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LINESHAPE AND LIFETIME STUDIES OF EXCITON LUMINESCENCE FROM CONFINED CuCl THIN FILMS

by

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ABSTRACT

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

I. INTRODUCTION

The study of excitons is entering 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 many different characteristic 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 emphasized as the space sampled by excitons is restricted to smaller regions. For instance, the binding energy should be affected 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 order 10-50Å in diameter) dispersed in an inert matrix have been reported.[2,3] This length scale is well below the wavelength (*ca.* 150Å), and approaches that of the Bohr radius (*ca.* 7Å) for CuCl free excitons. 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 examinations of a nominally two-dimensional CuCl system was the reflectance and transmittance study by Mita and Nagasawa[4] of a 1500Å unsupported platelet. These results have been analyzed by several workers, primarily with respect to determining which of the various forms of additional boundary conditions (ABC) are valid for the propagation of polaritons in CuCl.[4-6] There were no immediately apparent 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 (MBE) on Si(111), and the exciton photoluminescence was examined for different sample excitation conditions.[7] The width of the free exciton peak of the 150Å 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.[7] In the present investigation, the lifetimes as well as the spectral shapes of the free exciton luminescence of CuCl have been measured in the original 150Å 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 free exciton dynamics.

II. EXPERIMENTAL PROCEDURE

The new films were grown in the UHV chamber and by the procedure described previously.[7] 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 30Å, 500Å and 1200Å, and the CaF_2 confining layers were all 150Å 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 1.8K 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 (355 nm), or a frequency-doubled dye laser (375 nm) pumped by a 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 *ca.* 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 30Å film are clearly blue-shifted with respect to the thicker films, in agreement with the observations of Refs.[2] and [3].

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, which has a low average power. These spectra reveal significant differences in the relative peak intensities as a function of the thickness of the CuCl. The absolute intensity of the emission from the bound exciton of the 150Å-thick film was only a factor of three lower than that for the single crystal, which was 1.5μ thick, for identical excitation conditions. The spectra of the thin films reveal only two peaks, which are assigned to the CuCl free and bound excitons for the long and short 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 highest wavelength may be the result of free exciton decay after the loss of two quanta to optical phonons[2] (the single-phonon-loss sideband would be at nearly the same wavelength as the bound exciton, and may cause the prominent shoulder on the long-wavelength side of the bound exciton peak). The remaining features have been assigned to impurity states resulting from atmospheric exposure of the crystal.[9]

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 (*ca.* 10-nanosecond) pulses. Representative spectra from the single crystal, and the 1200Å, 150Å and

30Å films are shown in Fig. 3. These spectra also display striking differences. The intensity ratio of the free-to-bound excitons has become much larger for the films than for the bulk sample. The CuCl excitonic molecule can be observed, and an unassigned peak appears at high wavelength in all the spectra. All the spectral features for the films are significantly broader than for the corresponding peaks of the single crystal and, in particular, the free exciton of the 150Å film appears to have an exponential intensity decay toward lower values of wavelength. The spectral dependence on the excitation intensity is illustrated in Fig. 4 (which displays spectra from the 150Å film accumulated with four different values of the excitation power). This figure shows the extremely strong dependence on film thickness of the peak intensity and the width of the free exciton compared with the bulk exciton. The appearance and excitation density dependence of the CuCl biexciton are also apparent.

The time dependence of the free- and bound-exciton photoluminescence from both the single crystal and the 150Å film are shown in Fig. 5. The photoluminescence from the free exciton in all the thin film samples was essentially identical to that shown for the 150Å film, since they were all limited by the *ca.* 40-ps resolution of the doubled dye laser plus the SSC. The e^{-1} lifetimes determined from the plots in Fig. 5 are presented in Table I. The lifetimes of the thin film excitons 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_2O_3 $(1\bar{1}02)$ is often used as a substrate to grow (001)-oriented Si.[10] Thus, one would expect that all these materials are structurally compatible with one another. The results of x-ray and TEM studies of the CuCl films, which will be discussed in detail elsewhere, confirm that both the CaF_2 and CuCl form highly oriented films on both Si and Al_2O_3. The CaF_2 essentially serves three main functions: (1) as a structural template on which to grown CuCl, (2) as an optically transparent confinement layer for holes and electrons, and (3) as a chemically protective barrier that prevents interaction of the CuCl with either the substrate or the ambient air. This last consideration is extremely 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 the previous section 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 bandgap 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 to form a hot distribution of excitons, which also interacted with the acoustic phonons of the lattice. Thus, the effective temperature of the excitons observed via their photoluminescence signal will depend on the lifetime of the excitons; the shorter the lifetime, the hotter the excitons.

The exciton lifetime depends on a large number of 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.[11] 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 decay of 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 and may produce modes that are superradiant.[12] All the photoluminescence peaks for the free exciton from the thin film samples display an exponential decay toward shorter wavelengths that is characteristic of radiative decay from populations of excitons that are much hotter than the crystal temperature. This 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 may be 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, *et al.*[13] 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 microns for their samples, which were approximately 30 microns thick. Thus, at least for materials in the study of Ref.[13], the excitons traveled an average of 4.7 microns and had little opportunity to interact with the crystal surfaces before undergoing radiative decay. Since the films examined for this study were all significantly thinner than this length, boundary interactions may be important for all these thin films.

Another viewpoint is also of interest in this connection. If excitons are created uniformly throughout the thickness ℓ of a film and have an isotropic velocity distribution with a magnitude $\mathbf{v}$, then the time required for half of all the excitons to collide with one of the two walls of the film is simply

$$t_{1/2} = \ell/\mathbf{v} \ . \qquad (1)$$

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 $\mathbf{v}$, then the longest values of $t_{1/2}$ for the 30Å, 150Å, 500Å, and 1200Å films are 0.2 ps, 1 ps, 3 ps, and 8 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 100Å thick. For the 1.5μ-thick single crystal, the above analysis yields a $t_{1/2}$ of only

100 ps. This indicates that the polaritons must have scattered from the surfaces of the crystal many times before decaying, and thus boundary effects do not appear to be so important for the single crystal.

Since the time resolution of the lifetime measurements was not sufficient to distinguish among the different excitation conditions for the thin film samples, the lineshapes of the free exciton photoluminescence may be examined to see if they yield dynamical information. The high-energy side of the free exciton peaks can be fit to a Boltzmann-type distribution to determine an *effective temperature of the excitons* during the radiative decay process. Higher temperatures will indicate shorter lifetimes of the excitons, although no calibration to determine a value for the lifetime is available.

For the 150Å film, the effective temperature determined for the free exciton photoluminescence has been plotted in Fig. 6 as a function of the intensity of the excitation radiation. 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 probably the lifetimes, of the excitons are independent of the density. As the exciton density increases, however, so does the exciton temperature, with an approximate logarithmic dependence on the excitation intensity. This indicates that the lifetime of the excitons in the 150Å film decreases with density. This may be the reason why, although excitonic molecules are observed via their photoluminescence signal at high exciton densities,[7] the intensity of the biexciton photoluminescence does not become as large on a relative basis as that observed for a bulk crystal; the excitons in the thin films decay too quickly to form a high concentration of excitonic molecules.

The final point to note is whether or not the decay channels of the excitons in thin films are radiative. If the observed lifetime of the single crystal sample is used as an estimate of an intrinsic radiative lifetime for CuCl and the overall decrease in lifetime observed for the thin films is attributed to nonradiative effects, then only about 3% of the thin-film excitons would decay radiatively. Considering that the photoluminescence from the thin films is comparable in intensity to the single crystal, this is very unlikely. Therefore, the drastic decrease observed in the photoluminescence lifetime of the confined excitons is primarily the result of a decrease in the radiative lifetime, and there appear to be two different mechanisms involved in shortening the exciton lifetime. The first is related to the volume of space available to the excitons, as seen by comparing the free-exciton photoluminescence from the 30Å- and 150Å-thick samples in Fig. 2, and the second to increasing the density of the excitons, as revealed in Fig. 6. This probably means that the radiative lifetime is affected by collisions of the confined excitons both with the boundaries of the films and with each other.

The exciton dynamics in the thin films may be modelled by simple kinetic rate equations, assuming that all relavent rate constants and radiative decay channels are included. A schematic diagram of the processes accounted for in the kinetic model are shown in Fig. 7. The model accounts for the basic formation and decay channels of excitons in CuCl. At t=0, there is the direct recombination of electrons and holes, followed by the non-reversible formation of free excitons. Free excitons may decay via several possible channels; wall collisions, traps, collisions with other excitons, by formation of excitonic molecules, and by other radiative and non-radiative channels. The formation of an excitonic molecule is treated as a reversible process since the bi-exciton radiatively decays into an exciton and a photon, by wall collisions, collisions with other excitonic particles, and by other processes. Rate constants $\mathbf{k}_4$ and $\mathbf{k}_5$ are neglected in this discussion since the rate constants are much smaller than $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}_3$. The rate equations for the decay of free exciton density, ρ_x, may be expressed as:

normal radiative decay in bulk $\quad d\rho_x/dt = -\mathbf{k}_1\rho_x \quad$ (2)

wall collisions $\quad d\rho_x/dt = -\mathbf{k}_2\rho_x \quad$ (3)

exciton-exciton $\quad d\rho_x/dt = -\mathbf{k}_3\rho_x^2 \quad$ (4)

Eq.(3) may be re-written using Eq.(1) to solve for $\mathbf{k}_2$ as

$$d\rho_x/dt = v/n\ell\rho_x = 1/nt^{1/2}\rho_x \tag{5}$$

in which n represents the average number of wall collisions before radiative decay of the free exciton.

The overall rate expression is given by

$$d\rho_x/dt = -(\mathbf{k}_1 + 1/nt^{1/2} + \mathbf{k}_3\rho_x)\rho_x \qquad (6)$$

and the lifetime of the free exciton by the reciprocal of Eq.(6). The first term in Eq.(6) represents the normal radiative process and the trailing terms the radiative decay due to the perturbation of the quantum well barriers. Other radiative and non-radiative 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.(6), those involving wall collisions and normal radiative processes. Assuming an average collision frequency factor of five (n=5) collisions for radiative decay, the lifetime in the bulk single crystal would be 500 ps compared to the experimentally observed 850 ps. Therefore, it is quite plausible that the lifetime of the free exciton may solely depend on the physical boundaries of the sample, even in a bulk crystal. Re-writing Eq.(7) to reflect this yields

$$d\rho_x/dt = -(1/nt^{1/2} + \mathbf{k}_3\rho_x)\rho_x \qquad (7)$$

Equation (7) may be used to rationalize Fig. 6 into three distinct regimes of radiative decay: first, wall collision mediated, second, one of exciton-exciton interaction, and third, a region of radiative saturation. Thus, the flat region in the exciton temperature-peak-intensity in the low density excitation region can be rationalized as the regime in which wall collisions dominate the decay process. The linear increase of temperature and peak intensity in the central region of Fig. 6 is attributed to the quadratic term in Eq.(7). At high exciton densities, the increase in the radiative intensity is due to the opening of an additional radiative channel. There is no experimental data to assign a value to $1/\mathbf{k}_3$, although it is intuitive that $1/\mathbf{k}_3$ must be faster than that for wall collisions. The remaining regime of highest excitation density is the region in which there is radiative saturation. Combining intensity and temperature profiles, it is clear that this region is one in which the wall collision decay channels are swamped and non-radiative processes begin to limit radiative intensity from the free exciton.

V. CONCLUSIONS

The photoluminescence from excitons created by hot electrons and holes that combine after above-bandgap excitation in confined CuCl thin films has been investigated. The lifetime of the free-exciton photoluminescence from films with thicknesses of 1200Å and less was shorter than the 40-ps resolution of the instrumentation used, whereas the measured lifetime of that in a 1.5μ-thick CuCl single crystal was 850 ps. This dramatic decrease of the lifetime has been attributed mainly to a decrease of the radiative lifetime of the excitons in the thin films. By examining the lineshape of the free-exciton photoluminescence, an effective temperature of the excitons at the time of decay could be determined. This 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 radiative lifetime is rationalized by a kinetic model in which wall and exciton-exciton collisions are dominant modes of radiative decay.

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VII. REFERENCES

1. A collection of relevant reviews can be found in *Excitons,* edited by E.J. Rashba and M.D. Sturge (North-Holland, New York: 1982).
2. (a) T. Itoh and T. Kirihara, J. Lumin. **31/32,** 120 (1984);

   (b) T. Itoh, Y. Iwabuchi and M. Kataoka, Phys.Stat.Sol. **B 145,** 567 (1988).
3. (a) A.I. Ekimov, Al.L. Efros and A.A. Onushchenko, Solid State Commun. **56,** 921 (1985);

   (b) A.I. Ekimov, A.A. Onushchenkom M.É. Raîkh and Al.L. Éfros, Sov.Phys. JETP **63,** 1054 (1986).
4. T. Mita and N. Nagasawa, Solid State Commun. **44,** 1003 (1982).
5. Y. Segawa, Y. Aoyagi, S. Komura, S. Namba, S. Inoue and M. Nakayama, Physica B&C **117/118,** 309 (1983).
6. K. Cho and M. Kawata, J.Phys.Soc.Japan **54,** 4431 (1985).
7. R.S. Williams, D.K. Shuh and Y. Segawa, J.Vac.Sci.Technol. **A6,** 1950 (1988).
8. M. Itoh, Tohoku University, private communication.
9. D.C. Reynolds, P.J. Almassy, C.W. Litton, G.L. Koos, A.B. Kunz and T.C. Collins, Phys.Rev.Lett. **44,** 204 (1980).
10. C.C. Chang, J.Vac.Sci.Technol. **A8,** 500 (1971).
11. J.J. Hopfield, Phys.Rev. **112,** 1555 (1958).
12. K.C. Liu, Y.C. Lee and Y. Shan, Phys.Rev. **B11,** 978 (1975).
13. Y. Segawa, Y. Aoyagi and S. Namba, Solid State Commun. **39,** 535 (1981).

Table I. CuCl Photoluminescence Lifetimes*

	Free Exciton	*Bound Exciton*
Bulk Crystal	850 ps	1090 ps
1200Å Film	1090 ps	130 ps
500Å Film	< 40 ps	90 ps
150Å Film	< 40 ps	260 ps
30Å Film	< 40 ps	—

*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.

FIGURE CAPTIONS

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 1200Å. The absorption coefficient of CuCl is so large at the exciton frequencies that the peaks are saturated for the 1200Å film. The 30Å film displays a definite blue-shift of the absorption peaks with respect to the thicker films.

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.

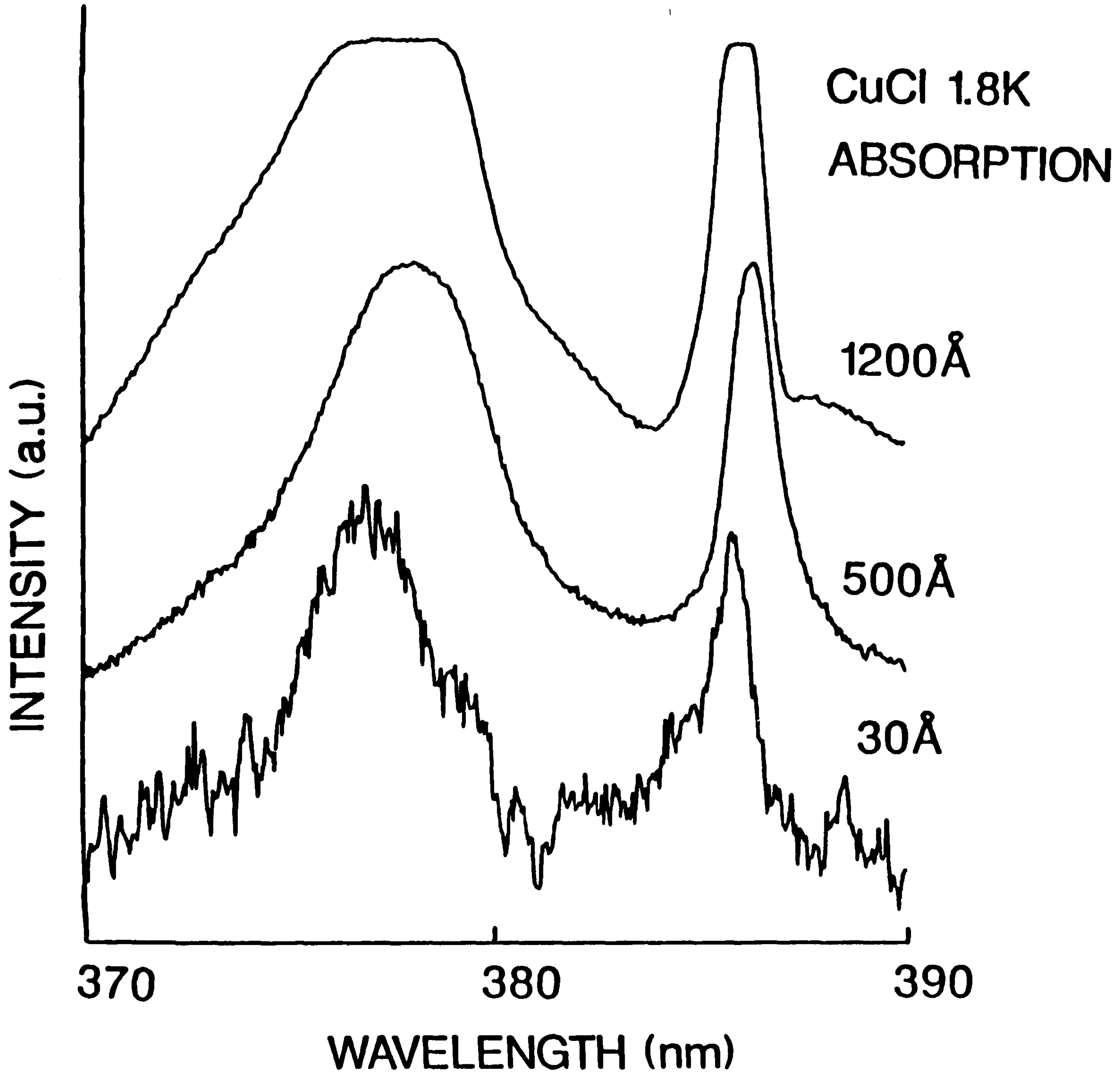
3. A comparison of the photoluminescence from the 30Å and 150Å films and the bulk CuCl samples for a high excitation density (third harmonic of a pulsed YAG laser). The free exciton peak (F.E.) in the thin film is much more intense and much broader than for the bulk crystal. Photoluminescence from the decay of bound excitons (B.E.) and excitonic molecules can also be clearly observed from the spectra.

4. Photoluminescence spectra from the 150Å CuCl film for four different light intensities incident on the sample (*i.e.*, the laser beam was attenuated by 0-3 10% neutral-density filters). The evolution of the free- and bound-exciton peaks can be followed as a function of excitation density.

5. A comparison of the time dependence of the photoluminescence from the free (a) and bound (b) excitons of the bulk CuCl sample and the 150Å-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.

6. A plot of the effective temperature of the free excitons, 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 is shown by the left y-axis. The right y-azis represents the peak intensities of photoluminescence for the free and bound excitons as a function of excitation density.

7. A schematic diagram of the proposed kinetic model, where ρ represents the effective density of subscribed particles (**e-** = electrons, **h+** = holes, **x** = free exciton, and **x-x** = excitonic molecule). The various **k**'s represent density independent rate constants.


CuCl 1.8K
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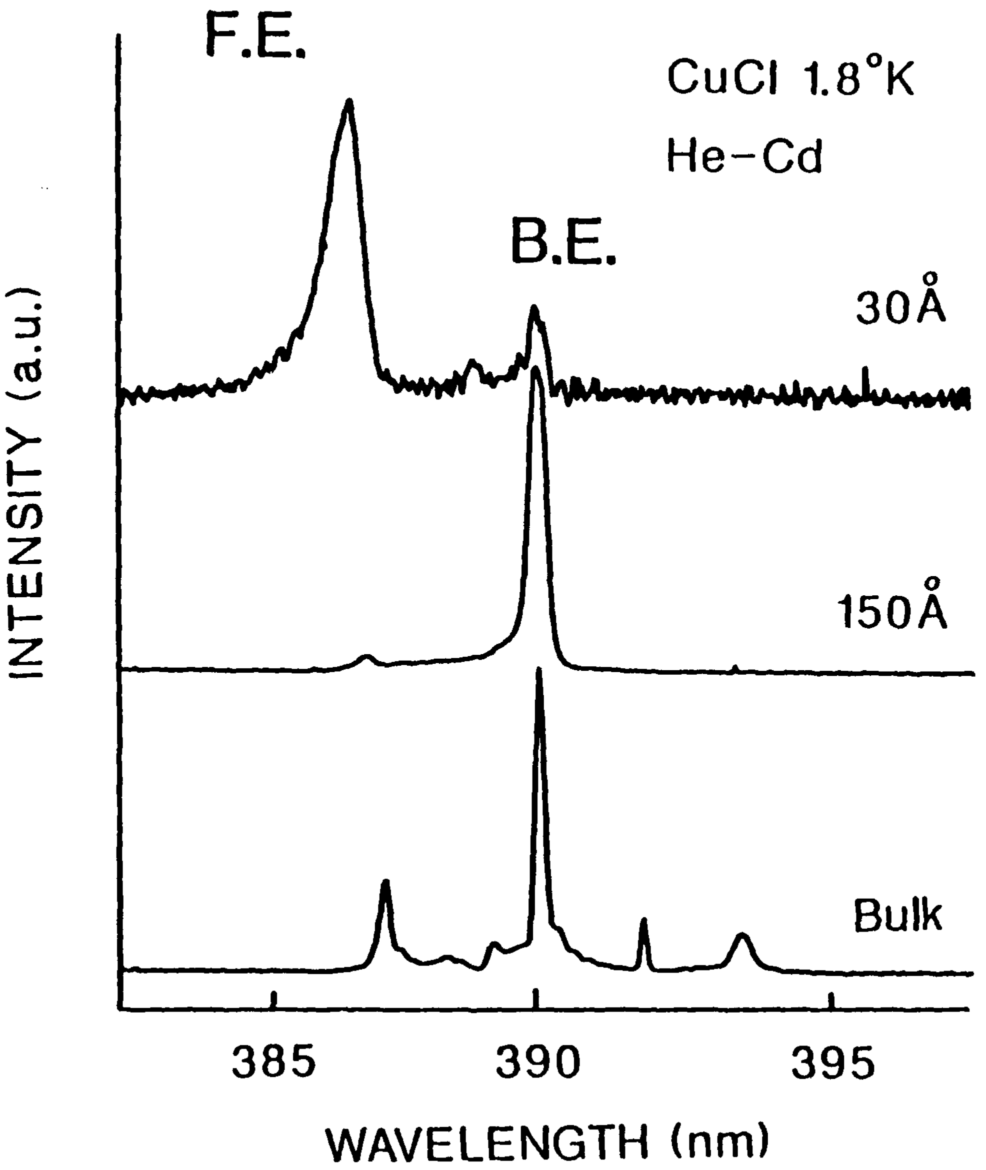
500Å
30Å
INTENSITY (a.u.)
370
380
390
WAVELENGTH (nm)

Fig. 1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CuCl 1.8°K
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Fig. 2

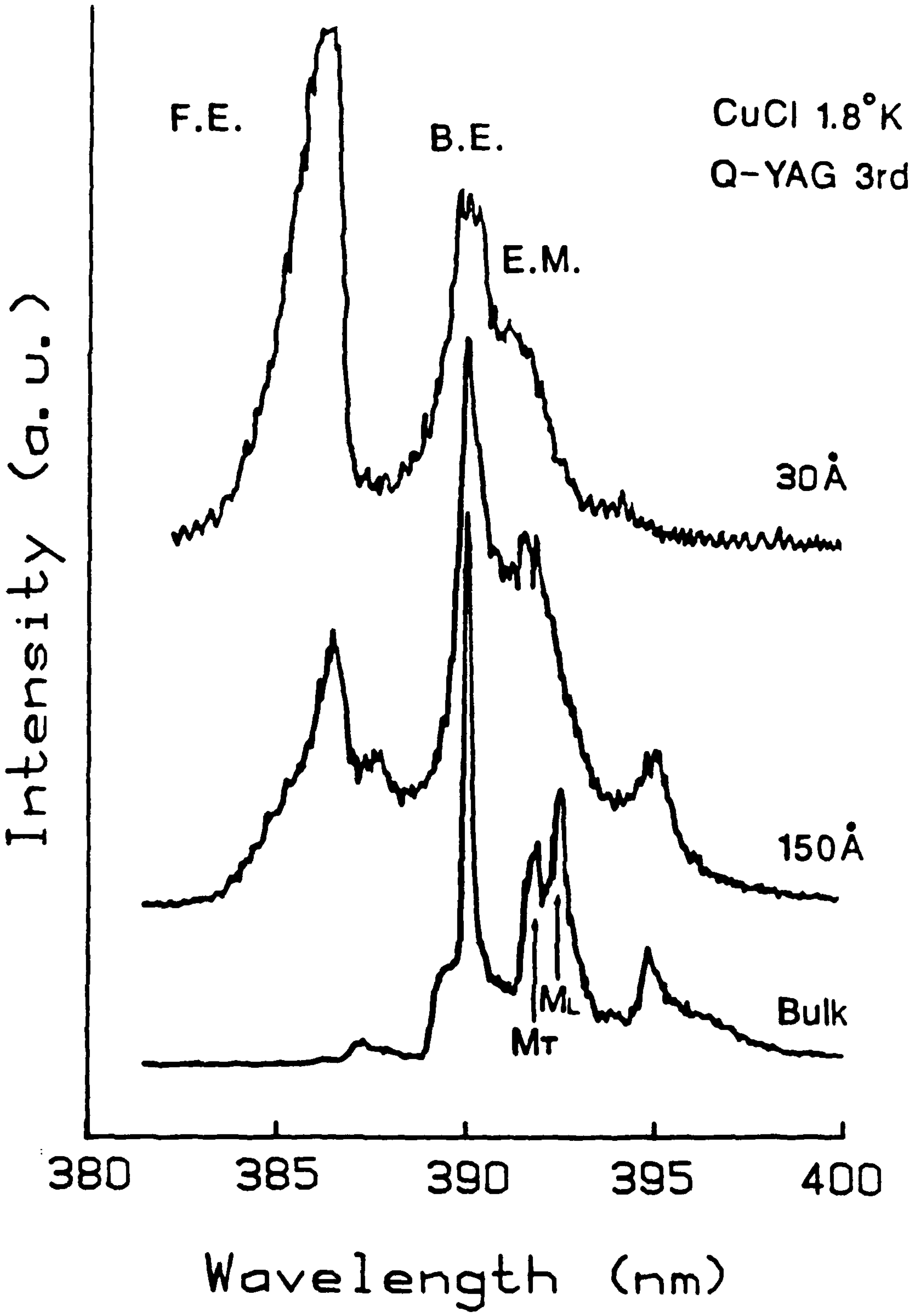
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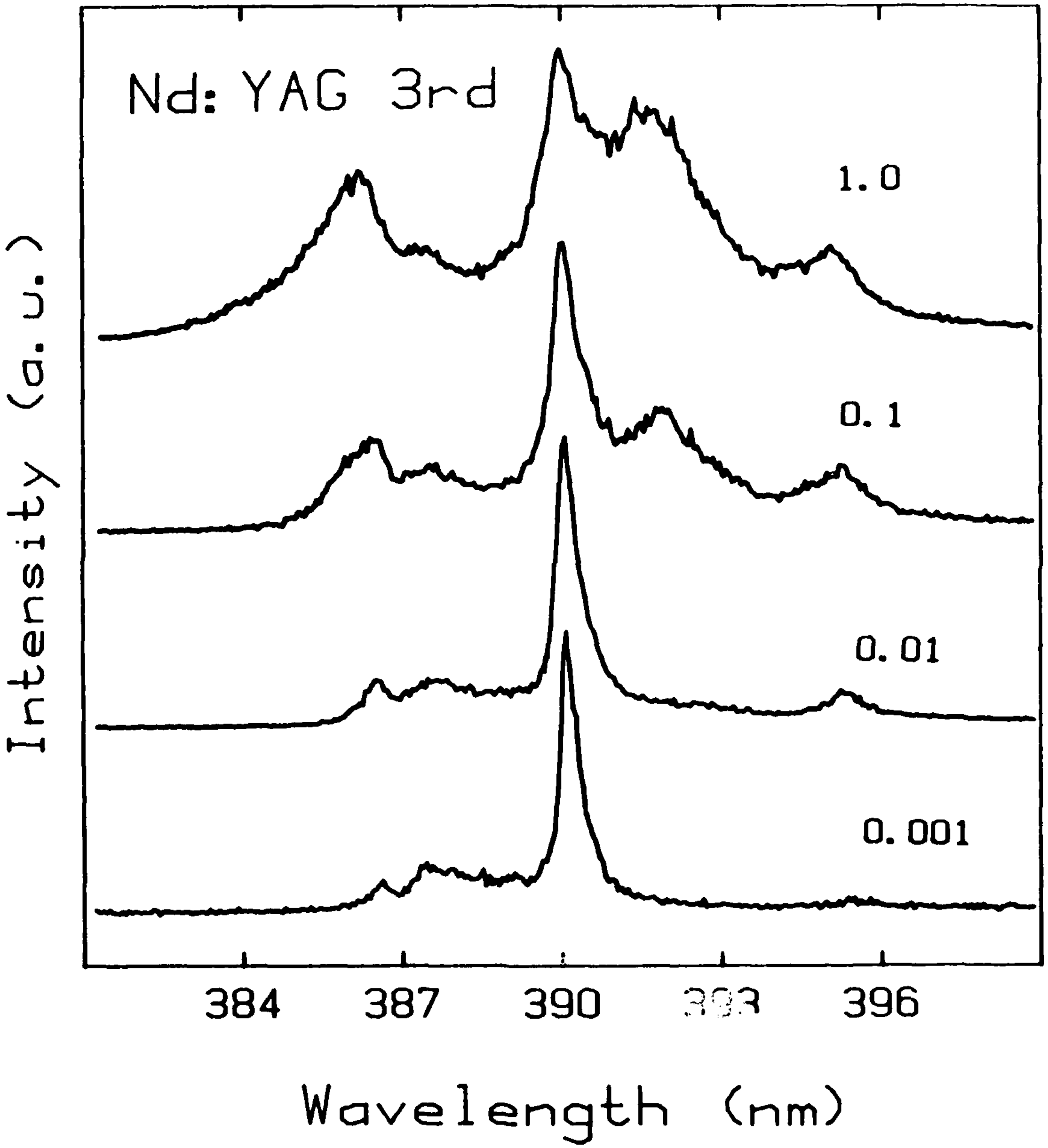
Fig. 3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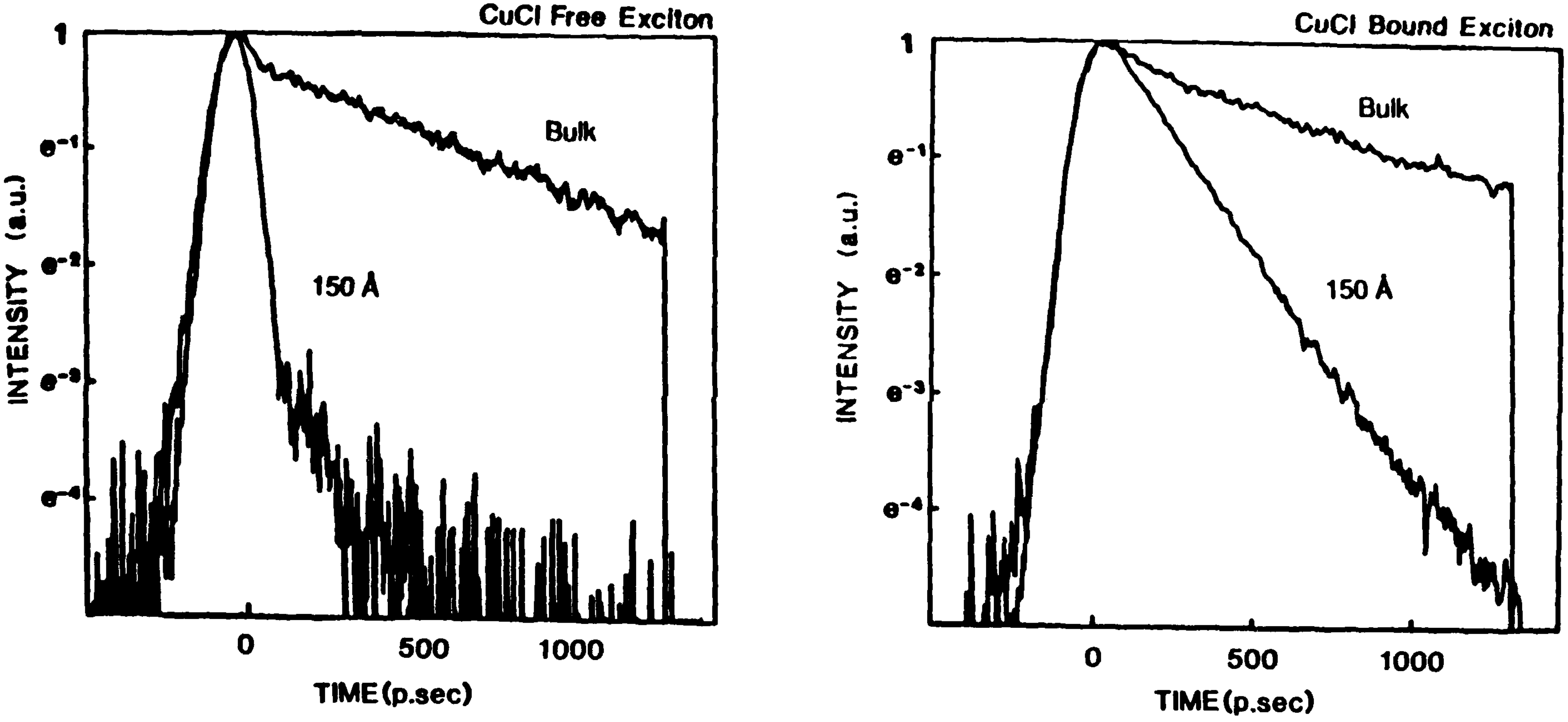
0.001
Intensity (a.u.)
384
387
390
393
396
Wavelength (nm)

Fig. 4


CuCl Free Exciton
INTENSITY (a.u.)
1
e⁻¹
e⁻²
e⁻³
e⁻⁴
Bulk
150 Å
0
500
1000
TIME (p.sec)
CuCl Bound Exciton
INTENSITY (a.u.)
1
e⁻¹
e⁻²
e⁻³
e⁻⁴
Bulk
150 Å
0
500
1000
TIME (p.sec)

a)

b)

Fig.5

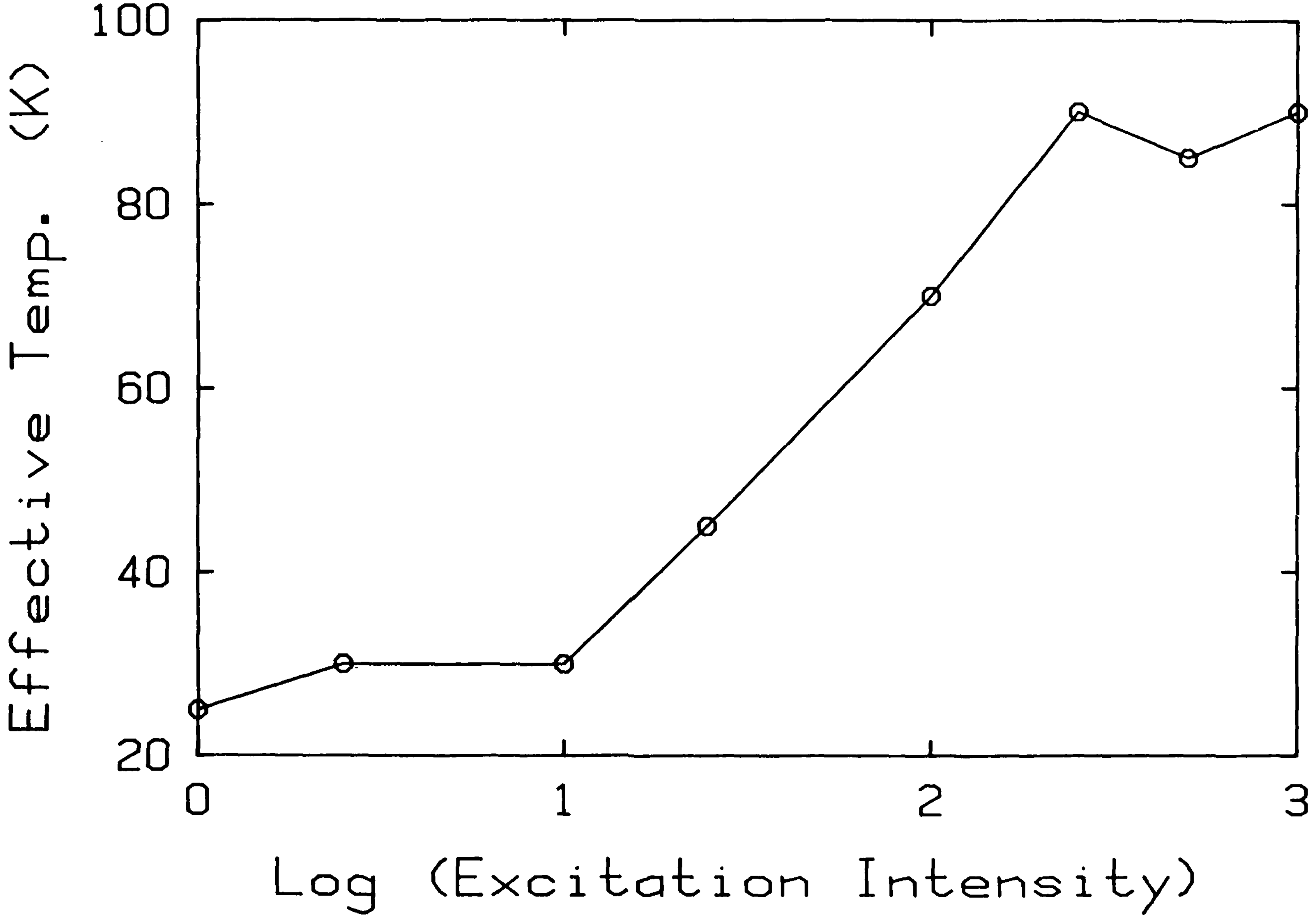
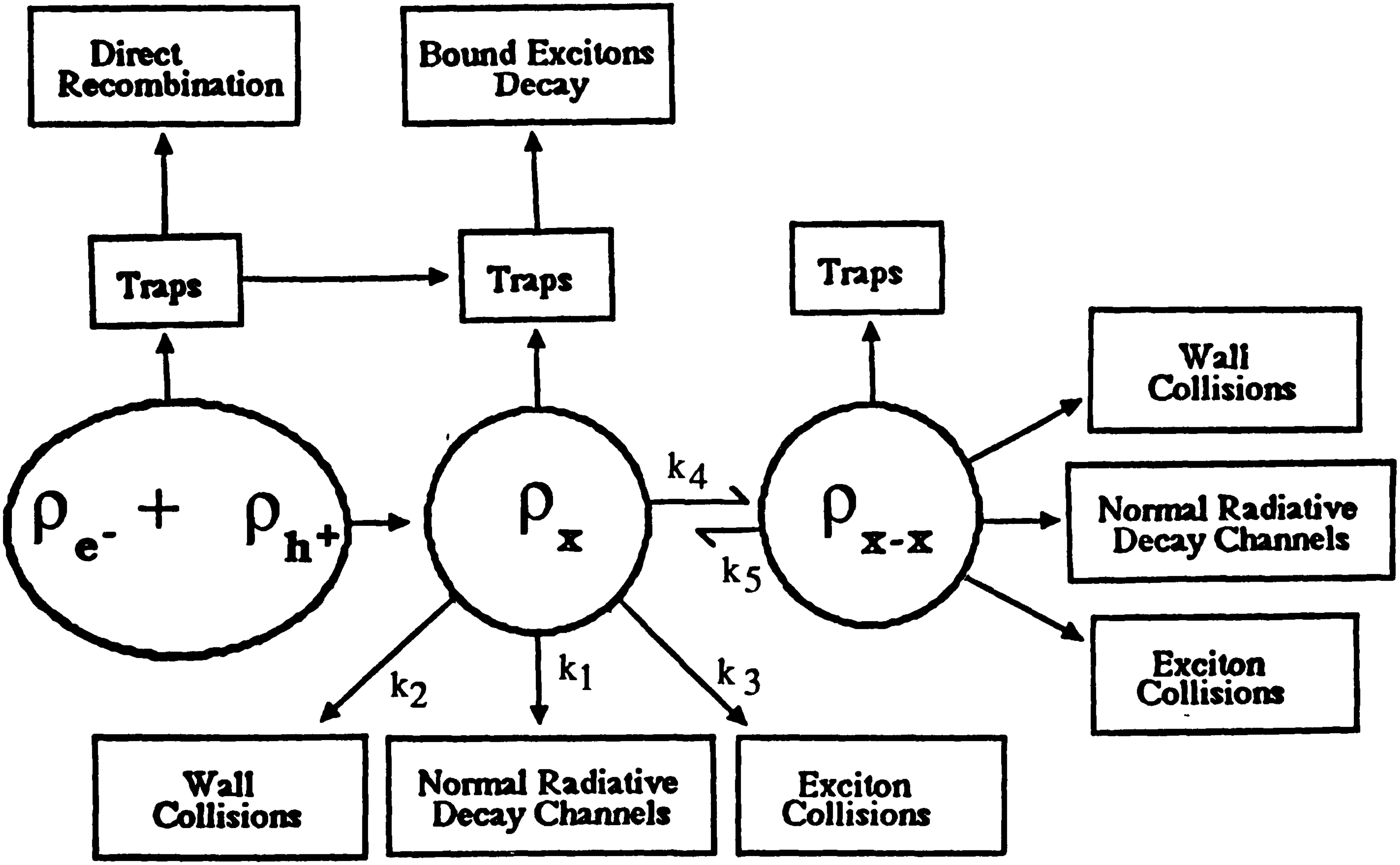

Effective Temp. (K)
100
80
60
40
20
0
1
2
3
Log (Excitation Intensity)

Fig. 6


Direct Recombination
Bound Excitons Decay
Traps
Traps
Traps
Wall Collisions
Normal Radiative Decay Channels
Exciton Collisions
$\rho_{e^-} + \rho_{h^+}$
ρ_x
ρ_{x-x}
k_4
k_5
k_2
k_1
k_3
Wall Collisions
Normal Radiative Decay Channels
Exciton Collisions

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