Line-shape and lifetime studies of exciton luminescence from confined CuCl thin films

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Photoluminescence studies have been performed on structures, grown by molecular-beam epitaxy, with thin films of CuCl (30–1200 Å) confined between layers of CaF_2. Excitons were formed by irradiation of these systems with uv frequencies above the CuCl band gap, and the spectral and temporal dependences of the recombination radiation were compared with those of a bulk CuCl single crystal. We employ a kinetic model to explain why the photoluminescence line shapes of the free excitons in the thin films were characteristic of a much hotter exciton temperature and the lifetimes were much shorter (< 40 ps) than those of the bulk CuCl crystal (850 ps).

I. INTRODUCTION

The study of excitons has entered a new phase with the creation of dimensionally constrained systems. In designing an experiment for which the size of the sample influences the properties of the system, the choice of the appropriate length scale is important. For excitons, there are several relevant lengths to consider, such as the Bohr radius, the wavelength, and the mean free path between inelastic collisions. Each of these length scales influences a different property of excitons, and different phenomena will be affected as the space sampled by excitons is restricted to smaller regions. For instance, the binding energy should be increased by confinement to spaces of the order of an exciton Bohr radius, and the dispersion relation should respond to distance scales on the order of the wavelength (quantum confinement). For confinement to length scales less than the inelastic mean free path, the dynamics of exciton interactions with the surroundings should be altered. This is one criterion that may be used to determine when the dimensionality of the excitons has been restricted.

The excitons of CuCl have been studied extensively over the past three decades, and their behavior in bulk material is well understood.[1] Recently, studies to observe the behavior of excitons in small CuCl particles ("zero-dimensional" quantum dots of diameter 10–50 Å) dispersed in an inert matrix have been reported.[2-5] This length scale is well below the wavelength (approximately 150 Å), and approaches that of the Bohr radius (approximately 7 Å) for CuCl free excitons (FE). In these studies, large blue shifts of the exciton photoluminescence have been observed and attributed to quantum confinement. There were other major spectral differences in the shapes and relative intensities of the peaks, but these have not yet been investigated in detail.

The first experimental examination of a nominally two-dimensional CuCl system was the reflectance and transmittance study by Mita and Nagasawa[6] of a 1500-Å unsupported platelet. These results have been analyzed by several workers, primarily with respect to determining which of the various forms of additional boundary conditions are valid for the propagation of polaritons in CuCl.[6-8] There were no obvious effects of exciton confinement in these studies.

In a different type of study, a thin-film structure of the type $CaF_2/CuCl/CaF_2$ was grown by molecular-beam epitaxy on Si(111), and the exciton photoluminescence was examined for different sample excitation conditions[9] The width of the FE peak of the 150-Å CuCl film was found to be much broader than that for a bulk single crystal. The thickness of the film was at the maximum at which one might expect to observe quantum-confinement effects, and thus the large spectral differences were attributed to a change in the dynamical interactions of the excitons with their surroundings.[9] In the present investigation, the lifetimes as well as the spectral shapes of the FE luminescence of CuCl have been measured in the original 150-Å film sample, as well as in three new films with thicknesses chosen to examine the effects of different length scales and excitation densities on the FE dynamics.

II. EXPERIMENTAL PROCEDURE

The films were grown in the UHV chamber and by the procedure described previously.[9] These layered structures were all grown on Al_2O_3 ($1\bar{1}02$) substrates to allow both transmission and photoluminescence studies of the films. The CuCl film thicknesses of the new samples were 30, 500, and 1200 Å, and the CaF_2 confining layers were all 150 Å thick. During growth, the material deposition rates were monitored with a quartz crystal oscillator and, after growth, the total film thickness was measured with a profilometer.

For the optical experiments, the samples were cooled

to 1.8 K by immersion into liquid helium in a specially constructed dewar from which vapor was continually pumped. The absorption measurements were performed with a commercial tungsten lamp, a 50-cm monochromator, a photomultiplier, and a lock-in amplifier to extract the signal from the chopped source. The photoluminescence was excited by UV light focused onto the samples from one of three sources: a He-Cd laser (325 nm), a frequency-tripled Nd:YAG laser (where YAG is yttrium aluminum garnet) (355 nm), or a frequency-doubled dye laser (375 nm) pumped by a mode-locked picosecond Kr-ion laser. For the first two sources, the photoluminescence was focused onto the entrance slit of a 50-cm monochromator and spectrally dispersed onto an optical multichannel analyzer (OMA) to record the spectra. For the last source, the photoluminescence was focused into a monochromator followed by a Hamamatsu Synchroscan Streak Camera (SSC), which also dispersed the signal temporally. The time resolution of the laser plus the SSC was approximately 40 ps. The data from the OMA and the SSC were transferred to a computer for storage and analysis.

III. RESULTS

Exciton-absorption spectra of the films grown on sapphire substrates are shown in Fig. 1. The peaks in the spectrum from the 30-Å film are clearly blue shifted with respect to the thicker films, in agreement with the observations of Ref. 2–5.

Photoluminescence spectra of a low density of excitons from two of the thin films and from a bulk CuCl crystal, shown in Fig. 2, were excited with the He-Cd laser,
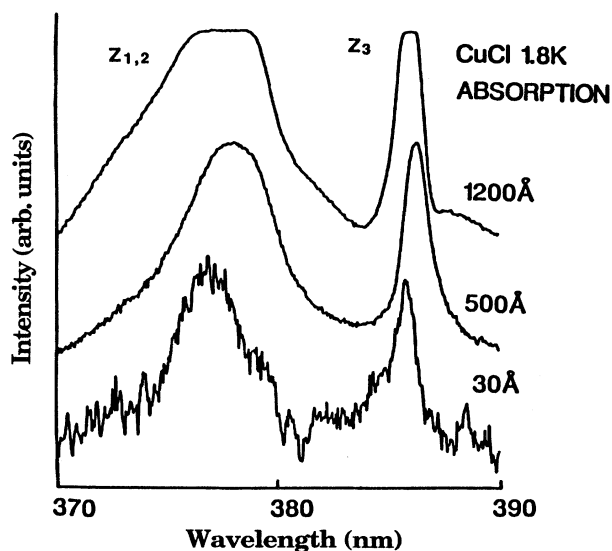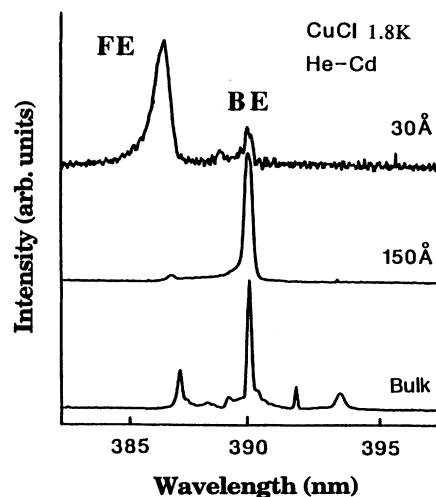

FIG. 2. Photoluminescence spectra excited by a low-intensity source, the He-Cd laser, for a bulk CuCl crystal and thin films of various thicknesses. As the film thickness decreases, the free-exciton photoluminescence peak becomes broader, indicating a higher effective temperature for the excitons during decay. The intensity of the free exciton (FE) relative to the bound exciton (BE) increases dramatically for the thinnest films examined.

which has a low average power. These spectra reveal significant differences in the relative intensities of the FE and bound exciton (BE) peaks as a function of the thickness of the CuCl. Also, the measured intensity of the emission from the BE of the 150-Å-thick film was only a factor of 3 lower than that for the single crystal, which was 1.5 μm thick, for identical excitation conditions. The spectra of the thin films reveal only two peaks, which are assigned to the CuCl FE and BE for the short- and long-wavelength features, respectively. The spectrum of the bulk sample reveals the same two peaks as well as several other peaks and shoulders. The peak at the longest wavelength may be the result of FE decay accompanied by the loss of two quanta to optical phonons (2LO), which have an energy of 25.7 meV for CuCl.[10] The single-phonon-loss sideband would be at nearly the same wavelength as the BE, and may cause the prominent shoulder on the long-wavelength side of the BE peak. The remaining features have been assigned to impurity states resulting from atmospheric exposure of the CuCl.[11]

Photoluminescence spectra from a much higher density of excitons in the samples were excited with the tripled Nd:YAG laser, which delivered a very high power in short (approximately 10 ns) pulses. Representative spectra from the single crystal and the 150-Å and 30-Å films are shown in Fig. 3. These spectra display striking differences from those in Fig. 2. The intensity ratio of the free to bound excitons has become much larger for the films than for the bulk sample. A photoluminescence peak arising from the decay of the CuCl excitonic molecule (EM), also called a biexciton, is observed for all three

FIG. 1. Absorption spectra for CaF_2/CuCl/CaF_2 structures grown on $Al_2O_3(1\bar{1}02)$ for CuCl thicknesses of 30, 500, and 1200 Å. The absorption coefficient of CuCl is so large at the exciton frequencies that the peaks are saturated for the 1200-Å film. The 30-Å film displays a definite blue shift of the absorption peaks with respect to the thicker films.
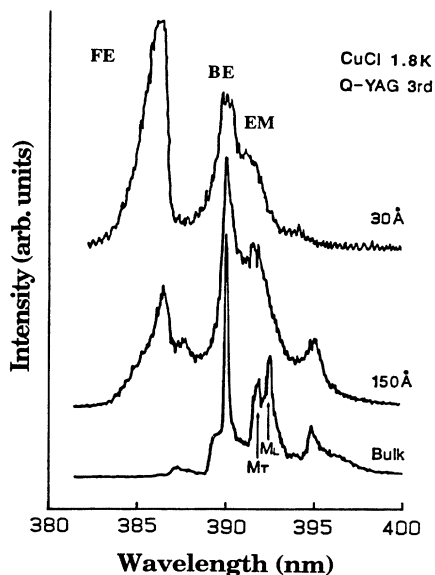
FIG. 3. Comparison of the photoluminescence from the 30 and 150-Å films and the bulk CuCl samples for a high excitation density (third harmonic of a pulsed YAG laser). The free-exciton peak in the thin film is much more intense and much broader than for the bulk crystal. Photoluminescence from the decay of bound excitons and excitonic molecules (EM) can also be clearly observed from the spectra.

samples, with the EM peaks from the films blue shifted substantially compared with the EM of the bulk crystal. The assignment of these peaks to an EM decay was confirmed by the fact that the peak intensities for all three samples were proportional to the square of the excitation density in power-dependent studies.[12] An unassigned peak, which is not the 2LO phonon loss, appears at long wavelength in all the spectra of Fig. 3. For the spectrum of the bulk sample at high excitation density, this peak overwhelms the 2LO peak.

All the spectral features of the films are significantly broader than the corresponding peaks of the single crystal. In particular, the FE peaks of the films exhibit an exponential intensity decay toward shorter wavelength, whereas the EM peaks are broadened to longer wavelength. The spectral dependence on the excitation density is illustrated in Fig. 4 (which displays spectra from the 150-Å film accumulated with four different values of the excitation power). This figure shows the extremely strong dependence of the peak intensity and width of the FE compared to the BE with respect to the relative excitation density. The appearance and excitation density
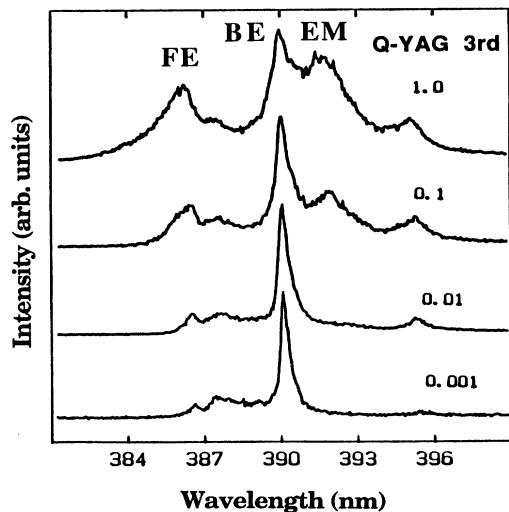

FIG. 4. Photoluminescence spectra from the 150-Å CuCl film for four different light intensities incident on the sample (i.e., the laser beam was attenuated by zero to three 10% neutral-density filters). The evolution of the free- and bound-exciton peaks can be followed as a function of excitation density. The effective temperature of the FE increases with increasing excitation density.
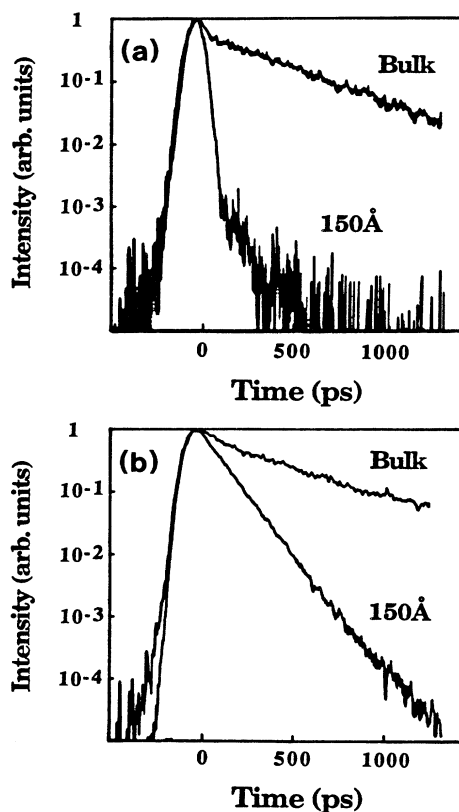

FIG. 5. Comparison of the time dependence of the photoluminescence from the (a) free and (b) bound excitons of the bulk CuCl sample and the 150-Å-thick film. The free-exciton lifetime obtained for the thin film was limited by the combined time resolution of the frequency-doubled dye laser and the synchroscan streak camera.

TABLE I. CuCl photoluminescence lifetimes (τ). Time required for the peak photoluminescence to decrease by a factor of e^{-1} over the region where the log of the intensity decreases linearly with time.

	Free exciton (ps)	Bound exciton (ps)	Wall collisions [a] (ps)
1.5-μm crystal	850	1090	140
1200-Å film	40	130	12
500-Å film	<40	260	4
150-Å film	<40	90	1
30-Å film	<40		0.3

[a] $\tau_{\text{wall}} \simeq nl/(v \ln 2)$.

dependence of the CuCl EM are also apparent for the 150-Å film.

The time dependence of the FE and BE photoluminescence decay from both the single crystal and the 150-Å film are shown in Fig. 5. The photoluminescence from the FE in all the thin-film samples was essentially identical to that shown for the 150-Å film, since they were all limited by the approximately 40-ps resolution of the doubled dye laser plus the SSC. The e^{-1} lifetimes determined from the plots in Fig. 5 and for the other samples investigated are presented in Table I. The lifetimes of the excitons in the thin film are considerably shorter than those of the corresponding excitons in the single crystal.

IV. DISCUSSION

There is a close lattice match for the cubic crystal structures of Si, CaF$_2$, and CuCl (0.543, 0.546, and 0.542 nm, respectively), and Al$_2$O$_3$($1\bar{1}02$) is often used as a substrate to grow (001)-oriented Si.[13] Thus one would expect that all these materials are structurally compatible with one another. The results of x-ray diffraction and transmission electron microscope studies of the CuCl films, which are discussed in detail elsewhere,[14] confirm that both the CaF$_2$ and CuCl form highly textured films on both Si and Al$_2$O$_3$. The CaF$_2$ essentially serves three main functions: (i) as a structural template on which to grow CuCl, (ii) as an optically transparent confinement layer for holes and electrons, and (iii) as a chemically protective barrier that prevents interaction of the CuCl with either the substrate or the ambient air. This last consideration is very important for thin film studies, since CuCl is extremely hygroscopic, and the entire sample could easily become contaminated in a humid environment.

The results presented in Sec. III will be discussed primarily in terms of a strictly excitonic model, although at some point a more complete analysis must include polaritonic effects. All the frequencies used for creating excitons in this study were above the CuCl band gap in energy. Thus the absorbed light created electrons and holes, which then began to thermalize with the phonons of the material. Some of the electrons and holes combined on a

subpicosecond time scale to form a hot distribution of excitons,[15] which also cooled via interactions with acoustic phonons. Thus the effective temperature of the excitons observed via the Boltzmann distribution evident in their photoluminescence signal will depend on the lifetime of the excitons, the shorter the lifetime, the hotter the exciton distribution.

The exciton lifetime depends on several different factors, such as the polaritonic nature, interactions with defects and impurities in the lattice, phonons, other excitons, and the boundaries of the sample. Some of these interactions will lead to nonradiative decay of the excitons, and some to radiative decay. For a perfect bulk system, the interaction of a photon and an exciton leads to a polariton, which does not decay radiatively.[16] Thus hot polaritons relax energetically to the bottleneck region of the polariton dispersion curve before finally decaying. This is observed, in the spectra from the CuCl single crystal in Figs. 2 and 3, as an abrupt decrease in the photoluminescence intensity from the free exciton to the short-wavelength side of the peak. However, for systems with broken symmetry, such as the thin films investigated here, radiative decay is allowed by the breakdown of k selection rules, which may produce modes that are super-radiant.[17] All the photoluminescence peaks for the FE from the thin-film samples displayed a decrease in intensity toward shorter wavelengths that provided excellent fits to a Boltzmann distribution. The temperature of each distribution was characteristic of radiative decay from populations of excitons that were much hotter than the crystal temperature. The fact that excitons that were well up the FE dispersion curve did decay is one of the justifications for treating the present results from the thin films in terms of an excitonic model.

As mentioned in the Introduction, the length scale that affects the dynamics of excitons is the inelastic mean free path. Of course, there are as many different mean free paths as there are scattering channels, and in general these are material dependent. A rough estimate of the mean free path for excitonic decay in bulk material can be obtained by multiplying the velocity of an exciton by its lifetime. Segawa, Aoyagi, and Namba[18] have made careful measurements of the lifetimes of cold CuCl excitons in a single crystal as a function of energy in the

bottleneck region of the dispersion curve, i.e., in the most excitonic portion. They observed that these lifetimes could be superimposed on the velocity curve obtained from the dispersion relation, which means that multiplying the observed lifetimes by the exciton velocity yielded a constant: essentially 4.7 μm for their samples, which were approximately 30 μm thick. Thus, at least for materials in the study of Ref. 18, the excitons traveled an average of 4.7 μm and had little opportunity to interact with the crystal surfaces before undergoing radiative decay. Since all the samples examined for the present study were significantly thinner than this estimate of the bulk radiative scattering length, boundary interactions may be important for all the thin films and even the single crystal.

Another viewpoint is also of interest in this connection. The propagation of free excitons is diffusional parallel to the quantum well walls, but should be essentially ballistic in the perpendicular direction. If excitons are created uniformly throughout the thickness l of a film and initially have an isotropic velocity distribution with a magnitude v, then the time required for half of all the excitons to collide with one of the two walls of the film is

$$t_{1/2} = \frac{l}{v} \ . \tag{1}$$

If an average of n bounces off a wall are required to cause an exciton to decay, then the e^{-1} lifetime for wall interactions can be estimated from

$$\tau_{\text{wall}} \simeq \frac{nl}{v \ln 2} \ . \tag{2}$$

Incorporating this quantity into the standard lifetime equations gives[19]

$$\frac{1}{\tau} = \frac{1}{\tau_{\text{nr}}} + \frac{1}{\tau_{\text{r}}} + \frac{1}{\tau_{\text{wall}}} \ , \tag{3}$$

where τ_{nr} and τ_{r} are the intrinsic CuCl nonradiative and radiative recombination lifetimes, respectively, of the free excitons and τ_{wall} is a radiative or nonradiative contribution that exists because of the size of the sample. If the slowest value of the exciton velocity in the bottleneck region of the dispersion curve (1.5×10^6 cm/s) is used for v and $n = 1$, then the longest values of τ_{wall} for the 30, 150, 500, and 1200 Å films are 0.3, 1, 4, and 12 ps, respectively, all of which are much shorter than the resolution of the time-dependent experiments in this investigation. Thus, if wall collisions are an important process in determining the lifetimes of excitons in confined films, time resolution better than 1 ps will be necessary to observe these effects for films on the order of 100 Å thick. For the 1.5-μm-thick single crystal, the above analysis yields a τ_{wall} of only 140 ps. The fact that the observed lifetime is much longer than this may be the result of diffusional transport of the excitons in the thicker material and/or values of n roughly equal to 6 (see Table I), i.e., the excitons may survive on average six wall collisions before decaying.

If the onset of a strictly nonradiative process was responsible for the observed lifetime of the excitons in the quantum-well samples, the photoluminescence yields would have been quenched to the point that they would not have been observable. Using the experimentally determined lifetime of the single crystal as an estimate of the radiative decay lifetime, the decrease in lifetime observed for the thin films would mean that only 3% of the thin-film excitons would decay via a radiative process. Since the films also have a much smaller excitation volume than the single crystal, the total photoluminescence yield for identical excitation conditions would be about three orders of magnitude smaller for the films than for the single crystal. The observed ratio of yields is of the order of a factor of 10 or less, so this observation is taken as evidence that at least part of the decrease in lifetime is caused by new radiative channels opened by the fact that the system is a thin film. Therefore there must be additional perturbations that increased the radiative recombination efficiency and shortened the exciton lifetime. There appear to be two different mechanisms involved, of which the first has been previously observed in semiconductor quantum wells.[20,21] This is related to the volume of space available to the excitons, as seen by comparing the free-exciton photoluminescence from the 30- and 150-Å-thick samples in Fig. 2. The second mechanism is related to increasing the density of the excitons, as revealed in Fig. 6. Thus the FE radiative lifetime is significantly affected by collisions of the confined excitons both with the boundaries of the films and with each other. In this context, it is important to realize that even at the highest excitation densities, the excitons did not form a Bose-Einstein condensate.[22] For the condensate, the luminescence appears at a photon energy intermediate between those of the FE and EM, and is only excited by resonant two-photon absorption.[14]
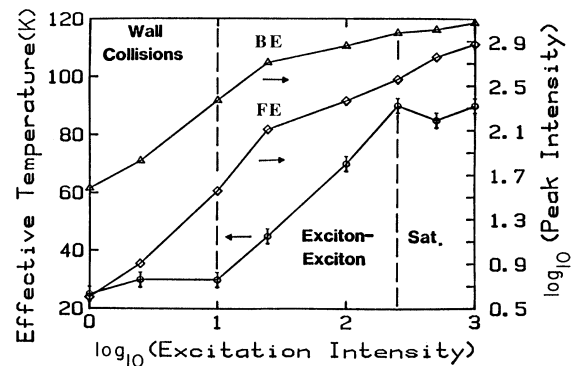

FIG. 6. Plot of the effective temperature (left vertical axis) of the free excitons (circles), determined by fitting the high-energy side of the photoluminescence peak to a Boltzmann distribution, as a function of the excitation density, which was varied by using different combinations of neutral-density filters. The right vertical axis represents the peak intensities of photoluminescence for the free (diamonds) and bound (triangles) excitons as function of excitation density, and shows the approach to saturation of the emission at high densities.

Since the time resolution of the pulsed laser/SSC system was not sufficient to measure the lifetimes of the thin-film samples, the line shapes of the FE photoluminescence may be examined to see if they yield dynamical information. The high-energy side of the free exciton peaks were fit to a Boltzmann distribution to determine an *effective temperature of the excitons* during the radiative decay process.[23] Higher temperatures will indicate shorter lifetimes of the excitons, although no calibration to determine a value for the lifetime is available.

For the 150-Å film, the effective temperature determined for the FE photoluminescence has been plotted in Fig. 6 as a function of the relative intensity of the laser beam. The density of the excitons created in the irradiated material will be roughly proportional to the light intensity. At low exciton densities, the temperature, and thus the lifetimes, of the excitons are independent of the density. As the exciton density increases, the exciton temperature increases with an approximate logarithmic dependence of the excitation intensity, which indicates that the lifetime of the excitons in the 150-Å film decreases with density. The rapid decay of the FE in the thin films may be the reason why the intensity of the EM photoluminescence does not become as large on a relative basis as that observed for the single crystal.[24] The FE decay so quickly, the EM population does not have a chance to build up. The binding energy of a CuCl EM is about 32 meV,[25] which is still large compared to the highest exciton temperature observed, 120 K, so temperature alone cannot explain the suppression of the EM.

The dynamics of the formation and decay of the excitons in the thin films may be modeled by simple kinetic rate equations, but the difficulty is making certain that all the relevant rate constants and radiative decay channels are included.[26] A schematic diagram of the processes that appear to be important for a kinetic model is given in Fig. 7. The model incorporates the basic formation
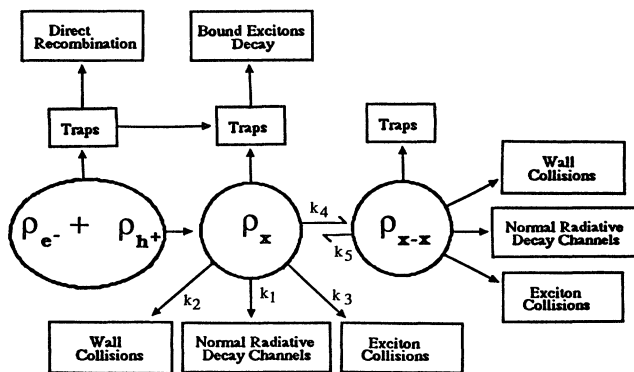

FIG. 7. Schematic diagram of the proposed kinetic model, where ρ represents the effective density of subscripted particles (e^- denotes electrons, h^+ denotes holes, x denotes free exciton, and $x-x$ denotes excitonic molecule). The various k's represent density-independent rate constants.

and decay channels of excitons in CuCl. At $t=0$, a hot gas of electrons and holes is created by the laser pulse, followed rapidly by some direct recombination and the nonreversible formation of free excitons as the system cools. Free excitons are removed from the system via several possible channels: traps, radiative decay induced by wall collisions and collisions with other excitons, formation of excitonic molecules, and other radiative and nonradiative channels. The formation of an EM is nearly a reversible process, since the EM radiatively decays into a FE and a photon. For the purposes of the following discussion, the dominant rate equations for the decay of FE density, ρ_x, may be expressed as

$$\frac{d\rho_x}{dt} = \begin{cases} -k_1\rho_x & \text{(normal radiative decay in bulk)} \quad (4) \\ -k_2\rho_x & \text{(wall collisions)} \quad (5) \\ -k_3\rho_x^2 & \text{(exciton-exciton collisions)} \quad (6) \end{cases}$$

The rate constant k_2 can be estimated from Eq. (1) to be

$$k_2 = \frac{1}{\tau_{\text{wall}}} \qquad (7)$$

where τ_{wall} was defined in Eq. (2). The overall rate expression for the FE decay is given by

$$\frac{d\rho_x}{dt} = -(k_1 + k_2 + k_3\rho_x)\rho_x \ . \qquad (8)$$

The nonradiative decay channels are neglected for the purpose of this discussion.

The dynamics of the free excitons under low density excitation are represented by the terms linear in ρ_x in Eq. (7), i.e., those involving wall collisions and normal radiative processes. A rough estimate for the value of k_1 is just the inverse of the FE lifetime for bulk CuCl (shown in Table I), or $k_1 = 1.2 \times 10^9$ s^{-1}. If the lifetimes listed in Table I represent low density limits, then k_2 for the 1200 Å film is approximately 2.5×10^{10} s^{-1}, which corresponds to a value of $n = 3.5$ for the average number of wall collisions. If this value of n is used to calculate a value of k_2 for the bulk crystal, then a value of 2.0×10^9 s^{-1} is obtained, which is larger than that actually observed. Given the crudeness of these estimates, this may mean that a primary mode for radiative decay of the excitons in the 1.5-μm single crystal is interactions with the physical boundaries of the sample. Rewriting Eq. (8) to reflect this yields

$$\frac{d\rho_x}{dt} = -(k_2 + k_3\rho_x)\rho_x \ . \qquad (9)$$

At present there are no data to estimate k_3, because the measured lifetimes are all shorter than the resolution of the laser plus streak camera system. However, Eq. (9) may be used to divide Fig. 6 into three distinct regimes of exciton formation and radiative decay: first, wall-collision-mediated decay; second, exciton-exciton interactions; and third, a region in which exciton formation is saturated. Thus, the flat region in the exciton-temperature versus excitation-density plot in the low-density excitation region can be understood as the regime

in which wall collisions dominate the decay process. The increase of the exciton temperature and the photoluminescence peak intensity in the central region of Fig. 6 is attributed to the quadratic term in Eq. (9). The remaining regime at the highest excitation density is the region in which the absorption of 355-nm light by the CuCl saturates.

V. CONCLUSIONS

The photoluminescence from excitons created by hot electrons and holes that combine after above band-gap excitation in confined CuCl thin films has been investigated. The lifetime of the free-exciton photoluminescence from films with thicknesses of 1200 Å and less was shorter than the 40-ps resolution of the instrumentation used, whereas the measured lifetime of that in a 1.5-μm-thick CuCl single crystal was 850 ps. By examining the line shape of the free-exciton photoluminescence, an effective temperature of the excitons at the time of decay could be determined. Since the temperature of the excitons should decay rapidly with time, hotter exciton distributions correspond to shorter lifetimes. The temperature was increased both by decreasing the thickness of the region available to the excitons and increasing the exciton density. Thus the decrease in exciton lifetime for the thin films is explained by a kinetic model in which wall and exciton-exciton collisions are dominant modes of radiative decay. The kinetic model also suggests that the radiative decay in the 1.5-μm single crystal of CuCl may be determined by wall interactions as well.

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