



.

LIBRARY Michigan State University PLACE IN RETURN BOX to remove this checkout from your record. TO AVOID FINES return on or before date due.

| DATE DUE | DATE DUE | DATE DUE |
|----------|----------|----------|
|          |          |          |
|          |          |          |
|          |          |          |
|          |          |          |
|          |          |          |
|          |          |          |
|          |          |          |

MSU is An Affirmative Action/Equal Opportunity Institution c:circidatedua.pm3-p.1 This is to certify that the

dissertation entitled

## HIGH RESOLUTION SPATIAL AND TEMPORAL

DEPENDENT LUMINESCENCE STUDIES OF SOLIDS

presented by

Ta-Ryeong Park

has been accepted towards fulfillment of the requirements for

Ph.D. degree in Physics

S.D. Mahanti S.D. Mahanti Major professor Centro

Date 8. 1. 1991

MSU is an Affirmative Action/Equal Opportunity Institution

0-12771

# HIGH RESOLUTION SPATIAL AND TEMPORAL

DEPENDENT LUMINESCENCE STUDIES OF SOLIDS

By

Ta-Ryeong Park

# A DISSERTATION

# Submitted to

Michigan State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Physics and Astronomy

### ABSTRACT

637-4002

HIGH RESOLUTION SPATIAL AND TEMPORAL DEPENDENT LUMINESCENCE STUDIES OF SOLIDS

By

#### **Ta-Ryeong** Park

By employing a pico-second pulsed dye laser system, we have performed spatially and temporally resolved luminescence experiments on various size crystals of sodium cryptand sodide (Na<sup>+</sup>C222Na<sup>-</sup>) to directly observe the spatial propagation of optically excited states as well as the dependence of the luminescence spectra on crystal size. The so called single photon counting method was used for the measurements of the time evolution of the photoluminescence. For the purpose of microluminescence experiment, we have constructed a vibration free sample mounting system in conjunction with a closed cycle helium cryostat and an optical microscope.

Small crystals ( $\leq 50 \ \mu$ m) of Na<sup>+</sup>C222Na<sup>-</sup> exhibit an emission lineshape at higher energy than that from larger crystals. An exciton-polariton dynamics model is used to obtain the rate equations which establish the polariton populations. These rate equations, which involve the Fokker-Planck equation, are shown to explain the time and energy dependence of the emission spectrum and the dependence of the luminescence on crystal size. The crystal size effect is explained by the fact that when the crystal size decreases, the non-uniform response of the radiative decay

rate leads to a decrease of the lower polariton branch (LPB) population and hence of the fluorescence intensity at energies relative to that at higher energies. It is also shown that the scattering of polaritons with acoustic phonons gradually alters the polariton population distribution and manifests itself as a constantly redshifting lineshape. This behavior leads to fast time decay of the fluorescence at high energies and slow decay at low energies. It is also shown that the time decay of the fluorescence can be approximated by a double exponential function that conforms to the experimental observations.

The temperature dependent photoluminescence from Na<sup>+</sup>C222Na<sup>-</sup> is presented. A red shift of the lineshape and a faster decay at a higher temperature is well explained by the above polariton model. As an experimental confirmation of this mechanism, we demonstrate that the time evolution of the lineshape maxima is nearly independent of temperature.

We also report an emission spectrum from defect sites of  $Na^+C222Na^$ as well as emission from other alkalides including  $Rb^+(15C5)_2Na^-$ ,  $K^+(15C5)_2Na^-$ , and  $K^+(15C5)_2K^-$ . Also it is found that the emission from  $Na^+C222Na^-$  shows interesting behavior in a high excitation power range: namely redshift of the lineshape, faster time decay, and an intensity decrease.

Photoluminescence from intercalated  $Cr(en)_3^{3+}$  ions in fluorohectorite clay was also measured by the time resolving technique. Upon intercalation, they show a redshift and a composition dependent lifetime change.

**iii** 

### ACKNOWLEDGEMENT

I wish to express my sincere gratitude to my former (now substantial) adviser Professor Stuart A. Solin for his invaluable help and support throughout all stages of this research. Although he left for NEC Research Institute in New Jersey two years ago, he has kindly continued to fully support me in every way. It is indeed one of the most wonderful and indelible experiences in my life to establish a research career under his supervision. Were it not for his intuition, fresh ideas for new experiments, generous help, and unusual enthusiasm, this dissertation could not exist even in its most primitive form.

It is a pleasure to acknowledge Professor James L. Dye in the chemistry department. He was kind enough to provide me with various alkalide samples which were the main subject of this research. The many discussions with him was essential in completing this dissertation.

With great pleasure I also acknowledge my adviser Professor S. D. Mahanti. He has taught me solid state physics which gave me valuable knowledge. With his vast amount of knowledge, he was also kind enough to read all of this dissertation and to make the invaluable suggestions.

I am also grateful to Professor W. Lynch and C. Foiles for their service on my guidance committee. Collaboration with Professor A. Sieradzan was a wonderful experience. Thanks are also due to M. Holtz, P. Zhou and G. Xu for their collaboration and many interesting discussions. I also appreciate the kind help from J. Muns, T. Palazzolo and P. Andrews.

Finally, I feel deep gratitude to my parents, sister, wife, son and wife's family. Without their support, I would not maintain my life.

iv

## TABLE OF CONTENTS

| Chapter | 1.  | Introduction1   |
|---------|-----|---|
| Chapter | 2.  | Experimental techniques and results                       |
|         | 2.1 | Light source7   |
|         | 2.2 | Detection equipment and methods12                         |
|         | 2.3 | Microluminescence experiment of sodium cryptand sodide21  |
| Chapter | 3.  | Theoretical analysis of the photoluminescence from sodium |
|         |     | cryptand sodide   |
|         | 3.1 | Motivation for the exciton-polariton picture              |
|         | 3.2 | A brief review of the exciton-polariton physics33         |
|         | 3.3 | Transport equations                                       |
|         | 3.4 | Approximate solutions                                     |
|         | 3.5 | Radiative loss and inter branch conversion of the         |
|         |     | polariton   |
| Chapter | 4.  | Comparison of the theory with experiment                  |
|         | 4.1 | Time resolved lineshapes                                  |
|         | 4.2 | Time evolution at fixed energies                          |
|         | 4.3 | Crystal size dependence of the lineshapes                 |
| Chapter | 5.  | Temperature dependence of the luminescence from sodium    |
|         |     | cryptand sodide72   |
| Chapter | 6.  | Other features of photoluminescence from alkalides80      |
|         | 6.1 | Photoluminescence from defect sites and other             |
|         |     | alkalides   |
|         | 6.2 | Excitation intensity dependence of the                    |

|         |        | photoluminescence                                    |
|---------|--------|--|
| Chapter | 7.     | Concluding remarks to aklalide research92            |
| Chapter | 8.     | Photoluminescence from intercalated clay compounds94 |
| List of | refere | ences  |

# LIST OF TABLES

| <u>Table</u> |   | Page |
|--------------|---|------|
| 4.1          | Physical parameters used for constructing theoretical | 58   |
|              | curves  |      |

# LIST OF FIGURES

| <u>Figure</u> |  | Page |
|---------------|--|------|
| 1.1           | Representations of 18-crown-6 and cryptand [p.q.r]       | 2    |
| 1.2           | Crystal structure of Na <sup>+</sup> C222Na <sup>-</sup> | 3    |
| 2.1           | Location of components on the Quantronix 416             | 8    |
| 2.2           | The dye laser configuration                              | 11   |
| 2.3           | Schematic diagram of the light source and detection      |      |
|               | equipment  | 13   |
| 2.4           | Diagram of the low temperature vibration isolated        |      |
|               | sample chamber with microscope                           | 23   |
| 2.5           | Time decay behavior of luminescence from the non-        |      |
|               | illuminated and illuminated spot                         | 23   |
| 2.6           | Experimental and theoretical time integrated lineshapes  |      |
|               | from three crystals                                      | 26   |
| 2.7           | Time evolution of the luminescence lineshapes            | 27   |
| 2.8           | Peak energy vs. time                                     | 28   |
| 2.9           | Time integrated lineshapes from illuminated and non-     |      |
|               | illuminated spot   | 30   |
| 3.1           | A schematic representation of polariton dispersion       | 35   |
| 3.2           | Theoretical time evolution of the function G(E,t)        | 51   |
| 3.3           | Energy dependence of $T_l v_{gl} / n_l^2$ and $G(E,t)$   | 52   |
| 4.1           | The (theoretical) time evolution of the maximum          |      |
|               | intensity energies $\xi(t)$ and $\eta(t)$                | 60   |

| 4.2 | The theoretical and experimental time resolved lineshapes                   | 61 |
|-----|---|----|
| 4.3 | Time dependence of the function F <sub>0</sub> (E,t)                        | 63 |
| 4.4 | Theoretical and experimental time decay of the                              |    |
|     | luminescence intensity I(E,t) at various energies                           | 64 |
| 4.5 | Lifetimes of the decay curves and the ratio of pre-                         |    |
|     | exponential factors   | 67 |
| 4.6 | The function $1/(\beta-\alpha c/(\beta-B)-k_1)$ for three cases             | 70 |
| 4.7 | Experimental time-integrated line shapes from a small                       |    |
|     | (-20µm) crystal   | 71 |
| 5.1 | Time integrated lineshapes at various temperatures                          | 73 |
| 5.2 | Time evolution of the maxima of energy of the fluorescence                  |    |
|     | lineshape at various temperatures   | 74 |
| 5.3 | Time evolution of the 1.8265eV photoluminescence                            | 75 |
| 5.4 | Theoretical plotting of $T_l v_{gl} / n_l^2$ and LPB population at          |    |
|     | 20K and 30K   | 76 |
| 5.5 | Experimental time evolution of the maximum intensity of                     |    |
|     | the lineshapes at 3 different temperatures                                  | 79 |
| 6.1 | Steady state double peaked spectra from Na <sup>+</sup> C222Na <sup>-</sup> | 81 |
| 6.2 | Time evolution of the double peaked spectra                                 | 83 |
| 6.3 | Emission from Rb <sup>+</sup> (15C5) <sub>2</sub> Na <sup>-</sup>           | 85 |
| 6.4 | Emission from K <sup>+</sup> (15C5) <sub>2</sub> Na <sup>-</sup>            | 86 |
| 6.5 | Emission from K <sup>+</sup> (15C5) <sub>2</sub> K <sup>-</sup>             | 89 |
| 6.6 | Lineshape vs. excitation intensity  | 90 |
| 6.7 | Time decay vs. excitation intensity   | 91 |
| 8.1 | Structure of fluorohectorite and $Cr(en)_{3}^{3+}$                          | 96 |
| 8.2 | Low temperature, cw spectra of the $Cr(en)_3^{3+}$ salt,                    |    |
|     | $Cr(en)_3^{3+}$ - FHT, and K-FHT  | 97 |

| 8.3 | Time resolved spectra of $Cr(en)_3^{3+}$ - FHT | 98  |
|-----|--|-----|
| 8.4 | Lifetime vs. concentration, x                  | 100 |
| 8.5 | Basal spacing vs. concentration, x             | 101 |

## 1. Introduction

Sodium cryptand sodide,  $Na^+(C222)Na^-$ , in which C222 represents the bicyclic polyether, cryptand[2.2.2],<sup>1</sup> is an ionic crystal in which both the positive and negative ions are derived from sodium atoms.<sup>2</sup> This rather unusual sodium oxidation state of -1 is made possible by enclosure of the sodium positive ion in the cage structure of the multiatomic cryptand molecule (Fig.1.1) which serves to separate the positive and negative ions in the solid. The crystal structure<sup>3</sup> (Fig.1.2) consists of close-packed cryptated cations with sodium anions in the pseudo octahedral holes. The packing has an A,B,C,A,... sequence within a hexagonal unit cell with a = 8.83 Å, and c = 29.26 Å.

Sodium cryptand sodide, abbreviated  $Na^+(C222)Na^-$ , is one member of a class of compounds which contain alkali metal anions. More than 40 such compounds, called alkalides have been synthesized and the crystal structures of 30 are known.<sup>4</sup> In the formation of alkalides, the alkali metal anions are stabilized by the complexation of the cation. The ideal complexant for the alkali cations should be non-reducible and of the right size and shape to accommodate the maximum coordination number of the particular alkali cations used. Cyclic polyethers of the crown-ether class, such as 18-crown-6 (18C6) (Fig.1.1), and bicyclic polyethers of the cryptand class, such as cryptand[2.2.2] (C222), are sufficiently resistant to reduction, at least at low temperatures, to permit isolation of salts that contain the complexed cation and alkali metal anions.<sup>2</sup> All alkalides are thermally unstable and reactive towards air and moisture, but can be handled and studied in vacuo or an inert atmosphere below about  $-40^{\circ}$ C. Of all the alkalides the sodide used in



(a)

(b)

Fig.1.1 Representation of (a) 18-crown-6 and (b)cryptand[p.q.r] (Cpqr), with p=m+1, q=n+1, r=o+1. The crown ethers form planar structures and the cryptands form 3-dimensional cages. Cryptand[2.2.2] (C222) has p=q=r=1.(from Ref.5)



**Fig.1.2** Crystal structure of Na<sup>+</sup>C222Na<sup>-</sup>: Packing of Na<sup>+</sup>C222 and Na<sup>-</sup> (solid circles) in the crystalline sodide Na<sup>+</sup>C222Na<sup>-</sup> (from ref.2)

the work of Chapter 1 through Chapter 5,  $Na^+(C222)Na^-$  is the most stable and defect free, and can be easily studied at low temperatures in an inert atmosphere. It can also be prepared as single crystals in the mm size range if desired.

Recently, Bannwart et al. measured the photoluminescence spectrum of polycrystalline and single crystal sodium cryptand sodide by using an ultrafast picosecond pulsed dye laser as the excitation source.<sup>5</sup> The photoluminescence was attributed to a 3P --> 3S bound-bound transition of the sodium anion. The peak of the fluorescence occurred at about 1.84 eV with an excitation photon energy of 2.1 eV at a nominal temperature of 7 K.<sup>6</sup> Also, it was shown that the time evolution of this spectrum after =lns could be fit with a double exponential function. On the high energy side of the band, two decay processes were observed, while on the low energy side growth was followed by decay. The two time constants were independent of wavelength except on the high energy edge, where they were both shorter. The results were interpreted as excitation from the narrow ground state 3s band to a broad 3p band, followed by shorttime emission from high energy states in the p band. After decay to the bottom of the 3p band, excited state relaxation (see the beginning of section 3.1) was presumed to occur so that the long-time emission was from the relaxed excited state. At the time there was no evidence for mobility of the excited state, so a localized picture was used to explain the results. Because conductivity measurements had shown<sup>7</sup> that Na<sup>+</sup>(C222)Na<sup>-</sup> behaves as an intrinsic semiconductor with a band gap of =2.4 eV, the luminescence signal could not have arisen from the conduction band.

A puzzling feature of luminescence studies of sodides was the extremely weak signals from other sodides compared with that from  $Na^+(C222)Na^-$ .<sup>8</sup> The optical absorption spectra are similar, the <sup>23</sup>Na NMR signals are virtually identical, and the crystal structures clearly show that Na<sup>-</sup> is present in all cases. The major difference between  $Na^+(C222)Na^-$  and other sodides is that the latter generally contain high concentrations (up to 1% or more) of electrons at defect sites, whereas  $Na^+(C222)Na^-$  has barely detectable levels of trapped electrons. Both magnetic susceptibilities and EPR spectra confirm this difference.<sup>9</sup> The weak luminescence from other sodides suggested that trapped electrons might be effective in quenching luminescence from sodides. If, however, the excitation remained localized, trapped electrons at low concentrations would not be effective quenchers. The experiments described in Chapter 2 were therefore performed to determine whether the excitation is localized or mobile.

Moreover the smallest separation between sodium anions is 8.83 Å while the effective radius of the sodium metal anion is 2.5 Å. This implies that the ground state wave function of the anion is well localized. However, despite the large separation, we expect sodium anions to interact through a dipole-dipole interaction (or higher order). Also the interstitial spaces and channels formed by packing of the large cations can provide room for the electron wavefunction to spread. This implies that there can be some overlap of the wavefunctions of neighboring sodium anions. The absorption spectrum of Na<sup>+</sup>(C222)Na<sup>-</sup> films has a half-width of  $0.62eV^{10}$  while that of the long time (about 30ns) luminescence spectrum is only 28meV.<sup>5</sup> This also suggests that the wavefunction of the excited state of Na is broad enough to overlap with adjacent ions. (The overlap causes an increase in band width.)

Consequently, in spite of the very short lifetime of the excited state (a few nanoseconds) the possibility of excitation energy transfer still remains. Thus, the experimental research effort in Chapter 2 was focussed on the search for mobile excited states that may exist in sodium cryptand sodide.

In Chapter 2 we present a new set of experimental data based on the micro-luminescence method. In Chapter 3 we point out some of the deficiencies of the model presented in Ref.5 and discuss the feasibility of the exciton-polariton picture as the process responsible for the photoluminescence signal. Also we develop a mathematical model that is compared with previous and current experimental results in Chapter 4. In Chapter 5 temperature dependent luminescence data is presented and compared with the theory developed in Chapter 3. In Chapter 6 the photoluminescence from other alkalides and from defect site of the Na<sup>+</sup>C222Na<sup>-</sup> is discussed. The excitation intensity-dependent photoluminescence from sodium cryptand sodide is also discussed.

Finally, in order to study the behavior of optically active molecules in a 2 dimensionally confined system, we have chosen clay intercalation compounds. In Chapter 8 the time evolution of the photoluminescence spectra from the intercalated  $Cr(en)_3^{3+}$  ions in clay gallery is discussed.

### 2. Experimental techniques and results

### 2.1 Light source

The light source consisted of a mode-locked Nd:YAG laser (Quantronix 416 MLSH) which provided 1.06  $\mu$ m, 100ps wide pulses at a 76MHz repetition rate. Its output was frequency doubled to give about 1.2 V of 532 nm light that was used to pump a dye laser. The dye laser (Coherent model 702-CD) gave continuously tunable 6 pico-second wide light pulses. Rhodamine 6G was used to provide a tuning range of 560-618 nano-meters. A cavity dumper was used to extract the laser pulse from the cavity and to reduce the pulse repetition rate. An average power of about 20mW was obtained at the repetition rate of 1 MHz. Neutral density filters were used to reduce the power.

The Quantronix model 416 used for this dissertation work is a solidstate laser, operable on a fundamental wavelength of either 1064 nm in the near infra-red or a second harmonic of 532 nm in the visible (Fig.2.1).<sup>11</sup> It consists of 4 major distinct parts: a laser head which contains a Nd:YAG rod and a krypton lamp, a front and a rear mirror, a mode locker, and a second harmonic generator assembly. A neodymium doped Yttrium Aluminum Garnet (Nd:YAG) crystal rod is used as a amplification medium. The pump lamp is a krypton-type unit because its emission spectrum is in the visible and near IR range and is therefore well matched to the absorption spectrum of the Nd:YAG rod. In addition to the above laser head, a partially transmissive (127) front mirror and a highly reflective rear reflector comprise the optical resonator. The rear mirror mount is adjustable (to set cavity length) by a differential



Fig.2.1 Location of components on the Quantronix 416 (from Ref.11)

micrometer. The cavity length is stabilized by the use of invar rod which connects the front and the adjustable rear mirror mount. High cavity length stability is required to avoid frequent cavity length adjustment in mode locked operation where a change in cavity length of  $l\mu m$  has a noticeable impact on pulse width and pulse-to-pulse timing jitter.

The mode locker used was an acousto-optic modulator acting as a very fast optical gate. When mode locked, harmonically spaced resonator modes have a coherent phase relationship. This leads to a repetitively pulsed output whose pulse width is determined by the laser bandwidth. (For a Gaussian distribution of the laser frequency, the product of the pulse width in time and the laser band width in frequency is about 0.5.<sup>11,12</sup>) If the period of the loss modulation is exactly equal to the round trip transit time of the photon in the resonator, then a pulse will traverse the modulator during the low loss state on every succeeding pass. The amplitude of such a pulse can grow to a stable value. However, any pulse traversing the modulator during the high loss state will not grow in amplitude. As a result, the output consists of repetitive pulses spaced by the round trip transit time. The loss is modulated at a frequency of c/2L where c is the velocity of light and L is the length of cavity resonator. Stable mode locking therefore depends on an exact match between this modulator frequency and the cavity length.

The cavity length, about 2m, determines the pulse repetition rate (76MHz) and the frequency of the (sinusoidal) RF input for the mode locker (38MHz).

The small leakage IR output pulse (1064nm and about 5mW of power) through the rear mirror of the resonator was focussed on a fast

photodiode (Antel AR-S2) which was connected to a fast oscilloscope (Tektronix Model 2465 Oscilloscope). The pulse shape monitored was about 100 ps FWHM and the cavity length was adjusted for a maximum performance of the Nd:YAG laser system.

The frequency doubled (532nm, by a second harmonic generator) output pulse of the Nd:YAG laser was used to excite the gain medium of the dye laser system. The dye laser system employed for this dissertation work was a Coherent Model 702-CD. See Fig.2.2 for a diagram. The amplification medium is a circulating dye jet (rhodamine 6G in most cases) which provides a tunable range of 560-618nm. In this configuration, the cavity length of the dye laser is matched within  $=2\mu$ m to the cavity length of the Nd:YAG pump laser. The synchronous pumping yields a dye laser output pulse of about 6 ps width in the absence of a saturable absorber jet. The pulse shape was monitored constantly by the use of an autocorrelator (Femtochrome FR-103) and the cavity length was adjusted accordingly.

The typical output power of the dye laser at 76MHz was about 80 mW when the average pumping power was about 1W. The role played by the cavity dumper in the dye laser system is essential in performing the experiments in this research work. With only a small power loss, the pulse repetition rate is controlled by the cavity dumper. Since the lifetime of sodium cryptand sodide was about a few nano-seconds, the dye laser output pulse repetition rate was chosen to be 1 MHz (with the corresponding pulse separation of  $1\mu$ s) for the time resolved luminescence experiments on alkalides. For the research on clay intercalation compounds discussed in Chapter 8 of this dissertation, a pulse repetition rate of 190 kHz was chosen due to a long lifetime (of a



Fig.2.2 The dye laser configuration. The dotted line on the right corresponds to the configuration for cavity dumping (from Ref.12).

few micro-seconds).

The shape of the extremely narrow dye laser output pulse was displayed on a conventional oscilloscope by means of an autocorrelator (Femtochrome FR-103) which is composed of a rotating parallel pair of mirrors, a second harmonic generator, and a photomultiplier tube.<sup>13</sup> The rotating mirrors introduce a periodically varying time delay in one arm of a Michelson interferometer. The split and then combined beam with time delay is focussed onto a nonlinear crystal and the generated second harmonic is detected by a photomultiplier which subsequently gives the input signal to the oscilloscope.

## 2.2 Detection equipment and methods

The signal was detected by a thermoelectrically cooled photomultiplier tube through a monochromator (Model 25-100 Jarrell-Ash One Meter Double Czerny-Turner Scanning Spectrometer). The latter had a double grating configuration and the number of grooves per mm was 1800. The focal length was 1 meter and the f-number of 8.7 whose matching to the external optical system was crucial in the case of a weak signal. Although this spectrometer was factory designed to be driven only manually, the author retrofitted a computer control by coupling a stepping motor with the drive assembly of the spectrometer.

For the time resolved photoluminesence experiments, a conventional time correlated single photon counting method<sup>14</sup> was employed. Fig.2.3 shows a schematic diagram of the setup used for this dissertation work. In a single photon counting method, when one records the detection of a fluorescence (or Raman or any other emission) photon one also measures



Fig.2.3 Schematic diagram of the light source and detection equipment: CFD=Constant Fraction Discriminator, TAC=Time-to-Amplitude Converter, MCA=Multi-Channel-Analyzer and PMT=Photo Multiplier Tube. Dashed lines denote the optical path and continuous lines the electrical connection.

the elapsed time after a sample was excited by a laser pulse and converts this time to an amplitude. This is accomplished as follows in a Normal time to amplitude converter (TAC) configuration:

(1) The dye laser beam is split into 2 pulses.

(2) One beam irradiates the photodiode whose output is used as a triggering pulse. The trigger pulse is routed, through a discriminator (Tennelec Model TC 455 Quad CF discriminator), to the start input of a time-to-amplitude converter (PRA Model 1701) which initiates charging of a capacitor.

(3) The other main laser pulse is used to excite the sample which subsequently fluoresces.

(4) The fluorescence signal (or any other kind of emission signal) photon is detected by a PMT through a spectrometer.

(5) The PMT signal, after being amplified and reshaped to a clean form by a discriminator (Tennelec TC 455), stops the charging process of the capacitor in the TAC.

(6) The TAC gives a pulsed output voltage which is proportional to the charge in the capacitor, hence to the time difference between the START and STOP pulses.

(7) An analog-to-digital converter in a multi-channel-analyzer (Nucleus Model PCA II-8000) converts the analogue voltage from the TAC into a digital signal and stores it in the corresponding channel of the MCA.
(8) The processes from (1) to (7) above is repeated until a sufficient amount of data is accumulated in the memory of the MCA.

(9) It is important to identify the channel number corresponding to the beginning of an excitation in an ideal case or in a case when the

detection equipment has infinitely fast response compared to the time scale of the emission process. When the overall response time of the detection equipment (a chain of objects: PMT, preamplifier, discriminator, TAC, inter connecting cables, delay box, and beam path of the signal, laser excitation pulse width, etc.) is nonnegligible, the time origin of the excitation is not well defined. Instead, it has a certain distribution in time and which is called the Instrument Response Function (IRF). The IRF or the time profile of the excitation pulse is recorded in the same way by replacing the sample with a light scatterer.

The normal TAC configuration described above is not efficient due to the recovery time of the TAC. Whenever the TAC is started, it waits for a stop signal up to a certain length of time. Therefore when the stop signal, supplied by the generally weak emission signal photon, occurs infrequently compared to the start pulse (laser excitation pulse), the electronics has a large amount of dead time. However full advantage of the high repetition rate of excitation is taken by 'inverting' the TAC configuration.

In an inverted configuration of the TAC, the laser triggering pulse is used for a stop pulse and the fluorescence photon for a start pulse. Since the stop pulse must arrive at the TAC later than the start pulse, an adjustable delay is inserted between the TAC stop input and the photodiode that is irradiated by the laser triggering pulse. Therefore, this usage of the inverted TAC configuration is possible only when there is a sufficiently long length of delay within which the fluorescence decay process is completed. For this reason, the inverted TAC

configuration was used in alkalide experiments and the normal configuration in intercalated clay experiments. (The maximum delay was about 330ns while the decay processes of the photoluminescence from alkalides and clay intercalants were finished in a few nano-seconds and in about 10 micro-seconds respectively.)

This time resolved experiment has an additional advantage: the signal to noise ratio is greatly enhanced. This is because the time interval chosen for the detection of an emitted photon is much smaller than the successive excitation pulse separation time. In alkalide experiments the former was about 30ns while the latter was  $l\mu$ s, which means that only for 3Z of time is un-correlated (or random) noise recorded in the MCA. In other words, 97Z of the steady state noise such as room light is eliminated by this method. This aspect was particularly beneficiary when doing microluminescence experiments on sodium cryptand sodide.

It was stated previously that the IRF should be recorded when it has a non-negligible spread compared to the experimental time scale. In this case the instrumental factors contribute significantly to the observed decay behavior. Mathematically, the observed decay curve is given by a convolution integral of the IRF and the real luminescence decay curve from a sample. This is expressed by<sup>14</sup>

$$I(t) = \int_{0}^{t} D(t-t') IRF(t') dt' \qquad (2.1)$$

where I(t)=observed luminescence decay behavior, IRF(t)=time dependence of the IRF, and D(t)=real luminescence decay behavior. The mathematical problem of solving for the function D(t) is commonly referred as deconvolution and in this research it was accomplished by using a commercial software package (from PTI Lasers). One more practical difficulty associated with Eq.(2.1) is that the IRF, in general, is photon energy dependent. If one could measure the IRF at every energy of interest and use successive deconvolution, then the energy dependence of the IRF would be mitigated. Fortunately, our measurements indicated that the IRF of our equipment is nearly energy independent. The fluorescence of the rhodamine 6G dye solution, which has about a 5ps lifetime, was used for a measurement of the IRF at various energies. The IRF at a laser excitation wavelength of 580nm and the R6G fluorescence decay curves at the wavelength of interest showed no noticeable differences. Finally, it has to be mentioned that in our measurements the number of detected photons per unit time (N<sub>1</sub>) was sufficiently smaller than the excitation pulse repetition rate (N<sub>2</sub>), to justify the use of a single photon counting method.<sup>14</sup> The ratio, N<sub>1</sub>/N<sub>2</sub>, was less than 0.001 in most cases.

As shown in Fig.2.3, all the detection equipment was controlled by a computer (IBM XT and 80386 CPU based PC). Computer software was developed to carry out the following tasks automatically:

(1) Assign the wavelengths at which the emission signal is measured
 (2) Preset the data aquisition time of the MCA at each wavelength
 (3) Set the spectrometer at a beginning wavelength
 (4) Control the MCA to start data acquisition (The format of the data is given by the number of count vs. channel (time).)
 (5) Read the exciting laser power many (about 9) times a second while the fluorescence data is being acquired by the MCA

(6) Stop data acquisition after a preset time has elapsed and store the data on a computer hard disk

(7) Store the laser power information on the computer hard disk(8) Drive the monochromator to the next wavelength position by operating the stepping motor coupled with the drive assembly

(9) Repeat the steps from (4) to (8) until acquisition at the last wavelength is finished

When the steady state luminescence spectrum was investigated, only a rate meter, the laser power meter and the monochromator were controlled by the computer. Since the outputs of the laser power meter and the rate meter were both given by voltage, a voltmeter (Keithly Model 199 System DMM/ Scanner) with an analog-to-digital converter was used to read the voltage and was interfaced with the computer through GPIB (National Instruments). The stepping motor was also controlled by the computer through the GPIB.

To obtain a time resolved line shape, the number of counts from one channel to another was integrated at all wavelengths. Since the dye laser power was generally fluctuating, the integrated count was normalized by using the laser power information in step (7) above.

Using the above-mentioned methods, the following experiments were performed:

A. Microluminescence experiments (Na<sup>+</sup>C222Na<sup>-</sup>)
(1) Crystal size dependence of line shape (CW and time resolved)
(2) Spatial distribution of the emission intensity
(3) Position dependent time decay

- (4) Position dependent line shape vs. energy
- (5) Excitation intensity dependence of

time decay,

line shape,

emission intensity

B. Normal luminescence experiment (without a microscope)

(6) Line shape (CW and time resolved; Na<sup>+</sup>C222Na<sup>-</sup>)

- (7) Time decay at various energies and lifetime measurement by deconvolution (Na<sup>+</sup>C222Na<sup>-</sup>)
- (8) Temperature dependence (Na<sup>+</sup>C222Na<sup>-</sup>)
- (9) Double peaked luminescence (Na<sup>+</sup>C222Na<sup>-</sup> and other alkalides)
- (10)Line shape (CW and time resolved; intercalated clay compounds)

(11)Composition dependence of time decay and life time measurement (intercalated clay compounds)

In order to observe the propagation of the optically excited states directly, we employed a position sensitive optical microscope whose objective was used both for focussing the laser light on the sample and for collecting the photoluminescence signal from the sample at a selected spot (Fig.2.4). Therefore in this micro-luminescence experiment, the signal was collected in the backward direction with a collection angle of about  $15^{\circ}$ . The size of the focussed laser beam on the sample was about  $10\mu m$ .

Since sodium cryptand sodide does not give a stable luminescence signal at high laser light intensities (the intensity of the emission signal decreases gradually with time), we had to use low enough excitation light intensity in most cases to maintain the emission signal and sample stability. About 1  $\mu$ V of time averaged laser power was focussed on the sample yielding a power density of about 1V/cm<sup>2</sup>. While performing experiments with a closed cycle helium cryostat (Cryosystems LTS-21-.1), samples were kept in a vibration isolated chamber (connected to a Cryosystems SCA-Vib Vibration Isolation Adapter) that was connected to the cold finger of the cryostat with flexible copper wires (Fig.2.4). The temperature sensor was attached to the sample chamber holder and the monitored temperature was about 26 K. An X-Y-Z translator was used to bring the selected spot/sample into focus. The sample vibration amplitude and frequency were less than a few  $\mu$ m and a few hundred Hz respectively. Moreover, considering the very fast optical and electronic processes which are nearly complete in 30 nsec, even slowly moving samples can be regarded as essentially stationary.

The laser beam position and the sample was monitored through the TV camera. The lenses A and B in Fig.2.4 were used to minimize the incident laser beam diameter while the lenses C and D were used to match the f-number of the monochromator. The lens A was moved in a plane perpendicular to the beam direction to bring the beam to a desired spot on the sample. When doing the measurements of the spatial distribution of the emission signal, the laser beam was scanned across the sample surface while fixing the signal collection position on the sample. The change in the IRF associated with this lens movement was negligible. The spatial resolution of data collection was about 25  $\mu$ m. This microscope system was very useful in choosing the crystal and identifying its size. Moreover, the laser power density could be accurately controlled owing to the knowledge on the focussed beam size.

Due to the low signal intensity, an inverted configuration of the time-to-amplitude converter was used. The overall instrument response time was about 0.7nsec. The dye laser pulse repetition rate was chosen to be 1MHz and the excitation photon energy was 2.1 eV.

### 2.3 Microluminescence experiment of sodium cryptand sodide

Typical time and spatially resolved single crystal data are shown in Fig.2.5.<sup>15</sup> Note the difference between the time decay curves that were taken from two different spots on the same sample. The signal (designated by (a) in Fig.2.5) emanating from a non irradiated area (about 80 µm distant from illumination and 25 µm in diameter for signal collection) has a broader width in time and a peak position shifted toward later time than the one (designated by (b) in Fig.2.5) from the illuminated area (25 µm in diameter for signal collection again). These time resolved emission signals and the direct measurement of emission intensity as a function of distance from illumination (Inset of Fig.2.5) provide unambiguous proof that the optically excited state is propagating through the crystal. If the signal (a) were caused by direct laser light illumination (the very weak stray exciting laser light present at the position of signal collection), then its time dependence would be almost identical to the one represented by the curve (b) considering the fact that one channel corresponds to 60 pico-seconds. In this experiment we scanned the exciting laser light across the sample surface with no change in the instrument response function within our experimental accuracy. Energy transport by a diffusion process can be considered to explain the slight peak position shift and the increase in



Fig.2.4 Diagram of the low temperature vibration isolated sample chamber with microscope.


Fig.2.5 Time decay behavior of luminescence from (a)the non-illuminated spot and (b)the illuminated spot from sample 3 at an emission energy of 1.843 eV.IRF means Instrumental Response Function. One channel=60ps. Inset: The spatial distribution of the laser excitation intensity (filled diamonds) and the emission signal intensity (squares) as a function of distance from the illumination spot with sample 3. Curve (c) is the time decay curve at the same energy from a large (~1mm in size) and shiny bright golden colored crystal.

decay width shown in Fig.2.5. The exciton-polariton (see section 3.2), which is constantly scattered by acoustic phonons while moving with the group velocity, is a viable medium for such energy transfer.

In the inset of Fig.2.5 we have shown the time integrated luminescence and exciting laser light (2.1eV) intensities at various positions in order to give direct evidence that the emission from the non-illuminated position does not come from the stray exciting laser light but rather from the migration of the excited states. Here again, the luminescence emission intensity would have the same spatial distribution as the exciting laser light were the former due to the latter. A rather broad distribution of the laser light, compared to the 10  $\mu$ m beam size, is partially due to the wide signal collecting area (about 25µm in diameter) and partially to the roughness of the sample surface that causes irregular reflection. Normally, the time decay (curve (c) in Fig.2.5) at this energy (1.843 eV) from the large (order of 1mm in size) and best quality (see below for the description of crystal quality.) crystals is much slower than that shown by curves (a) and (b) in Fig.2.5. The abnormally fast decay observed in Fig.2.5 is attributed to lattice defects or impurities inside the crystal which enhance the non-radiative decay process. Sample quality is clearly discernible by the color it exhibits: this sample showed a less bright golden color than the one with best quality.) Therefore it should be noted that the emission intensity distribution appearing in the Inset of Fig.2.5 is only specific to the sample mentioned above.

Spectral line shapes have also been measured many times from various sized crystals (1)shiny, bright golden crystal, =0.5mm diameter (sample 1), (2)shiny bright golden powder =50µm crystallite diameter (sample 2),

and (3)less bright golden crystal, =1mm diameter (sample 3). Sample 3 was also used in obtaining the signal shown in Fig.2.5. Fig.2.6a shows time integrated line shapes. The time integrated line shapes from powders ( $\leq 50 \ \mu m$  in size) show a peak at 1.852 eV, which differs from the case of the larger samples. The spectrum of sample 3 has a dip at 1.845 eV and a larger width of 38 meV while sample 1 shows no dip and a peak at lower energy with a width of 28 meV. Fig.2.6b shows the theoretical plotting of the time integrated line shapes that correspond to the three experimental cases in Fig.2.6a. We will discuss this figure later.

Fig.2.7 shows the normalized time resolved spectral line shapes of sample 3. We can see from Fig.2.7 that the time integrated line shape is largely composed of two components: (1)a narrow component with a relatively narrow width that decays rapidly with a peak at 1.852eV and (2)a wide component which grows with time relative to the narrow one (Fig.2.8b). A careful examination of Fig.2.7 also shows that the narrow component has a peak position that is nearly unchanged but the wide one changes continuously with time from a short wavelength to a long wavelength with time (Fig.2.8a).

The time denoting our experimental line shapes is accurate only within our experimental time resolution limit, 0.7 nsec, determined by the instrumental response time. Therefore this limited time resolution does not give us true line shapes but only an average. This inaccuracy will be particularly large in the very short time region, less than -Insec. Nevertheless, these curves are sufficient to provide us with a very clear trend.

From the above observations we conclude that the time integrated photoluminescence line shapes are mainly determined by the crystal size



Fig.2.6 (a) Experimental time integrated luminescence line shapes from three crystals:(1) large (=0.5mm in size) and shiny bright golden colored crystal (sample 1), (2) small (=50 $\mu$ m) and shiny bright golden colored powder (sample 2) and (3) large (=1mm in size) and less shiny bright golden colored crystal than sample 1 (sample 3). (b) Corresponding theoretical time integrated line shapes: (1)  $S_c/V_c$ =0.5/cm and  $R_{\alpha 0}$ =2x10<sup>8</sup>/sec (2)  $S_c/V_c$ =50/cm and  $R_{\alpha 0}$ =2x10<sup>8</sup>/sec and (3)  $S_c/V_c$ =0.5/cm and  $R_{\alpha 0}$ =2x10<sup>9</sup>/sec.



Fig.2.7 Time evolution of the luminescence line shapes from sample 3.  $t_1 < t_2 < t_3 < 1$  nsec.



Fig.2.8 (a) Peak energy vs. time: (1) narrow and (2) wide component. (b) Peak intensity ratio of narrow component to wide component.

and quality. A larger crystal yields a line shape with a peak at lower energy. A good quality large crystal also has a much longer lifetime than either small crystals or large crystals with defects.

Fig.2.9 shows the normalized time integrated line shapes from illuminated and non illuminated spots (sample 3). They are nearly identical except that the one from the illuminated area is slightly broader than the other. Neglecting this small difference, we will later use this observation as the experimental justification for the uniform distribution of polaritons which we assume for simplicity.

Fig ill



Fig.2.9 Time integrated line shapes from (1) illuminated and (2) non illuminated spot with sample 3.

- e 0
- pc
- in
- ev
- th
- cor

3. Theoretical analysis of the photoluminescence from sodium cryptand sodide

## 3.1 Motivation for the exciton-polariton picture

In Ref.5, the photoluminescence from sodium cryptand sodide was envisioned as coming from the excited p-level and an additional energy level with lower energy which was introduced to explain the experimental observation of a double exponential decay. However, the 3-level mechanism proposed in Ref.5 is incomplete in accounting for various experimental observations. The proposed lower energy level of the excited state, which is generated by relaxation of the surroundings would be determined by local interactions rather than long-distance effects. Hence it can be said that the nature of the proposed induced energy level would be independent of the macroscopic geometry of the crystal. Therefore, this model does not provide a natural explanation for our crystal size dependent line shape. Moreover, with a fixed low energy level, one can not account for the continuous red shift of the lineshape with time.

However, the interpretation of our data in terms of a mobile exciton-polariton<sup>16-21</sup> has many advantages. The spatial migration of the optical excitation can be understood as a result of diffusion of polaritons that are scattered by phonons. As was pointed out previously in Section 2.3, the behavior shown in Fig.2.5 is at least qualitative evidence for this diffusion. In order for the polaritons to luminesce, they first must gain access to the crystal boundary where they are converted into photons. Consequently, the spectrum and time evolution

(for example, lifetimes) of the polariton are affected by the crystal geometry which controls the radiative decay rate.

The crystal size dependent line shape, shown in Fig.2.6, is a convincing signature of exciton-polariton luminescence. Also, the continuous red shift of the spectrum as a function of time (Fig.2.8, 4.1 and see Ref.5) is in qualitative agreement with polariton dynamics as was considered by Toyozawa<sup>19</sup> who calculated the rate of energy decrease of a polariton as a result of scattering with phonons.

In addition to the above aspects, the time decay characteristics of the photoluminescence signal from sodium cryptand sodide are similar to those of CdS,  $CdSe^{21}$  and  $CdTe^{22}$  which are known to exhibit polariton luminescence. In general, these materials do not show mono-exponential time decay behavior(see Ref.5 for the case of sodium cryptand sodide which was fitted with a bi-exponential time decay). Also they show fast time decay at higher energy and slow decay at low energy, which means they have a time-dependent line shape.

Although many authors have addressed the theory of exciton-polariton luminescence<sup>20,21,23-26</sup>, none of their treatments was completely suitable for our purpose. In Ref.20 steady state luminescence from only the lower polariton branch was studied with a numerical method. In Ref.23, the position-dependent but steady state luminescence without radiative loss terms in the equations was considered. The treatments of Refs.25 and 26 were also for steady state luminescence only. In Ref.21 the time-dependence of the luminescence was investigated but numerical methods were used and crystal size dependence was not considered.

3.2 A brief review of the exciton-polariton physics

Near exciton-photon resonance energies, both modes tend to couple to form a new mode. This mixed mode of photon and exciton is called an exciton-polariton. When the polarization is caused by transverse optical phonons instead of transverse excitons, the mixed mode is called a phonon-polariton. Polaritons were first studied quantum mechanically by Hopfield.<sup>16</sup> Hereafter, the term "polariton" will be understood to denote the exciton-polariton unless otherwise stated.

Since the electromagnetic wave is transverse, only the transverse crystal field is coupled with the photon field. In the exciton-polariton system, the energy is exchanged between the exciton and the photon. The excitation energy is shared between the exciton and the internal photons. Hopfield described this mutual exchange of energy by constructing new eigenstates of the complete Hamiltonian comprised of the crystal, radiation field and the interaction between them.<sup>16</sup> The new eigenstates have infinite optical lifetime and thus constitute bona-fide propagating modes inside a crystal. However, decay occurs when they meet the crystal boundary and the photon escapes from the crystal. The decay rate is proportional to the propagation velocity and surface to volume ratio of the crystal. It is therefore large with small crystals and is small with large crystals. It is this crystal size dependent decay rate that motivated us to interpret luminescence from Na<sup>+</sup>C222Na<sup>-</sup> as arising from an exciton-polariton. CdS is a good example material which shows polariton luminescence.<sup>21</sup> (See Section 3.1.)

The classical theory of polaritons  $^{16,18}$  starts by formulating the equation of motion for the polarization P,

Iı at

$$\frac{1}{\omega_0^2} \frac{\partial^2 \mathbf{P}}{\partial t^2} - \frac{\hbar}{\mathbf{m}_e \omega_0} \nabla^2 \mathbf{P} + \mathbf{P} = \beta \mathbf{E}$$
(3.1)

where **E** is the electric field,  $\beta$  is the static polarizability, and  $\omega_0$  is the resonance frequency at k=0, m<sub>e</sub> is the effective exciton mass, and in order to include the spatial dispersion term involving  $\nabla^2 P$  the dispersion relation between wave vector k and the frequency  $\omega$  $\hbar\omega = \hbar\omega_0 + \frac{\hbar^2 k^2}{2m_e}$  was assumed. When Eq.(3.1) and Maxwell's equations are solved, we obtain the dispersion relation

$$\epsilon(\omega) = n(\omega)^2 = \frac{c^2 k^2}{\omega^2} = \epsilon_{\omega} + \frac{4\pi \beta \omega_0^2}{\omega_0^2 + (\hbar \omega_0 / m_e) k^2 - \omega^2}$$
 (3.2)

where  $n(\omega)$  is the index of refraction,  $\epsilon(\omega)$  is the dielectric constant,  $\epsilon_{\infty}$  is the background dielectric constant, and c is the speed of light in vacuum. The solution of Eq.(3.2) is plotted in Fig.3.1. The finite effective mass of the exciton makes the lower polariton branch (LPB) bend upwards. In the case of an infinite exciton mass (no spatial dispersion term in Eq.(3.1)) a forbidden band is established between  $\omega_{\rm T}=\omega_0$  and  $\omega_{\rm L}=\omega_0\sqrt{\left\{1+\frac{4\pi\beta}{\epsilon_{\infty}}\right\}}$ , where no electromagnetic wave can propagate. In the large k region, the LPB behaves like an exciton and the upper polariton branch (UPB) behaves like a photon whereas in small k region they show the opposite behavior.

In Hopfield's microscopic theory of the exciton-polariton<sup>16</sup>, the total Hamiltonian for the interacting system of exciton and photon is given by

$$H = H_{exciton} + H_{photon} + H_{exciton-photon}$$
(3.3)

In Eq.(3.3),  $H_{exciton}$  denotes an exciton Hamiltonian and it contains an atomic part  $H_{atom}$  and an interaction part  $H_{atom-atom}$  between atoms. The



Fig.3.1 A schematic representation of exciton-polariton dispersion with finite effective exciton mass. UP=upper polariton branch, LP=lower polariton branch, LE=longitudinal exciton dispersion, TE=transverse exciton dispersion (from Ref.18)

a V 81 0 Th

Vi

Ħ

interaction between neighboring atoms determines the effective exciton mass. The interaction is caused by a dipole-dipole interaction (Eq.3.4) in Frenkel case and a wavefunction overlap (Coulomb or exchange) in Wannier case.) In a tight binding limit (Frenkel exciton), in which the overlap between atomic wavefunctions centered at different sites is neglected, one can approximate the interaction by a dipole-dipole interaction.<sup>16,18</sup> (The transport equations in Section 3.3 do not depend on the the type of exciton in sodium cryptand sodide. We need to assume only the dispersion relation of the exciton band which is determined by the effective exciton mass.) Therefore

$$H_{atom-atom} = \sum_{m \neq m'} e^{2 \frac{|\mathbf{n} - \mathbf{n}'|^2 \mathbf{X} \cdot \mathbf{X}_{m'} - 3(\mathbf{n} - \mathbf{n}') \cdot \mathbf{X}_{m}(\mathbf{n} - \mathbf{n}') \cdot \mathbf{X}_{m'}}{2|\mathbf{n} - \mathbf{n}'|^5}}$$
(3.4)

where m and m' denote atomic sites and X is the total electronic dipole moment of the atom at site m.

Eq.(3.4) can be second quantized in terms of a creation operator for an excited atomic state n at site  $\mathbf{m}$ .

$$d_n^{\dagger}(\mathbf{m}) = |n, \mathbf{m} > 0| \qquad (3.5)$$

where  $|n,m\rangle$  is the wavefunction of the excited atomic state n at site m and  $|0\rangle$  is the ground state wave function. Using Eq.(3.5) the dipole operator is reexpressed as<sup>16</sup>

$$\mathbf{X}_{\mathbf{m}} = \sum_{\mathbf{n}\neq\mathbf{0}} \left\{ <0 \left| \mathbf{X}_{\mathbf{m}} \right| \mathbf{n}, \mathbf{m} > \mathbf{d}_{\mathbf{n}}(\mathbf{m}) + <\mathbf{n}, \mathbf{m} \right| \mathbf{X}_{\mathbf{m}} \left| 0 > \mathbf{d}_{\mathbf{n}}^{\dagger}(\mathbf{m}) \right\} + \sum_{\mathbf{n}, \mathbf{n}'\neq\mathbf{0}} <\mathbf{n}, \mathbf{m} \left| \mathbf{X}_{\mathbf{m}} \right| \mathbf{n}', \mathbf{m} > \mathbf{d}_{\mathbf{n}}^{\dagger}(\mathbf{m}) \mathbf{d}_{\mathbf{n}'}(\mathbf{m}).$$
(3.6)

Then one obtains, keeping only terms quadratic in d and  $d^{\mathsf{T}}$ ,

$$H_{\text{exciton}} = \sum_{\mathbf{k},\mathbf{n}} E_{\mathbf{n}}^{\text{atom}} b_{\mathbf{n}\mathbf{k}}^{\dagger} b_{\mathbf{n}\mathbf{k}} + \frac{1}{2} \sum_{\mathbf{k},\mathbf{n}} \Delta_{\mathbf{n}}(\mathbf{k}) (b_{\mathbf{n}\mathbf{k}} + b_{\mathbf{n},-\mathbf{k}}^{\dagger}) (b_{\mathbf{n},-\mathbf{k}} + b_{\mathbf{n},\mathbf{k}}^{\dagger}) \quad (3.7)$$
with<sup>18</sup>

$$\Delta_{n}(\mathbf{k}) = \frac{4\pi N}{3 V} e^{2} \{ 3 | \frac{\mathbf{k}}{\mathbf{k}} \cdot \mathbf{X}_{0n} |^{2} - | \mathbf{X}_{0n} |^{2} \} \{ 1 - \frac{1}{10} (ka)^{2} + \dots \}$$
(3.8)

where N and V are the number of atoms in the crystal and the crystal volume respectively, and a is the lattice constant. The matrix element  $\mathbf{X}_{0n} = \langle 0 | \mathbf{X}_{m} | n, m \rangle$  was assumed to be real and  $\mathbf{E}_{n}^{\text{atom}}$  is the atomic energy state. The operator  $\mathbf{b}_{n\mathbf{k}}^{\dagger}$  is the delocalized exciton creation operator and is given by

$$b_{nk}^{\dagger} = \frac{1}{\sqrt{N}} \sum_{\mathbf{n}} e^{i\mathbf{k}\cdot\mathbf{n}} d_{n}^{\dagger}(\mathbf{n}). \qquad (3.9)$$

As is evident from Eq.(3.8), the magnitude of  $\Delta_n(\mathbf{k})$  depends on whether  $\mathbf{k}$  is parallel (longitudinal exciton) to or perpendicular (transverse exciton which couples with the photon) to the matrix element  $\mathbf{X}_{0n}$ .

Hexciton in Eq.(3.7) can be diagonalized exactly by a Bogolyubov transformation

$$B_{nk} = b_{nk} \cosh(\theta_{k}/2) + b_{n,-k}^{\dagger} \sinh(\theta_{k}/2)$$
(3.10)

Then

$$H_{\text{exciton}} = \sum_{n,k} \hbar \omega_{nk} B_{nk}^{\dagger} B_{nk}$$
(3.11)

with

$$\hbar\omega_{n\mathbf{k}} = \mathbf{E}_{n}^{\text{atom}} + \Delta_{n}(\mathbf{k}). \qquad (3.12)$$

The exciton-photon interaction Hamiltonian is given by

$$H_{\text{exciton-photon}} = -\frac{e}{mv} \sum_{\mathbf{n}} \sum_{\mathbf{i}} \mathbf{A}(\mathbf{n}+\mathbf{r}_{\mathbf{i}\mathbf{n}}) \cdot \mathbf{P}_{\mathbf{i}\mathbf{n}} + \frac{e^2}{2mv^2} \sum_{\mathbf{i}} \mathbf{A}(\mathbf{n}+\mathbf{r}_{\mathbf{i}\mathbf{n}})^2 \qquad (3.13)$$

where A is the vector potential, m is the electron mass, v is the speed of light in the medium, and  $r_{im}$  is the position of the i<sup>th</sup> electron in the atomic site m. The quantized form of Eq.(3.13) is obtained by expanding the vector potential according to

$$\mathbf{A}(\mathbf{m}+\mathbf{r}_{\mathbf{i}\mathbf{m}}) = \sum_{\mathbf{k}} \left\{ \frac{2\pi\hbar\mathbf{v}}{\mathbf{k}\mathbf{V}} \right\}^{1/2} \epsilon_{\mathbf{k}}^{\mathbf{a}}(\mathbf{a}_{\mathbf{k}}+\mathbf{a}_{-\mathbf{k}}^{\dagger}) \exp(\mathbf{i}\mathbf{k}\cdot\mathbf{m})$$
(3.14)

and using

$$\sum_{i} \mathbf{P}_{im} = -im \sum_{n} \sigma_{0n} \mathbf{X}_{0n} (\mathbf{d}_{n} - \mathbf{d}_{n}^{\dagger})$$
(3.15)

where 
$$\hbar\sigma_{0n} = E_n^{atom} - E_0^{atom}$$
. Then the total Hamiltonian in Eq.(3.3) becomes  

$$H = \sum_{k} \hbar v k (a_k^{\dagger} a_k + 1/2) + \sum_{k} \sum_{n} \hbar \omega_{nk} B_{nk}^{\dagger} B_{nk}$$

$$+ \sum_{k} \sum_{n} \left\{ i C_{nk} (a_k^{\dagger} + a_{-k}) (B_{nk} - B_{n,-k}^{\dagger}) + D_{nk} (a_k^{\dagger} + a_{-k}) (a_k + a_{-k}^{\dagger}) \right\}$$
(3.16)

where

$$C_{nk} = \hbar \sigma_{0n} \left\{ \frac{2\pi e^2 |\mathbf{X}_{0n}|^2}{\hbar \sigma_{0n}} \frac{N}{v} \frac{\omega_{nk}}{vk} \right\}^{(1/2)}, \qquad (3.17)$$

$$D_{nk} = \hbar \sigma_{0n} \frac{2\pi e^2 |\mathbf{X}_{0n}|^2}{\hbar \sigma_{0n}} \frac{N}{V} \frac{\sigma_{0n}}{vk}.$$
 (3.18)

The Hamiltonian in Eq.(3.16), based on the microscopic theory, has the same form as the phenomenological Hamiltonian 16,18 (which is not shown here). Comparison of them gives

$$\frac{\beta}{\epsilon_{\infty}} = \frac{2e^2 |\mathbf{X}_{0n}|^2}{\hbar\sigma_{0n}} \frac{N}{V}$$
(3.19)

Eq.(3.16) can be diagonalized exactly by generalized Bogolyubov's transformation<sup>16,29</sup>

$$\mathbf{a}_{\mathbf{k}} = \sum_{\mu} \left\{ \alpha_{\mu}(\mathbf{k}) \mathbf{Y}_{\mu}(\mathbf{k}) + \alpha_{\mu}^{\dagger}(-\mathbf{k}) \mathbf{Z}_{\mu}^{*}(-\mathbf{k}) \right\}$$
  
$$\mathbf{B}_{\mathbf{nk}} = \sum_{\mu}^{\mu} \left\{ \alpha_{\mu}(\mathbf{k}) \mathbf{u}_{\mu\mathbf{n}}(\mathbf{k}) + \alpha_{\mu}^{\dagger}(-\mathbf{k}) \mathbf{v}_{\mu\mathbf{n}}^{*}(-\mathbf{k}) \right\}, \quad \mu = \ell, \mathbf{u} \quad (3.20)$$

In this representation, Eq.(3.16) becomes

$$H = \sum_{\mu=l,u} \hbar \omega_{\mu}(\mathbf{k}) \alpha_{\mu}^{\dagger}(\mathbf{k}) \alpha_{\mu}(\mathbf{k}) + \text{const.} \qquad (3.21)$$

where  $\hbar w_{\mu}(\mathbf{k})$  is the exciton-polariton energy of the  $\mu^{\text{th}}$  branch (the indices  $\boldsymbol{l}$  and u indicate the lower and the upper polariton branch respectively) and is the root of Eq.(3.2) in case of single exciton

band. Hereafter, we consider only the single exciton band and the subscript will be suppressed. The transformation coefficients are given by

$$Y_{\alpha}(\mathbf{k}) = \frac{\mathbf{v}\mathbf{k} + \boldsymbol{\omega}_{\alpha}(\mathbf{k})}{2\left[\mathbf{v}\mathbf{k}\boldsymbol{\omega}_{\alpha}(\mathbf{k})\mathbf{L}_{\alpha\mathbf{k}}\right]^{1/2}}, \quad (\alpha = \ell, \mathbf{u}) \quad (3.22)$$

$$Z_{\alpha}(-\mathbf{k}) = \frac{\nabla \mathbf{k} - \omega_{\alpha}(\mathbf{k})}{\nabla \mathbf{k} + \omega_{\alpha}(\mathbf{k})} Y_{\alpha}(\mathbf{k}) , \qquad (3.23)$$

$$u_{\alpha}(\mathbf{k}) = i \left[ \frac{\pi \beta}{\epsilon_{\infty} \omega_{\alpha}(\mathbf{k}) \omega_{\mathbf{k}} L_{\alpha \mathbf{k}}} \right]^{1/2} \left[ \frac{\omega_{\alpha}(\mathbf{k}) + \omega_{\mathbf{k}}}{1 - \omega_{\alpha}(\mathbf{k})^{2} / \omega_{\mathbf{k}}^{2}} \right], \qquad (3.24)$$

$$L_{\alpha k} = \frac{4\pi\beta/\epsilon_{\infty}}{(1-\omega_{\alpha}^{2}(k)/\omega_{k}^{2})^{2}}, \qquad (3.25)$$

$$\mathbf{v}_{\alpha}(-\mathbf{k}) = -\left[\frac{\omega_{\mathbf{k}} - \omega_{\alpha}(\mathbf{k})}{\omega_{\mathbf{k}} + \omega_{\alpha}(\mathbf{k})}\right] \mathbf{u}_{\alpha}(\mathbf{k})$$
(3.26)

where

$$\hbar\omega_{\rm k} = \hbar\omega_{\rm 0} + \frac{\hbar^2 {\rm k}^2}{2m_{\rm e}}$$
(3.27)

and  $\hbar\omega_{\alpha}(\mathbf{k})$  is the polariton energy of the branch  $\alpha$  with wavevector  $\mathbf{k}$ .

## 3.3 Transport equations

Before writing down the transport equations, it will be appropriate to speculate on the qualitative aspects of the processes occurring inside Na<sup>+</sup>C222Na<sup>-</sup>. When the laser photons are incident on sodium cryptand sodide, they combine with the excitonic states of the solid to create exciton-polaritons. The transition  $(3S)^2 \longrightarrow 3S3P$  of the sodium negative ion is responsible for the excitonic state. Since the incident photon has a wavevector of small magnitude , it will populate the UPB initially (see Fig.3.1). These UPB polaritons are scattered by phonons into the UPB itself and into the LPB. The huge difference between the density of states of the LPB and UPB makes the LPB population dominant. The LPB polaritons are scattered by phonons into themselves and into the UPB. However the intra-branch scattering within the LPB dominates.

When the LPB polaritons are scattered by phonons they either lose energy (phonon emission) or gain energy (phonon absorption). Therefore the energy distribution of the polaritons becomes wider as the number of scatterings increases. This scattering process is similar to a random walk problem. On the average, the LPB polariton loses energy after experiencing a scattering with a phonon since the transition probability for a phonon emission is larger than the opposite process, the former being proportional to  $(N_p + 1)$  while the latter to  $N_p$  when  $N_p$  is the phonon occupation number.

With decreasing energy (wavevector), the magnitude of the density of states decreases. When the LPB polariton approaches the photon-like region (see Fig.3.1), the scattering rate reduces severely due to the small magnitude of the density of states and the wavevector. Thus in this region, the redshift of the LPB polariton's distribution slows down and with Na<sup>+</sup>C222Na<sup>-</sup> it apparently ceases to redshift after =30 nsec. This is the so-called bottle-neck phenomenon which was proposed by Toyozawa.<sup>19</sup>

From the above description it is evident that the population of the UPB polaritons is redshifting, which is represented as a redshifting fluorescence. In order for the polaritons to fluoresce, they have to escape from the crystal. With a smaller crystal, a polariton experiences a smaller number of scatterings with phonons before it leaves the crystal. Therefore a photon emerging from a smaller crystal has a higher

average energy, which qualitatively accounts for our crystal size dependent luminescence from Na<sup>+</sup>C222Na<sup>-</sup> in section 2.3.

It is well known that the strong coupling between photons and excitons<sup>16,18</sup> results in an exciton-polariton mode whose dispersion relation, in the isotropic case<sup>28</sup>, is given by Eq.3.2 or more explicitly<sup>27</sup>

$$n_{\ell,u}(\omega)^{2} = \frac{c^{2}k_{\ell,u}^{2}}{\omega^{2}}$$
$$= \frac{1}{2} \left[ \epsilon_{\omega}^{-} (1 - \frac{\omega^{2}}{\omega_{0}^{2}}) - \frac{m_{e}c^{2}\omega_{0}}{\hbar\omega^{2}} \right] \pm \left[ \frac{1}{4} \left\{ \epsilon_{\omega}^{+} (1 - \frac{\omega^{2}}{\omega_{0}^{2}}) - \frac{m_{e}c^{2}\omega_{0}}{\hbar\omega^{2}} \right\}^{2} + 4\pi\beta - \frac{m_{e}c^{2}\omega_{0}}{\hbar\omega^{2}} \right]^{1/2} (3.28)$$

where the + sign refers to  $n_{l}$ ,  $k_{l}$ , and the - sign refers to  $n_{u}$ ,  $k_{u}$  in Eq.(3.28). In this equation,  $n_{l}$  and  $n_{u}$  are the indices of refraction of the lower polariton branch (LPB) and upper polariton branch (UPB) respectively, c is the speed of light in vacuum,  $\vec{k}_{l,u}$  is the wave vector, and  $\beta$  satisfies<sup>15,18</sup> (from Eq.(3.8) and (3.19))

$$\Delta E_{LT} = E_{L}(0) - E_{T}(0) = \frac{2\pi\beta}{\epsilon_{\infty}} E_{T}(0)$$
(3.29)

Here,  $E_{T}(0) = \hbar \omega_{0}$  and  $E_{L}(0)$  are the transverse and longitudinal energy at k = 0 respectively.

Following Askary and Yu<sup>21</sup>, we did not introduce a phenomenological damping constant in Eqs. (3.2) and (3.28) because we include radiative and non-radiative loss terms explicitly in our transport equations.

Since the observed luminescence spectrum depends on the polariton distribution function at the boundary of the crystal, it is necessary to set up transport equations appropriate to polariton dynamics. The transport equations are greatly simplified if we adopt a model that has an isotropic and spatially uniform polariton distribution. The latter can be partially justified with the experimental data displayed in Fig.2.9 which shows that the normalized spectral distributions at illuminated and unilluminated positions are nearly identical. The position dependent amplitude factor can be effectively compensated for by adjusting the geometry of the crystal appropriately. This will become clear in the discussion below.

Let  $\mathbf{\tilde{f}}_{\alpha}(\mathbf{\vec{k}},t)d^{3}rd^{3}k$  be the number of polaritons at branch  $\alpha$  ( $\alpha$ - $\mathbf{l}$ , u) in the volume element  $d^{3}rd^{3}k$  at time t, position  $\mathbf{\vec{r}}$  and wavevector  $\mathbf{\vec{k}}$ . Then in the small  $\mathbf{\tilde{f}}_{\alpha}(\mathbf{\vec{k}},t)$  limit(weak excitation intensity limit) the transport equation for the LPB, after excitation by a laser pulse, is given by

$$\frac{\partial}{\partial t} \bar{f}_{l}(\vec{k},t) = \frac{V_{c}}{(2\pi)^{3}} \int d^{3}k' \{ \bar{\Psi}_{ll}(\vec{k}' \rightarrow \vec{k}) f_{l}(\vec{k}',t) - \bar{\Psi}_{ll}(\vec{k} \rightarrow \vec{k}') f_{l}(\vec{k},t) \} 
+ \frac{V_{c}}{(2\pi)^{3}} \int d^{3}k' \{ \bar{\Psi}_{ul}(\vec{k}' \rightarrow \vec{k}) f_{u}(\vec{k}',t) - \bar{\Psi}_{lu}(\vec{k} \rightarrow \vec{k}') f_{l}(\vec{k},t) \} 
- \frac{S_{c}}{V_{c}} \bar{\nabla}_{gl}(\vec{k}) \{ \bar{\Sigma}_{l}(\vec{k}) + \bar{\Gamma}_{l}(\vec{k}) \} \bar{f}_{l}(\vec{k},t) - \bar{R}_{l}(\vec{k}) \bar{f}_{l}(\vec{k},t) 
+ \frac{S_{c}}{V_{c}} \bar{\nabla}_{gu}(\vec{k}) \bar{\Gamma}_{u}(\vec{k}) \frac{g_{u}(E)}{g_{l}(E)} \bar{f}_{u}(\vec{k}'')$$
(3.30)

in which  $\mathbf{E}_{\underline{\ell}}(\vec{\mathbf{k}})=\mathbf{E}_{\mathbf{u}}(\vec{\mathbf{k}}'')=\mathbf{E}$  representing the same energy of the LPB and UPB that have different wavevectors. We obtain a similar equation for the UPB by exchanging the indices  $\underline{\ell}$  with u in Eq. (3.30). Here  $\bar{\mathbf{v}}_{g\alpha}(\vec{\mathbf{k}})$  is the group velocity of the polariton at branch  $\alpha$ ,  $\mathbf{V}_{c}$  and  $\mathbf{S}_{c}$  are the crystal volume and surface area respectively,  $\bar{\mathbf{R}}_{\alpha}(\vec{\mathbf{k}})$  is the non-radiative loss rate of the branch  $\alpha$ ,  $\bar{\mathbf{W}}_{\alpha\beta}(\vec{\mathbf{k}}'\rightarrow\vec{\mathbf{k}})$  is the transition rate due to scattering with phonons from polariton branch  $\alpha$  with wavevector  $\vec{\mathbf{k}}'$  to  $\beta$  with  $\vec{\mathbf{k}}$ ,  $\mathbf{g}_{\alpha}(\mathbf{E})$  is the density of states at branch  $\alpha$  and  $\bar{\mathbf{\Sigma}}_{\alpha}$  and  $\bar{\mathbf{\Gamma}}_{\alpha}$  will be defined later. In Eq. (3.30) the first term on the right hand side represents the intra-branch scattering in the LPB, the second term the inter-branch scattering from and to the UPB. The term  $(S_c/V_c)\bar{v}_{gl}(\vec{k})\bar{E}_{l}(\vec{k})\bar{F}_{l}(\vec{k},t)$ represents the radiative loss due to the transmission of polaritons into the vacuum as photons,  $(S_c/V_c)\bar{v}_{gl}(\vec{k})\vec{F}_{l}(\vec{k},t)$  is the inter-branch c on v e r s i on l o s s f r o m L P B t o U P B and  $(S_c/V_c)\bar{v}_{gu}(\vec{k})\bar{F}_{u}(\vec{k})(g_{u}(E)/g_{l}(E))\bar{F}_{u}(\vec{k}'',t)$  is the inter-branch conversion gain from UPB to LPB. (As in Ref.21 we have neglected the longitudinal exciton band in these transport equations, for simplicity. However, it is not neglected in calculating the transmission coefficient etc., in Section 3.5.)

All those processes that involve transmission to vacuum and the inter-branch conversion occur at the crystal to vacuum boundary. Therefore these terms are directly responsible for the crystal size dependence of the spectra that we have observed experimentally.

Since the experimental observations are usually made in terms of energy (or wavelength), it is convenient to rewrite Eq.(3.30) and its companion equation for the UPB in terms of energy instead of wavevector. We construct equations regarding the number of polaritons per unit energy interval,  $\phi_{\alpha}(E,t)$ . Then with

$$\phi_{\alpha}(\mathbf{E},t) = \mathbf{V}_{c} \mathbf{g}_{\alpha}(\mathbf{E}) \mathbf{f}_{\alpha}(\mathbf{k}(\mathbf{E}),t) = \mathbf{V}_{c} \mathbf{g}_{\alpha}(\mathbf{E}) \mathbf{f}_{\alpha}(\mathbf{E},t)$$
(3.31)

and

$$\frac{\mathbf{v}_{c}}{(2\pi)^{3}}\int d^{3}\mathbf{k}' \left\{ \bar{\mathbf{w}}_{\alpha\beta}(\vec{\mathbf{k}} \cdot \vec{\mathbf{k}}')\phi_{\alpha}(\mathbf{E}(\vec{\mathbf{k}}), t) = \int d\mathbf{E}' \mathbf{z}_{\alpha\beta}(\mathbf{E} \cdot \mathbf{E}')\phi_{\alpha}(\mathbf{E}, t) \right.$$
(3.32)

Eq.(3.30) becomes

$$\begin{aligned} \frac{\partial}{\partial t} \phi_{\underline{\ell}}(E,t) &= \int dE' \left\{ \phi_{\underline{\ell}}(E',t) Z_{\underline{\ell}\underline{\ell}}(E' \rightarrow E) - \phi_{\underline{\ell}}(E,t) Z_{\underline{\ell}\underline{\ell}}(E \rightarrow E') \right\} \\ &- \left\{ \frac{S_{c}}{V_{c}} v_{\underline{g}\underline{\ell}}(E) \left[ \Sigma_{\underline{\ell}}(E) + \Gamma_{\underline{\ell}}(E) \right] + R_{\underline{\ell}}(E) \left\{ \phi_{\underline{\ell}}(E,t) + \int dE' \left\{ \phi_{\underline{u}}(E',t) Z_{\underline{u}\underline{\ell}}(E' \rightarrow E) - \phi_{\underline{\ell}}(E,t) Z_{\underline{\ell}\underline{u}}(E \rightarrow E') \right\} \end{aligned}$$

and there is a corresponding equation for the UPB, where

$$v_{gl}(E(\vec{k})) = \bar{v}_{gl}(\vec{k})$$
 etc. (3.34)

In the equation for the UPB we neglect the intra-branch scattering since, because of the small density of states and the small magnitude of the wavevector of the UPB, it is much smaller than the inter-branch scattering rate. (See the expression for  $\bar{\Psi}_{\alpha\beta}(\vec{k}' \rightarrow \vec{k})$  below and the intrabranch scattering term in Eq.(3.30).)

The expression for the polariton scattering rate with longitudinal acoustic phonons has been taken from Ref.29 as follows (we consider only LA phonons as the dominant scattering source responsible for the polariton evolution while scattering with optical phonons is assumed to occur just after the excitation by the laser pulse) :

$$\begin{split} \bar{\mathbb{W}}_{\alpha\beta}(\vec{k}' \rightarrow \vec{k}) = (\frac{2\pi}{\hbar}) \left(\frac{\hbar D^2}{2\rho\mu V_c}\right) q \Lambda_{\alpha\beta}(\vec{k}' \rightarrow \vec{k}) \left[ N_p(\hbar\mu q) \delta(E_f - E_i - \hbar\mu q) + [N_p(\hbar\mu q) + 1] \delta(E_f - E_i + \hbar\mu q) \right] \quad (3.35) \end{split}$$

where  $q = |\vec{k}' - \vec{k}|$ ,  $\mu$  is the speed of sound, D the exciton deformation potential,  $\rho$  the density of the crystal,  $N_p(\hbar\mu q)$  the number of the phonons per state with energy  $\hbar\mu q$  at a given temperature,  $E_i(E_f)$  the initial(final) state polariton energy and  $\Lambda_{\alpha\beta}(\vec{k}' \rightarrow \vec{k})$  is given by

$$\Lambda_{\alpha\beta}(\vec{k}' \rightarrow \vec{k}) = \left| u_{\beta}^{*}(\vec{k}) u_{\alpha}(\vec{k}') + v_{\beta}(\vec{k}) v_{\alpha}^{*}(\vec{k}') \right|^{2}$$
$$= \Lambda_{\beta\alpha}(\vec{k} \rightarrow \vec{k}') \quad . \tag{3.36}$$

In evaluating the inter-branch scattering terms due to LA phonons in Eq.(3.33), we have adopted some simplifying approximations from Ref.29. Owing to the small magnitude of the LA phonon wave vector in the region

of interest, the inter-branch scattering was regarded as elastic and in considering the intra-branch scattering, we have neglected the change in the magnitude of the LPB polariton wave vector after being scattered by a phonon. (See Section III.A of Ref.29 for details.) Then we have

$$\int dE' \phi_{u}(E',t) Z_{ul}(E' \rightarrow E) = \Delta(E) g_{l}(E) k_{l}(E) \phi_{u}(E,t) \Theta(E-E_{l})$$
(3.37)

$$\int dE' \phi_{l}(E,t) Z_{lu}(E \rightarrow E') = \Delta(E) g_{u}(E) k_{l}(E) \phi_{l}(E,t) \Theta(E-E_{L})$$
(3.38)

and the corresponding equations for the UPB. Here

$$\Delta(E) = \left[\frac{\pi D^2}{\rho \mu}\right] \left[2N_p(\hbar \mu k_l(E)) + 1\right] \Lambda_{ul}(k_u(E) \rightarrow k_l(E))$$
(3.39)

and  $k_{\alpha}(E)$  is the wavevector of the polariton branch  $\alpha$  whose energy is E.

The intra-branch (LPB) scattering term due to LA phonons in Eq.(3.33) plays a very important role in determining the time evolution of the polariton luminescence. By its appearance only, we see that the LPB polaritons are undergoing a diffusion process in energy space. (If we relax the condition of a spatially uniform distribution, polaritons will also diffuse over space.) We can simplify the intra branch scattering term in a manner analogous to the procedure used for deriving the Fokker-Planck equation.<sup>30</sup> For this purpose we define, for  $\epsilon > 0$ ,

$$Z_{gg}(E \rightarrow E + \epsilon) = Z_{+}(E;\epsilon) \qquad (3.40)$$

and

$$Z_{00}(E \rightarrow E - \epsilon) = Z_{(E;-\epsilon)}$$
(3.41)

Then since in our approximation(see Ref.29)

$$q = |\vec{k}' - \vec{k}| = 2k \sin(\phi/2)$$
 (3.42)

where  $\phi$  is the angle between  $\vec{k}$ ' and  $\vec{k}$ , we have

$$0 \le \epsilon \le 2k\hbar\mu = \epsilon_{\rm m} \tag{3.43}$$

Therefore the first term on the right hand side of Eq.(3.33) is approximated by

$$\int dE' \left\{ \phi_{\ell}(E',t) Z_{\ell\ell}(E' \rightarrow E) - \phi_{\ell}(E,t) Z_{\ell\ell}(E \rightarrow E') \right\}$$

$$= \frac{\partial}{\partial E} \left[ \phi_{\ell}(E,t) \int_{0}^{\epsilon_{m}} dS \cdot S \left\{ Z_{-}(E;-S) - Z_{+}(E;S) \right\} \right]$$

$$+ \frac{1}{2} \frac{\partial^{2}}{\partial E^{2}} \left[ \phi_{\ell}(E,t) \int_{0}^{\epsilon_{m}} dS \cdot S^{2} \left\{ Z_{-}(E;-S) + Z_{+}(E;S) \right\} \right] \qquad (3.44)$$

and for 
$$E' \geq E$$

$$\int_{\mathbf{E}' \geq \mathbf{E}} \int_{\mathbf{E}' \geq \mathbf{E}'} \int_{\mathbf{E}' \geq \mathbf{E}' \geq \mathbf{E}' \geq \mathbf{E}' \geq \mathbf{E}'} \int_{\mathbf{E}' \geq \mathbf{E}' \geq \mathbf{E}' \geq \mathbf{E}' = \mathbf{E}$$

where

$$d^{3}k_{l}^{\prime}(E) = k_{l}^{\prime}^{2}(E) dk_{l}^{\prime}(E) d\Omega \qquad (3.46)$$

Thus we obtain

$$Z_{+}(E;\epsilon) = \left(\frac{\pi D^{2}}{\rho \mu}\right) \Lambda_{ll}(\vec{k}_{l}(E) \rightarrow \vec{k}_{l}(E)) \frac{g_{l}(E)N_{p}(\epsilon)\epsilon^{2}}{2k_{l}^{2}(E)(\hbar \mu)^{3}}$$
(3.47)

and a corresponding expression for  $Z_{(E;-\epsilon)}$  with  $N_{p}(\epsilon) \rightarrow (N_{p}(\epsilon)+1)$ .

Combining Eqs.(3.33), (3.37)-(3.39), (3.44) and (3.47), we obtain the following balance equations for the lower and upper polaritons:<sup>15</sup>

$$\frac{\partial}{\partial t} \phi_{\underline{l}}(E,t) = \frac{\partial}{\partial E} \{ A(E) \phi_{\underline{l}}(E,t) \} + \frac{1}{2} \frac{\partial^2}{\partial E^2} \{ H(E) \phi_{\underline{l}}(E,t) \}$$
  
-  $B(E) \phi_{\underline{l}}(E,t) + C(E) \phi_{\underline{u}}(E,t) , \qquad (3.48)$ 

$$\frac{\partial}{\partial t} \phi_{u}(E,t) = -\beta(E) \phi_{u}(E,t) + \alpha(E) \phi_{l}(E,t) \qquad (3.49)$$

where

$$\alpha(\mathbf{E}) = \left[ \frac{\mathbf{S}_{c}}{\mathbf{V}_{c}} \mathbf{v}_{g} \mathbf{l}^{(\mathbf{E})} \mathbf{\Gamma}_{\mathbf{l}}^{(\mathbf{E}) + \Delta(\mathbf{E})} \mathbf{g}_{u}^{(\mathbf{E})} \mathbf{k}_{\mathbf{l}}^{(\mathbf{E})} \right] \Theta(\mathbf{E} - \mathbf{E}_{L}) , \qquad (3.50)$$

$$\beta(\mathbf{E}) = \left[\frac{S_{c}}{V_{c}} \mathbf{y}_{u}(\mathbf{E}) \left\{ \Sigma_{u}(\mathbf{E}) + \Gamma_{u}(\mathbf{E}) \right\} + R_{u}(\mathbf{E}) + \Delta(\mathbf{E}) \mathbf{g}_{l}(\mathbf{E}) \mathbf{k}_{l}(\mathbf{E}) \right] \Theta(\mathbf{E} - \mathbf{E}_{L}) , \quad (3.51)$$

$$A(E) = \left(\frac{D^2}{\pi\rho}\right) \frac{k_{\ell}^4}{v_{g\ell}(E)} \Lambda_{\ell\ell}(k_{\ell}(E) \rightarrow k_{\ell}(E)) , \qquad (3.52)$$

$$B(E) = \frac{S_c}{V_c} g_l(E) \left\{ \sum_{l} (E) + \Gamma_l(E) \right\} + R_l(E) + \Delta(E) g_u(E) k_l(E) \Theta(E - E_l) , \qquad (3.53)$$

$$C(E) = \left[\frac{S_{c}}{V_{c}} v_{gu}(E) \Gamma_{u}(E) + \Delta(E) g_{l}(E) k_{l}(E)\right] \Theta(E - E_{L}) , \qquad (3.54)$$

and

$$H(E) = \left(\frac{\pi D^{2}}{\rho \mu}\right) \Lambda_{II}(k_{I}(E) \rightarrow k_{I}(E)) \frac{g_{I}(E)}{2k_{I}^{2}(E)(\hbar \mu)^{3}} \int_{0}^{2\hbar \mu k_{I}(E)} \left\{2N_{p}(S) + 1\right\} S^{4} dS . \qquad (3.55)$$

The intra-branch scattering within the UPB has been neglected in Eq.3.49. (See the comments following Eq.3.34.) In Eq.3.48 the terms involving A(E) and H(E) represent the intra-branch scattering of the polaritons with LA phonons. They are independent of the crystal geometry and the process represented by them is similar to the random walk problem. Also,  $-B(E)\phi_{j}(E,t)$  in Eq.3.48 and  $-\beta(E)\phi_{u}(E,t)$  in Eq.3.49 represent the LPB and UPB loss and include radiative, non-radiative, inter-branch conversion and the inter-branch scattering contributions. Among these, the radiative losses and the inter-branch conversion occur at the crystal to vacuum boundary. The terms  $C(E)\phi_{u}(E,t)$  and  $\alpha(E)\phi_{j}(E,t)$ represent, respectively, the gain from the UPB and the LPB which is caused by the inter-branch conversion and the inter-branch scattering by the phonons. As for the non-radiative decay rate  $R_{\alpha}(E)$  due to either lattice defects or impurities, we have taken Sumi's expression<sup>20</sup> which is given by

$$R_{\alpha}(E) = R_{\alpha 0} \left| u_{\alpha}(E) \right|^{2}$$
(3.56)

where  $R_{\alpha 0}$  is a constant.

## 3.4 Approximate solutions

Since the photons incident on the crystal are converted into excitons at t=0, the initial conditions will be

$$\phi_{ij}(E,0)=0 \text{ and } \phi_{j}(E,0)=0$$
 (3.57)

Therefore

$$\phi_{u}(E,t) = \alpha(E)e^{-\beta(E)t} \int_{0}^{t} e^{\beta(E)t'} \phi_{\ell}(E,t')dt' \qquad (3.58)$$

Equation (3.48) for the LPB population in its present form is difficult to solve. The terms  $-B\phi_{l}$  and  $C\phi_{u}$  contribute to the loss and gain respectively. Without those loss and gain terms, Eq.(3.48) becomes a Fokker-Planck equation that describes the diffusion of LPB polaritons in energy space. And our earlier choice of  $\phi_{l}(E,t)$  is compatible with this picture in the respect that the integration of  $\phi_{l}(E,t)$  over the entire energy space gives a time independent constant in the absence of loss and gain terms, as is readily checked with Eq.(3.30). Consequently, the two terms including A(E) and H(E) are crucial in determining the time evolution of the observed line shape. (Of course the line shape is determined not only by population but also by other factors such as the transmission coefficient.)

Therefore we approximate  $\phi_{j}$  by the product of a steep energy dependent part G(E,t) determined by the Fokker-Planck equation and an overall time evolution part  $\Omega(E,t)$  which is dominated by gain and loss terms. We write

$$\phi_{l}(E,t) = \Omega(E,t)G(E,t), \quad \frac{\partial\Omega}{\partial E} = 0$$
 (3.59)

and the equation for G(E,t) is chosen to be

$$\frac{\partial}{\partial t}G(E,t) = \frac{\partial}{\partial E} \left\{ A(E)G(E,t) \right\} + \frac{1}{2} \frac{\partial^2}{\partial E^2} \left\{ H(E)G(E,t) \right\}$$
(3.60)

Then we obtain

$$\phi_{f}(E,t) = G(E,t)e^{-Bt} \cdot \{1+C \int_{0}^{t} e^{Bt'} \frac{\phi_{u}(E,t')}{G(E,t')}dt'\}$$
(3.61)

Therefore, in this approximation our problem reduces to solving the Fokker-Planck equation given by Eq.(3.60) and solving Eq.(3.58) and (3.61) simultaneously. As a further approximation for solving Eq.(3.60), we can replace A(E) and H(E) with  $A(E_m)$  and  $H(E_m)$  where  $E_m$  is the energy at which the maximum of G(E,t) occurs at time t. This is a reasonable approximation because the FWHM of the experimental line shape is about 28 meV while the energy range in which polaritons evolve is about 310 meV (from 2.1 eV to 1.79eV). (The FWHM of the function G(E,t=30ns) is about 50 meV (Fig.3.3) by this approximation with the parameters in Table 4.1) Consequently A(E) and H(E) are treated as if they were functions of time since  $E_m=E_m(t)$ . Hence Eq.(3.60) is rewritten as

$$\frac{\partial}{\partial t}G(E,t) = A(E_{m}(t))\frac{\partial}{\partial E}G(E,t) + \frac{1}{2}H(E_{m}(t))\frac{\partial^{2}}{\partial E^{2}}G(E,t)$$
(3.62)

In order to solve Eq.(3.62) we define  $\xi(t)$  and v(t) as follows:

$$\xi(t) = \int \frac{dE}{A(E)} = t , \qquad (3.63)$$

$$\xi(t) - \int \frac{H(E)}{A(E)} d(E) = v(\xi(t)) = v(t)$$
 (3.64)  
  $E_0$ 

where  $\xi = \xi(E_0, t) = \xi(t)$  and  $E_0$  is the appropriate initial onset energy (taken as a parameter) at which the diffusion of polaritons by the scattering with LA phonons begins. (This initial onset energy can be lower than the laser excitation energy since polaritons are scattered by optical phonons at very early times.) Then we see that

$$G(E,t) = \frac{1}{\sqrt{[\nu(t)]}} e^{-\frac{(E-\xi(t))^2}{2\nu(t)}}$$
(3.65)

satisfies Eq.(3.62) with

$$E_{m}(t) = \xi(t)$$
 (3.66)

Thus we see that  $E_m(t)$  is indeed the maximum energy corresponding to the peak of G(E,t) at time t. With Eq.(3.63) it is evident that the maximum energy decreases monotonically as time increases and that the rate of change slows down since the magnitude of A(E) becomes smaller at smaller energies. As was mentioned in the beginning of the Section 3.3, the overall intra-branch scattering rate of the LPB is proportional to the density of states and the magnitude of the LPB wavevector, k. (See Eqs.3.35 and 3.42.) Both factors decrease simultaneously with decreasing energy (see Fig.3.1). Therefore the rate of energy decrease slows down with decreasing energy also. When the LPB polariton approaches the photon-like region of the dispersion curve, the extremely small values of the factors render the energy change rate negligible.

Eqs.(3.58) and (3.61) for  $\phi_u(E,t)$  and  $\phi_l(E,t)$  can be solved by iteration, for  $E > E_L$ . Since G(E,t) approaches its long time value rapidly (Fig.3.2), it can be approximated by its latest value when it appears in the integrand of Eqs.(3.58) and (3.61). Then we have

$$\phi_{u}^{(N)}(E,t) = \alpha e^{-\beta t} \int_{0}^{t} e^{\beta t'} \phi_{l}^{(N-1)}(E,t') dt', \quad (N \ge 1) \quad (3.67)$$

$$\phi_{\underline{\ell}}^{(N)}(E,t) = Ge^{-Bt} + Ce^{-Bt} \int_{0}^{t} e^{Bt'} \phi_{\underline{u}}^{(N)}(E,t')dt', \quad (N \ge 1) \quad (3.68)$$

where  $\phi_{\alpha}^{(N)}(E,t)$ ,  $\alpha=1,u$ , denotes the value of  $\phi_{\alpha}(E,t)$  obtained after



Fig.3.2 Theoretical time evolution of the function G(E,t) at energies (1) 1.91eV and (2)1.926eV.



Fig.3.3 Energy dependence of (1) multiplicative factor  $T_{l}v_{gl}/n_{l}^{2}$ ; (2) G(E,t=lnsec); and (3)G(E,t=30nsec).

performing the N-th integration. Obviously, the LPB population  $\phi_{l}(E,t)$ dominates over the UPB  $\phi_{u}(E,t)$ , since the probability for a transition from the LPB to the UPB is much smaller than the opposite transition due to the difference in density of final states.(Eqs.(3.37), (3.38) and the corresponding equations for the UPB) Hence we choose

$$\phi_{l}^{(0)}(E,t) = G(E,t)e^{-B(E)t}, \qquad (3.69)$$

$$\phi_{\rm u}^{(0)}$$
 (E,t)=0 . (3.70)

Successive iteration with the terms of small contribution neglected leads to a convergent result that is given by

$$\phi_{l}(E,t) \approx G(E,t)e^{-\left(B-\frac{\alpha C}{\beta-B}\right)t}, \qquad (3.71)$$

$$\phi_{u}(E,t) = G(E,t) \cdot \frac{\alpha}{\beta} \cdot \left\{ e^{-\left[B - \frac{\alpha C}{\beta - B}\right]t} - e^{-\beta t} \right\}.$$
(3.72)

Eqs.(3.71) and (3.72) give self-consistent results when inserted into Eqs.(3.58) and (3.61) since  $\beta >> B$  and  $\beta >> \alpha C/\beta$ .

## 3.5 Radiative loss and inter branch conversion of the polariton

The transmission coefficient as a function of energy and incident angle of the polariton directly determines the radiative loss, and this has been considered by many workers.<sup>19-21</sup> A larger transmission means a larger radiative loss. Therefore it has a simple relationship with  $\Sigma_{\alpha}(E)$ :

$$\Sigma_{\alpha}(E) = \frac{1}{2} \int_{0}^{\Theta_{\alpha}^{T}} \cos\Theta\sin\Theta_{\alpha}(E;\Theta) d\Theta , \quad (\alpha = \ell, u) \quad (3.73)$$

where  $T_{\alpha}(E;\theta)$  is the transmission coefficient of the polariton branch  $\alpha$ at energy E with an incident angle of  $\theta$ . In the same way the interbranch conversion rate is given by

$$\Theta_{\alpha}^{\text{IC}} = \frac{1}{2} \int_{0}^{\alpha} \cos\Theta\sin\Theta I_{\alpha\beta}(E;\Theta) d\Theta, \quad (\alpha\beta = \text{lu or ul}) \quad (3.74)$$

where  $I_{\alpha\beta}(E;\Theta)$  is the inter-branch conversion coefficient from polariton branch  $\alpha$  to  $\beta$ ,  $\alpha \neq \beta$ , at energy E with incident angle  $\Theta$ . In Eqs.(3.73) and (3.52) the angles  $\Theta_{\alpha}^{T}$  and  $\Theta_{\alpha}^{IC}$  are determined by the relations

$$in\Theta_{\alpha}^{T} = \frac{1}{n_{\alpha}(E)}$$
,  $(\alpha = \ell, u)$  (3.75)

and

$$\sin \Theta_{l}^{IC} = \frac{n_{u}(E)}{n_{l}(E)}, \quad \sin \Theta_{u}^{IC} = \frac{\pi}{2} \quad \text{for } E \ge E_{L}$$
 (3.76)

Here for an angle greater than  $\Theta_{\alpha}^{T}$ , total reflection occurs. And for an angle greater than  $\Theta_{\ell}^{IC}$ , the wave vector of the polariton converted from the LPB to the UPB becomes complex with a pure imaginary component which is normal to the surface. It is given by

$$[k_{u}^{R}]_{z} = -ik_{l}^{I} [\sin^{2}\theta - \sin^{2}\theta_{l}^{IC}]$$
(3.77)

(see Ref.31 for a similar argument in the case of total reflection) where  $k_{l}^{I}$  is the magnitude of the incident LPB polariton. Therefore for  $\Theta > \Theta_{l}^{IC}$  the converted UPB polaritons do not propagate and there is no inter-branch conversion from the LPB to the UPB.

Following Selkin,<sup>32</sup> the transmission coefficient has been obtained by taking the ratio of the magnitude of the time averaged transmitted energy flux to the magnitude of the incident flux. (In our case we are considering the transmission from inside the crystal to vacuum.) The inter branch conversion coefficient has been similarly obtained. Using
the expression for the time averaged energy flux of Ref.32 we find explicitly:

$$T_{\alpha}(E;\Theta) = \left| \frac{E_{\alpha}^{T}}{E_{\alpha}^{I}} \right|^{2} \left| \frac{\operatorname{Re}(k_{\alpha}^{T})}{\operatorname{Re}(k_{\alpha}^{I})} \right| \frac{1}{[1+\zeta\chi_{\alpha}^{2}]}$$
(3.78)

and

$$I_{\alpha\beta}(E;\Theta) = \left| \frac{E_{\beta}^{R}}{E_{\alpha}^{I}} \right|^{2} \left| \frac{\operatorname{Re}(k_{\beta}^{R})}{\operatorname{Re}(k_{\alpha}^{I})} \right|^{\frac{1+\zeta \chi_{\beta}^{2}}{1+\zeta \chi_{\alpha}^{2}}}, \quad (\alpha,\beta=\ell, u \text{ and } \alpha\neq\beta) \quad (3.79)$$

where

$$\chi_{\alpha} = (n_{\alpha}^{2} - \epsilon_{\infty}) / 4\pi \quad \text{and} \quad \zeta = \frac{4\pi\hbar\omega^{2}}{\beta m_{e}c^{2}\omega_{0}}$$
(3.80)

and  $E_{\alpha}^{I}$  is the incident electric field amplitude of the branch  $\alpha$  with angle  $\Theta$ ,  $E_{\alpha}^{T}$  is the corresponding transmitted vacuum amplitude,  $E_{\beta}^{R}$  is the converted (reflected) amplitude inside the crystal and the k's are the wavevectors that carry a similar meaning.

In evaluating the various ratios of the electric fields for Eqs.(3.79) and (3.80), we have used Pekar's ABC (Additional Boundary Condition) (see Ref.21 and the references therein for a discussion of the ABC). In the case of p-polarization, we have included the contribution from the longitudinal exciton band also. Then we have used the average value over s- and p-polarizations for  $T_{\alpha}$  and  $I_{\alpha\beta}$ . 4. Comparison of the theory with experiment

#### 4.1 Time resolved lineshapes

We begin our discussion with the expression of the line shape from polariton luminescence. When the luminescence signal is collected with a fixed small solid angle  $\Delta\Omega_{ex}$  at normal emergence of the luminescence, we have<sup>23,29</sup> as the relationship for the line shape I(E,t)

$$I(E,t)\Delta\Omega_{ex}\Delta E = \sum_{\alpha=\ell,u} T_{\alpha}(E;0) v_{g\alpha}(E) g_{\alpha}(E) f_{\alpha}(E) \frac{\Delta\Omega_{ex}}{n_{\alpha}^{2}(E)}$$
(4.1)

or

$$I(E,t) \propto \sum_{\alpha=l,u} \frac{\frac{T_{\alpha}(E;0)v_{g\alpha}(E)}{n_{\alpha}^{2}(E)}}{\phi_{\alpha}(E,t)} \qquad (4.2)$$

Since  $\beta(E) >> \alpha(E)$  through the contribution of the density of states, the surface terms (radiative loss and inter branch conversion) and the non-radiative decay term (see Eqs.(3.50) and (3.51)) we have  $\phi_{\downarrow}(E,t) >> \phi_u(E,t)$ . Therefore the main contribution to the total luminescence arises from the LPB even with the multiplicative terms  $T_{\alpha}(E;0)v_{g\alpha}(E)/n_{\alpha}^{2}(E)$ . (However, it should be noted that without the surface terms and the non-radiative loss term in Eqs.(3.50) and (3.51), the UPB makes an equally important contribution to the total luminescence due to the modulating multiplicative factors.) Therefore, as was pointed out by Askary and Yu,<sup>21</sup> the UPB mainly manifests itself not through a sizable luminescence in comparison to the LPB but by affecting the transmission coefficient of the LPB through the additional boundary condition and affecting the overall decay rate of the LPB which depends on the ABC through the surface terms. Since in the region of interest  $\phi_{\underline{l}}(E,t)$  and G(E,t) are increasing functions of energy and  $T_{\underline{l}}(E;0)v_{\underline{g}\underline{l}}(E)/n_{\underline{l}}^{2}(E)$  is a rapidly decreasing function of energy (see Fig.3.3) their product shows a curve that has a well defined peak which shifts in time according to the evolution of the function G(E,t). It is worth emphasizing that the observed luminescence distribution is different from the polariton population distribution because of the extremely small overall escape probability of LPB polaritons due to their excitonic nature at higher energy.

Fig. 4.1 shows a theoretical plot of the energy at maximum intensity as a function of time with the parameters given in Table 4.1 and Fig.4.2a shows the time evolution of the line shape from 1 nsec to 30nsec. They show a very good agreement with the experimental observation shown in Fig.4.2b and reported in Ref.5. Fig.4.2b shows the corresponding experimental time resolved line shapes from a large (~1mm in size) crystal. In choosing the parameters listed in Table 4.1, the non-radiative decay loss constant,  $R_{\alpha 0}$ , defined in Eq.(3.56) had to be fixed at 2x10<sup>8</sup>/sec for a shiny bright golden colored (of best quality) and large (=1mm in size) crystal in order to match the long lifetime of about 5ns measured in Ref.5. This value of  $R_{\alpha 0}$  is required because the radiative decay loss rate of the LPB decreases severely near and above the longitudinal exciton band minimum energy for reasonable combinations of parameters. (See below for the discussion of the lifetimes.) Therefore it can be said that the long lifetimes of the shiny bright golden colored and large (~1mm in size) crystals of Ref.5 are mainly determined by lattice defects and impurities, according to the parameter combination of Table 4.1.

Table 4.1 Physical parameters used for constructing theoretical curves

4.2 Time evolution at fixed energies

In order to make a direct comparison with experiment it is very helpful to examine the time evolution of the luminescence at fixed energies, in addition to the information shown in Fig.4.1 and 4.2.

Eq.(4.2) for the total luminescence becomes approximately

$$I(E,t) = \text{Const.} \frac{T_{\ell}(E;0)v_{g\ell}(E)}{n_{\ell}^{2}(E)} G(E,t)e^{-\left[B-\frac{\alpha C}{\beta-B}\right]t}$$
$$= \text{Const.}F(E,t)e^{-\left[B-\frac{\alpha C}{\beta-B}\right]t}$$
$$= F_{0}(E,t)e^{-k_{1}t}e^{-\left[B-\frac{\alpha C}{\beta-B}\right]t}$$
$$= F_{0}(E-\eta(t))e^{-k_{1}t}e^{-\left[B-\frac{\alpha C}{\beta-B}\right]t}$$
(4.3)

When  $B(E) - \alpha(E)C(E)/(\beta(E)-B(E))$  in Eq.(4.3) changes slowly in the region of interest, which conforms to our case, the line shape at each instant is determined by the function F(E,t). Fig.3.3 indicates that the product of the curves (1) and (3) (30 ns) has larger magnitude than the product of the curves (1) and (2) (1 ns), which shows that the function F(E,t)is an increasing function of time. Therefore in Eq.(4.3) we have used the factorized form for F(E,t) in which the function  $F_0(E,t)$  is assumed to represent the normalized line shape at each instant. The choice of the exponential form,  $\exp(k_1t)$ , for the growth of the function F(E,t) is for comparison with lifetime measurements. However, since  $F_0(E,t)(F(E,t))$  is a shifting function (Fig.4.2a) with its peak energy defined by curve 2 in Fig.4.1, its time dependence at fixed energies is represented by two different aspects (Fig.4.3). At energies (for example curves (4) and (5) in Fig.4.3) higher than  $E_c$ , which is the peak



Fig.4.1 The (theoretical) time evolution of the maximum intensity energy, (1)  $\xi$ (t) of the function G(E,t) and (2)  $\eta$ (t) of the luminescence line shape with the parameters in Table 4.1. The squares are the experimental peak energy positions of the line shapes taken from Ref.5.



Fig.4.2 (a) The theoretical and (b) experimental time resolved line shapes (1) I(E,t=1nsec), (2)I(E,t=3nsec), (3) I(E,t=6nsec) and (4)I(E,t=30nsec).

intensity energy of the function  $F_0(E,t)$  at long time (about 30 nsec),  $F_0(E,t)$  increases to the maximum (which occurs when the peak intensity energy,  $\eta(t)$ , coincides with that energy E, if the 4th equality in Eq.(4.3) is exact) followed by a decrease to its long time value  $F_0(E,t=30nsec)$ . For  $E < E_c$  (for example curve (1) in Fig.4.3),  $F_0(E,t)$ gradually increases to  $F_0(E,t=30nsec)$ , because in this case the peak intensity energy never coincides with that energy, E. Note that G(E,t)behaves in the same manner as  $F_0(E,t)$  with  $E_c$  replaced by  $E_f$  which is the peak energy of the polariton distribution at long time (see Fig.3.2.).

From the above argument it is obvious that the time evolution of the polariton luminescence described by these equations shows a very rapid increase followed by a rapid decrease at high energy and a slow growth followed by a slow decay at low energy. Fig.4.4 shows such a behavior. (Fig.4.4a was plotted using Eq. (4.2).) Fig.4.4b shows the experimental data (from a large (=lmm in size) and shiny bright golden colored crystal) which show narrower widths than in Fig.4.4a. This quantitative deviation is due to the slow increase of the function F(E,t) in our theory. A different combination of parameters may reduce this deviation.

In the work of Ref.5, the experimental time decay data were fitted in terms of a double exponential decay. In the present case, we can also approximate our theoretical solution in terms of a double exponential decay. This can be achieved by writing

$$F_{o}(E,t)=F_{o}(E,t=30nsec)+\delta(E)e^{-\sigma(E)t}$$
(4.4)

An examination of Fig.4.3 shows that the approximation of Eq.(4.4) is a reasonable one. We see that for  $E < E_c$ ,  $\delta(E) < 0$  and for energies much



Fig.4.3 Time dependence of the function  $F_0(E,t)=G(E,t)(T_lv_{gl}/n_l^2)EXP(-k_1t)$  with  $k_1=1\times10^7/sec$  at (1) E =1.798eV, (2) E =1.814eV (3) E=1.842eV, (4) E =1.874eV and (5) E =1.89eV.



Fig.4.4 (a)Theoretical time decay of luminescence intensity the I(E,t) at (1) E =1.89eV .(2) E =1.874eV. (3) E =1.854eV. (4) E=1.834eV. (5) E =1.818eV and (6) E =1.802eV with the parameters in Table 1. (b)Experimental counterparts: (1)IRF. (2)E =1.868eV. (3)E =1.850eV. (4)E =1.841 eV. (5)E =1.832eV and (6)E =1.814eV.

higher than  $E_c$  (for example, E = 1.874, 1.89 eV in Fig.4.3,  $\delta(E) > 0$  if we use Eq.(4.4) for the range of time after  $F_0(E,t)$  has attained its maximum value. However for the range of energies which are higher than  $E_c$  but close to  $E_c$ , it is better to approximate  $F_0(E,t)$  with positive  $\delta(E)$  (for example, E = 1.842 eV in Fig.4.3.) If Eq.(4.4) were an identity, we obviously would have  $\delta(E) = -F_0(E,t=30 \text{nsec})$  for  $E < E_c$ , since G(E,t) approaches zero as time goes to zero for the energy range of interest. Therefore we have a rough estimate of

$$\delta(E) \propto -F_{c}(E, t=30nsec)$$
(4.5)

Now we identify  $1/[(B-\alpha C/(\beta-B))-k_1]$  as the long lifetime,  $F_0(E,t=30nsec)$  as the pre-exponential factor of the long lifetime,  $1/(B-\alpha C/(\beta-B)-k_1+\sigma)$  as the short lifetime and  $\delta(E)$  as the preexponential factor of the short lifetime. Consequently, this provides a natural explanation for the experimental data in Ref.5 which implies the coincidence of the three peak positions of the pre-exponential factors and the long time line shape: all these peaks occur around 1.835eV which corresponds to  $E_c$  in the present case.

Eq.(4.2) was fitted with a double exponential form to obtain Fig.4.5, with the long lifetime  $1/((B-\alpha C/(\beta-B))-k_1)$  fixed at 5.26 ns (with  $k_1=1\times10^7$ /sec). The decrease of short lifetime at high energy in Fig.4.5a is associated with the fact that at higher energy the rate of peak energy decrease is larger. The latter is due to the larger density of states and the wavevector of the LPB at higher energy. (See Eqs.(3.52) and (63).) Therefore at higher energy the function  $F_0(E,t)$ ascends quickly and also descends quickly so that it is represented by a smaller short lifetime. Fig.4.5b shows the theoretical and experimental ratios of the short lifetime pre-exponential factor to the long one. Again their quantitative deviation is due to the slow increase of the function F(E,t) in our theory. Nevertheless, the qualitative comparison shows good agreement: both ratios are negative at low energy and positive at higher energy.

In short, the continuous red shift of the polariton distribution arising from the scattering of the acoustic phonons results in the red shift of the observed luminescence. And this is also represented as the fast decay at high energy and the slow decay at low energy.

## 4.3 Crystal size dependence of the lineshapes

We now consider the size dependence of the line shape. When the crystal size decreases ( $S_c / V_c$  increases) B(E) increases for energies smaller than E, due to the increased radiative loss. However, for the energy range slightly below and above  $E_L$ , B(E) is quite insensitive to the change of the crystal size because of the extremely small transmission coefficient of the LPB polaritons and the inter-branch conversion coefficient to the UPB in addition to the extremely large index of refraction of the LPB. Instead, the value of B(E) for that energy range is mainly determined by crystal size independent factors which are the inter-branch scattering rate due to phonons plus the nonradiative decay rate (see Eq.(3.53)). Fig.4.6 plots the energy dependence of  $1/(B-\alpha C/(\beta-B)-k_1)$  for the three cases:  $(1)S_C/V_C=0.5/cm$  and  $R_{\alpha 0} = 2 \times 10^8 / \text{sec}$ ,  $(2) S_c / V_c = 50 / \text{cm}$  and  $R_{\alpha 0} = 2 \times 10^8 / \text{sec}$  and  $(3) S_c / V_c = 0.5 / \text{cm}$  and  $R_{\alpha 0} = 2 \times 10^9$ /sec. Hence, in the case of a small crystal (eg. large value of energy range slightly below and above  $E_{I_{c}}$ , B(E) is quite insensitive to the ratio  $S_c^{}/V_c^{}$ ) this non uniform change of decay rate leads to the



Fig.4.5 (a) Lifetimes of the decay curves when the function I(E,t) was fitted with a bi-exponential decay. The value of the theoretical long lifetime was fixed at 5.26nsec. (1)Theoretical and (2)experimental long lifetime, (3)theoretical and (4)experimental short lifetime. (b) The ratio of the short lifetime pre-exponential factor to the long one. The theoretical curve (1) was obtained from the I(E,t) and the experimental curve (2) was reconstructed from the data in Ref.5. Both are negative at low energy and positive at high energy.

reduction of the luminescence intensity at long wavelength (Eq.(4.3)), which is in agreement with the experimental data shown in Fig.2.6a. Note the three corresponding theoretical plots in Fig.2.6b that use Eq.(4.2) with the parameters used for plotting Fig.4.6. They show results that are consistent with experiment.

Also it was found experimentally that the line shape shift of a powdered crystal (=20 $\mu$ m in size) is different from that of a large crystal (=1mm in size)(Fig.4.7): the long time line shape shifts by only a small amount compared to the large crystal (=1mm in size). In the case of a small crystal (S<sub>c</sub>/V<sub>c</sub>=50/cm), our theoretical analysis showed smaller red shifts than the case of a large crystal (S<sub>c</sub>/V<sub>c</sub>=0.5/cm) at early time and some blue shifts at long time, although the function G(E,t) does not depend on crystal size. This indicates again that our parameter combination in Table 4.1 is not a perfect choice. Further independent experiments (see, for example, Ref.18 for the discussion of various experimental methods) are required to improve the parameter values.

Note that we have used a smaller value of  $S_c/V_c$  (or larger crystal) in plotting our calculation in Fig.2.6b than its actual value estimated by the physical size of the crystal. This is because we have assumed a uniform distribution of the polaritons: in reality the magnitude of polariton distribution decreases as the polariton moves from the position at which it was generated (inset of Fig.2.5), which means a smaller radiative loss than in the case of a uniform distribution.

We do not have a theoretical explanation for the narrow high energy peak that looks stationary in Fig.2.7 and 2.8. The early time line shape that is obtained with Eq.(4.2) is not narrow enough to compare with the experimental one nor is it stationary. It is, however, possible that the narrow local maximum of the transmission coefficient of the LPB near the longitudinal exciton minimum energy is responsible for that narrow peak. Then the position of the peak would also remain stationary at near  $E_L$ . As a second strong possibility, the narrow and stationary component can be regarded as stemming from the localized exciton energy level that was formed by crystal lattice defects or impurities. At a defect site, the trapped polaritons will be converted into a localized exciton and radiate subsequently.<sup>20</sup>



Fig.4.6 The function  $1/(B-Cc/(B-B)-k_1)$  for three cases: (1)S /V =0.5/cm and R = 2x10 / sec (2) S /V = 50/cm and R = 2x10 / sec and (3) S /V = 0.5/cm and R = 2x10 / sec.



Fig.4.7 Experimental time-integrated line shapes from a small (=20 $\mu$ m) crystal. Dashed curve denotes the time integrated shape over the whole time range (from 0 to 30 nsec) while the solid curve refers to the late time range (from 3 to 30 nsec).

5. Temperature dependence of the luminescence from sodium cryptand sodide

Since the photoluminescence spectrum from sodium cryptand sodide was successfully described by the exciton-polariton mechanism at a fixed temperature in previous chapters, it is the purpose of this chapter to represent the experimental observations at elevated temperatures and to compare them with theory.

The sodium cryptand sodide crystal used for our measurements was of the highest quality (shiny golden bright color) and its size was about lmm.

Fig.5.1a shows the experimental time integrated line shapes at 3 different temperatures, with  $20K < T_1 < T_2 < T_3 < =50K$ .<sup>33</sup> The estimated temperatures of the  $T_1$ ,  $T_2$ , and  $T_3$  are about 25 K, 30 K, and 35 K respectively. It exhibits a red shift of the line shape as temperature increases. The energies of the time resolved line shape maxima are shown in Fig.5.2a at corresponding temperatures. Fig.5.3a shows the time evolution of the fluorescence at a fixed energy of 1.8265eV. We see a faster decay (or a faster growth at early time region) as temperature increases.

Among the functions  $\alpha(E)$ ,  $\beta(E)$ , A(E), B(E), C(E), and H(E), which were defined in Eqs.(3.50)-(3.55) of Chapter 3, only H(E) shows explicit temperature dependence because it depends on the number of phonons per state. Since H(E), and hence v(E) defined in Eq.(3.64), is an increasing function of temperature, the FWHM of the LPB population also increases with temperature. Fig.5.4 shows the function  $T_{\parallel}v_{g\parallel}/n_{\parallel}^2$  and the LPB population  $\phi_{\parallel}(E,t=1nsec)$  at T=20K and T=30K.<sup>34</sup> (In plotting the

72



Fig.5.1 (a)Experimental time integrated lineshapes at temperatures  $(1)T_1$ ,  $(2)T_2$  and  $(3)T_3$  with  $20K < T_1 < T_2 < T_3 < 50K$ . The estimated temperatures of the  $T_1$ ,  $T_2$ , and  $T_3$  are about 25 K, 30 K, and 35 K respectively. (b)Theoretical lineshapes calculated using Eq.(1) at (1)25K, (2)30K and (3)35K.



Fig.5.2 (a)Experimental time evolution of the maxima of energy of the fluorescence line shape at temperatures  $(1)T_1$ ,  $(2)T_2$  and  $(3)T_3$ . The estimated temperatures of the  $T_1$ ,  $T_2$ , and  $T_3$  are about 25 K, 30 K, and 35 K respectively. (b)Theoretical counterparts at (1)25K, (2)30K and (3)35K.



Fig.5.3 (a) Experimental time evolution of the 1.8265eV photoluminescence at temperatures  $(1)T_1$ ,  $(2)T_2$  and  $(3)T_3$ . The estimated temperatures of the  $T_1$ ,  $T_2$ , and  $T_3$  are about 25 K, 30 K, and 35 K respectively. Curve (4) represents Instrumental Response Function. (b) Theoretical plotting of 1.8265eV photoluminescence at (1)25K, (2)30K and (3)35K.



Fig.5.4 (1)Theoretical plot of the multiplicative factor  $T_{l}v_{gl}/n_{l}^{2}vs$ . energy. The LPB population,  $\phi_{l}(E,t=1nsec)$ , at (2)T=20K and (3)T=30K.

theo evi reso conc frec dep in 1 the the tem evo god Vid th evo Whe еx of Þo li s h η( ٧a ir Cd theoretical figures, the parameter values in Table 4.1 were used. As is evident from the example of Fig.5.4, Eq.(4.2) shows that the time resolved lineshape has a redshift as temperature increases. Thus we conclude that the LPB population broadening, which is caused by the more frequent scattering with LA phonons, is responsible for the temperature dependence of the fluorescence from Na<sup>+</sup>C222Na<sup>-</sup>. Using Eq.(4.2), we plot in Figs.5.1b and 5.2b the theoretical counterparts of this red shift and the qualitative agreement with experiment is good. Note also that both the experiment and theory show lineshape broadening with increasing temperature.

Fig.5.3b shows the theoretical temperature dependence of the time evolution of the fluorescence at a fixed energy E=1.8265eV. They give a good qualitative consistency again: with increasing temperature, the width of the time decay curve becomes smaller and the peak position of the decay curve occurs at earlier time. The reason for the time evolution difference between different temperatures is easily explained. When the function  $B - \frac{\alpha C}{\beta - B}$  in Eq.(3.71) is energy independent (in the experimental range of interest), which is our case, the time evolution of the luminescence at a certain energy E is chiefly determined by the position of E and the long time (=30 nsec) energy maximum of the lineshape,  $\eta$ (t=30nsec;T) in Fig.5.2b. The function I(E,t) in Eq.(4.2) shows growth followed by decay process(es) and the larger is  $\eta$ (t=30nsec;T)-E, the slower is the growth of the I(E,t). At a fixed value of E the quantity  $\eta$  (t=30nsec;T)-E decreases as temperature increases, due to the redshift of the lineshape (see Fig.5.2), which completes our explanation for Fig.5.3.

That the above argument is correct can be shown in a different way. After =lnsec the value of  $\sqrt{[\nu(t)]}$  in Eq.(3.71) is nearly unchanged. (Note that in a high temperature limit where  $\hbar\mu k_{0}/k_{\rm B}T$  << 1 is satisfied, by Eqs.(3.52) and (3.55) Eq.(3.64) is approximated by  $v(t)=2k_BT \cdot (E_0-t_0)$  $\xi(t)$ ) where  $k_B$  is Boltzman's contant.) Therefore, after =lnsec the time evolution of the maximum value of the LPB population,  $\phi_{\theta}(E=\xi(t),t)$ , is  $e^{-\left(B-\frac{\alpha C}{\beta-B}\right)t}$ , which is independent of governed by the function temperature. The observed fluorescence I(E,t) in Eq.(4.2) acquires an additional time evolution factor because of the multiplicative function  $T_{\rho}v_{\alpha\beta}/n_{\beta}^2$ . But this additional time evolution factor is quite insensitive to temperature. Hence by the same token, we expect that the time evolution of the maximum intensity of the lineshapes,  $I(E=\eta(t;T),t)$ , is (nearly) independent of temperature. This behavior is very well confirmed experimentally in Fig.5.5. Not surprisingly, the time evolution curves from 3 different temperatures overlap nearly exactly.

In conclusion, we have demonstrated that the exciton-polariton dynamics model developed in previous chapters consistently explains the temperature dependence of the photoluminescence spectrum from sodium cryptand sodide.



Fig.5.5 Experimental time evolution of the maximum intensity of the lineshapes at 3 different temperatures  $T_1(-)$ ,  $T_2(\times)$  and  $T_3(\Box)$ . The estimated temperatures of the  $T_1$ ,  $T_2$ , and  $T_3$  are about 25 K, 30 K, and 35 K respectively.

# 6. Other features of photoluminescence from alkalides

# 6.1 Photoluminescence from defect sites and other alkalides

In the experiments discussed in the previous chapters the time integrated lineshapes from Na<sup>+</sup>C222Na<sup>-</sup> samples showed single peak structures, although their detailed shapes depended on the sample quality and size. Those experiments were understood in terms of an exciton-polariton mechanism which includes the non-radiative decay rate. The quality of a sample was revealed by the color it exhibits and by the time decay behavior. A poor quality sample was recognized by a darker color, a faster time decay, and a higher energy peaked time integrated lineshape than those from a good quality crystal. (Since the lineshape is red shifted, a faster time decay means a smaller contribution from the long time spectra. Therefore when integrated over time, the lineshape has a peak at higher energy position.) With a possible exception of the narrow peak component observed in Figs.2.7 and 2.8, the Na<sup>+</sup>C222Na<sup>-</sup> crystals studied in previous chapters did not show any clear indication of an additional peak in the lineshape. Therefore it is evident that the crystal defects or impurities, which were imagined to be responsible for the poor crystal quality, mainly acted only as fluorescence quenchers which enhanced the non-radiative decay rate.

In this chapter, we report a set of experimental data which show two peaks in the steady state line shapes from various alkalides  $(Na^{+}C222Na^{-}, Rb^{+}(15C5)_{2}Na^{-}, K^{+}(15C5)_{2}Na^{-}, and K^{+}(15C5)_{2}K^{-}).$ 

Fig.6.1 shows the steady state lineshapes from  $Na^+C222Na^-$ . Fig.6.1a and Fig.6.1c show the lineshapes at 20K and at room temperature,

80



Fig.6.1 Steady state double peaked spectra from Na<sup>+</sup>C222Na<sup>-</sup> from (a) normal quality crystals at 20 K, (b) crystals with light-induced defects at 20 K, and (c) normal quality crystals at room temperature

respectively. The sample in Fig.6.1c had a "normal" lineshape like that in Fig.6.1a at 20K. The relative magnitude of the 2 peaks in Fig.6.1c was sample dependent. It is not clear whether the higher energy peak in Fig.6.1c is related to the lower energy peak in Fig.6.1a, partially due to the lack of experiments at intermediate temperatures.

Fig.6.1b shows the double peaked lineshape from a collection of "damaged" Na<sup>+</sup>C222Na<sup>-</sup> crystals at 20K. Thus the signal is an average over many crystals. The sample was irradiated by intense dye laser pulses for at least several hours. The laser pulse repetition rate was 1MHz and about 20-30mW of time averaged output was focussed on the area of about 1mm<sup>2</sup>. The power density here was, therefore, at least a few times greater than the one in previous experiments.

Fig.6.2 shows the time resolved lineshapes from such crystals with light-induced defects. At very early time, the main component which has its peak at around 1.84eV dominates. This main component is the one we described in terms of the exciton-polariton mechanism in previous chapters. With increasing time, the secondary component centered at 1.758eV(=7050Å) grows relative to the main component, followed by a relative re-growth of the main component. After a long time (about 24 nsec), we observe only the main component which is superimposed on a broad background which is from defect sites. When the sample configuration was changed by a random mixing of the crystals the secondary peak was removed completely, leaving only the main component. Therefore it is reasonable to conclude that the defect sites were generated by the intense laser light and they resided only within a skin depth of the crystal surface. At this point, it is not obvious how these defect sites were generated. A deformed complexant and/or a



Fig.6.2 Time evolution of the double peaked spectra from  $Na^+C222Na^-$  crystals with light-induced defects

local deformation of the anion's environment or a color center may be responsible for the secondary peak. However, from the time evolution of 2 components in Fig.6.2, it is evident that the secondary component is fed by the main component. When the exciton-polaritons arrive at the defect sites, they are trapped and their exciton components could be converted into photons.

Beside sodium cryptand sodide, photoluminescence was observed from  $Rb^{+}(15C5)_{2}Na^{-}$ ,  $K^{+}(15C5)_{2}Na^{-}$ , and  $K^{+}(15C5)_{2}K^{-}$  at 20K with low laser power density.

Rb<sup>+</sup>(15C5)<sub>2</sub>Na<sup>-</sup> (Fig.6.3) also shows a double peaked (steady state) lineshape when excited by yellow light (581nm). It consists of a narrow peak centered at 1.671eV(=7420Å) and a wide peak at 1.791eV(=6920Å). When excited by green light (532 nm), the wide component was removed (Fig.6.3b). K<sup>+</sup>(15C5) Na<sup>-</sup> in Fig.6.4 shows a lineshape with only one peak at 1.664eV(=7450Å). However the width of the lineshape depended on the wavelength of the exciting light. With green light the width was about 74meV(=330Å), while with yellow light the width was about 200meV(=900Å). Thus, with  $K^+(15C5)_{2}Na^-$  it appears that the 2 peak positions of the narrow and wide components roughly coincide. From the experiments on Rb<sup>+</sup>(15C5)<sub>2</sub>Na<sup>-</sup> and K<sup>+</sup>(15C5)<sub>2</sub>Na<sup>-</sup> we find that green light is not efficient in getting the wide component while yellow light is efficient. It is rather unlikely that sodium cryptand sodide is the only compound with a bound excited state of an alkali anion. In comparison with the case of Na<sup>+</sup>C222Na<sup>-</sup>, the narrow component from other alkalides is likely to be the main luminescence which has its origin in the transition of the sodium anion's electron (and, of course, possibly exciton-polariton luminescence). Then the broad component is attributable to the defect



**Fig.6.3** Emission from  $Rb^+(15C5)_2Na^-at 20 K$ , (a) with 581nm (yellow) excitation light and (b) with 532nm (green)



Fig.6.4 Emission from  $K^{+}(15C5)_2Na^{-}$ , (a) with 532nm (green) excitation light and (b) with 581nm (yellow)

sites. Actually, it is hard to prepare alkalides without defects. Among alkalides  $Na^+C222Na^-$  is the most defect free, which is the reason for the observation of a single peak from this compound in most cases.

Fig.6.5 shows the line shape from  $K^+(15C5)_2 K^-$ . It has only one peak centered at 1.828eV(=6780Å). Compared to the yellow light the green was very inefficient (=10% of the yellow) in producing photoluminescence from this compound. This supports our conjecture that the observed signal is from the defect sites.

## 6.2 Excitation intensity dependence of the photoluminescence

Fig.6.6 shows the steady state lineshape from sodium cryptand sodide at various excitation intensities. The experimental arrangement in Chapter 2 was used for this experiment and the laser beam was focussed on a single crystal. In a low enough laser power range, the intensity of photoluminescence from  $Na^+C222Na^-$  is proportional to the excitation power. However, there are 3 major effects associated with laser power increase above a certain limit, but in the realm of stable emission:

(1) Redshift of the lineshape vs. laser power, (Fig.6.6)

- (2) Continuous decrease in photoluminescence intensity vs. laser power,
- (3) A faster decay at a higher laser power. (Fig. 6.7)

In Fig.6.6, the number of counts per second (in arbitrary unit) at the lineshape maxima was in curve (a) 200 with excitation intensity I = 40 I<sub>0</sub>, in curve (b) 1200 with I = 10 I<sub>0</sub>, and in curve (c) 200 with I =  $I_0 = 1 \text{ W/cm}^2$ .

When the laser power exceeds the second limit, the photoluminescence intensity gradually decreases with respect to time. In the power range of this experiment, the signal was stable over time and the sample gave consistent results after cycling the laser power.



**Fig.6.5** Emission from  $K^+(15C5)_2K^-$


Fig.6.6 Lineshape vs. excitation intensity (Na<sup>+</sup>C222Na<sup>-</sup>) with (a) excitation laser power I = 40 I<sub>0</sub>, (b) I = 10 I<sub>0</sub>, and (c) I = I<sub>0</sub>  $\approx$  1W/cm<sup>2</sup>



Fig.6.7 Time decay vs. excitation intensity at E = 1.841 eV, with (a) excitation laser power I = 40 I<sub>0</sub>, (b) I = 10 I<sub>0</sub>, and (c) I = I<sub>0</sub><sup> $\approx$ </sup> 1W/cm<sup>2</sup>

## 7. Concluding remarks to alkalide research

Our results show that the exciton-polariton mechanism is consistent with a variety of experimental observations on Na<sup>+</sup>C222Na<sup>-</sup>. It provides a very plausible explanation for the size dependence of the luminescence line shape in the sense that the polariton dynamics are affected by the geometry of the crystal. Also our experimental data shown in Fig.2.5 relating to the migration of the excited state are a natural consequence of the polariton mechanism because the polaritons have a good propagating property (group velocity  $\geq 1.5 \times 10^7$  cm/sec with the physical parameters given in Table 4.1)). The scattering of polaritons with phonons alters the polariton population distribution and manifests itself as a constantly red shifting line shape (Fig. 4.1 and 4.2), which is directly responsible for the different time evolution behavior at different energies (Fig. 4.4). We have shown that all of these effects are well described by the exciton-polariton formalism, although there are some quantitative deviations. It was also shown that the time and wavelength dependence of the luminescence decay can be described by a bi-exponential process as found in the work of Ref.5. In summary, the formalism based on polariton transport explains the spatial transport of the optically excited state, the crystal size and quality dependence of the line shape, the time evolution of the line shape, the fast decay at high and slow decay at low energies and the observed double exponential decay from Na<sup>+</sup>C222Na<sup>-</sup>. Also due to the increased scattering of acoustic phonons with polaritons at elevated temperatures the polariton populations have wider distribution. This explains the redshift of the luminescence, faster decay, and wider lineshape at a higher temperature.

We have observed a secondary luminescence peak from the defect sites of the Na<sup>+</sup>C222Na<sup>-</sup> crystal which was generated by strong irradiation by laser light. Double peaked lineshapes were observed from other alkalides  $(Rb^+(15C5)_2Na^-, K^+(15C5)_2Na^-)$  whose main peaks originate from the transition of the alkali metal anions' electrons. In analogy with Na<sup>+</sup>C222Na<sup>-</sup>, the secondary peaks are attributed to defect sites. It was also found that the photoluminescence from Na<sup>+</sup>C222Na<sup>-</sup> strongly depended on the excitation intensity.

## 8. Photoluminescence from intercalated clay compounds

There are several kinds of layered materials which show extreme anisotropy. Among these graphite is composed of atomically thin layers while the host layers in layer dichalcogenides such as TiS<sub>2</sub> and HfS<sub>2</sub> are a few atoms thick. The host layers in layered silicate clays are many atoms thick so that they are relatively rigid and thus can be propped apart or pillared by widely-spaced intercalant molecules without sagging. All of these layered materials accommodate intercalant materials between adjacent layers without affecting the physical properties of the layers themselves.<sup>35</sup>

Fluorohectorite is a trioctahedral 2:1 layered silicate<sup>36</sup> (see Fig.8.1a). Its layers are formed from a sheet of edge-connected octrahedra which is bound to two sheets of corner-connected tetrahedra. Charged ions can be inserted into the inter gallery space bounded by adjacent two layers.

To observe the effects of intercalation on optically active molecules, we have measured<sup>37</sup> continuous and time resolved photoluminescence spectra from the ion exchanged complex layered oxide fluorohectorite (FHT) (chemical formula =  $F_4Si_8(Mg_{5.34}Li_{0.66})O_{20})$ . The ions were  $Cr(en)_3^{3+}$  (see Fig.8.1b) and  $Co(en)_3^{3+}$  (en = ethylenediamine). The ion exchanged films were annealed at 140 °C for 12 hours to eliminate water from the galleries, then mounted to the cold finger of a closed-cycle helium cryostat and cooled to a nominal temperature of 20K. The experimental method described in Chapter 2 was used. Time resolved

spectra were measured in the normal configuration of the time-toamplitude converter (TAC). The pulse repetition rate of the dye laser was chosen to be 190KHz for the time resolved measurements.

Fig.8.2 shows the low temperature cw emission lineshapes of the pure  $Cr(en)_3$  salt, the  $Cr(en)_3$  intercalated clay  $(Cr(en)_3 - FHT)$ , and the potassium-intercalated clay (K-FHT). For the salt, we see a strong band at 1.797eV which corresponds to the chromium ion d- to s- state spin forbidden transition.<sup>38</sup> This band is seen to redshift by 36 meV and broaden upon intercalation. The additional broad band emission from 1.8 to 2.1 eV comes from the host material and is unaffected by the presence of  $Cr(en)_3^{3+}$ . K-FHT shows the luminescence from the host layer.

In Fig.8.3 we show time resolved photoluminescence spectra of the  $Cr(en)_3$ -FHT clay. Snapshots are taken at t=0, 0.5, and 3.0  $\mu$ s with a corresponding exposure time of 0.05  $\mu$ s. The t=0 spectrum shows the strong broadband intrinsic clay emission to dominate the  $Cr(en)_3^{3+}$  band, even when plotted on a logarithmic scale. The background quickly quenches, leaving only the intercalant portion of the spectrum shown at t=0.5 and 3.0  $\mu$ s in Fig.8.3. The  $Cr(en)_3^{3+}$  emission in the FHT has a lifetime of 3.9  $\pm$  0.2  $\mu$ s, compared to the 13.6  $\pm$  1.3  $\mu$ s lifetime of the pure salt.<sup>37</sup>

Thus, there are two primary consequences for the  $Cr(en)_{3}^{3+}$  ion upon intercalation into FHT, namely redshift of the emission and a factor of 3 decrease in lifetime. The latter cannot be accounted for solely by relaxation via phonon decay into the neighboring silicate layers -- this would reduced the lifetime to nanoseconds. We believe instead that molecular deformation plays the key role in explaining the observed effects. The basal spacing (c-axis repeat distance), a measure of the



Fig.8.1 Structure of (a) fluorohectorite and (b)  $Cr(en)_3^{3+}$ . (a) Open circles are oxygen, closed circles are cations in tetrahedral (Si) and octahedral (Mg, Li) positions. Fluorines (not distinguished from oxygen in the figure) are located in the second and third basal planes of oxygens.



Fig.8.2 Low temperature, cw spectra of the  $Cr(en)_{3}^{3+}$  salt,  $Cr(en)_{3}^{3+}$  - FHT, and K-FHT



**Fig.8.3** Time resolved spectra of  $Cr(en)_{3}^{3+}$  - FHT at very short time and much later, showing fast quenching of the high energy background and the long lived red emission band of the chromium ion (T = 20 K)

clay gallery height, increases from 12.2Å to 14.5Å when exchanging  $Cr(en)_{3}^{3+}$  for Li<sup>+</sup> implying that the  $Cr(en)_{3}^{3+}$  molecules prop up the galleries. Conversely, the molecules are being compressed by the silicate layers. This stress serves to further mix d and p orbitals of the chromium ions, already overlapping due to the  $Cr(en)_{3}^{3+}$  molecular ligand field. The p  $\rightarrow$  s transition is allowed; d and p mixing would thereby reduce the lifetime of our "forbidden" transition.

Fig.8.4 shows the lifetimes of the photoluminescence from  $[Cr(en)_3]_x[Co(en)_3]_{1-x}$  - FHT compounds as a function of the concentration, x, of the Cr(en)\_3 ion. Besides the emission from the host layer, there was not any photoluminescence detected for x = 0 case. Therefore the luminescence in question can be safely assumed to be originating from the Cr(en)\_3^{3+} ions only. Fig.8.4 indicates a increase of lifetime below x = 0.35. Fig.8.5 shows that the basal spacing also has a increase below x = 0.35. The two figures show a good correlation, which can be a justification of our argument in that the variation of the lifetime is associated with the basal spacing change which modulates the wavefunction of the Cr(en)\_3^{3+} ions.

In conclusion we suggest that the deformation of the  $Cr(en)_3^{3+}$  ions, which is introduced by the mechanical stress generated by the host layers, reduces the lifetime of the photoluminescence from the  $Cr(en)_3^{3+}$ ions.



Fig.8.4 Lifetime of the photoluminescence vs. concentration, x, of  $[Cr(en)_3]_x[Co(en)_3]_{1-x}$  - FHT compounds



Fig.8.5 Basal spacing vs. concentration, x, of [Cr(en)] [Co(en)] - FHT compounds

LIST OF REFERENCES

•

## LIST OF REFERENCES

<sup>1</sup> Cryptand[2.2.2] is a biclyclic polyether that encapsulates the Na<sup>+</sup> ion. It has the molecular formula  $N(CH_2CH_2OCH_2CH_2)_3N$ .

<sup>2</sup> J.L Dye, Prog. Inorg. Chem. 32, 327 (1984); J. L. Dye and M. G. DeBacker, Ann. Rev. Phys. Chem. 38, 271 (1987)

<sup>3</sup> F. J. Tehan, B. L. Barnett and J. L. Dye, J. Am. Chem. Soc., 96, 7203 (1974)

<sup>4</sup> J. L. Dye, R. H. Huang and D. L. Ward, J. Coord. Chem. B, 18, 121 (1988)

<sup>5</sup> R. S. Bannwart, S. A. Solin, M. G. DeBacker and J. L. Dye, J. Am. Chem. Soc., Vol. 111, No. 15, 5552 (1989)

<sup>6</sup> Recent measurements showed that the same machine used in the work of Ref.5 had a temperature difference between the cold finger and the sample site: when the cold finger was at 11 K, the sample site was at 22 K. Therefore we have used a temperature of 20 K in constructing the theoretical curves.

7 J. Papaioannou, S. Jaenicke and J. L. Dye, J. Solid State Chem., 67, 122 (1987)

<sup>8</sup> M. G. DeBacker, A. Sieradzan, G. Xu, Ta-Ryeong Park and J. L. Dye, unpublished results, this laboratory.

<sup>9</sup> D.-H. Shin, A. S. Ellaboudy, J. L. Dye and M. G. DeBacker, unpublished results, this laboratory.

10 J. L. Dye, M. R. Yemen, M. G. DaGue and J.-M. Lehn, J. Chem. Phys. 68, 1665 (1975) 11 User's manual of Quantronix Model 416 laser system

<sup>12</sup> B. Couillaud and V. Fossati-Bellani, Lasers & Applications, Jan, 79 (1985) & Feb, 91 (1985); B. Couillaud, V. Fossati-Bellani and G. Mitchell, Proceedings of SPIE-The International Society for Optical Engineering, Vol. 533, Ultrashort Pulse Spectroscopy and Applications, January 22-23, 1985, Los Angeles, California

<sup>13</sup> Instruction Manual of Model FR-103 Autocorrelator of Femtochrome Research, INC.; Z. A Yasa and N. M. Amer, Optics Commun., 36, 406 (1981) <sup>14</sup> D. V. O'Connor and D. Phillips, *Time-Correlated Single Photon Counting* (Academic Press, London, 1984)

<sup>15</sup> Ta-Ryeong Park, Stuart A. Solin and James L. Dye, submitted to Phys. Rev. Lett.; Ta-Ryeong Park, Stuart A. Solin and James L. Dye, submitted to Phys. Rev. B

16 J. J. Hopfield, Phys. Rev. 112, 1555 (1958)

<sup>17</sup> S. I. Pekar, Sov. Phys. JEPT 6(33), 785 (1958)

<sup>18</sup> F. Bassani and L. C. Andreani, in *Excited-State Spectroscopy in Solids*, edited by U. M. Grassano and N. Terzi (North-Holland, 1987), p.1
<sup>19</sup> Y. Toyozawa, Suppl. Prog. Theor. Phys. 12, 111 (1959)

<sup>20</sup> H. Sumi, J. Phys. Soc. Japan 41, 526 (1976)

<sup>21</sup> F. Askary and P. Y. Yu, Phys. Rev. B 31, 6643 (1985)

<sup>22</sup> D. E. Cooper and P. R. Newman, Phys. Rev. B 39, 7341 (1988)

23 V. V. Travnikov and V. V. Krivolapchuk, Sov. Phys. JEPT 58(6),1210 (1983)

<sup>24</sup> T. Steiner, M. L. W. Thewalt, E. S. Koteles and J. P. Salerno, Phys. Rev. B 34, 1006 (1986)

<sup>25</sup> A. Bonnot and C. Benoit a la Guillaume, in *Polaritons*, edited by E. Burstein and F. De Martini (Pergamon, New York, 1975), p. 197

<sup>26</sup> V. V. Rossin, Sov. Phys. Solid State 32(3), 472 (1989)
 <sup>27</sup> J. J. Hopfield and D. G. Thomas. Phys. Rev. 132, 563 (1963)

28 The actual structure of sodium cryptand sodide is anisotropic. See Ref.3

29 W. C. Tait and R. L. Weiher, Phys. Rev. 178, 1404 (1969)

30 D. A. McQuarrie, Statistical Mechanics (Harper & Row, 1976)

<sup>31</sup> R. H. Good, Jr and T. J. Nelson, *Classical Theory of Electric and Magnetic Fields* (Academic Press, 1971), p.351

32 A. Selkin, Phys. Stat. Sol. (b) 83, (47) 1977

<sup>33</sup> The values of the temperatures read by a sensor at cold finger were 15K, 20K and 25K for  $T_1$ ,  $T_2$  and  $T_3$  respectively. See the comment at Ref.6.

<sup>34</sup> We assume that other parameters does not change with temperature. For example, we ignore the effects associated with thermal lattice expansion.

<sup>35</sup> S. A. Solin, J. of Molecular Catalysis, 27, 293 (1984)

<sup>36</sup> G. W. Brindley and G. Brown, Crystal Structures of Clay Minerals and Their X-Ray Identification (Mineralogical Society, 1980)

<sup>37</sup> Chaper 8 is based on the presentation given in 1991 APS March Meeting, held in Cincinnati Ohio; M. Holtz, Ta-Ryeong Park, J. Amarasekara, T. Pinnavaia and S. A. Solin, Bull. Am. Phy. Vol. 36, No. 3, 1001 (1991)

<sup>38</sup> C. J. Ballhausen, Introduction to Ligand Field Theory (McGraw-Hill, New York, 1962)