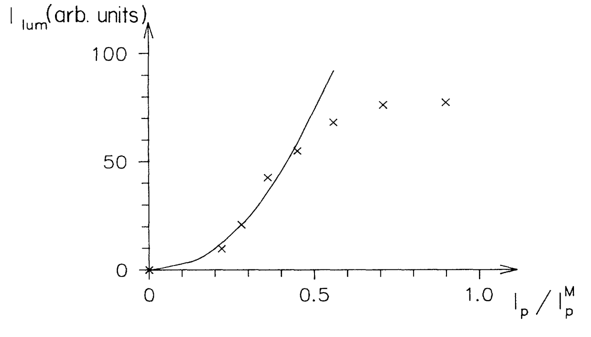

FIG. 6. Intensity of the A line of Figs. 3 and 4 for $\hbar\omega_p = 3.204$ eV as a function of the excitation intensity ($I_p^M = 5$ MW/cm^2).

Finally, the emission band A can be attributed to the biexciton-exciton decay, as we will see. Let us first separate the A band from the other emission bands by subtracting from the total luminescence spectrum the last spectrum of Fig. 3 in which the A band does not appear. The spectrum obtained, after being normalized on the high-energy part of the B line, is finally plotted in Fig. 4. The emission band obtained is not structured at all. It has a maximum which slightly shifts when the pump-beam excitation is tuned through the exciton resonance. The pump-beam excitation spectrum is plotted in Fig. 5. Except for a saturation effect, it is very similar to the excitonic absorption spectrum given in the same figure. We can therefore conclude from this observation that biexcitons are very likely created from the exciton population in these experiments. The variation of the A-line intensity as a function of the laser intensity is plotted in Fig. 6. We observe a nonlinear increase before a saturation at high intensities of excitation. This behavior is consistent with a generation process of biexcitons by the coupling of two excitons. The spectral position of the maximum of the B band plotted in Fig. 4 is at about 3.165 eV, its high-energy side being at 3.17 eV, as for the biexciton band in bulk CuCl.

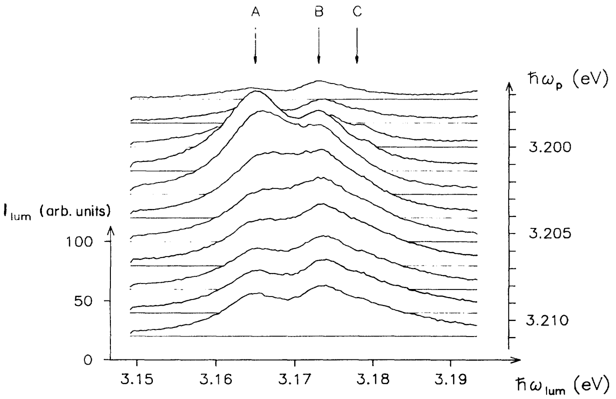

FIG. 7. As Fig. 3 but for microcrystallites of mean radius of 55 Å.

We have also performed similar experiments with samples containing smaller microcrystallites (55-, 45-, and 35-Å mean radius). As shown in Fig. 7 for crystallites with a mean radius of 55 Å, the C line decreases in intensity as the quantum dot size, but does not shift in energy as stated above. The A line is always present and does not shift either with the size of the microcrystallites. The excitonic resonance, on the contrary, shifts by 20 meV for samples containing the smallest microcrystallite.

DISCUSSION OF BIEXCITON LUMINESCENCE

In order to analyze in detail the experimental results obtained on the biexciton luminescence, let us first consider the contribution of electron-hole and hole-hole exchange interactions to the energy of excitons and biexcitons, respectively, in large microcrystallites, when the quantization of the kinetic energy of the quasiparticles does not show up.

In bulk material, following Ref. 1, the degeneracy of the different exciton states is lifted by electron-hole exchange interaction. We obtain the following energies at $k=0$ for the longitudinal and transverse excitons:

$$E_T = E_{\Gamma_2} + \Delta_{ST} ,$$

$$E_L = E_T + \Delta_{LT} ,$$

where Δ_{ST} is the singlet-triplet splitting due to the analytic exchange interaction, and Δ_{LT} the longitudinal-transverse splitting due to the nonanalytic exchange interactions. This latter interaction gives rise to the typical polariton dispersion where the coupling of the Γ_5 transverse exciton to the electromagnetic radiation field appears. The oscillator strength, per unit volume of the exciton, is proportional to Δ_{LT}.

In microcrystallites, the translational invariance is broken. Since the size of microcrystallites is small compared to the wavelength of the light field, this field can be considered as homogeneous inside the microcrystallites. No propagation and no polariton effects occur. In addition, the dilution of CuCl is so important (a density $<10^{-4}$ of the bulk CuCl density) that the oscillator strength per unit volume gives rise to an energy gap at the exciton resonance which is so small (5.10^{-7} eV) that it cannot be resolved here. The energy of dipole-active Γ_5 excitons in microcrystallites is given by[1]

$$E_{\Gamma_5} = E_{\Gamma_2} + \Delta_{ST} + \tfrac{1}{3}\Delta_{LT} .$$

Using the well-known values of the parameters of the bulk CuCl,[1] we obtain $E_{\Gamma_5} = 3.2043$ eV for CuCl microcrystallites at liquid helium temperature. As it can be seen in Fig. 2(a), this value corresponds nicely to the observed maximum of the exciton absorption line.

If we apply the same argumentation to the biexciton ground state, we find its energy E_{bind} in the bulk material[1] to be

$$E_{\text{bind}}=2E_{\Gamma_2}-E^{d}_{\text{bind}}+\tfrac{3}{2}(\Delta_{\text{ST}}+\tfrac{1}{3}\Delta_{\text{LT}})\ ,$$

where E^{d}_{bind} is the biexciton binding energy, as calculated when all exchange interactions are neglected. Its value is $E^{d}_{\text{bind}}=34.5$ meV. This is the same as in bulk material. As shown in the introduction, the absorption lines of excitons and of biexcitons can be both inhomogeneously broadened, but the center of the lines should be found at the values given above.

If we assume that biexcitons recombine radiatively from their ground state, creating excitons of Γ_5 symmetry, the luminescence line shape should be the inverse of the excitonic absorption line shape. In Figs. 8(a) and 8(b), we compare this line-shape (dotted curve) to the line shape of the observed biexciton luminescence (solid curve) measured when we excite our samples with a laser intensity of 5 MW/cm^2 at photon energies of $\hbar\omega_p=3.210$ eV and $\hbar\omega_p=3.2055$ eV.

As can be seen in Figs. 8(a) and 8(b), at higher photon energies ($E \gtrsim 3.17$ eV), we do not detect any luminescence, independently of the photon energies of the pump excitation. This behavior remains valid even if we vary the excitation intensity. Small differences can be observed between the high-energy sides of the observed luminescence bands and the calculated ones. These discrepancies can be due to the contribution of biexcitons to the inhomogeneous broadening of the luminescence band which has not been taken into account in the theoretical model. On the red side of the luminescence bands, on the contrary, important differences show up which depend on the photon energy and on the intensity of the laser excitation. They are not explained by our linear model, as can be seen when we compare the observed luminescence bands to the calculated ones.

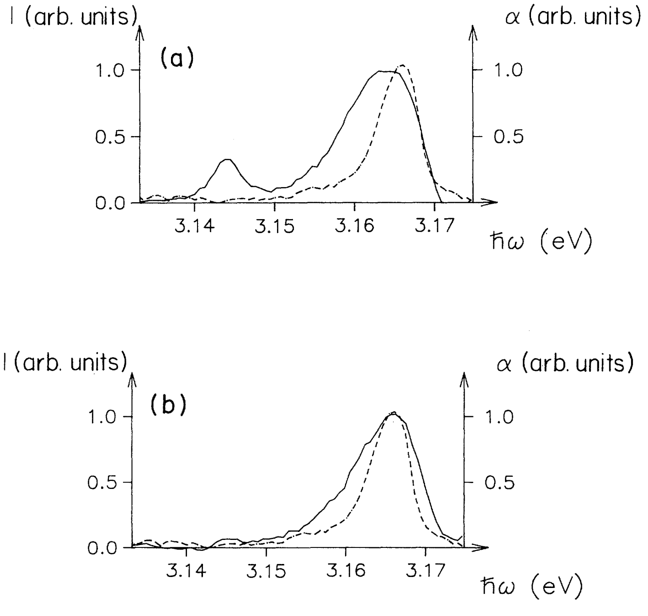

FIG. 8. Spectra from Fig. 4 for (a) $\hbar\omega_p=3.210$ eV and (b) 3.2055 eV (solid line) compared to the line shape deduced from linear absorption (dotted line) as explained in the text.

These results may, however, be explained if the exciton nonlinearity is taken into account as sketched in Fig. 9. Biexcitons are created from the coupling of excitons. They relax to their ground state. Then they recombine, emitting photons and creating excitons of Γ_5 symmetry. If we assume that the density of states of Γ_5 excitons is proportional to the linear absorption of excitons (the fine curve in Fig. 5), we can expect an emission line shape as drawn (the dotted curve) in Figs. 8(a) and 8(b). We know, however, from Fig. 2 that the shape of the absorption line changes with the pumping intensity, i.e., it shows a blue shift (solid line in Fig. 9). This effect should modify the luminescence line shape at small photon energies, during the biexciton recombination (Fig. 9). However, the biexciton luminescence, given in Figs. 8 and 9, is time integrated and corresponds to the integration of the recombination of biexcitons which changes in time. This explains its larger spectral width on its red side when compared to the calculated luminescence line and also the changes observed when the intensity and photon energy of the excitation are varied.

Since the rising part of the biexciton luminescence on the blue side of the spectrum is almost independent of the excitation conditions and does not show any appreciable broadening, we conclude that the initial biexciton distribution is also independent of the excitation conditions. The situation is completely different in bulk material, where the distribution of the initial biexcitons gives rise to the broad M_{L} and M_{T} lines which are very dependent on the excitation conditions.

Another peculiar observation to discuss is the fact that the spectral position of the biexciton emission line is independent of the mean radius of the microcrystallites

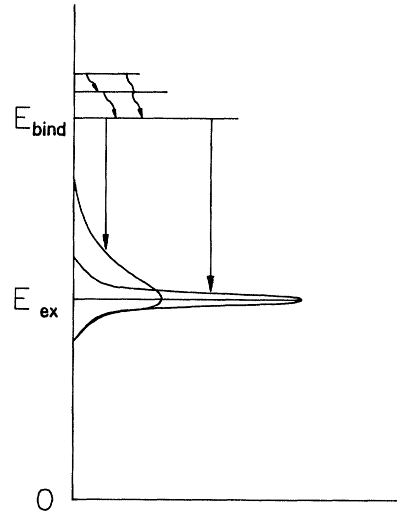

FIG. 9. Schematic density of states of excitons and biexcitons giving rise to the biexciton luminescence.

while the exciton line in the same excitation conditions strongly shifts to higher energies with a decreasing radius. As discussed by Efros and Efros,[12] the existence of the excitonic state in a microcrystallite depends on the ratio between the microcrystal radius and the exciton Bohr radius. When this ratio is smaller than 1, the Coulomb interaction between charged carriers is negligible and one observes only transitions between quantized valence and conduction-band levels. This is not the case for copper chloride because in this material the Bohr radius of the exciton is so small (7 Å) that the quantum dots are always bigger than the exciton radius. If we apply the same model to the biexciton and quantize its center-of-mass motion, we find that the biexciton-level shift to the blue is half that of the exciton level, because the biexciton total mass is nearly twice the exciton mass. The *A* line, which corresponds to the transition from the biexciton level to the exciton one, should then shift to the red, contrary to our observations. Moreover, if we follow the theory of Efros and Efros, biexcitons should in fact disappear as bound states when the microcrystallite radius is smaller than the biexciton Bohr radius, because the quantized kinetic energy would become larger than the binding energy. The situation is here also different in our experiments, where the biexciton emission is still observed in very small microcrystallites of mean radius of 20 Å.

Recent theoretical predictions for the lowest two-pair state show, however, that biexcitons are stable in this limit. Indeed, calculations by Banyai *et al.*[14] in the asymptotic limit where the quantum dot radius tends to zero and by Hu *et al.*[16,29] on a larger size range demonstrate that the biexciton binding energy increases when the crystal radius decreases. Our measurements, which show that the *A* line stays at a fixed spectral position, indicate that the increase of the energy due to the confinement is compensated for by the increase of the binding energy in such a way that the separation between biexciton and exciton levels remains almost constant when the crystal radius changes.

CONCLUSION

We have measured the luminescence spectra of CuCl microcrystals near the excitonic resonance in high excitation conditions. The *C* line, due to an exciton bound to a neutral impurity (copper vacancy), is detected at the same spectral position as in bulk crystals. We have also observed a luminescence band due to transitions between biexciton and exciton states. The absence of a shift of this band, when the quantum dot size diminishes, confirms that the biexciton binding energy increases when the microcrystal radius decreases. The absence of strong modifications on its high-energy tail when we increase the excitation intensity or its photon energy indicates that biexcitons recombine from their ground state to which they first thermalize.

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