RELAXATION KINETICS OF EXCITONS IN CUPROUS OXIDE

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THESIS

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RELAXATION KINETICS OF EXCITONS IN CUPROUS OXIDE

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Cuprous oxide is a thoroughly studied semiconductor with long-lived, mobile excitons. The kinetic energy distribution of the excitons is reproduced in phonon-assisted luminescence spectra. When non-equilibrium excitons are produced by a laser pulse, nanosecond-time-resolved luminescence reveals the relaxation of their kinetic energy distribution.

It has been known for several years that, when the excitons are produced with the highest attainable densities, the time-sequence of exciton kinetic energy distributions closely resembles a sequence of Bose-Einstein distributions, with apparent temperatures greater than that of the lattice. A widely used hypothesis is that the excitons exchange energy through elastic collisions quickly enough to establish a quasi-equilibrium, with the exciton gas having a temperature distinct from that of the lattice. The transient kinetic energy distributions have thus been interpreted simply as quasi-equilibrium distributions, with the gas density near enough the quantum density that the Bose statistics of the excitons is noticeable.

This work is an experimental and theoretical study of such luminescence spectra. The absolute brightness of the photoluminescence, compared with that of a known number of excitons, indicates that the density of excitons is at all times too low to reveal their Bose statistics—assuming they act as an ideal gas. The assumption of a quasi-equilibrium among the excitons is abandoned, and the relaxation problem is treated through a Boltzmann equation. Only relaxation processes which have been measured experimentally are included: acoustic phonon emission and absorption, interconversion between spin states, and non-radiative two-exciton decay. Numerical modeling reproduces most of the experimental observations, without invoking Bose statistics.
ACKNOWLEDGMENTS

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1. OVERVIEW

1.1 The virtues of cuprite

Cuprous oxide, Cu$_2$O, is a semiconductor with a band gap of 2173 meV, in the yellow part of the visible spectrum. Cuprous oxide is the mineral cuprite, and sufficiently large single crystals are available from mineral sources. The experiments described here used a single crystal of cuprite donated by the Smithsonian Institute.

The low-energy excitations of cuprite are quite simple. The band edges are at zone center and have only the two-fold Kramers' degeneracy stemming from the two spin states of the electron. The electron and hole effective masses are isotropic and small, 0.99 and 0.58 free electron masses respectively [Ohyama, 1997]. An electron and a hole bind to form an exciton with the unusually high binding energy of 150 meV. More precisely, 150 meV is the binding energy of the 1s exciton; one can observe a complete Rydberg series of hydrogen-like states of the electron and hole.

As the bound state of two fermions, excitons should obey Bose statistics. In thermal equilibrium, we expect the occupation number of the exciton kinetic energy eigenstate with energy $\varepsilon$ to be given by the Bose-Einstein distribution

$$f_B(\varepsilon) = \frac{1}{\exp[(\varepsilon - \mu) / k_B T] - 1}$$

where $\mu$ is the chemical potential and $T$ the temperature of the exciton gas. This distribution becomes noticeably different from the classical Maxwell-Boltzmann distribution, $\exp(-\varepsilon / k_B T)$, when the exciton density is sufficiently high that the occupation numbers $f_B$ become greater than one. Based on the density of exciton states in Cu$_2$O, the Bose statistics of excitons should become noticeable at an exciton density of 10$^{17}$/cm$^3$ if the exciton gas temperature is 2K.

The 1s exciton is split by electron-hole exchange into a singlet and triplet. The singlet state, called the paraexciton, lies 12 meV lower than the triplet orthoexciton. Here cuprous oxide is less simple than one might hope, as spin-orbit coupling thoroughly confuses the spin states. It happens that the singlet paraexciton has an electron-hole combined spin wavefunction which is entirely spin-$1$. Since creation or destruction of a paraexciton requires flipping an electron spin, radiative recombination of the paraexciton is extremely weak.

The band edges in cuprous oxide both have even parity, so the direct radiative recombination of any 1s exciton is dipole-forbidden. Thus radiative recombination is relatively slow: 0.1/$\mu$s for orthoexcitons in a crystal at 2K. The lifetime of the lower-energy paraexciton is limited by non-radiative recombination and can reach several microseconds in good samples.
There are optical phonons which induce a dipole moment between the bands, making dipole-allowed the recombination of an exciton through simultaneous emission of a photon and optical phonon. This phonon-assisted luminescence is still too slow to affect the exciton population dynamics; the rates are 70/ms for orthoexcitons and 0.14/ms for paraexcitons.

Slow as it is, phonon-assisted luminescence is extremely useful. The optical phonon accepts the difference between the momenta of recombining exciton and the photon, allowing excitons of any momentum to luminesce with equal probability. The energy of the emitted photon is the total energy of the exciton, less that of the optical phonon — but the phonon energy is nearly independent of the momentum it was required to accept from the recombining exciton, thanks to the flat dispersion curves of the optical phonons involved [Beg, 1976]. Therefore, the phonon-assisted luminescence spectra closely reproduce the exciton kinetic energy distribution (figure 1).

Figure 1: a) The energy-momentum relations for orthoexcitons and ($\Gamma_{12}$) optical phonons in cuprous oxide. The arrows indicate the quadrupole allowed optical recombination and two possible dipole allowed phonon-assisted recombinations.
b) The photoluminescence spectrum resulting from these transitions. The broad asymmetric line peaked at 2020meV is phonon-assisted luminescence, which duplicates the exciton kinetic energy distribution.

The phonon-assisted luminescence from the orthoexcitons is bright enough to provide good spectra using time-slices as short as 0.1ns, but the paraexciton luminescence has two shortcomings. First, the rate of phonon-assisted luminescence from the paraexcitons is 500 times weaker than from the orthoexcitons. Second, the paraexciton phonon-assisted luminescence lies only 3.6 meV below one of the stronger orthoexciton phonon replicas, which obscures the high-energy part of the paraexciton kinetic-energy distribution. Therefore the paraexciton kinetic energy distributions are known with less confidence, especially during and for the first few
nanoseconds after the laser excitation, when the excitons are relatively hot and orthoexcitons abundant.

Exciton scattering by acoustic phonons is well-understood, thanks largely to the study of exciton diffusivity by David Trauernicht [1986a] in this laboratory. The temperature dependence of the paraexciton diffusivity was accounted for using the deformation potential model of exciton-phonon scattering. Hot excitons cool by acoustic phonon emission, and the same deformation potential predicts close to the observed rate of cooling [Snobe, 1990c]. Phonon emission rates are around 10/ns for excitons with 1 meV (12K) of kinetic energy.

Acoustic phonons can potentially scatter excitons not only between momentum states, but between the ortho and para spin states. Snobe, Trauernicht and Wolfe [1990a] demonstrated that the dominant mechanism of conversion from orthoexcitons to paraexcitons does in fact involve the emission or absorption of just one acoustic phonon. The rate of interconversion is 0.3/ns at 2K.

Auger recombination—a collision between two excitons in which one exciton recombines without emitting a photon—has been established as important in cuprous oxide, but it had not previously been measured quantitatively [Mysyrowicz, 1981]. Some of the bandgap energy released in the Auger recombination appears as kinetic energy in the remaining excitons, an effect we call Auger heating. One of the conclusions of this thesis is that Auger recombination in cuprous oxide is too strong to allow excitons to exhibit Bose statistics. We estimate that the density-dependent Auger decay rate reaches 1/ns at an exciton density of approximately 10^{16}/cm^3.

1.2 The experiments

The green light from an argon ion laser falling on a sample of cuprite creates electron-hole pairs within 3μm of the surface. In a crystal at 2K, these carriers combine to form excitons with a quantum yield near 30%. Previous work in this lab used low intensity argon ion excitation to measure exciton diffusivity (60 μm^2/ns at 2K [Trauernicht, 1986a]) and thermalization rate [Snobe, 1990c].

With our argon-ion laser capable of producing 10^{11} photons per pulse (0.03-μJ, sub-nanosecond pulses obtained by dumping the cavity of a mode-locked laser) by focusing the laser to a 10-μm spot on the crystal we can obtain excitation densities in excess of 10^{20} photons absorbed per cubic centimeter. The resulting high density of excitons suffers Auger recombination with a sub-nanosecond lifetime [Snobe, 1990c]. Due to Auger heating, the temperature of the dense exciton gas remains high much longer than that of a low density gas. With an excitation density of 10^{20} photons per cm^3, in a 2K lattice, the average orthoexciton kinetic energy remains above 10K for about 1ns. Also, for the first nanosecond after the laser
pulse, the exciton kinetic energy distribution is very close to the Bose-Einstein distribution which one would expect to see for a gas of excitons in thermal equilibrium at a density of around $10^{19}$/cm$^3$. Several groups have reported the observation of Bose-Einstein distributions of excitons in Cu$_2$O, when using intense photoexcitation [Hulin, 1980; Snoke 1987, 1990c; Lin, 1996; Naka, 1996; Goto 1997].

In this work we use the brightness of the observed luminescence to determine the number of excitons in the crystal. Then with an estimate of the volume the excitons occupy, we estimate their density. The density obtained in this way never exceeds $10^{17}$/cm$^3$. This new information is inconsistent with the simple explanation of the observed distributions in terms of Bose statistics in an ideal gas. The goal of this thesis is a quantitative explanation of these distributions consistent with the measured gas density.

To produce excitons at a controlled density within the bulk of the crystal, we use phonon-assisted absorption — the reverse of the phonon-assisted luminescence process illustrated in figure 1. Photons having energy less than the bandgap can be absorbed through creation of an orthoexciton and an optical phonon. This absorption process creates exactly one orthoexciton per photon absorbed, with a specific kinetic energy, and at a known density (derived from the power absorbed and the absorption length). The ability to produce a known density of excitons is essential for the density calibration of chapter 3, and for the measurement of the Auger decay constant by Jeremy Warren.

We can confine excitons to a region in the bulk of the crystal, tens of microns in diameter, by using a favorite technique of this laboratory: the strain well. A ball bearing or convex lens pressed against the surface of the crystal creates a strain field inside the crystal. Near the contact area, the strain is mainly compressive, which increases the bandgap in cuprite. Further into the crystal, there is more shear strain, which splits otherwise degenerate electronic states, pushing the lowest exciton states down in energy. The net effect is a potential well for excitons, which can be made at least 20 meV (230K) deep in cuprite without damage to the crystal. Confining the excitons allows us to maintain a moderate density (say, $10^{13}$/cm$^3$) for hundreds of nanoseconds, so as to measure the rate of Auger decay of essentially thermalized excitons.

1.3 Excitons far from equilibrium

Given the knowledge we have about the various relaxation and recombination mechanisms of the excitons, it has proven worthwhile to create a detailed computer model of the first several microns near the surface of a Cu$_2$O crystal. The model results, presented in chapter 6, reproduce most of the experimental observations, including exciton kinetic energy distributions which are well-fit by the Bose-Einstein distribution — even though the Bose statistics of the excitons is neglected in the model.
In the experiments in cuprous oxide, three effects become apparent at about the same excitation intensity: the apparent exciton gas temperature becomes higher than that of the lattice, the exciton kinetic energy distribution is no longer a Maxwell-Boltzmann distribution, and Auger decay reduces the luminescence yield (the number of orthoexcitons that survive long enough to luminesce, per excitation photon). It is natural to suppose that the resulting non-Maxwellian distribution is the product of a competition between Auger heating and phonon-emission cooling of the excitons.

The exciton relaxation processes can be expressed in terms of a Boltzmann equation, or master equation, for the non-equilibrium occupation number \( \tilde{n}(\varepsilon) \) of the exciton quantum state with kinetic energy \( \varepsilon \). The following simplified Boltzmann equation describes the relaxation of the excitons as they emit and absorb acoustic phonons of momentum \( q \), thereby losing or gaining an energy equal to the phonon energy \( sq \), where \( s \) is the speed of sound in cuprite. From section 4.3 we have

\[
\frac{\partial}{\partial t} \tilde{n}(\varepsilon, t) = \frac{\Xi_0^2 m^3 s}{4\pi \rho \hbar^4 k(\hbar s)^2} \int_0^{2k+2ms} \left[ f_q \tilde{n}(\varepsilon-sq, t) - (1+f_q) \tilde{n}(\varepsilon, t) \right] q^2 dq \Theta(k>ms)  \\
+ \frac{\Xi_0^2 m^3 s}{4\pi \rho \hbar^4 k(\hbar s)^2} \int_0^{2k+2ms} \left[ (1+f_q) \tilde{n}(\varepsilon+sq, t) - f_q \tilde{n}(\varepsilon, t) \right] q^2 dq
\]

where the deformation potential \( \Xi_0 \) indicates the strength of the electron-lattice coupling, \( m \) is the exciton effective mass, \( \rho \) is the density of cuprite, and for brevity \( k = \sqrt{2m\varepsilon} \). We neglect any lattice heating, so for the phonon occupation numbers \( f_q \) we use the equilibrium values \( f_q = [\exp(sq/k_BT) - 1]^{-1} \). I purposefully omit the identical-particle scattering enhancement \([1+\tilde{n}]\) so as to model only kinetic effects, and not the effect of Bose statistics.

In the limit of small sound velocity \( s \), the energy of each emitted phonon becomes infinitesimal, but the phonon emission rate increases as \( 1/s \), so the exciton cooling rate through phonon emission reaches a finite limit. The Boltzmann equation reduces to partial differential equation in time and exciton energy [Inoue, 1976]. This limit does not apply in Cu_2O, but it will provide an analytical solution from which we can begin to understand what is happening in the real material. Taking the limit \( s \to 0 \), we have

\[
\frac{\partial}{\partial t} \tilde{n}(\varepsilon, t) \to \frac{\Xi_0^2 m^3 s}{4\pi \rho \hbar^4 \sqrt{ms^2/2}} \left\{ \varepsilon k_BT \frac{\partial^2}{\partial \varepsilon^2} + \frac{8\sqrt{\varepsilon}}{\sqrt{ms^2/2}} \left( \varepsilon k_BT \frac{\partial^2}{\partial \varepsilon^2} + (\varepsilon + 2k_BT) \frac{\partial}{\partial \varepsilon} + 2 \right) \tilde{n}(\varepsilon, t) - A \tilde{n}(\varepsilon, t) \right\}.
\]

I have added the term \(-A \tilde{n}(\varepsilon, t)\) to describe Auger decay. I have assumed that Auger recombination is independent of the relative velocities of the excitons so that the decay rate of the occupation number \( \tilde{n}(\varepsilon, t) \) is proportional to the exciton gas density \( n = \int \tilde{n}(\varepsilon, t) g(\varepsilon) d\varepsilon \), where \( g(\varepsilon) \) is the exciton density of states.
Suppose that excitons are being continuously created at high energy, $\varepsilon = \infty$, and cooling according to the differential equation above. The steady-state exciton distribution will be a solution to

$$\{ \varepsilon k_B T \frac{\partial^2}{\partial \varepsilon^2} + (\varepsilon + 2k_B T) \frac{\partial}{\partial \varepsilon} + 2 - \frac{a}{\sqrt{\varepsilon}} \} \tilde{n}(\varepsilon) = 0$$

where

$$a = A n \frac{4\pi \rho \hbar^4}{\varepsilon_0^2 m^3 s} \frac{\sqrt{m^2 s^2/2}}{8}.$$

When there is no decay, $a = 0$, a solution is $\tilde{n}(\varepsilon) \propto \exp(-\varepsilon/k_B T)$ — a Maxwell-Boltzmann distribution at the lattice temperature.\(^1\) If there is finite Auger decay, the steady state solutions must be determined by numerical integration of the differential equation, but at high kinetic energy they approach $\tilde{n}(\varepsilon) \sim 1/\varepsilon^2$. At low exciton kinetic energy, the steady state solution remains a Maxwell-Boltzmann at the lattice temperature $T$, so long as $a^2/k_B T$ is not too large.

![Figure 2: a) A numerical solution of the differential equation for $\tilde{n}(\varepsilon)$ in the text, which describes excitons, with an inverse lifetime of $A n = 10/\text{ns}$, exchanging phonons with a 2K lattice, under a simplified model which includes acoustic phonons only, and takes the limit of zero sound velocity (which is inappropriate for Cu$_2$O at 2K). Plotted is the steady-state kinetic energy distribution $\tilde{n}(\varepsilon) g(\varepsilon)$.

b) An experimental spectrum recorded during a 10ns pulse which from which the sample, at 2K, absorbed $2 \times 10^{15}$ photons per cm$^2$. The dominant broad feature is phonon-assisted luminescence which reproduces the orthoexciton kinetic energy distribution. The dashed curve is a Maxwell-Boltzmann distribution with the same apparent gas temperature of 40K.

c) Results of numerical integration of the full Boltzmann equation developed in chapter 6 assuming creation of $2 \times 10^{15}$ excitons per cm$^2$ in a 10ns pulse. The time shown is during the center of the generation pulse.](image)

In figure 2a is plotted the steady state kinetic energy distribution $\tilde{n}(\varepsilon)$ $g(\varepsilon)$ from this simple model with a lattice temperature of $T = 2K$ and $A n = 10/\text{ns}$ — appropriate for the experimentally reasonable case of $A = 10^{-16}$ cm$^3$/ns and $n = 10^{17}$/cm$^3$. This solution is qualitatively similar to the experimental spectrum in part b of the figure, which was observed during a 10ns laser pulse.

\(^1\)The second solution is $\tilde{n}(\varepsilon,t) \propto (k_B T/\varepsilon) - \exp(-\varepsilon/k_B T) \times Ei(\varepsilon/k_B T)$, which goes as $1/\varepsilon$ at low $\varepsilon$ and $-1/\varepsilon^2$ at high $\varepsilon$. It cannot be present in a physical solution because it would make $\tilde{n}(\varepsilon,t)$ negative for some $\varepsilon$. 

---

\(6\)
Comparing the data from an experiment using a 10ns pulse to a predicted steady-state
distribution is not unreasonable, because under this simplified model the time required for
acoustic phonon cooling to reduce the exciton energy to about 0.4meV (5K) is only
$$\frac{4\pi \rho \hbar^4}{\Xi_0^2 m^3 s} \frac{\sqrt{m s^2/2}}{4\sqrt{0.4\text{meV}}} \approx 1\text{ns}.$$ 

Both the theoretical and experimental distributions in figure 2 contain more weight at high
energies than a Maxwell-Boltzmann distribution at the 2K (0.17meV) lattice temperature, and
neither resembles the higher-temperature Maxwell-Boltzmann distribution which would fit the
high-energy tail.

This steady-state solution to the simplified model is even more strikingly different from a hot
Maxwell-Boltzmann than is the data. This is partially due to the unrealistic limit of zero sound
velocity. In real cuprite, acoustic phonon cooling is very slow for excitons with kinetic energy
on the order of $ms^2 = 0.34\text{meV (4K)}$. Incorporating this fact into the model lowers the peak at
low exciton energy, and reduces the similarity to the observed distributions. The competition
between phonon cooling and Auger decay is only part of the explanation of the observed
distributions.

We must also consider the spatial inhomogeneity of the exciton gas. In the experiments, a
pulse of light having a short absorption length creates excitons in a distribution which decays
exponentially with depth into the sample. High-density creation of excitons requires light with
an absorption length on the order of microns, so in most experiments the spectra represent the
superposition of local exciton distributions at various depths from the excited surface. The
exciton density, and through Auger heating the mean exciton energy, vary significantly with
depth into the crystal.

The model developed in chapter 6 follows the exciton occupation numbers as a function of
three variables: the distance $z$ from the crystal surface, the magnitude $k$ of the exciton
momentum, and to account for motion of excitons into the crystal, the component $k_z$ of the
exciton momentum normal to the surface. Optical phonon emission and conversion between
orthoexciton and paraexciton spin states must also be included. Still, the integration of the
Boltzmann equation can be done on a personal computer. Figure 2c presents the results of such a
simulation, assuming intense surface excitation creates $2\times10^{15}$ excitons per cm$^2$ in a distribution
with an exponential penetration depth of 2.5μm. The exciton occupation numbers computed

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2 Numerical modeling of elastic scattering between excitons is beyond the scope of this thesis.
Evidence that my conclusions survive in the presence of a reasonable elastic scattering cross-
section are presented in Appendix B.
from the model never exceed 0.03. Nevertheless, the transient kinetic energy distribution from
the model is just as suggestive of Bose-Einstein statistics as is the experimental spectrum.

In summary, cuprous oxide is a simple semiconductor with strongly bound excitons which
display their kinetic energy through phonon-assisted luminescence. It is possible to produce the
excitons at various energies and densities, allowing measurement of exciton-exciton interactions
and exciton energy relaxation rates. Using high excitation density, very interesting kinetic
energy distributions have been observed by our group and by several other groups [Hulin, 1980;
Naka, 1996; M. Y. Shen, 1997] and have thus far been interpreted only as a manifestation of the
Bose statistics of the excitons [Mysyrowicz, 1996; Swope, 1995]. Using a method I have
developed to measure the exciton gas density, I have found that I am unable to produce a gas of
excitons of sufficiently high density to exhibit quantum statistics. Nevertheless, I do find that the
transient kinetic energy distributions of the excitons have the Bose-Einstein shape. This thesis
draws upon our thorough understanding of excitons in cuprous oxide in order to explain the
observed distributions as the net result of the various known relaxation and decay processes for
excitons in Cu$_2$O. The resulting model is consistent with my observations of the exciton kinetic
energy distributions and exciton gas density.
2. THE STRUCTURE OF CUPRITE

2.1 Atomic structure and phonons

Cu$_2$O has an uncommon crystal structure, named the *cuprite* structure. The crystal is best described as two interpenetrating diamond lattices. The oxygen atoms sit where the carbon atoms do in diamond, and O-Cu-O chains replace the covalent carbon-carbon bonds. When the two diamond lattices are interwoven, a smaller unit cell appears. The Bravais lattice is simple cubic, with a lattice constant 0.427 nm. There is a center of inversion about each copper atom.

![Diagram of atomic structure](image)

Figure 3: The atomic structure of cuprous oxide. The larger circles are oxygen atoms. 

a) Copper in the center. The copper atoms form an FCC sublattice.

b) Oxygen in the center. The oxygen atoms form a BCC sublattice.

<table>
<thead>
<tr>
<th>$\Gamma$</th>
<th>Energy (meV)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3\Gamma_{15}^-$</td>
<td>0</td>
<td>acoustic modes</td>
</tr>
<tr>
<td>$^3\Gamma_{25}^-$</td>
<td>10.7</td>
<td>rigid rotation of the Cu$_4$O tetrahedron, bending the O-Cu-O bonds</td>
</tr>
<tr>
<td>$^2\Gamma_{12}^-$</td>
<td>13.6</td>
<td>all four Cu move toward the equator, then toward poles; Cu move along lines of constant latitude, twisting the tetrahedron</td>
</tr>
<tr>
<td>$^3\Gamma_{15}^-$</td>
<td>18.8 (TO) 19.1 (LO)</td>
<td>all Cu move North, then South, along lines of constant longitude; O move in opposition along [001] to keep the center of mass fixed</td>
</tr>
<tr>
<td>$^1\Gamma_{2}^-$</td>
<td>43.4</td>
<td>breathing mode of the Cu tetrahedron</td>
</tr>
<tr>
<td>$^3\Gamma_{25}^+$</td>
<td>63.8</td>
<td>relative motion of the two simple cubic O lattices</td>
</tr>
<tr>
<td>$^3\Gamma_{15}^+$</td>
<td>78.5 (TO) 82.1 (LO)</td>
<td>while northern Cu move toward the central O, the southern Cu move away; all O move in opposition along [001] to keep the center of mass fixed</td>
</tr>
</tbody>
</table>

Table 1: Symmetries, energies, and descriptions of the zone center phonons in cuprite. The descriptions refer to a globe centered on an oxygen, large enough to put sea level through the center of the four nearest copper atoms, with the equator lying in the (001) plane.
Six atoms per unit cell form $6 \times 3 = 18$ phonon modes, all of which can be seen in some way in luminescence spectra. Table 1 describes the phonon modes at zone center (zero wavevector, all the unit cells vibrating in phase). In the symmetry designations of these modes, $\Gamma$ refers to the center of the Brillouin zone; I use the historical notations to designate the symmetries of the phonons and electronic states, but denote parity by $'+'$ and $'-'$ (rather than with primes); and the left superscripts, when present, are the degeneracies of the states. The phonon energies in the table are taken from Petroff et al. [1975] but all are confirmed by my luminescence spectra, such as figure 7 in chapter 3.

### 2.2 Electronic structure

The Cu$^+$ ion electronic structure ends $3d^{10}\ 4s^0$, with the 4s levels only slightly higher in energy than the 3d levels. The Cu 3d levels form the valence band in Cu$_2$O, and the empty Cu 4s levels form the conduction band [Elliot, 1961]. Both the highest-energy state in the valence band and the lowest state in the conduction band are at the center of the Brillouin zone, meaning both states have the full periodicity of the lattice; Cu$_2$O has a direct bandgap.

Figure 4 depicts the band edge wavefunctions. Ignoring for the moment the spin part of the wavefunctions, the highest valence band state is triply degenerate. The wavefunction shown in the figure could be denoted by $xy$, taking the z-axis to be vertical. There are states $yz$ and $zx$ which have the same energy. This set of three states {$xy, zx, yz$} forms the representation $\Gamma^+_{25}$ of the cubic point group. (Appendix A collects the group theory used in this thesis.)

![Figure 4: The electronic wavefunctions that build the excitons in Cu$_2$O.](image)

a) A cartoon representation of the $\Gamma^+_6$ state at the bottom of the conduction band.

b) A cartoon of the spatial part of the $\Gamma^+_7$ and $\Gamma^+_8$ states at the top of the valence band.

The single spatial wave function at the bottom of the conduction band, call it $s$, forms the completely symmetric representation $\Gamma^+_1$. Including spin, the pair of states { $s^\uparrow$, $s^\downarrow$ } transforms as a spinor, $\Gamma^+_6$. Including spin in the valence band wavefunctions makes six degenerate states. Spin-orbit coupling lifts the degeneracy, separating two $\Gamma^+_7$ states from four $\Gamma^+_8$ states. (Formally, the product of the space and spin wavefunctions is reducible as $\Gamma_{25}^+ \times \Gamma^+_6 = \Gamma^+_7 + \Gamma^+_8$.)

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1For example, the notation for the zone center modes is that of that of Bouckaert, Smoluchowski and Wigner, 1936, Phys Rev 50, 58.
experiments on excitonic absorption in Cu₂O determined that the Γ⁻⁷ valence band states are higher in energy. Using tables in Koster [1963], we can write the Γ⁺⁷ states explicitly as \{ (yz+izx)↓ + xy↑, (yz-izx)↑ - xy↓ \}.

Figure 5 shows the band structure of Cu₂O near zone center, showing the experimentally determined separations. The higher Γ⁻⁸ conduction band, made from Cu 4p orbitals, is included because it is important as an intermediate state for the electron in phonon-assisted exciton luminescence, and because it is close enough in energy that it could contain the electron emitted from an Auger recombination.

The Γ⁺⁷ to Γ⁺⁶ bandgap is called the yellow bandgap, and electron-hole pairs across this bandgap form an entire Rydberg series of exciton states, including the ortho and paraexcitons studied in this thesis. The Γ⁻⁸-to-Γ⁺⁶ bandgap supports the green exciton series. Optical excitation of a valence band electron to the Γ⁻⁸ conduction band is dipole-allowed, producing the strong blue and indigo absorption bands.

I should point out that my earlier statement, “the band edges in cuprous oxide both have even parity”, refers only to the band extrema at zone center. Parity is a “good quantum number” at only two points in the Brillouin zone: the zone center point Γ and the corner point R. Most band structure calculations [Dahl, 1966; Kleinman, 1980; Ruiz, 1997] for Cu₂O predict that the lowest conduction band center has even parity at the zone center point Γ, and odd parity at the point R. The highest valence band has even parity at both points.

For this reason, optical transitions between the highest valence and lowest conduction bands is dipole forbidden only at zone center. The vertical transitions induced by argon ion laser light for example, with photon energy 2409 meV, take place far from zone center. These transitions are dipole-allowed, and strong enough to absorb the light within 3μm. From this absorption length we can estimate the dipole matrix element between the bands. Using the effective mass approximation for the joint density of states in the transition, the absorption coefficient is given by the expression [Madelung, 1978, section 6.2.2]

\[ \alpha = \frac{4\pi e^2}{\varepsilon_0} \frac{\hbar^2}{m^2 \omega c n} \sum_{\alpha,\beta} \langle \alpha|k|\beta k \rangle^2 \left( \frac{m_{\text{red}} k}{\pi^2 \hbar^2} \right) \]

where the vertical transition takes place at wavevector \( k = \sqrt{2\mu(\hbar\omega - E_{\text{gap}})} / \hbar \), \( m_{\text{red}} \) is the reduced mass \( 1/m_{\text{red}} = 1/m_e + 1/m_h \), and α and β are band indices. Assuming the three valence bands
stemming from the \( \Gamma_7^+ \) and \( \Gamma_8^+ \) states at zone center contribute equally to the absorption, the 3\( \mu \)m absorption length of 2049 meV light, for which \( k=1.6/\text{nm} \), implies a dipole matrix element of magnitude \( \langle c, k|\nabla|v, k\rangle \approx 0.3/\text{nm} \) between each of these valence bands and the \( \Gamma_6^+ \) conduction band. Since this dipole matrix element is zero at zone center, one might reasonably assume that \( \langle c, k|\nabla|v, k\rangle \approx k/5 \).

2.3 Building excitons

The Rydberg formula, taking the dielectric constant \( \varepsilon \approx 7\varepsilon_0 \) and using SI units,

\[
E_{\text{binding}}, n = \frac{m_{\text{red}} e^4}{2(4\pi \varepsilon_0 h)^2} \frac{1}{n^2} = \frac{100 \text{meV}}{n^2},
\]

correctly predicts the binding energies of all the yellow exciton energies within a few meV — except for the \( n=1 \) state. The 1s yellow paraexciton binding energy is 152meV. Most authors agree that the extra binding energy is due to ‘central cell corrections’ to the effective mass approximation, which should arise when the electron and hole are likely to be found in the same unit cell.\(^2\) The Bohr radius, \( a_0 = 4\pi \varepsilon_0 h^2/m_{\text{red}} e^2 = 1.0 \text{nm} \), is in fact comparable to the size of a the unit cell. We will, however, follow the convention [Yu and Shen, 1975] to define the Bohr radius of the 1s exciton so as to agree with the actual 1s exciton binding energy:

\[
152 \text{meV} = \frac{e^2}{2a_0} \frac{1}{4\pi \varepsilon_0}; \quad a_0 = 0.7 \text{nm}.
\]

(This is equivalent to using a 50% larger reduced mass \( m_{\text{red}} \) for the 1s exciton only.) The fact that the binding energy of the 1s exciton is comparable to the spin-orbit splitting between the highest valence bands (figure 5) forces us to consider both the yellow and green excitons as we turn to consideration of the internal structure of the 1s excitons.

For reference, the various masses referred to are:

\[
\begin{align*}
  m_0 & \quad \text{free electron mass} \quad 9.1 \times 10^{-31} \text{ kg} \\
  m_e & \quad \Gamma_6^+ \text{ electron effective mass} \quad 0.99 m_0 \quad \text{[Ohyama, 1997]} \\
  m_h & \quad \Gamma_7^+ \text{ electron effective mass} \quad 0.58 m_0 \quad \text{[Ohyama, 1997]} \\
  m_{\text{red}} & \quad \text{electron-hole reduced mass} \quad 0.37 m_0 \\
  m & \quad \text{1s exciton effective mass} \quad 3.0 m_0 \quad \text{[Yu, 1975]}
\end{align*}
\]

\(^2\)That is, on the scale of the unit cell, plane waves are not sufficient approximations to the Bloch wavefunctions of the electron and hole. Alternatively, thinking in momentum space, the small 1s exciton wavefunction needs considerable contributions from Bloch functions with large wavevectors, for which the effective mass approximation is not good. All calculated band structures agree that at large wavevector, the band energy is less than that predicted by the effective mass approximation. The 1s exciton gets the spatial sharpness it needs to take advantage of the Coulomb attraction at a bargain price in kinetic energy. Kavoulakis et al. [1997] have shown that the extra binding energy and extra mass (\( 3m_0-0.58m_0+0.99m_0 \)) of the 1s exciton can be simply and consistently explained in this way.
Figure 6: An energy-level diagram for the 1s excitons in Cu$_2$O. Moving away from the
center, interactions are switched off one at a time as indicated by the column headings. All
the states shown are even parity, so the parity symbols are omitted.

Using the one electron state and three degenerate hole states shown in figure 4, with two spin
states for each electron and hole, we can build twelve different 1s excitons. Figure 6 shows how
spin-orbit coupling and the exchange interaction split these excitons into the ortho- and
paraexcitons of the yellow and green exciton series. Each time we add an interaction which
breaks a degeneracy, we move from a degenerate set of product wavefunctions, designated in
figure 6 by the product of representations, to non-degenerate sets of intertwined wavefunctions.
The pattern by which the degeneracies split can be predicted by reducing the product
representations using a cubic group multiplication table (one is reproduced in appendix A). For
example, 1s excitons built from an electron in the $\Gamma_6^+$ conduction band and a hole in the $\Gamma_7^+$
valence band would split (looking up $\Gamma_6^+ \times \Gamma_7^+ = \Gamma_2^+ + \Gamma_{25}^+$) into a $\Gamma_2^+$ singlet and a $\Gamma_{25}^+$ triplet under
the exchange interaction.

If we start with the crystal in the ground state, both of the $\Gamma_7^+$ valence band states are filled.
Their wave function is the antisymmetrized product of $(yz + izx)\downarrow + xy\uparrow$ and $(yz - izx)\uparrow - xy\downarrow$:

\[
(-i\ yz\ zx + i\ zx\ yz)(\downarrow\uparrow + \uparrow\downarrow) + (xy\ yz - yz\ xy)(\uparrow\uparrow + \down\down) + (xy\ zx - zx\ xy)(-\down\up + i\down\down) \\
+ (yz\ yz + zx\ zx + xy\ xy)(\down\up - \down\down)
\]
where spatial and spin parts have been factored as far as possible and each product denotes a product wavefunction with electron number one in state listed first in the product, electron number two in the state listed second.

Now apply an oscillating electric quadrupole field oriented as \( xy \), and tuned to the 1s yellow exciton absorption line. It will boost one electron from an \( xy \) state into an conduction band state \( s \) without flipping the spin. The new wave function of these two electrons is

\[
(s \, yz - yz \, s)(\uparrow\uparrow + \downarrow\downarrow) + (s \, zx - zx \, s)(-i\uparrow\uparrow + i\downarrow\downarrow) + (s \, xy + xy \, s)(\downarrow\uparrow - \uparrow\downarrow).
\]

To write this more concisely, let \( \theta_z \) denote the spin state with total spin 1 and zero spin component along \( z \) and let \( \phi \) denote the spin state with total spin 0. Now we have

\[
(s \, yz - yz \, s)\theta_y - (s \, zx - zx \, s)\theta_x - (s \, xy + xy \, s)\phi.
\]

Two other degenerate wave functions can be constructed from this one by cycling \( x-y-z \), so this is one of the three orthoexcitons, which have the designation \( \Gamma_2^+ \).

The remaining combination of a \( \Gamma_6^- \) electron and a \( \Gamma_7^- \) hole is the paraexciton, designated \( \Gamma_2^- \):

\[
(s \, yz - yz \, s)\theta_x + (s \, zx - zx \, s)\theta_y + (s \, xy - xy \, s)\theta_z.
\]

To produce the paraexciton from the ground state would require something on the order of a simultaneous electric quadrupole field oriented as \( xy \) and magnetic field along \( z \).

The exchange splitting raises the orthoexciton triplet 12meV above the paraexciton singlet. This seems opposite from the usual rule—"spin-singlet implies a symmetric spatial wavefunction and higher Coulomb energy"—but spin-orbit coupling has made the hole states more complicated than pure spin states. The singlet paraexciton is not a spin-singlet; in the last paragraph we found the spin part of its wave function to be purely spin-one. It is the orthoexciton which has a spin-singlet, spatially symmetric, term in its wavefunction and thus an enhanced Coulomb repulsion between the conduction-band electron and the unpaired valence-band electron.

The orthoexciton wave functions given above are not perfect, as revealed experimentally by the splitting of the orthoexciton triplet to first order in strain. The states above, being formed by electron and hole wavefunctions each with Kramers' degeneracy, remain degenerate in a strained crystal. The real orthoexciton must have some of the \( \Gamma_6^+ \) band mixed into its hole wavefunction [Waters et al., 1980]. The only rigorously true statement we can make about the orthoexcitons is that they transform as \( \Gamma_2^+ \), so we will forget the detailed wavefunctions and refer to them simply as the \( yz, zx, \) and \( xy \) orthoexcitons from now on.

Finally, it is enlightening to consider spin-orbit and exchange interactions in the "wrong" order, as is done in figure 6 working right to center. Starting fresh with the twelve degenerate states (which we can factor into spin parts times spatial parts) we apply exchange coupling to the spin parts only and get the familiar result: the spin-0 state higher than the spin-1 state. The spin-
1 are optically forbidden. The spin-orbit interaction splits the 9-fold degeneracy of this lower level into 1, 3, 5-fold degenerate levels, the same pattern which results from coupling two systems each with angular momentum 1. The spin-orbit energy increases with total angular momentum, just like in the Hydrogen atom.

From this point of view, it would seem that all of the yellow excitons would be optically forbidden because their electronic spin is 1. However the spin-orbit interaction will mix the $^{3} \Gamma_{25}^{+}$ yellow orthoexciton with the green exciton of the same symmetry, giving the yellow orthoexciton some spin-0 character, and the ability to luminesce through its electric quadrupole. Despite their weak interaction with light, the 1s yellow excitons are the lowest-energy electronic excitations in Cu$_2$O, and they dominate the luminescence spectrum.
3. OPTICAL ABSORPTION AND LUMINESCENCE

3.1 Luminescence Spectra

In figure 7 we see luminescence due to direct radiative recombination of the orthoexciton at the energy of an orthoexciton at rest, 2033.2 meV. The paraexciton direct luminescence would appear at 2021.2 meV if its direct radiative recombination were allowed. Most of the other lines are due to phonon-assisted recombination of 1s yellow excitons. Each of these lines reproduces the exciton kinetic energy distribution. For example, close examination of the high-energy tail of the orthoexciton $\Gamma_{12}$-assisted line indicates that the orthoexcitons are not quite thermalized.

![Cu$_2$O luminescence at 2K](image)

Figure 7: Luminescence under continuous illumination by the 514.5nm (2409meV) Argon ion laser line. The luminescence was collected from the same side of the sample as the incident light to reduce reabsorption of the luminescence by the crystal.

The line marked ‘unknown’ at 1912 meV was once thought to be due to excitonic molecules. Petroff et al. [1972] found that this line increased only linearly with excitation intensity, and that it disappeared at higher lattice temperatures, indicative of a bound exciton. A wider luminescence spectrum, observed in a sample cut from the same crystal of mineral cuprite as were all the samples used in this work, has been published by Ohyama et al. [1997]. Our sample source, a crystal donated by the Smithsonian Institute, shows far fewer bound excitons and oxygen vacancies than another mineral sample evaluated by Ohyama et al.
<table>
<thead>
<tr>
<th>Orthoexcitons</th>
<th>Paraexcitons</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{15}$ (90meV)</td>
<td>$\Gamma_{25}^+$</td>
</tr>
<tr>
<td>$\Gamma_{25}$</td>
<td>$\Gamma_2$</td>
</tr>
<tr>
<td>$\Gamma_{15}$ (19meV)</td>
<td>$\Gamma_{12}$</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>21</td>
<td>500</td>
</tr>
<tr>
<td>17</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 2: The relative phonon-assisted luminescence rates for ortho- and paraexcitons.

In table 2 the relative efficiencies for the various phonon-assisted luminescence processes of orthoexcitons were obtained from luminescence spectra such as figure 7. These spectra do not indicate the luminescence efficiency of the paraexciton relative to that of the orthoexcitons, because the relative numbers of orthoexcitons and paraexcitons is not known. The relative luminescence efficiencies for paraexcitons versus orthoexcitons is determined by comparing the corresponding phonon-assisted absorption coefficients, first reported by Bloch and Schwab [1978], and then applying the detailed balance argument of section 3.3.

3.2 Absorption spectra

Figure 8 shows the optical absorption of cuprous oxide in the immediate vicinity of the exciton energy. Although optical creation of 1s excitons is dipole-forbidden, the orthoexciton can be created through an electric quadrupole transition. At the peak of this absorption line, the absorption length is on the order of 2mm, depending on the crystal axis and polarization of the light.

The absorption bands to the blue of the direct absorption line are due to phonon-assisted exciton absorption. This process is the dipole-allowed simultaneous creation of an orthoexciton and an optical phonon. Any photon energy above the threshold goes into orthoexciton kinetic energy, with the phonon completing the momentum conservation triangle. In the 2K spectrum, the $\Gamma_{25}$-assisted absorption is barely visible, starting at 2044meV, then the $\Gamma_{12}$-assisted absorption begins with absorption coefficient (the inverse of the absorption length)

$$\alpha(\epsilon) = 8.0 \pm 0.5 \text{ cm}^{-1} \sqrt{\epsilon / \text{meV}}$$

where $\epsilon$ is the amount by which the photon energy exceeds the threshold; $\epsilon$ is also the kinetic energy of the orthoexciton produced. (Previous measurements of the prefactor above are 12cm$^{-1}$meV$^{-1/2}$ [Grun, 1961] and 3.7cm$^{-1}$meV$^{-1/2}$ [Gorban', 1962].) The energy dependence of

---

1 In thermal equilibrium in a 2K lattice the ratio of paraexcitons to orthoexcitons would be $10^{30}:1$. It would take several hundreds of nanoseconds to reach this ratio, in which time a considerable fraction of the paraexcitons may have decayed or diffused out of the region from which luminescence is collected.

2 Despite the direct absorption line, we often use an experimental arrangement in which the luminescence travels through the sample, typically 2mm thick, before collection. Therefore some of the spectra in this thesis have the direct luminescence line distorted due to reabsorption of the luminescence. The effect is typically a 50% reduction in height at the peak.
the absorption has the same shape, $\sqrt{\varepsilon}$, as the density of final states for the exciton, indicating that the matrix element for absorption is independent of the momenta of the orthoexciton and phonon produced.

![Graph](image)

**Figure 8:** Optical absorption by $1s$ orthoexcitons. The sharp absorption lines are due to resonant creation of excitons. The strong absorption band at 2K is due to creation of an exciton and a $\Gamma_{12}$ phonon. The dashed curve through the data is $\alpha(\varepsilon) = 8.0 \sqrt{\varepsilon}$. If this absorption band is multiplied by $f$ and $(1+f)$, where $f$ is the thermal occupation at 77K of the $\Gamma_{12}$ phonon, it fits the absorption bands at 77K (dashed lines at right).

If there are ambient optical phonons, there can be phonon-assisted absorption events in which an optical phonon is destroyed. At higher lattice temperatures, an anti-Stokes absorption band appears with its threshold one optical phonon energy to the red of the direct line. The absorption coefficient is $\alpha(\varepsilon)$ as quoted above, multiplied by the occupation number of the optical phonon. The blue-shifted Stokes absorption band is also enhanced due to stimulated phonon emission at higher lattice temperatures. Once $\alpha(\varepsilon)$ was determined from the 2K spectrum in figure 8, the 77K spectra was fit using no adjustable parameters.

For light traveling along a $(001)$ direction, the direct absorption line is unpolarized, and its integral is $1.8 \text{ cm}^{-1} \text{ meV}$ for a crystal at 77K. At 2K the integrated absorption is only $0.6 \text{ cm}^{-1} \text{ meV}$. This reduction in the direct absorption strength below around 40K was studied by Kreingol'd and Makarov [1975], who attribute it to insufficient exciton-phonon scattering, using the model of J. J. Hopfield. Hopfield [1958] pointed out that the exciton-photon coupling alone would allow an excitation to propagate through the crystal as an exciton-polariton, oscillating between exciton and photon, then emerge as a photon on the other side. Dissipation is required for absorption of light. The absorbance is limited by the slower of the two processes: the exciton-photon oscillation and scattering of the exciton out of the momentum states which can directly luminesce. Later in this chapter we find that the exciton-photon coupling strength, expressed as a frequency, is $\gamma = 260/\text{ns}$. In chapter 4 we discuss the rate at which excitons are scattered out of the lowest kinetic-energy states, which M. Y. Shen *et al.* [1997] measured to be only $0.8/\text{ns}$ at 1.8K in a 2K crystal.
For ease of comparison with other reports, we can convert the direct line absorption strength $\alpha_d$ into an oscillator strength $f$ defined by [Dexter and Knox, 1965]

$$f = \frac{2c}{\pi\hbar \omega_p^2} \int n \alpha_d(\varepsilon) \, d\varepsilon$$

$$= 7.1 \times 10^{-10} \text{ cm/meV} \int n \alpha_d(\varepsilon) \, d\varepsilon$$

where $\omega_p$ is the plasma frequency for one electron per unit cell ($\omega_p = 6.4 \times 10^{15}/s$ in Cu$_2$O). For direct absorption along a $<001>$ direction, $f = 3.8 \times 10^{-9}$. For the index of refraction $n$ we refer to Karlsson et al. [1982] who find that $n$ increases from near 2.6 in the infrared, to a peak of 3.1 at 2500meV. In the region of exciton luminescence, around 2100meV, the index of refraction is 3.0.

![Absorption curve](image)

**Figure 9:** Absorption curve for cuprous oxide measured using a slice of cuprite approximately 10µm thick. The thickness was determined by counting interference fringes where the absorption is weak. The inset shows the yellow exciton Rydberg series, n=2 through 6; the green exciton Rydberg series is in the center of the main figure. The strong argon ion laser transition at 514.5nm has photon energy 2409meV.

Most of the experiments we will be discussing use argon ion laser light with wavelength 514.5nm, photon energy 2409meV. Published absorption strengths at this wavelength are hard to find. This section of the absorption curve, midway in between the green exciton series, and the blue and indigo absorption bands, seems too boring to merit publication. Since it is of great interest to me, I measured the absorbance of a 10µm slab of mineral Cu$_2$O. The thickness of the sample was determined from interference fringes seen in the transmission curve below 2100meV,
assuming an index of refraction $n = 3.0$. My measured absorbance, figure 9, is roughly 30% less than that reported by Grun et al. [1961] in the region they publish. Pending a better absorption measurement, I use the average of my measurement ($\alpha = 3300\text{cm}^{-1}$) and extrapolation of the data of Grun et al. ($\alpha = 5000\text{cm}^{-1}$) and use $2.5\mu\text{m} \pm 0.5\mu\text{m}$ for the absorption length of 2409meV photons.

### 3.3 Detailed balance

Since Cu$_2$O has a dipole-forbidden direct gap, exciton luminescence is quite slow — much too slow, it turns out, to be seen in the exciton lifetime. However, in figure 8 we have a measure of the rate of the inverse process. From the strength of the absorption and a detailed model of the absorption process, one could obtain numerical estimates of the matrix elements involved. Then with those matrix elements and the same detailed model, one could work out the rate of spontaneous emission. Alternatively, we can avoid the need for a detailed model by using thermodynamic arguments and the principle of detailed balance, which was first applied to luminescence in semiconductors by van Roosbroeck and Shockley [1954].

Consider a material which supports optical excitations with a density in energy of $g(h\omega)$ and an absorption coefficient $\alpha(h\omega)$. A photon moving through the crystal at speed $c/n$, where $n$ is the index of refraction, has a probability per unit time of being absorbed which is equal to $\alpha(h\omega) c/n$. The rate of absorption of thermal radiation per unit volume of material is then

$$\alpha(h\omega) \frac{c}{n} \rho(h\omega) f_\rho(h\omega) \left[1 \pm f_x(h\omega)\right]$$

where $\rho(h\omega) = n^3 \omega^3 / \pi^2 c^3 h$ is the photon density of states, $f_\rho$ is the thermal occupation number for the photons. The last factor describes either saturation or stimulated absorption depending on the statistics of the excitations, whose occupation number is denoted by $f_x$.

Defining $\gamma(h\omega)$ to be the rate of spontaneous emission for the excitation at energy $h\omega$, the total rate of emission of radiation per unit volume of material is then

$$\gamma(h\omega) g(h\omega) f_x(h\omega) \left[1 + f_\rho(h\omega)\right].$$

When the material is in thermal equilibrium with the radiation field, by the principle of detailed balance the absorption and emission rates match at each energy $h\omega$. Solving for the spontaneous emission rate,

$$\gamma(h\omega) = \frac{c \alpha(h\omega) \rho(h\omega) f_\rho(h\omega) \left[1 \pm f_x(h\omega)\right]}{n g(h\omega) f_x(h\omega)} \frac{1}{1 + f_\rho(h\omega)}.$$

If the $f$'s are thermal equilibrium occupation numbers, then the last two fractions above are equal to $\exp(-h\omega/kT)$ and $\exp(+h\omega/kT)$ respectively, regardless of the Bose- or Fermi statistics of the excitations. We have the general relation

$$\gamma(h\omega) = \frac{c \alpha(h\omega) \rho(h\omega) \left[1 \pm f_x(h\omega)\right]}{n^2 \omega^2 \pi^2 c^2 h g(h\omega)}.$$

20
The applicability of detailed balance to luminescence in solids has been confirmed precisely for the R lines of ruby [Nelson, 1964] in which case the absorption and luminescence lines are narrow and coincident. On the other hand, the detailed balance argument fails to correctly predict the luminescence rate of the F-center in the alkali halides [Fowler, 1966] where the absorption and luminescence lines are separated by 1eV. In the alkali halides, the ions near the color center move in response to the electronic excitation, so the emission occurs in a different environment than the absorption. This difference in environment changes both the position and the oscillator strength of the emission line. The detailed balance argument cannot relate absorption observed in one environment with emission observed in a different environment.3

The detailed balance argument can be successfully applied to Cu2O, so long as we are careful to use an absorption process which is truly the inverse of the luminescence process.

3.4 Phonon-assisted luminescence rates

In spectra from a 2K crystal, such as figure 7, the phonon-assisted luminescence lines appear red-shifted from the direct line. The luminescence process is

\[ \text{exciton} \rightarrow \text{phonon} + \text{photon} \]

so the inverse process must be

\[ \text{photon} + \text{phonon} \rightarrow \text{exciton} \]

which is the red-shifted absorption band, visible only when the lattice is warm enough to have optical phonons in the initial state. This red-shifted absorption is visible in the 77K spectrum in figure 8 at the start of this chapter, but not in the 2K spectrum. Even though the red-shifted absorption in a 2K crystal is too weak to measure directly, we know that its strength is that of the blue-shifted absorption, times the occupation number of the assisting phonon.

We generally express the absorption coefficient \( \alpha(\varepsilon) \) as a function of the kinetic energy \( \varepsilon \) of the exciton. The photon energy is then \( h\omega = \varepsilon - E_{12} \), where \( E_{12} \) is the energy of the \( \Gamma_{12} \) optical phonon. Letting \( f_{12} \) denote the phonon occupation number, the rate of absorption is

\[ \alpha(\varepsilon) \left( \frac{c}{n} \rho(\hbar\omega) f_p(\hbar\omega) f_{12}(E_{12}) [1 + f_x(\varepsilon)] \right) \]

and the luminescence rate is

\[ \gamma_{12}(\varepsilon) g(\varepsilon) f_x(\varepsilon) [1 + f_{12}(E_{12})] [1 + f_p(\hbar\omega)]. \]

Balancing these rates and solving for \( \gamma \),

\[ \gamma_{12}(\varepsilon) = \frac{c}{n} \frac{\alpha(\varepsilon) \rho(\hbar\omega) f_p(\hbar\omega) f_{12}(E_{12}) [1 + f_x(\varepsilon)]}{g(\varepsilon) f_x(\varepsilon) [1 + f_{12}(E_{12})] [1 + f_p(\hbar\omega)]} \]

3Jordan Markham [1965] proposed a modification to the detailed balance method which changes the results even if there is no shift between the emission and absorption lines. I choose not to apply his method.
\[ \frac{n^2 \omega^2}{\pi^2 c^2 \hbar} \frac{\alpha(\varepsilon)}{g(\varepsilon)} \exp(h\omega/kT) \exp(E_{12}/kT) \exp(-\varepsilon/kT) \]
\[ = \frac{n^2 \omega^2}{\pi^2 c^2 \hbar} \frac{\alpha(\varepsilon)}{g(\varepsilon)}. \]

The density of states for free excitons of mass \( m \) and spin degeneracy \( g_0 \) is
\[ g(\varepsilon) = \frac{g_0}{4\pi^2} \left[ \frac{2m}{\hbar^2} \right]^{3/2} \varepsilon^{3/2}. \]

For orthoexcitons in Cu$_2$O, with \( g_0 = 3 \) and \( m = 3m_o \) [Yu, 1975] and using \( n=3 \) [Karlsson, 1982], the phonon-assisted luminescence rate is
\[ \gamma_{12} = \frac{\sqrt{2}}{c^2 g_0} \frac{n^2 (\hbar\omega)^2}{m^{3/2}} \frac{\alpha(\varepsilon)}{\sqrt{\varepsilon}} = 7.0 \pm 1.3 \times 10^4 /s \]

where most of the uncertainty is due to the uncertainty in the exciton effective mass.

3.5 Direct luminescence rate

Only those orthoexcitons whose momenta are the same as that small momentum of a 2033meV photon are able to directly luminesce. Therefore the spontaneous luminescence rate \( \gamma(\varepsilon) \) and absorption coefficient \( \alpha_\lambda(\varepsilon) \) are both sharply peaked near \( \varepsilon=0 \). We can use the result of section 3.3 by integrating both sides:
\[ \gamma D = \int \gamma(h\omega) g(h\omega) dh\omega = \frac{n^2 \omega^2}{\pi^2 c^2 \hbar} \int \alpha_\lambda(h\omega) dh\omega. \]

We imagine \( \gamma \) to be the luminescence rate for those excitons in momentum states which can directly luminesce, of which there are \( D \) per unit volume of crystal. Using the full value of the direct absorption coefficient along [100], \( \int \alpha_\lambda(h\omega) dh\omega = 1.8 \text{ cm}^{-1} \text{ meV}, \) we find \( \gamma D = 26 \text{ /ns /\mu m}^3. \)

We can roughly separate the factors \( D \) and \( \gamma \). The orthoexcitons which can directly luminesce lie in a spherical shell in \( \mathbf{k} \)-space which has radius \( k_o = \omega n/c = 3.1 \times 10^7 / \text{m}. \) The thickness of this shell is estimated by broadening the orthoexciton energy by \( \hbar \gamma \) in accordance with the uncertainty principle. This allows the photon wavevector to vary by \( \Delta k = (\gamma/\omega) k_o. \) The number of orthoexciton states which can directly luminesce is then
\[ D = \frac{1}{(2\pi)^3} \int_{\text{shell}} d^3k = \frac{4\pi}{(2\pi)^3} k_o^2 \Delta k = \frac{k_o^3}{2 \pi^2} \frac{\gamma}{E_x}. \]

This relation allows us to separate the product \( \gamma D = 26 / \text{ns /\mu m}^3 \) into \( \gamma \approx 260 / \text{ns} \) (\( \hbar \gamma = 0.15 \text{ meV} \)) and \( D \approx 0.1 / \text{\mu m}^3. \) A more detailed investigation of the direct absorption by Frölich et al. [1991] treats this issue more rigorously.

Gross and Kaplyanskii [1962] used the direct absorption strength and Smakula’s equation, which relates spontaneous emission rates to the oscillator strength of the corresponding absorption line, to estimate the orthoexciton lifetime against direct recombination to be 20 seconds, much longer than \( (1/260) \text{ns} \) ! This discrepancy can be resolved. In 1962, it was not
clear whether the excitons in Cu$_2$O were localized or free, and Gross simply treated them as one Lorentz oscillator per unit cell. We regain his estimate by taking $\gamma(\varepsilon)$ to be a constant over the entire band.\footnote{There are other corrections necessary to reconcile the calculation here with that of Gross and Kaplyanskii. They used an integrated absorption of only 1.3cm$^{-1}$meV, and included two correction factors, a factor of $[1 + (n^2-1)/3]^2$ for the Lorentz local field and a factor of $n$ for the photon density of states, for emission but not for absorption.} Equivalently, we can take $D$ to be one state per unit cell, $D = (0.427\text{nm})^{-3}$. The actual lifetime against direct recombination of a gas of thermalized orthoexcitons would be 20 seconds if the bands were so narrow that thermal energies spread the exciton momentum distribution uniformly across the Brillouin zone.

3.6 Ratio of direct to phonon assisted luminescence

In a gas of orthoexcitons exhibiting Bose-Einstein statistics, one would expect the high occupation of low-energy states to show itself in the direct luminescence intensity. For an equilibrium Bose distribution of orthoexcitons, the ratio of direct to phonon-assisted luminescence observed along a $\langle 100 \rangle$ direction should be

$$\frac{I_{\text{direct}}}{I_{\text{assisted}}} = \frac{\gamma D f_x(0)}{\gamma_{12} \Omega f_x g e^{-\frac{\Omega}{T}}} = \left(10 \pm 1\right) \left[\frac{10^6 K}{T}\right]^{5/2} \frac{n_q}{n} \frac{1}{\exp(\mu/kT) - 1} \rightarrow \text{low density} \left(10 \pm 1\right) \left[\frac{10^6 K}{T}\right]^{5/2}$$

where $n_q$ is the quantum density, $n_q = g_\text{o} (mk_BT/2\pi\hbar^2)^{3/2}$, and $\mu$ is the chemical potential of the orthoexcitons relative energy of an orthoexciton with zero kinetic energy. As the gas density approaches the critical density for Bose-Einstein condensation, the chemical potential $\mu$ goes to zero, and this ratio $I_{\text{direct}}/I_{\text{assisted}}$ increases as $1/|\mu|$. First, we should check the prediction of our formula at low exciton density.

![Figure 10: Luminescence spectra a long time (30ns) after an argon-ion laser pulse. Spectra were collected from the same (001) face of the crystal as was excited. In the spectrum from the crystal at 2K at left, weak luminescence from the paraexcitons is visible at 2010 meV. In the 70K spectrum, the anti-Stokes phonon-assisted luminescence band is visible at 2040 meV.](image)
Figure 10 consists of luminescence from low-density exciton clouds collected from the (001) face of a cuprite sample at two different lattice temperatures. At 70K, the ratio of the direct luminescence intensity to the integral of the phonon-assisted line is 0.018 as predicted in the preceding paragraph (after factoring out $(1+f_{12})$ so as to count only spontaneous phonon emission). At a crystal temperature of 2K, the ratio is 1.1, about one third the prediction above. This factor of three shortfall is close to the reduction in the direct absorption upon cooling the crystal to 2K, and appears for the same reason. Phonon scattering is not fast enough to fully repopulate those orthoexciton momentum states which can directly luminesce.

If, however, the excitons are exchanging energy quickly through elastic collisions, the low momentum orthoexcitons states which can directly luminesce will be repopulated through these collisions. Then the direct line strength should then increase. Snoke et al. [1987] did report an increase, at high excitation density, of the direct line height ($S_d$) relative to the height of the phonon assisted line ($S_p$). At the highest densities reported by Snoke et al. the ratio $S_d/S_p$ was more than twice its limiting value at low densities. Snoke et al. presented this effect as strong evidence for quantum degeneracy—that is, occupation numbers greater than one.

However, I have found that the ratio $S_d/S_p$ is independent of excitation intensity over a wide range. Figure 11 shows the results of an attempt to observe an increase in the relative strength of the direct line. The upper two spectra result from low-power continuous excitation of cuprite held at 2K, and show orthoexcitons in a Maxwellian distribution at 3K. The lower two spectra result from intense pulsed excitation (about $5 \times 10^5$ W/cm$^2$ peak incident power in 10ns pulses). The relative heights of the direct and phonon-assisted luminescence lines change very little—the height ratio moving slightly in favor of the phonon-assisted line at higher power density—despite the dramatic change in the exciton kinetic energy distribution. This data directly contradicts the earlier report.

The spectra at the left of figure 11 were collected from the same side of the sample as was illuminated by the laser, so that the luminescence passed through only a few microns of cuprite before being collected. Checking for the possibility that the previously reported relative increase in direct luminescence intensity may have been an artifact of reabsorption by the crystal, we also collected luminescence which had passed through the 2.5mm thick crystal. The sole effect of this change in geometry was the expected reduction in the observed direct line height.

To ensure that the “intense” excitation which produced the lower spectra in figure 11 did in fact produce kinetic energy distributions indicating quantum degeneracy, I fit the time-resolved luminescence from the experiment of figure 11b. Figure 12 shows the spectrum during the 10ns laser pulse (recorded with 3ns time-resolution) and a fit to a highly degenerate Bose distribution. I am resigned to disregard the earlier observation without an explanation of its origin.
Figure 11: a) Luminescence spectrum resulting from continuous wave argon ion laser excitation of cuprite at 2K, with the luminescence collected from the same side of the crystal as was illuminated. (The spectrometer resolution function is a triangle with full-width at half-maximum equal to 0.14meV.)
b) Time-integrated luminescence resulting from intense pulsed excitation. The laser was focused to a 20µm diameter spot and the crystal absorbed 0.2µJ from each 10ns pulse.
c) The same experiment as in part a, but viewed through the 2.5mm crystal.
d) The experiment of part b, viewed through the 2.5mm crystal.

Figure 12: Time-resolved luminescence spectrum from part b of the previous figure, fit to a Bose distribution with T=120K and µ=−1.3K. This distribution would be seen in a gas of bosons in equilibrium at 86% of the critical density for Bose-Einstein condensation. The fitting function is broadened by the monochromator resolution function, and by a Lorentzian with a 0.15meV full-width at half-maximum. The direct line is cut off; its full height is 7.5×10⁷ counts per second per meV.
3.7 Counting excitons in the lab

Our goal is to measure the exciton density, the number of excitons occupying a certain volume. The radiative rate derived in section 3.4 gives the photons flux produced by a given number of excitons. In this section we estimate the efficiency with which we count these photons, using the optical system diagrammed in figure 13.

![Diagram of optical system](image)

Figure 13: Typical experimental arrangement, with transmission efficiencies of the various components (measured using 633nm He-Ne laser light). The counting efficiency \( \eta \) defined in the text is the product of all the efficiencies to the right of the sample.

The collection lens is a 90mm fixed-focus \( f/2.0 \) camera lens. Focusing the luminescence on the monochromator entrance slit requires moving the lens further from the source than its design working distance. The most restrictive aperture is then the 28mm diameter aperture on the cryostat side of the lens, which is 70mm from the luminescence, giving an effective aperture of \( f/2.5 \). The cone of light accepted by this lens has a half-angle \( \theta = \tan^{-1}(1/5) \). Snell's law reduces the cone of acceptance inside the crystal to \( \theta' = \sin^{-1}(n^{-1} \sin \theta) \). The solid angle, inside the cuprite, of the collected light is then

\[
\Omega_{\text{collection}} = \int_{0}^{2\pi} d\phi \int_{0}^{\theta'} \sin \theta \, d\theta = 2\pi(1-\cos \theta')
\]

\[
\approx \pi \theta'^2 \approx \pi \theta^2 / n^2
\]

\[
\approx \pi / (5^2 \times n^2) = 0.014.
\]

The efficiency of the monochromator is measured in conjunction with that of the photo-multiplier tube (PMT) and associated electronics. Typically the combined efficiency is 1.8% for \( E \) vertical, 4.2% for \( E \) horizontal, using the monochromator in second order at 610nm. The efficiency was checked at least every six months, as the PMT degrades with age and with use.

We assume that photons reflected from each optical surface are not re-reflected in such a way as to be counted. Combining the reflective losses with the monochromator and PMT efficiencies results in a counting efficiency \( \eta \) which is typically 1%. The conversion from number of orthoexcitons to PMT count rate is

\[
y_1 y_2 \frac{\Omega_{\text{collection}}}{4\pi} \eta \approx 0.8 \text{ cps / orthoexciton}.
\]

26
The front slit of the monochromator (typically 100µm wide) admits only a portion of the image of the exciton cloud. The magnification factor between the exciton cloud in the crystal to its image on the monochromator entrance was 5.4, so a typical 100µm-wide entrance slit admits photons from a 19µm-wide section in the sample.

Of the photons which enter the monochromator, the rear slit allows only those with energy in a certain range to fall on the photocathode of the PMT. We have a monochromator with focal length $F=1m$ using a grating with line spacing $d=833nm$ in order $m=2$ and with an angle $2\phi=9.8^\circ$ between incident and diffracted beams. A back slit width $w$ will pass photons with wavelength in a range $\delta\lambda$ (wavenumber in a range $\delta\nu$) given by

$$\frac{\delta\lambda}{\lambda} = \frac{\delta\nu}{\nu} = \frac{1}{2} \frac{w}{F} \sqrt{\left[\frac{2d \cos \phi}{m\lambda}\right]^2 - 1}.$$ 

For the case of $h\nu=2024meV (\lambda=612nm)$ and $w=100\mu m$, this formula predicts $\delta(h\nu)=0.09meV$ and we have measured $\delta(h\nu)=0.08meV$.

When recording time-resolved luminescence, we accumulate photon counts resulting from $N_{\text{pulses}}\approx10^6$ laser pulses; typically one photon is counted for every $10^3$ laser pulses. Each counted photon increments one counter in an array of counters, based on the time between the laser pulse and the luminescence photon detection. To record a time-resolved spectrum, this process is repeated for the set of wavelengths we wish to sample. Thus each counter represents the number of luminescence photons counted within an energy range $\delta(h\nu)$, within a time range $\delta t$, accumulated over $N_{\text{pulses}}$ repetitions of the experiment.

The results of a time-resolved luminescence experiment can be put into a canonical form by dividing the final value in each counter by $N_{\text{pulses}}$, by $\delta t$, and by $\delta(h\nu)$. The result is the number of counts per second per meV per laser pulse collected from the sample. The spectrum in figure 12 was normalized in this way. The integral over the $\Gamma\overline{12}$ phonon assisted line in figure 12 is $1.3\times10^8$ counts per second, indicating that at this instant there were $1.3\times10^8$ cps $\pm \left[\gamma_{12} \frac{\Omega_{\text{collection}}}{4\pi} \eta\right] = 1.5\times10^8$ orthoexcitons in view of the spectrometer.

We check this calibration by creating a known number of orthoexcitons and counting the luminescence. Using light with photon energy in the $\Gamma\overline{12}$ phonon assisted orthoexciton absorption band, seen in figure 8, we produce one orthoexciton per photon absorbed. The number of orthoexcitons produced by a laser pulse would be equal to the cumulative number of photons absorbed (the indefinite integral of the laser pulse) were it not for the fact that orthoexcitons are converted to paraexcitons, with a decay time of 3.5ns at 2K. Allowing for the down conversion, we expect to see a number of orthoexcitons equal to
\[ \int_{-\infty}^{t} I(\tau) \exp[(\tau-t)/3.5\text{ns}] \, d\tau \]

where \( I(t) \) is the instantaneous flux of laser photons, which is known from the measured laser power, and the measured laser pulse shape.

![Graph showing number of excitations over time for red, yellow, and green wavelengths](image)

Figure 14: Production of orthoexcitons by 10ns laser pulses using laser light with three different wavelengths. The upper curves show the cumulative number of photons absorbed within the observed volume; the lower curves include the effects of 3.5ns decay time for orthoexcitons. The circles indicate the instantaneous number of orthoexcitons within the observed volume, derived from the spectral integrals of the \( \Gamma_{12} \) phonon assisted orthoexciton luminescence line.

a) Photon energy 2050meV, which produces orthoexcitons with 3meV kinetic energy  
b) Photon energy 2100meV.  
c) Photon energy 2409meV.

Figure 14a compares the expected number of orthoexcitons with the number observed,\(^5\) based on the luminescence intensity and using our calibration. The excellent agreement is partially due to good fortune. Based on earlier checks of the calibration, and after eighteen months of practice in counting excitons, I am confident that I can report the actual number of excitons within a factor of two.

The other two parts of the figure show the results of excitation using higher and higher photon energies. The curves derived from the laser intensity fall on the circles indicating orthoexciton number if they are multiplied by 110%, 50%, and 30% respectively. The reduced production efficiency of shorter excitation wavelengths could be due to surface recombination, as the absorption lengths were 700μm, 50μm, and 3μm for these three wavelengths.\(^6\) Another

---

\(^5\)For this experiment the front monochromator slits were opened to accept the entire image of the exciton cloud.

\(^6\)The \( \text{Cu}_2\text{O} \) surfaces used in this work were prepared either by a final etch in 2vol% bromine-methanol solution, which removes 5μm/min, or by using Syton™ for the final polish. Etching with \( \text{HNO}_3 \) is faster, but leaves a rougher surface. Luminescence yield does not vary greatly (by less than a factor of two) between these surface preparations.
possibility is that some orthoexcitons are lost before they shed their excess kinetic energy. The yellow laser produced excitons with 50meV kinetic energy; the green laser produces free electron-hole pairs with about 100meV kinetic energy (and some of the holes are produced in the slightly deeper $\Gamma_{\frac{1}{8}}^+$ valence band). The numbers of orthoexcitons plotted in figure 14 are derived from the integral of nearly thermalized kinetic-energy distributions, so the production efficiencies we infer from this figure are thermalized orthoexcitons per photon.

Figure 15: Experimental arrangement showing the 50μm-diameter aperture in the center of an aluminum disk. The small rectangle represents the inverse image of the monochromator entrance slit.

Figure 15 shows the arrangement we use to produce excitons in a known volume. A 50μm aperture is lightly pressed against the surface of the sample. The laser beam is first focused through this aperture. Then the laser is brought out of focus, but kept centered, until the amount of light passing through the aperture is reduced by one half. The relative amount of laser light absorbed by the crystal can be monitored by the luminescence it produces, if the laser intensity is sufficiently low during the focusing procedure. This procedure floods the $\pi(50\mu m)^2/4$ area inside the aperture nearly uniformly with half the laser power entering the cryostat.

Usually luminescence is collected from only part of this disk shaped region. As mentioned on page 27, the front monochromator slit width determines the area from which luminescence is collected. For a typical front slit width of 100μm, the observed area is 900μm².

The distribution of excitons in the third dimension, the distance from the excitation surface, cannot be controlled. It is determined by the absorption length of the incident light, by the density-dependent decay of excitons, by exciton diffusion, and by surface recombination.

3.8 Observed luminescence compared to quasi-equilibrium distributions

Excitons are bosons, so their equilibrium distribution is a Bose-Einstein distribution,

$$f_B(\varepsilon) = \frac{1}{\exp[(\varepsilon - \mu) / k_B T_{\text{gas}}] - 1}.$$  

In this expression $\mu$ is the chemical potential relative to the energy of an exciton at rest; $\mu$ is a negative quantity. When $|\mu|$ is large compared with $k_B T_{\text{gas}}$ the Bose distribution reduces to the Maxwell-Boltzmann distribution, $g(\varepsilon) \exp[-\varepsilon / k_B T_{\text{gas}}]$. Higher (less negative) chemical potentials correspond to higher gas densities, and more sharply peaked kinetic energy distributions. Specifically, the gas density is
\[
n = \int_0^\infty \frac{g(e)}{\exp[(e-\mu) / k_B T_{\text{gas}}] - 1} \, de.
\]

For small \(\mu/k_B T_{\text{gas}}\), \(n \approx n_Q \cdot 2.612 \cdot \left\{ 1 - 1.357 \sqrt{-\mu/k_B T_{\text{gas}}} \right\}\),

where the quantum density is \(n_Q = g_0 \cdot (m k_B T_{\text{gas}}/2\pi \hbar^2)^{3/2}\).

As chemical potential \(\mu\) approaches zero, \(n_{\text{fit}}\) approaches the critical density \(n_{\text{crit}} = 2.612 \cdot n_Q\) which for orthoexcitons is \(n_{\text{crit}} = 1.0 \times 10^{17} / \text{cm}^3 \cdot (T_{\text{gas}} / \text{Kelvin})^{3/2}\). The excited state distribution is saturated at the critical density. Any density in excess of \(n_{\text{crit}}\) goes into the zero-kinetic-energy state, forming a Bose-Einstein condensate.

![Figure 16: Orthoexciton luminescence resulting from a 0.5ns argon ion laser pulse which deposited 1.3\times10^{14} photons per cm^2 in the sample. While fitting we allowed the overall scale of the Bose distribution to vary independently of \(T_{\text{gas}}\) and \(\mu\).](image)

- a) Time-resolved luminescence during the laser pulse fit to a Bose distribution with the parameters shown in the figure. The integral of the \(\Gamma_{12}\) phonon-assisted luminescence indicates \(8.1 \times 10^7\) orthoexcitons in the observed volume.
- b) The luminescence 0.3ns after the center of the laser pulse indicates \(6.5 \times 10^7\) orthoexcitons in view.

Some instantaneous orthoexciton distributions are fit to the Bose distribution function in figure 16 (and in figure 12 on page 25). This good agreement of the orthoexciton distribution, following intense pulsed excitation, with the Bose distribution has been seen repeatedly [Hulin, 1980; Snoke 1987, 1990c; Lin, 1996; Naka, 1996; Goto 1997]. Generally the luminescence follows the exponential tail of the Bose distribution down to 1% the peak luminescence intensity. In these experiments both \(T_{\text{gas}}\) and \(\mu\) vary substantially during and after the laser pulse, with \(T_{\text{gas}}\) always greater than the lattice temperature.

The interpretation of these distributions as quasi-equilibrium distributions was supported by Snoke et al. [1987] with an independent estimate of the exciton density. Supposing that nearly every photon absorbed created an orthoexciton, they estimate the number of orthoexcitons as \(l\tau\) where \(l\) is the photon flux and \(\tau\) the exciton lifetime. This estimate of the exciton number divided by the observed volume of the exciton cloud, predicted an exciton density within a factor...
of two of \( n_{\text{crit}} \). During and after the laser pulse, there was continuous agreement between the density \( n \) derived from the fit parameters \( T_{\text{gas}} \) and \( \mu \), and the density given by the ratio of the luminescence intensity to the measured exciton cloud volume [Snoke, 1987, 1990c].

However, analysis of the absolute luminescence intensity shows that the exciton density is two orders of magnitude below \( n_{\text{crit}} \). The spectra in figure 16 were collected from a 900\( \mu \)m\(^2\) area of the sample surface, using the arrangement of figure 15. Using 2.5\( \mu \)m for the absorption length of the argon ion 514.5nm line in Cu\(_2\)O, we estimate an effective volume of the observed cloud of excitons to be 2300\( \mu \)m\(^3\); exciton diffusion may make the actual cloud volume larger than this estimate. The integrals of the phonon-assisted luminescence spectra in figure 16, and the calibration from the previous section, indicate that there were less than \( 10^8 \) orthoexcitons within the observed volume, giving a maximum orthoexciton density of \( 4 \times 10^{16}/\text{cm}^3 \). The Bose distributions in figure 16, which fit the data so well, would be seen in an equilibrium ideal gas with density \( 2 \times 10^{19}/\text{cm}^3 \).

The argument leading to the discrepancy in the previous paragraph can be condensed, combining the Bose distribution at the start of this section with the collection efficiencies of the previous section into one expression. The expected number of counts recorded in the \( \Gamma_{12} \) phonon assisted spectrum for a gas of orthoexcitons filling a box of volume \( V \) is, denoting the actual occupation numbers of the quantum states by \( \bar{n}(\varepsilon) \),

\[
\text{CountRate}(E_{x} - E_{12} + \varepsilon) = \frac{\eta \omega^2 \alpha(\varepsilon)}{\pi^2 c^2 \hbar} V \bar{n}(\varepsilon) = 3 \times 10^9 \frac{\text{counts}}{\text{s meV}} \sqrt{\frac{\varepsilon}{\text{meV}}} \bar{n}(\varepsilon)
\]

where the factor of 100 is the square of four times the collection lens effective \( f \)-number, and I have estimated the volume \( V \) at 2300\( \mu \)m\(^3\). (Some of the more poorly-known quantities, such as the index of refraction \( n \) and exciton mass \( m \), have canceled out in this relation.) We can use this formula to read occupation numbers off the spectra in figure 16. For example, at \( \varepsilon = 1 \text{meV} \) we see that the count rate is between one and two times \( 10^7 \) counts/s/meV, so the exciton occupation number \( \bar{n}(\varepsilon) \) is less than 0.01. The Bose distributions which fit the shape of the observed exciton distribution have occupation numbers \( f_B(\varepsilon) \) around 2 at \( \varepsilon = 1 \text{meV} \). The magnitudes of the exciton occupation numbers \( \bar{n}(\varepsilon) \) do not fit the same Bose distribution that the shape of \( \bar{n}(\varepsilon) \) fits so well.

In the experiment of figure 16, \( 1.3 \times 10^{14} \) photons were absorbed per cm\(^2\), but the maximum observed areal density of orthoexcitons was only \( 0.9 \times 10^{13} \) per cm\(^2\). The ratio is less than the 30% production efficiency observed at low excitation density. The missing excitons were lost to Auger decay, discussed in chapter 5. Auger decay also provides a likely explanation, proposed by Mysyrowicz et al. [1981], of the excess kinetic energy (higher apparent \( T_{\text{gas}} \)) observed at
higher excitation density, as each Auger decay event recombines one electron-hole pair and releases an amount of energy equal to the band gap.

The experiment of figure 16 used only 3mW\(^7\) of laser power, and the laser was defocused to overfill the 50\(\mu\)m aperture. A focused argon ion laser beam, with 15mW in the same pulse train, produced the spectra shown in figure 17, which were recorded 0.3ns after the center of a 0.25ns laser pulse. The spectrum produced with the crystal at 2K crystal is fit by an even more spectacular Bose distribution, with \(T_{\text{gas}}=140\text{K}\). If this spectrum is actually coming from a gas with effective temperature 140K, we should be able to reproduce it with the crystal temperature raised to 70K. The same spectrum in a 70K crystal would show an exciton distribution much more narrow than \(k_B T_{\text{lattice}}\), and would be strong evidence for effects of Bose statistics.

![Graphs a) 2K crystal and b) 70K crystal](image)

**Figure 17**: Orthoexciton luminescence spectra 0.3ns after the center of a 0.25ns, 10nJ, focused green laser pulse. Time resolution was 0.3ns.  
- a) Crystal held at 2K, fit to a Bose distribution with \(T_{\text{gas}}=140\text{K}\) and chemical potential \(\mu=-1.0\text{K}\). The integral of the spectrum is \(9 \times 10^7\) counts/s.  
- b) Crystal held at 70K, fit to a Maxwell-Boltzmann distribution with \(T_{\text{gas}}=100\text{K}\). An anti-Stokes luminescence replica is visible at 2037meV. The integral of the spectrum is \(7 \times 10^7\) counts/s (after dividing by \(1+f_{1.2}\) to correct for stimulated-phonon-emission luminescence). This fit, shifted along the energy axis only, is repeated as the dashed line in the upper plot.

The results of the same experiment with the crystal at 70K are disappointing, but enlightening. The kinetic energy distribution is best described as a Maxwell-Boltzmann distribution with \(T_{\text{gas}}=100\text{K}\). The integrated luminescence indicates essentially the same number of excitons. While I did not measure the volumes of the exciton clouds directly, we know that exciton diffusivities decrease with increasing lattice temperature [Trauernicht, 1983]. Therefore the exciton density is probably higher in the 70K crystal than in the 2K crystal, but the spectrum from the 70K crystal shows the energy distribution of a low-density gas.

\(^7\)Average laser power measured at the cryostat window.
Given that the density of excitons is low enough that we should expect to see only the Maxwell-Boltzmann limit of the Bose distribution, we are led to consider the possibility that the observed Bose-like distributions at low lattice temperatures are a superposition of many Maxwell-Boltzmann distributions. David Snoke considered reasonable spatial distributions of exciton density and temperature, and found that, to fit the data, Bose distributions were required [Snoke, 1990b]. A good fit to the spectral shapes under this model required a peak exciton density larger than the density derived from fitting the data to a single Bose distribution.

Is there any set of Boltzmann distributions, with different gas temperatures, whose sum has the shape of a Bose distribution? Mathematically, the answer is yes, and the solution comes from simply expanding the Bose occupation number in powers of \( \exp(e/kT) \):

\[
\frac{\sqrt{e}}{\exp[(e-\mu)/k_BT_o] - 1} = \sum_{m=1}^{\infty} \sqrt{e} \exp(me/k_BT_o) \exp(m\mu/k_BT_o).
\]

A discrete set of temperatures \( \{T_o, \frac{1}{2}T_o, \frac{1}{3}T_o, \ldots\} \) seems unreasonable, especially since the series includes arbitrarily small temperatures while the exciton gas must be at least as warm as the lattice. However, the factor \( \exp(m\mu/k_BT_o) \) reduces the contribution of terms with temperatures below \( |\mu/k_B| \).

We can create a continuous distribution of temperatures similar to the discrete distribution implied by the sum above. Instead of a Dirac \( \delta \)-functions for each term in the sum, we use a Gaussian, and we give each Gaussian a width proportional to the distance to its neighbors. This yields the continuous distribution shown in figure 18a.

Also shown in figure 18a is an ad hoc temperature distribution which shares the general shape of the series expansion of the Bose distribution. This distribution sets the number of excitons in a region of gas with temperature \( T \), denoted \( n(T) \), to be proportional to \( T^{-2} \), and includes only temperatures between the lattice temperature \( T_L=2K \) and a maximum gas temperature of \( T_H=30K \).

Continuing in this vein, we postulate an exponential spatial distribution of excitons, as would be produced by optical excitation. We then find the temperature profile \( T(z) \) which would produce our ad hoc temperature distribution through the relation \( n(T) dT = n(z) dz \). One such choice is shown in figure 18b. We see that we need a small region of very hot gas, which we choose to place at the crystal surface, with the gas temperature quickly falling to that of the lattice deeper into the crystal. The overall kinetic energy distribution resulting from this temperature and density profile is

\[
n(\varepsilon) = n_0 \frac{\exp(-\varepsilon/k_BT_H) - \exp(-\varepsilon/k_BT_L)}{(\sqrt{\pi T_H} - \sqrt{\pi T_L}) \sqrt{\varepsilon}},
\]
which is shown in part d of the figure. In general, the function above fits our data as well as a Bose distribution, with the same number of free parameters.

Figure 18: a) Inverse Laplace transform of a Bose distribution ($\mu=-1.4K$ and $T_{gas}=20K$) with heavy smoothing, and the similar $n(T) \propto T^{-2}$ distribution.

b) A reasonable spatial distribution of excitons $n(z)$, and the spatial temperature distribution $T(z)$ which results in the $n(T) \propto T^{-2}$.

c) Orthoexciton photoluminescence 6ns after the center of a 10ns argon-ion laser pulse with intensity $10^{16}$ photons absorbed per cm$^2$. The fit is to a Bose distribution.

d) The same data as in (c) fit to the distribution of exciton temperature and density in (b).

The temperature distribution in figure 18b is extreme, with a very small region of very hot gas. Heating of the lattice by the incident laser pulse would not produce such a sharp peak in $T(z)$. The measured low temperature specific heat [Gregor, 1962] has the Debye form $c_v \propto T^3$, so the lattice internal energy $U \propto T^4$. Laser light with an absorption length $l$ would produce a heat distribution $U \propto e^{-z/l}$ so that $T \propto e^{-z/4l}$ —assuming that a constant fraction of the light energy goes directly into lattice heat. We believe the exciton density should be proportional to the square root of the locally absorbed power, $n \propto e^{-z/2l}$. Thus $T(z)$ is less sharply peaked than $n(z)$ under this model, and the distribution of excitons in temperature is $n(T) = n(z) \frac{dz}{dT} \propto T$, which is
very different from what was used in figure 18. (Lattice heating in considered quantitatively in section 5.1.)

More realistically, the exciton gas is not at the local lattice temperature during the pulse. A likely cause of the elevated exciton gas temperatures is Auger decay, which releases an amount of energy equal to the band gap on each decay event. The rate of energy release is proportional to the rate of exciton collisions, proportional to \( n^2 \). Exciton cooling by acoustic phonon emission allows the gas to shed energy at a rate proportional to \( n \ T_{\text{gas}}^{3/2} \). Balancing these energy fluxes leads to the much smoother temperature profile \( T_{\text{gas}} \propto n^{2/3} \). Assuming again that \( n(z) \propto e^{-z/2d} \) leads to a distribution of excitons in temperature of \( n(T) = n(z) \frac{dz}{dT} \propto T^2 \). We have not yet imagined any physical model which would produce the temperature distribution in figure 18b.

In summary, as the excitation density is raised the quantum yield of excitons falls, the average kinetic energy of the excitons (at any given time relative to their creation) rises, and the transient kinetic energy distribution of the orthoexcitons have the shape of a nearly saturated Bose distribution. The observed exciton density, however, is low enough that the quasi-equilibrium distribution of excitons should be Maxwell-Boltzmann. Decomposing the observed kinetic energy distribution into a sum of Maxwell-Boltzmann’s results in an implausible distribution of gas temperatures.

It has been suggested that interactions between the excitons may be responsible for the observed spectra [Snoke, 1995]. Certainly the excitons interact, but at the highest exciton densities we can create there is no clearly observable (that is, greater 0.05meV=0.6K) shift of the direct luminescence line. We would expect to see a mean field shift as the first sign of the exciton interaction potential.

Rather than abandon the assumption of an ideal gas, I will abandon the assumption of quasi-equilibrium. At the measured exciton densities, the mean time between elastic collisions between excitons\(^8\) may well be comparable with the acoustic phonon emission times. In this case the exciton kinetic energy distribution would be determined by the relative phonon emission rates of the various states. In the following chapters, we consider the cooling and decay mechanisms of the excitons, considering the system as a non-equilibrium ideal gas.

\(^8\)For an order-of-magnitude guess, we could take the scattering length to be about 3 Bohr radii, and the exciton density about \( 10^{16}/\text{cm}^3 \), so the elastic scattering rate may be about \( \tau^{-1} = n \sigma v = 10^{16}/\text{cm}^3 \ 4\pi(2\text{nm})^2 \ 10^6 \text{cm/s} = 5/\text{ns} \). In the next chapter we find that the phonon emission rates are around 3/\text{ns} for excitons moving at about \( 10^6 \text{cm/s} \).
4. EXCITON-LATTICE INTERACTION

4.1 Excitons in a strained crystal

Strain affects the electronic states in two ways. Uniform compression, as would result from hydrostatic pressure, simply shifts the bands. In cuprous oxide, uniform compression happens to increase the band gap.

Shear strain removes some of the symmetry of the crystal and splits degenerate bands. In particular, shear strain removes the three-fold degeneracy of the top of the valence band states. The strain hamiltonian in the basis of three \( \Gamma_{25}^+ \) states must have the form [Pikus and Bir, 1959]

\[
\mathbf{H}^{\text{strain}}_{\text{hole}} = -a (\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}) + \begin{bmatrix}
 b (2\varepsilon_{xx} - \varepsilon_{yy} - \varepsilon_{zz}) & \sqrt{3} d \varepsilon_{xy} & \sqrt{3} d \varepsilon_{xz} \\
 \sqrt{3} d \varepsilon_{xy} & b (-\varepsilon_{xx} + 2\varepsilon_{yy} - \varepsilon_{zz}) & \sqrt{3} d \varepsilon_{yz} \\
 \sqrt{3} d \varepsilon_{xz} & \sqrt{3} d \varepsilon_{yz} & b (\varepsilon_{xx} - \varepsilon_{yy} + 2\varepsilon_{zz})
\end{bmatrix}
\]

where the states are ordered \( \{yz, xz, xy\} \).

The strain hamiltonian for the three \( \Gamma_{25}^+ \) yellow orthoexciton states will have the same form, but with different coefficients. Since each of the three orthoexciton states contains considerable contributions from all three hole wavefunctions, the anisotropic deformation potentials for the yellow orthoexcitons are somewhat smaller than those for the bare holes.

\[
\mathbf{H}^{\text{strain}}_{\text{ortho}} = \Xi_0 (\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}) + \begin{bmatrix}
 \Xi_{zz} (2\varepsilon_{xx} - \varepsilon_{yy} - \varepsilon_{zz}) & \sqrt{3} \Xi_{xy} \varepsilon_{xy} & \sqrt{3} \Xi_{xz} \varepsilon_{xz} \\
 \sqrt{3} \Xi_{xy} \varepsilon_{xy} & \Xi_{zz} (-\varepsilon_{xx} + 2\varepsilon_{yy} - \varepsilon_{zz}) & \sqrt{3} \Xi_{xy} \varepsilon_{yz} \\
 \sqrt{3} \Xi_{xz} \varepsilon_{xz} & \sqrt{3} \Xi_{xy} \varepsilon_{yz} & \Xi_{zz} (-\varepsilon_{xx} - \varepsilon_{yy} + 2\varepsilon_{zz})
\end{bmatrix}
\]

The best source for \( \Xi_0 \) is the shift in the exciton energies with hydrostatic pressure measured by Reimann and Syassen [1989] which gives \( \Xi_0 = 1.68 \pm 0.02 \) eV. The shear deformation potentials are best determined from the splitting of the orthoexciton line under shear strain. Adjusting \( \Xi_{zz} \) and \( \Xi_{xy} \) to fit the strain splitting data of Waters [Waters et al., 1980; Trebin et al., 1981] yields:

\[
\begin{align*}
\Xi_0 &= -1.68 \text{ eV}, \\
\Xi_{zz} &= -0.29 \text{ eV}, \\
\Xi_{xy} &= 0.18 \text{ eV}.
\end{align*}
\]

where I have used the elastic compliances\(^1\) measured by Manghani et al. [1974]:

\(^1\)These compliances are for room temperature. Hallberg and Hanson [1970] made the only measurement of the elastic constants down to helium temperatures and found that Cu\(_2\)O stiffens by about 4% between room temperature and 4.2K. However, at room temperature their sample is generally softer (by about 4%) than what seem to be better samples measured by Manghani et al. and by other groups. Pure Cu\(_2\)O at 4.2K may be slightly stiffer than any published values attest.
\[ S_{11} = 4.17 \text{ Mbar}, \]
\[ S_{12} = -1.94 \text{ Mbar}, \]
\[ \text{and } S_{44} = 8.26 \text{ Mbar}. \]

Table 3 presents the fit. The orthoexciton shifts are the eigenvalues of their strain hamiltonian, \( H_{\text{ortho}}^{\text{strain}} \). The paraexciton sees only the isotropic part of the deformation potential, \( \Xi_0(\varepsilon_{xx}+\varepsilon_{yy}+\varepsilon_{zz}) \), because it is composed of equal parts of yz, xz and xy holes. The paraexciton shifts are small because the cuprous oxide has a large Poisson’s ratio, \( -S_{12}/S_{11} = 0.46 \) and expands sideways under stress, so uniaxial stress causes very little isotropic strain (volume change).

All the yellow excitons shift to lower energy to second-order in strain. This is due to the raising of the \( \Gamma_7^+ \) valence band to second-order in the strain splitting of the nearby \( \Gamma_8^+ \) band. The magnitude of the shift of the \( \Gamma_7^+ \) band, from second-order perturbation theory, is

\[
\frac{b^2}{\Delta} \{(\varepsilon_{xx} - \varepsilon_{yy})^2 + (\varepsilon_{yx} - \varepsilon_{zy})^2 + (\varepsilon_{xx} - \varepsilon_{zz})^2\} + \frac{2d^2}{\Delta} \{(\varepsilon_{yz}^2 + \varepsilon_{xz}^2 + \varepsilon_{xy}^2)\}
\]

where \( \Delta = 131 \text{ meV} \) is the separation between the \( \Gamma_7^+ \) and \( \Gamma_8^+ \) bands. The ratio \( b:d \) is the same as the ratio between the corresponding orthoexciton potentials \( \Xi_{zz} : \Xi_{xy} \), so there is only one independent parameter to fit to the data. From the published second-order shifts, I obtain \( b = -1.18 \text{ eV} \) and \( d = 0.73 \text{ eV} \) which produces the last line in table 3.

<table>
<thead>
<tr>
<th>Stress axis:</th>
<th>[001]</th>
<th>[110]</th>
<th>[111]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strains (( \times 10^{-3} ) per kbar compression):</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \varepsilon_{xx} = \varepsilon_{yy} = 1.94 ) ( \varepsilon_{zz} = -4.17 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>first-order orthoexciton shifts (meV per kbar)</td>
<td>4.04</td>
<td>2.27</td>
<td>0.93</td>
</tr>
<tr>
<td>(-1.27)</td>
<td>(-1.27)</td>
<td>0.26</td>
<td>0.93</td>
</tr>
<tr>
<td>(-1.27)</td>
<td>(-1.27)</td>
<td>(-1.03)</td>
<td>(-0.36)</td>
</tr>
<tr>
<td>first-order paraexciton shift (meV per kbar)</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>second-order shift (meV per kbar(^2))</td>
<td>(-0.79)</td>
<td>(-0.23)</td>
<td>(-0.05)</td>
</tr>
</tbody>
</table>

Table 3: The shifts of the yellow exciton levels caused by uniaxial compressive stress. The strain components are the tensor components defined by \( \varepsilon_{xy} = \frac{1}{2}(\partial u_x/\partial y + \partial u_y/\partial x) \).

### 4.2 Strain wells

A strain well forms a potential minimum for excitons within the interior of the crystal. The strain well technique takes advantage of two facts: 1) the strain field surrounding a punch pressed into a flat face of an elastic material is mainly compressive near the contact area, but contains a shear component which is greatest at some depth inside the material. 2) shear strain breaks
degeneracies and mixes electronic states, pushing the lowest electronic states (in our case the 1s yellow excitons) to lower energies.

The problem of a sphere pressing into a semi-infinite solid was solved by H. Hertz, for the case of elastically isotropic materials. From the textbook by Timoshenko [1934], if a glass sphere with radius R is pressed with force F onto a planar face of cuprite, the contact area is a circle of radius \( a \), with

\[
a = \sqrt[3]{\frac{3}{4} \frac{F R}{E_{\text{cuprite}}} \left[ 1 - \frac{\nu_{\text{cuprite}}^2}{E_{\text{cuprite}}} + \frac{1 - \nu_{\text{glass}}^2}{E_{\text{glass}}} \right]}
\]

Using the isotropic\(^2\) Young's modulus \( E_{\text{cuprite}} = 301 \text{kbar} \) and the Poisson's ratio is \( \nu_{\text{cuprite}} = -0.46 \) from Manghani et al. [1974] and handbook values for glass, 600 kbar and 0.25.

\( E_{\text{eff}} = 320 \text{kbar} \).

If we use a lens as the curved surface, the contact area can be seen as a dark circle inside the usual Newton's ring pattern formed by interference between the lens and crystal surfaces\(^3\). All lengths in the problem scale linearly with the contact radius \( a \).

All stresses in the problem scale with the average pressure in the contact area, \( F/\pi a^2 \). There are algebraic expressions for the stress on an axis normal to the crystal face, through the center of the contact area [Timoshenko, 1934]. If \( z \) denotes the distance from the center of contact,

\[
-\sigma_{xx} = -\sigma_{yy} = -\frac{3F}{2\pi a^2} \left( 1 + \nu_{\text{cuprite}} \right) \left[ 1 - \frac{z}{a} \arctan(a/z) \right] - \frac{1}{2} \frac{3F}{2\pi a^2} \frac{1}{1 + z^2/a^2}
\]

\[
-\sigma_{zz} = -\frac{3F}{2\pi a^2} \frac{1}{1 + z^2/a^2}
\]

(By convention, negative diagonal components of the stress tensor denote compression.) This can be expressed as the sum of a pressure \( p = -\sigma_{xx} = -\sigma_{yy} \) plus a uniaxial stress \( \sigma = -\sigma_{zz} - p \).

Using table 3, the energy shifts of the ortho- and paraexcitons are, as a function of position along this axis, with energies in meV and stresses in kbar,

\[
\Delta E_{\text{ortho}} = 0.50 \begin{bmatrix} 3p \end{bmatrix} + \begin{bmatrix} +4.04 \end{bmatrix} \sigma - 0.79 \sigma^2
\]

\[
\Delta E_{\text{para}} = 0.50 \begin{bmatrix} 3p \end{bmatrix} - 0.79 \sigma^2
\]

These strains and energies are plotted in figure 19 for typical parameters.

\(^2\)Cuprous oxide is moderately elastically anisotropic, with \( A \equiv 2(S_{11} - S_{12})/S_{44} = 1.4 \). The Hertz contact problem has been solved for transversely isotropic materials [Conway, 1956; Elliot, 1946]. One could approximate \( \text{Cu}_2\text{O} \) as transversely isotropic, rather than completely isotropic as in the text. However, this makes only a 1% difference in the effective modulus \( E_{\text{eff}} \).

\(^3\)If this is done under a microscope at room temperature, one must remember that \( \text{Cu}_2\text{O} \) cannot withstand as much stress at room temperature as it can at liquid helium temperatures.
As an aside, I point out that the orthoexciton doublet will cross the paraexciton level when \( \sigma \) exceeds about 10kbar. The doublet should retain its larger radiative rate as its energy sinks below that of the paraexciton, giving us a bright exciton as the lowest-energy state. (The crossing is allowed for perfectly uniaxial strain, as these states form different representations of \( D_{4h} \). Realistically, we should expect some mixing of the states when the energies are very close, but still a relatively bright state will become the lowest.) Using the strain well apparatus, this would require a peak surface strain of about 20kbar, almost three times the most I have applied.

![Graphs showing pressure and exciton energy](image)

Figure 19: a) Pressure and uniaxial stress due to a spherical surface being pressed into the flat surface of a material with Poisson's ratio equal to 0.46, as a function of distance from the point of contact along a line normal to the contact surface. b) Exciton energies as a function of distance in the crystal for the case of an 8.15mm-radius sphere pressed onto a (100) face of Cu_2O with 285N force, for which case \( a = 0.417 \text{mm} \).

The experimental conditions for which figure 19 was generated produce a well located slightly further into the crystal than predicted (270\( \mu \)m from the contact rather than the 250\( \mu \)m predicted) and somewhat less deep in energy (paraexciton well bottom at 2011.0meV rather than the predicted 2009.0meV). Treating \( E_{\text{eff}} \) as an adjustable parameter, we can closely match the experimental results. In figure 20 the curves in part b) are from the theory for isotropic materials using the slightly softer value \( E_{\text{eff}} = 300 \text{kbar} \).
Figure 20: a) Experimental arrangement for depositing excitons in a strain well. Excitons produced at the surface are pulled into the well by the potential gradient.
b) Exciton energies as a function of position, using the theory for an isotropic material with $F=285\text{N}$, $R=8.15\text{mm}$, and $E_{\text{eff}}=300\text{kbar}$. The confinement strengths are $\alpha = 232\text{meV/mm}^2$ for the paraexcitons and $\alpha = 269\text{meV/mm}^2$ for the orthoexcitons.
c) Luminescence spectrum produced by 25mW continuous argon ion laser excitation of a strain well produced by pressing a lens with radius of curvature $8.15\pm0.30\text{mm}$ with $285\pm15\text{N}$ of force onto a (001) face of Cu$_2$O. Luminescence is collected along [110] from both the well and the path between the center of contact and the well. The spectrum is affected by absorption lines near 2030meV and absorption band starting at 2047meV.

The worth of a strain well for confining excitons is in the steepness of its walls. The potential is parabolic near the center of the well, $E = E_0 + \alpha(z-z_0)^2$, and $\alpha$ is a measure of the confinement strength. Considering for the moment only the paraexcitons and only the term in $\sigma^2$ in the paraexciton energy, the confinement strength for paraexcitons is

$$\alpha \approx 0.19 \frac{\text{meV}}{\text{kbar}^2} \frac{(E_{\text{eff}})^2}{R^2} = \frac{17 \text{eV}}{R^2}$$

from numerical differentiation of the curve in figure 19a. Due to the non-linear relation between the stresses and exciton energies, the size and shape of the well depend on the magnitude of the
force applied. The rule of thumb above should work well for the stress we typically use for wells in Cu_2O, namely \( \sigma_{zz} \approx 7 \text{kbar} \) at the center of the contact area, \( \sigma \approx 4 \text{kbar} \) at the center of the well.

When the excitons in the well have come to thermal equilibrium, if their density is low enough that we may approximate the Bose distribution as a Boltzmann distribution, their spatial distribution will be a Gaussian, \( \exp[-\alpha(z-z_0)^2 / k_B T] \), with a full width at half maximum \( \text{FWHM}_z = \sqrt{\frac{16}{\ln 16} \frac{k_B T}{\alpha}} \approx \frac{R}{260} \sqrt{\frac{T}{K}} \).

Real exciton clouds in real strain wells tend to be larger than this prediction. In the well shown in figure 20, the paraexciton cloud\(^4\) had a transverse width \( \text{FWHM}_x = 120 \pm 20 \mu m \). The width along the strain axis was not measured for this well, but having measured the slightly oblate shape of another well of the same peak strain, we can infer that along the strain axis \( \text{FWHM}_z = 95 \pm 20 \mu m \), which is significantly larger than the predicted 45 \( \mu m \) full-width. The exciton clouds are larger than they would be in thermal equilibrium because (at experimentally convenient exciton densities) the exciton lifetime is determined by Auger recombination. Auger recombination preferentially destroys excitons at the center of the cloud where the density is highest, and adds energy to heat the exciton gas.

One last feature of the experimental geometry in figure 20a deserves mention here. If an argon-ion laser is used to fill the well, it creates excitons within a few microns of the crystal surface. The excitons move quickly down the potential gradient into the strain well, forming a tight stream. For the conditions of figure 20 the potential gradient between the center of contact and the well is about 1eV/cm. Trauericht and Wolfe [1986a] measured the paraexciton mobility to be \( 7 \times 10^{5} \text{cm}^2/(\text{eV s}) \) under these conditions.\(^5\) This would imply a drift velocity of \( 7 \times 10^{5} \text{cm/s} \), but as this is slightly greater than the average thermal velocity of the excitons, we should not expect the mobility to predict the drift velocity exactly. In fact, through time-resolved luminescence we see the excitons move at approximately \( 5 \times 10^{5} \text{cm/s} \) over the first half of their trip into the well.

The narrow stream follows an arcing path into the well if the laser focus is moved off-center. Once the laser moves outside the contact area, however, the stream disappears abruptly. We suspect that the reason for this is in the shape of the potential. Near the surface, the hydrostatic pressure \( p \) is the most important in determining the potential energy of an exciton. At the center of the contact area, the pressure decreases rapidly with distance from the surface, resulting in a

\(^4\)The paraexciton density was measured through its \( \Gamma_{25} \) phonon assisted luminescence. The strain well was filled using continuous laser light, of which 0.2mW was absorbed in the well through phonon-assisted optical creation of orthoexcitons.

\(^5\)Specifically, in a crystal at 2K and an average shear strain \( (\sigma_{zz} - \sigma_{xx}) \) of 3kbar over the drift path.
strong potential gradient pulling the exciton away from the surface. The situation off-center will be similar. The force $F$ exerted through the lens is distributed over contact area as

$$
\sigma_{zz} = \frac{3F}{2\pi} \sqrt{1 - r^2/a^2},
$$

and the other diagonal components of the strain tensor have values close to this [Timoshenko, 1934]. The pressure drops abruptly near $r=a$, the edge of the contact area, and is zero along the free surface outside the contact area. Where the surface pressure disappears, so does the exciton potential energy at the surface, so does the potential gradient driving the excitons to the interior of the crystal, and so does the well-defined exciton stream.

We have also made strain wells by pressing a sphere against a (110) of the cuprite sample. Two wells form, approximately one contact radius $a$ from the center of contact, along each of the [100] and [010] directions. To understand why two wells form, one can ignore the elastic anisotropy of cuprous oxide and simply refer to the second-order exciton shifts in Table 3. Approximate the stress field as pure radial uniaxial compression around the center of contact. That is, take the stress tensor at any point in the crystal to have one non-zero eigenvalue, with the corresponding eigenvector pointing toward the center of the contact area. (This approximation is exact for a point contact when Poisson’s ratio is $\frac{1}{2}$.) At several kbar stress, the exciton energy shift is dominated by the second-order term. The exciton energy at a point in any particular direction from the center of contact depends mainly on the size of the coefficient for the second-order shift for strain in that direction. The wells form along (100) directions, for which this coefficient is the largest.

We found that a small mis-cut of the sample caused the two wells to have different depths. We found the assignment of the luminescence lines complicated but interesting, and have not yet found an experiment for which the double strain well is well suited. The single strain well, however, is used for the measurement of the Auger decay rate in section 5.4.

4.3 Longitudinal acoustic phonon scattering by paraexcitons

Longitudinal acoustic (LA) phonons, unlike uniaxial compression, are effective in producing isotropic compression, because the crystal cannot spread sideways under a planar longitudinal sound wave. The exciton-phonon interaction for both ortho- and paraexcitons is dominated by the largest deformation potential $\Xi_o$. In this approximation the scattering potential seen by an exciton is

$$
V(x) = \Xi_o \nabla \cdot u.
$$

Expanding the local displacement of the lattice $u$ in normal modes [Kittel, 1987],

$$
u = \sum_{q, \mu} \hat{e}_{q\mu} \sqrt{\frac{\hbar}{2 \rho \Omega q s_\mu}} (a_{q\mu} e^{iq \cdot x} + a_{q\mu}^\dagger e^{-iq \cdot x})$$
where $\hat{e}_{\mathbf{q}\mu}$ is the polarization of the mode $\mu$ with wavevector $\mathbf{q}$, $\rho$ is the density and $\Omega$ is the volume of the crystal, and $s_\mu$ is the speed of sound. The scattering potential, in terms of phonon creation and annihilation operators, is then

$$V(x) = \Xi_0 \sum_{\mathbf{q}} \sqrt{\frac{\hbar}{2 \rho \Omega s_L}} (a_{\mathbf{q}L} e^{i\mathbf{q} \cdot \mathbf{x}} - a_{\mathbf{q}L}^* e^{-i\mathbf{q} \cdot \mathbf{x}}).$$

Let $V_\mathbf{q}^2$ denote $\Xi_0^2 \frac{\hbar q}{2 \rho \Omega s_L}$.

By Fermi's Golden Rule\(^\text{6}\), the phonon-scattering rate for an exciton with wavevector $\mathbf{k}$ is

$$\gamma_{\text{LA}}(\mathbf{k}) = \frac{2\pi}{\hbar} \sum_{\mathbf{q}} V_\mathbf{q}^2 \left\{ f_q \delta\left(\hbar^2 k^2/2m + \hbar s_L q - \hbar^2 |\mathbf{k} + \mathbf{q}|^2/2m\right) + (1 + f_q) \delta\left(\hbar^2 k^2/2m - \hbar s_L q - \hbar^2 |\mathbf{k} - \mathbf{q}|^2/2m\right) \right\}$$

$$= \frac{2\pi}{\hbar} \frac{\Omega}{(2\pi)^3} \int d^3q \Xi_0^2 \frac{\hbar q}{2 \rho s_L} \left\{ f_q \delta\left(\hbar^2 k^2/2m + \hbar s_L q - \hbar^2 |\mathbf{k} + \mathbf{q}|^2/2m\right) + (1 + f_q) \delta\left(\hbar^2 k^2/2m - \hbar s_L q - \hbar^2 |\mathbf{k} - \mathbf{q}|^2/2m\right) \right\}$$

$$= \frac{\Xi_0^2 m^3 s_L}{4\pi \rho \hbar^4} \left\{ \theta(q<0) (1 + f_{|q|}) + \theta(q>0) f_q \right\} \frac{q^2 dq}{k (m s_L / \hbar)^2}$$

$$= \frac{\Xi_0^2 m^3 s_L}{4\pi \rho \hbar^4} \left\{ \theta(q<0) (1 + f_{|q|}) + \theta(q>0) f_q \right\} \frac{q^2 dq}{k (m s_L / \hbar)^2}$$

where $f_q$ is the phonon occupation number, given in thermal equilibrium by the Planck function $f_q = [\exp(\hbar s_L q / k_B T) - 1]^{-1}$, and the step function $\theta(q)$ is one if the condition in its argument is satisfied and zero otherwise. The integral is dimensionless and the prefactor is

$$\Xi_0^2 m^3 s_L = 0.71 \text{ ns}^{-1}$$

where I have used the density $\rho = 6.1 \text{ g/cm}^3$ and longitudinal sound velocity $s_L = 4.5 \text{ km/s}$ from Manghani et al. [1974] and the exciton mass $m = 3.0 m_o$ reported by Yu and Shen [1975].

For large exciton momentum $k$, phonon emission events dominate over phonon absorption. From the expression for $\gamma_{\text{LA}}$ above, dropping terms in $f_q$ and performing the integration gives

$$\gamma_{\text{LA}}(\mathbf{k}) \rightarrow \frac{\Xi_0^2 m^3 s_L}{4\pi \rho \hbar^4} \left( \frac{\hbar k}{3 m s_L} \right)^2 \approx 11/\text{ns} \frac{\varepsilon}{\text{meV}},$$

where $\varepsilon$ is the exciton kinetic energy. The rate of energy-loss to LA phonon emission comes from a similar integration with additional factor of the energy of the emitted phonon energy $\hbar s_L q$ in the integrand. For large $k$,

$$\frac{\partial \varepsilon}{\partial t} \rightarrow -\frac{\Xi_0^2 m^3 s_L}{4\pi \rho \hbar^4} \frac{8 \sqrt{2}}{\sqrt{m s_L^2}} \varepsilon^{3/2}.$$

---

\(^6\)The use of first order perturbation theory for deformation potential scattering is justifiable because the interaction is weak. Kittel [1987, chapter 7] quantifies the weakness by estimating the number of virtual phonons in the cloud surrounding a carrier to be $\langle N \rangle = (m^2 \Xi_0^2 / \pi^2 \hbar^3 ps) \times \log(\pi \hbar^2 msa)$ where $a$ is the lattice constant. For Cu$_2$O, this estimate is $\langle N \rangle = 0.006$. 

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For scattering out of the $k=0$ state, the LA phonons required have energy $8K$. Such phonons are largely frozen out at $2K$, so the scattering rate is slow:

$$
\gamma_{\text{LA}}(0) = \frac{\Xi_\alpha^2 m^3 s_L}{4 \pi \rho \hbar^4} \frac{1}{16} \frac{1}{\exp(8K/k_B T) - 1} = 0.21 \text{ ns}^{-1} \text{ at } 2K.
$$

4.4 Longitudinal and transverse acoustic phonon scattering by orthoexcitons

Transverse acoustic (TA) phonons cause a shear field, and scatter orthoexcitons through the shear deformation potentials $\Xi_{zz}$ and $\Xi_{xy}$. Since the paraexciton energy does not depend on shear strain to first order, and since TA phonons produce mainly shear in a nearly elastically isotropic crystal, TA phonons interact very weakly with paraexcitons.

To treat the complete interaction of orthoexcitons with both LA and TA phonons we must use the $3 \times 3$ matrix $H_{ortho}^{\text{strain}}$ from section 2.4 as the scattering potential. Fermi's Golden Rule for orthoexciton scattering will contain the following average over initial spin states and sum over final spin states in place of $V_q^2$:

$$
V_q^2 = \frac{1}{3} \sum_{\alpha} \frac{1}{\sum_{\beta}} |\langle \alpha | H_{ortho}^{\text{strain}} | \beta \rangle|^2.
$$

Ignoring acoustic anisotropy and averaging over all directions of phonon wavevector $q$,\(^7\)

$$
V_q^2 \approx \frac{\hbar q}{2 \rho \Omega s_L} \left\{ \Xi_\alpha^2 + \frac{4}{5} \Xi_{zz}^2 + \frac{2}{5} \Xi_{xy}^2 \right\} (a_{qL} a_{qL} + a_{-qL} a_{-qL})
$$

$$
+ \frac{\hbar q}{2 \rho \Omega s_T} \left\{ \frac{8}{15} \Xi_{zz}^2 + \frac{1}{2} \Xi_{xy}^2 \right\} (a_{qT} a_{qT} + a_{-qT} a_{-qT}).
$$

This calculation predicts that LA-phonon scattering is only about 3% faster for orthoexcitons than for paraexcitons. I ignore the difference.

Most importantly, we now have an estimate of the TA-phonon scattering rate. The squared matrix element $|V_q|^2$ is only 7% that for LA-phonon emission, so in the limit of large orthoexciton wavevector $k$,

$$
\gamma_{\text{TA}}(k) \to \frac{8}{3} \left\{ \frac{8}{15} \Xi_{zz}^2 + \frac{1}{2} \Xi_{xy}^2 \right\} \frac{m k^2}{4 \pi \rho s_T} \approx 0.7 \text{ /ns} \cdot \frac{\epsilon}{\text{meV}}.
$$

The rate of scattering out of the ground state due to TA phonons is considerable, since the required phonons have energy only $0.7K$:

$$
\gamma_{\text{TA}}(0) = \frac{8}{15} \Xi_{zz}^2 + \frac{1}{2} \Xi_{xy}^2 \right\} \frac{m^3 s_T}{4 \pi \rho \hbar^4} \frac{16}{16} \frac{1}{\exp(0.7K/k_B T) - 1} = 0.18 \text{ ns}^{-1} \text{ at } 2K.
$$

---

\(^7\)The first line of this result agrees with the result of Snoke et al. [1991], except that these authors used the deformation potentials $b$ and $d$ of the bare holes.
4.5 Measured acoustic phonon emission rates

There have been a few direct measurements of the orthoexciton LA-phonon emission rates. Snoke et al. [1991] used picosecond dye laser pulses to produce orthoexcitons with a few meV of kinetic energy. Tens of picoseconds after the pulse they observed luminescence of orthoexcitons which had emitted only a few phonons since their creation. They fit their data using the deformation potential model, considering LA-phonon scattering only, with an isotropic deformation potential $\Xi_0 = 1.8$ eV.

The energy relaxation rate of orthoexcitons produced by above-bandgap excitation was measured by Snoke and Wolfe [1990c]. They report that $\Xi_0$ near 1.0 eV best fits their measurements. However, they compared their data with a well known theoretical result [Cornwell, 1967, p122] which uses the limit $s_L \to 0$. In section 6.3 we will see that a more complete model of LA phonon emission with finite $s_L$ predicts slower exciton cooling for exciton energies on the order of $m s_L^2 = 4K$. The more complete model closely matches the data of Snoke and Wolfe by using the larger deformation potential $\Xi_0 = 1.7$ eV.

The rate of scattering of orthoexcitons out of the $k=0$ state has been measured by M. Y. Shen et al. [1997] to be and 0.8/ns at 1.8K. This is about twice the prediction of sections 4.3 and 4.4; the sum of $\gamma_{LA}(0)$ and $\gamma_{TA}(0)$ is only 0.4/ns.

On the other hand, the paraexciton diffusivities measured by Trauernicht and Wolfe [1986a] imply that acoustic phonon scattering is slower than predicted in the previous sections. Trauernicht and Wolfe used the deformation potential model, with $\Xi_0 = 1.2$ eV, to fit their measured paraexciton diffusivities with great success. One might argue with their use of the relaxation time approximation in their calculation of the diffusivity, but in their treatment of exciton mobility they use a more sophisticated model and find an even smaller deformation potential, $\Xi_0 = 0.7$ eV, is required to match their measured paraexciton mobility. In summary, orthoexcitons emit LA phonons at a rate consistent with $\Xi_0 = 1.7$ eV, while the high diffusivity of paraexcitons implies an emission rate about half as fast.

One might suspect at this point that the relative importance of the shear deformation potentials have been underestimated, since $\Xi_{22}$ and $\Xi_{xy}$ contribute to LA phonon scattering by orthoexcitons only. However, $\Xi_{22}$ and $\Xi_{xy}$ also determine the TA phonon emission rate, and a measurement of the relative emission rates of LA and TA phonons by orthoexcitons [Yu and

---

8The system for integrating the Boltzmann equation developed in chapter 6 is capable of an exact prediction of the diffusivity based on the deformation potential model; this has not yet been done. To do this one should add a uniform driving force and observe the resulting drift velocity, thus calculating the mobility. This avoids simulating exciton transport in real space, which is the weakest part of the algorithm.
Shen, 1975] yields $\gamma_{TA}(k) - (1/45) \gamma_{LA}(k)$ in the limit of large orthoexciton wavevector $k$. This measurement puts TA phonon emission three times slower than the estimate on page 44, suggesting that the relative importance of the shear deformation potentials has been underestimated.

The simulations of chapter 5 use the deformation potentials listed on page 36, with no adjustment, except as explicitly noted.

4.6 Exciton mobility

One remarkable feature of the paraexciton diffusivity is that it increases dramatically below 10K. There are two reasons [Traurnicht and Wolfe, 1986a]. First, the number of ambient LA phonons is lower at lower temperatures. Second, energy and momentum conservation prevents LA phonon emission by paraexcitons moving slower than the longitudinal speed of sound, and the kinetic energy of a paraexciton moving at $s_L$ is 2K; at low temperature few paraexcitons have enough kinetic energy to emit an LA phonon. For the present work, an important question is: "What is the effective diffusivity of hot excitons in a cold lattice?"

Figure 21 shows that, in a 2K lattice, the phonon scattering rate for excitons is strongly dependent on the exciton velocity. Excitons with very high kinetic energy travel short distances between phonon emissions, and lose a small fraction of their kinetic energy with each emission. We can estimate an effective diffusivity for these hot excitons using the formula from the kinetic theory of gasses, $D = v^2 \tau / 3$. This pseudo-diffusivity approaches $6\mu m^2/\text{ns} = 60\text{cm}^2/\text{s}$ for very hot excitons in a 2K lattice; this is one-tenth the diffusivity of thermalized paraexcitons in a 2K crystal reported by Traurnicht and Wolfe [1986a]. The orthoexciton mobility is also limited by TA-phonon scattering, shown as dashed curves in figure 21, but at high exciton velocity LA-phonon scattering dominates, so hot orthoexcitons should have essentially the same pseudo-diffusivity.

The fact that low energy excitons, especially low energy paraexcitons, have such a long free path was the original motivation for simulating the relaxation of excitons as a function of position as well as energy. The suspicion was that during after a high intensity argon laser pulse low-energy excitons could exit the high-density cloud of excitons near the crystal surface, escape Auger decay, and contribute to the low-energy peak in the observed kinetic energy distributions. In numerical simulations presented in section 6.4, precisely this effect is seen. However, the explanation of the qualitative features of the observed exciton spectra do not depend on exciton motion.
4.7 Optical phonon emission

The deformation potential model postulates a potential energy for excitons that varies as
\[ V(x) = \sum_a D_a u_a \] where \( u_a \) is the displacement field for the \( a^{th} \) atom in each unit cell. If the atomic displacements are expressed in normal mode coordinates, a calculation parallel to that for acoustic phonon emission leads to a matrix element of the form \( D_{25} \, \hbar / \sqrt{2\rho \Omega E_{25}} \), where \( D_{25} \) is the appropriate linear combination of the \( D_a \) for, say, a \( \Gamma_{25} \) phonon.

In Cu2O, the coefficients \( D_{0p} \) vanish by symmetry for the important phonon modes. This is because all the optical phonons with energy less than 64meV have odd parity, and a set of atomic displacements \( u_a \) having odd parity can neither raise nor lower the energy of an even parity exciton. However, the emission of single optical phonons by orthoexcitons is observed.

Most likely the matrix element for emission is proportional to the wavevector of the phonon emitted [Cornwell, 1967]. Yu and Shen [1975] did not use the deformation potential model, but
instead considered the Coulomb interaction of the exciton’s electron and hole with the longitudinal branch of the $\Gamma_{15}$ optical phonon. (This Fröhlich-type interaction couples the excitons to $\Gamma_{15}$ LO phonons and no others.) For phonon wavelengths long compared with the exciton Bohr radius, this interaction also has a matrix element proportional to the wavevector of the phonon emitted.

We therefore take the matrix element for optical phonon scattering to be proportional to the phonon wavevector $q$. Since the average value of $q^2 = (k-p)^2$ for scattering excitons from momentum $k$ to momentum $p$ is just $k^2 + p^2 = (2\varepsilon - E_{op}) 2m/\hbar$, the optical phonon emission rate for excitons of energy $\varepsilon$ has the form

$$\gamma_{op} = R_{op} \sqrt{\varepsilon - E_{op}}$$

where the square root factor comes from the density of final states for the exciton.

Resonant Raman spectroscopy by Yu and Shen [1975] shows the relative emission rates of various types of phonons. These experiments used an orthoexciton with several meV kinetic energy as the intermediate (resonant) state. Each phonon emission experienced by the orthoexciton produces a Raman line. When the exciton kinetic energy is greater than $E_{op}$, optical phonons can be emitted. For orthoexcitons with 22 meV kinetic energy, Yu and Shen report that the emission rates of various phonons are in the following ratio:

$$\gamma_{LA} : \gamma_{25} : \gamma_{12} : \gamma_{15} = 1 : 0.14 : 0.18 : 0.21.$$  

Using the deformation potential $\Xi_0 = 1.7$eV, the $\gamma_{LA}$ for 22-meV orthoexcitons is 240/ns, so the ratio above implies optical phonon emission rates of about 30, 40 and 50/ns respectively. In another measurement of optical phonon emission rates, this time for 20-meV orthoexcitons, Snoke et al. [1991] found an optical phonon emission rate of 30/ns.

Despite the fact that these optical phonon emission rates are about five times slower than the LA phonon emission rates for orthoexcitons with the same kinetic energy, optical phonon emission is important in cooling the orthoexciton gas. Each optical phonon carries away about 15meV from an orthoexciton with initial kinetic energy around 20meV, compared with about 5meV in each LA phonon.

The paraexcitons probably interact less strongly with the optical phonons, because the symmetry requirements for phonon emission by paraexcitons are more stringent than for orthoexcitons. Within the models and in the approximations we have considered so far, only the emission of $\Gamma_{15}$ LO phonons is allowed. In chapter 6 I do not allow paraexcitons to emit optical phonons.

---

\(^9\)The corresponding values of $R_{op}$ are $R_{25} \approx 0.3$, $R_{12} \approx 0.5$, and $R_{15} \approx 1 \text{ ns}^{-1} \text{meV}^{-3/2}$. 

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Finally, both Yu and Shen [1975] and Snake et al. [1991] suggest that the emission of pairs of $\Gamma_{12}$ phonons is especially fast. However, Yu and Shen show that the Raman line due to emission of this pair\(^{10}\) is roughly the same strength as that due to emission of a single optical phonon. Both groups point to a deficit of luminescence from orthoexcitons with kinetic energy greater than twice the $\Gamma_{12}$ energy. This deficit can more easily be explained by reabsorption, as the luminescence from these excitons (or outgoing Raman signal) has energy above the phonon-assisted absorption edge shown in figure 8 of chapter 3. Assuming that emission of pairs of optical phonons emission is no more important than the Raman spectra indicate, and realizing that our experiments and simulations follow only those excitons with kinetic energy below about 25 meV, I ignore emission of pairs of optical phonons.

4.8 Conversion between exciton spin states

In a crystal held at 2K orthoexcitons convert to paraexcitons at a rate of 0.3/ns. As the crystal temperature is raised, the interconversion rate increases approximately as $T^{3/2}$ [Weiner et al., 1983]. Since I am concerned with the relaxation of hot excitons in a cold lattice, I need to separate the $T^{3/2}$ into dependencies on exciton kinetic energy and on lattice temperature. That is, I need a model for the interconversion.

When an orthoexciton becomes a paraexciton, the 12-meV ortho-para exchange energy must be shared between the paraexciton kinetic energy and any excitation emitted in the process. Energy and momentum conservation could easily be satisfied by emission of a phonon. The problem is, if we take all states to be at zone center, symmetry requires that to transform a $\Gamma_{25}^+$ orthoexciton into a $\Gamma_2^+$ paraexciton, the excitation(s) emitted must transform as $\Gamma_2^+ \times \Gamma_{25}^+ = \Gamma_{15}^+$. (Physically, we need a rotation to re-orient the electron spin with respect to the hole angular momentum, and a rotation transforms as $\Gamma_{15}^+$ in the cubic group.) There are no $\Gamma_{15}^+$ phonons in cuprous oxide.

Emission of one acoustic phonon and one $\Gamma_{15}$ optical phonon would satisfy the symmetry requirement [Caswell and Yu, 1982]. However, Snake et al. [1990a] used a strain well to adjust the orthoexciton-paraexciton splitting to less than the energy of a $\Gamma_{25}$ phonon, and the tiny change in the down-conversion rate they measured was inconsistent with any mechanism involving $\Gamma_{25}$ emission. Two acoustic phonons could also satisfy the symmetry requirement; this possibility is not treated in the literature. I ignore this possibility in view of the success of the one-phonon-emission mechanisms discussed next.

Snake et al. [1990a] pointed out that if a single-phonon emission did convert an orthoexciton to a paraexciton, the wavevectors of the final state excitations would be considerable, so it makes

\(^{10}\)by orthoexcitons with kinetic energies in the range 30-45 meV.
sense to look at processes which become allowed away from zone center. There are three wavevectors to consider: phonon, orthoexciton, and paraexciton. These lead to three possible channels for orthoexciton to paraexciton conversion.

Channel 1: A finite-wavevector transverse acoustic phonon contains some $\Gamma_{15}^+$ character. Physically, a TA phonon rotates the lattice as it passes. If we take the part of the hamiltonian which connects ortho- and paraexcitons to be of the form $L \nabla \times \mathbf{u}$, the down-conversion rate calculation parallels that in section 2.5, and the rate is proportional to the phonon wavevector. Considering both spontaneous and stimulated phonon emission, and phonon absorption, this down-conversion rate should be proportional to $(1 + f_p) + f_p$, where $f_p$ is the occupation number of the (about 1 meV energy) acoustic phonons involved. The temperature dependence would then be roughly $1 + 2 \left( \frac{T_{\text{lattice}}}{1 \text{meV}} \right)$.

Channel 2: A finite-wavevector orthoexciton, expanded in wavefunctions within one unit cell, contains some $\Gamma_{25}^-$ character. This odd-parity part of the orthoexciton is allowed by symmetry to convert to a paraexciton through acoustic phonon emission. ($\Gamma_{25}^- \times \Gamma_{25}^+ = \Gamma_{15}^-$ and infinite-wavelength acoustic phonons are $\Gamma_{15}^-$.) The matrix element for this process would be proportional to the orthoexciton wavevector; the rate is then proportional to the orthoexciton wavevector squared, $k_0^2$. Including phonon-absorption and stimulated emission as before gives an overall temperature dependence of the down-conversion rate of essentially $T_{\text{gas}} \left( 1 + 2 \frac{T_{\text{lattice}}}{1 \text{meV}} \right)$. (If we imagine longitudinal phonons to be involved, 1 meV becomes 3 meV.) This is the channel that Snoke et al. [1990a] used to fit the experimental rates.

Channel 3: A finite-wavevector paraexciton has some $\Gamma_{25}^-$ character, again making a one-phonon conversion process allowed. The temperature dependence, and the orthoexciton velocity dependence, of the down-conversion rate through this channel would be similar to that of channel 1.

Figure 22 shows that, while each of these channels provides a good fit to the observed ortho-paraexciton conversion rates for thermalized orthoexcitons, they make vastly different predictions for the behavior of hot orthoexcitons in a cold lattice. Channel 2, by selectively removing the fastest orthoexcitons, can result in transient distributions which appear colder than the lattice. In the simulations of chapter 6, this mechanism produced orthoexciton distributions 25% below the lattice temperature; such an effect has not been seen in experiments. Also, channel 2 predicts a linear temperature dependence in the conversion rate at low temperatures.

---

$^{11}$In order to fit the experimental results of figure 6, the prefactor $L$ must be 80 meV. My own attempt to work out this model in detail (assuming that spin-orbit coupling locks the hole spin to the rocking lattice and the exchange coupling then flips the electron spin relative to the hole angular momentum) yielded a prefactor $L$ six times smaller.
Figure 22: a) and c) Down-conversion rates as a function of orthoexciton speed (in a 2K lattice) predicted by two of the three channels discussed in the text. b) and d) Average down-conversion rates of a gas of orthoexcitons in equilibrium with the lattice, as a function of lattice temperature, compared with the data of Weiner et al. [1983].

Figure 23: Numbers of ortho- and paraexcitons following a 10-ns dye laser pulse tuned to the 1s orthoexciton absorption line.

The observed orthoexciton decay rate changes only 10% from 2.0 K to 4.2 K. The orthoexciton decay is dominated by conversion to paraexcitons at these temperatures, as seen in figure 23, which shows paraexcitons appearing quickly after resonant creation of orthoexcitons by a dye laser pulse. This experiment can and should be done with a short (sub-nanosecond) dye-laser pulse tuned to the orthoexciton direct absorption line, recording the rise in the paraexciton signal and the fall in the orthoexciton signal, with the crystal at both 2K and 4K.
Channels 1 and 3 have similar dependence on the orthoexciton velocity, and I find channel 1 physically more plausible. In this thesis, I assume that channel 1 is the dominant mechanism of orthoexciton-to-paraexciton conversion.

Finally, acoustic phonon scattering through the deformation potential also contributes to the rate of interconversion between orthoexciton states. The off-diagonal elements in $H^{\text{strain}}_{\text{ortho}}$ cause transitions between states, and in the basis of orthoexciton states $\{yz, xz, xy\}$ the off-diagonal elements are those elements involving $\Xi_{xy}$. The rate of interconversion is just that term in $\gamma_{\text{TA}}$ which is proportional to $\Xi_{xy}^2$; for thermalized orthoexcitons in a 2K lattice, this is $0.1/\text{ns}$.

Jia Ling Lin [thesis, 1995] measured the rate of decay of population of $xy$ orthoexcitons in a crystal under compressive strain along [001] which raises the energy of the $xy$ orthoexciton above that of the other two. The measured decay rates at 2K were closer to $1.0/\text{ns}$, which is faster than the sum of ortho-to-para conversion and the interconversion between orthoexciton states predicted above. Either the $xy$ orthoexcitons are being lost by other means (the conclusion reached by Lin) or this is another clue that orthoexciton-TA phonon scattering is faster than I have estimated.
5. AUGER RECOMBINATION

5.1 The effects of Auger recombination

There is a density-dependent, non-radiative decay mechanism for excitons that tends to limit their density. Figure 24 shows that for pulsed argon ion laser excitation above about $10^{13}$ photons absorbed per cm$^2$ per pulse, the observed number of orthoexcitons increases sub-linearly with laser power. That this is due to a shortened exciton lifetime is confirmed by observing the decay in the number of excitons after a short laser pulse.

![Graph showing orthoexcitons per cm$^2$ as a function of time.](image)

Figure 24: Areal density of orthoexcitons as a function of time relative to the center of the argon ion laser pulse which created them. These experiments used the 50μm aperture on the sample surface and the sample was immersed in a 2K helium bath. Pulse intensities were, in units of $10^{11}$ photons absorbed per cm$^2$ per pulse, 5, 13, 50, 130, 500, 1300, 5000, and 12500. a) 10ns pulses. b) 0.5ns pulses.

In semiconductors in which the electrons and holes remain unbound in a plasma, one can observe a process in which an electron recombines with a hole and transfers its bandgap energy to another nearby electron or hole. This three-body process is called Auger recombination. In Cu$_2$O at low temperatures, the excitons are the dominant species, and the density-dependent decay is due to the collision of two excitons. One exciton recombines and the other is split into a free electron and hole which carry away the bandgap energy. Following Hulin et al. [1980] we refer to this two-exciton decay process as Auger recombination.

The instantaneous decay rate of excitons due to this two-body decay is $(\partial n/\partial t)_A = -An^2$ where $A$ is the Auger constant. If continuous excitation creates $G$ excitons per unit time per unit volume, balancing the generation rate with the Auger decay rate leads to $n = \sqrt{GiA}$. This square-root dependence can be seen in the peak exciton densities created by the long pulses, but only at sufficiently high power that the Auger decay rate $An$ is fast on the scale of the pulse length.
Figure 25: a) The maximum observed areal density of orthoexcitons using 10ns argon ion laser pulses. The line is $n = \sqrt{G/A}$ as described in the text. b) The fastest observed orthoexciton decay rates after 0.5ns laser pulses.

We can find the order of magnitude of $A$ using $n = \sqrt{G/A}$ and figure 25a, which plots the peak orthoexciton density as a function of excitation intensity. I determine the exciton generation rate $G$ in two steps. First, the quantity plotted along the horizontal axis in figure 25a, divided by the 10ns pulse length, is the flux of argon ion photons; call it $J_0$. The photons are absorbed with absorption length $d$, and we have the estimate of section 3.7 for the number of orthoexcitons created per photon absorbed: $G = 30\% \frac{d J_0}{d} e^{-zd}$. The quantity plotted along the vertical axis is the density of orthoexcitons integrated over the depth $z$ from the excitation surface. When Auger decay is the dominant decay mechanism for the orthoexcitons, it limits their areal density to

$$
\int_0^\infty n \, dz = \int \sqrt{\frac{G}{A}} \, dz = \int \sqrt{\frac{30\% J_0}{d A}} e^{-zd} \, dz = 2 \sqrt{\frac{30\% J_0 d}{A}}.
$$

The line in the figure is this equation plotted with $d = 2.5\,\mu m$ and $A = 10^{-16} \, cm^3/ns$.

The Auger constant $A$ could vary by a factor of ten in either direction and still produce a curve within the error bars in figure 25a. These wide error bars require explanation. They denote the range of values obtained in two repetitions of the experiment separated by one year's time. The upper limits of the error bars come from an experiment in which time-resolved spectra were recorded; spectral integration of the orthoexciton phonon-assisted luminescence determined the orthoexciton density. The lower limits come from an experiment which used the monochromator with wide slits to accept most of the $\Gamma_2\rightarrow\Gamma_2$-phonon-assisted orthoexciton luminescence band; the orthoexciton density was determined from the instantaneous photon count rate during the laser pulse. These differences in technique do not explain all of the difference in the measured densities; there were additional, unintentional and unrecorded, differences in the experimental situation. All my other measurements of the orthoexciton yield fall within the band formed by these error bars.
Higher excitation density than shown in figure 25 is possible with our laser and 10ns pulses. At higher excitation levels the orthoexciton luminescence grows even more slowly with laser power. This is likely due to the formation of a bubble in the 2K superfluid helium bath. When the average power absorbed by the cuprite is greater than 400W/cm² I hear a faint whining sound from cryostat, especially when the laser hits the aluminum forming the 50μm aperture. (Greenstein and Wolfe [1981] found that an oscillating bubble formed when more than 100W/cm² fell on the surface of germanium-immersed in superfluid helium.)

Another estimate of the size of $A$ comes from the instantaneous decay rate. In figure 25b are plotted the fastest orthoexciton decay rates observed after 0.5ns pulses of different intensity. These fastest decay rates are the tangents to the curves in figure 24b at their inflection points, that is, they are the maximum values of

$$
\tau^{-1} = \frac{\int (dn/dt) \, dz}{\int n \, dz}
$$

because what we observe is $\int n \, dz$. At low excitation density the observed decay rate $\tau^{-1}$ is dominated by the orthoexciton to paraexciton conversion rate of 0.3/ns. At high excitation density it is limited by both the turn-off rate of the laser pulse and the 0.4ns timing resolution of our photon-counting system. When the observed decay rates lies between these limits, we can estimate $A$ through

$$
\tau^{-1} = 0.3/\text{ns} + A \frac{\int n^2 \, dz}{\int n \, dz} \approx 0.3/\text{ns} + A \frac{\int n \, dz}{2 \, d},
$$

where the densities are the observed densities at the inflection points. In the last step above I approximate the integral of the squared density by taking the density to have an exponential decay with decay length equal to our assumed absorption length $d = 2.5\mu$m for argon ion laser light. Using the rightmost four data points in figure 25b, and the uppermost four curves in figure 24b, the values of $A$ obtained by this method are 0.8, 1.1, 0.8, and $0.6 \times 10^{-16}$ cm$^3$/ns.

It is worthwhile to plot some solutions of a model equation for the rate of change of orthoexciton density. I include the rate of orthoexciton generation $G$, Auger decay, and a rate $B$ of conversion from orthoexcitons to paraexcitons$^1$:

$$
\frac{d \, n}{dt} = G - A \, n^2 - B \, n.
$$

After a short laser pulse, $G=0$, and the equation has the free solution, shown in figure 26a,

$$
n(t) = \frac{n_0 \, e^{-Bt}}{1 + (An_0/B) (1 - e^{-Bt})}.
$$

No matter how high the initial density $n_0$, the instantaneous density $n(t)$ is bounded by

$$
n(t) < \frac{B / A}{e^{Bt} - 1} < (A t)^{-1}.
$$

---

$^1$I am postponing consideration of the role of paraexcitons in Auger decay.
Experiments like those presented in figure 24 produce excitons through absorption of light. The excitons are created in a distribution proportional to $e^{-z/d}$ with $z$ the depth into the crystal. Then the excitons in the high-density region near the surface suffer faster Auger decay, so the shape of the cloud changes with time. This effect can be handled neatly by integrating the free solution $n(t)$ over depth $z$ into the crystal, with $n_0$ proportional to $e^{-z/d}$. The resulting areal density of excitons is

$$\int n \, dz = \frac{Bd}{A} \frac{\log[1 + (An_0/B)(1 - e^{-Bt})]}{e^{-Bt} - 1}$$

which is plotted in figure 26b. Despite the firm limit which Auger decay puts on the exciton density (the inequality at the bottom of the previous page) the experimentally observable spatial integral $\int n \, dz$ continues to increase with increasing excitation density.

Finally, I model the laser pulse $G(t)$ as a Gaussian and numerically integrate the population equation. These results, again integrated over $z$, are plotted in figure 26c.

![Figure 26: Solutions of the simplified population equation $dn/dt = G - A \, n^2 - B \, n$, with $A/d = 10^{16}$ cm$^3$ ns$^{-1}$ / 2.5$\mu$m and $B = 3.0$ ns$^{-1}$. The ordinate is $\int n \, dz$. Total exciton densities deposited were $4 \times 10^{10}$ through $4 \times 10^{15}$ per cm$^2$, so as to include the range of powers used in the experiment of figure 24. a) Generation rate $G$ homogeneous in space, and a $\delta$-function in time. b) $G$ decaying exponentially with $z$, again a $\delta$-function in time. c) $G$ again exponential in space, now a Gaussian with full-width 0.5$\mu$s in time.](image)

Each Auger recombination releases an amount of energy equal to the band gap. Initially, the energy is probably carried by the remaining separated electron and hole. We see that part of the released energy appears in the exciton gas, as the orthoexciton average kinetic energy begins to increase at the same excitation level where Auger decay begins to shorten the orthoexciton lifetime. Figure 27 shows the apparent "temperatures" of the gas extracted from fits to equilibrium distributions.

Heating of the lattice could make only a minor contribution to these higher exciton gas energies. First, the exciton gas heating is a function of only the pulse energy, rather than of average power absorbed. The experiment of figure 27b, at the excitation level $10^{16}$ photons per
cm² per pulse, gave the same results when the pulse train frequency was changed from 820kHz to 82kHz to 8.2kHz, an overall reduction by a factor of 100 in average power. Therefore we need consider only the energy absorbed by one pulse.

![Graphs showing maximum average gas temperature and possible lattice temperature versus photons/cm² for 10ns and 0.5ns pulses.](image)

**Figure 27:** The apparent exciton gas temperatures observed during the 0.5ns laser pulse, determined by fitting the orthoexciton phonon-assisted luminescence to a Bose-shaped distribution as discussed in section 3.8. The curves show the possible lattice temperature increase corresponding to the absorbed laser power as discussed in the text.

a) The results of 10ns pulses. The laser pulse produced by our two-pass acousto-optic cavity dumper is modulated at 779MHz, twice frequency of the acoustic wave used. The resulting ripple in the apparent temperature has been averaged to find the ‘maximum average’ temperatures, which are plotted.

b) The results of 0.5ns pulses.

Suppose all the energy absorbed from each laser pulse was converted directly into lattice heat, with the distribution of heat determined by the illumination area and absorption length. We ignore the diffusion of heat during the tens of nanoseconds of interest. The specific heat of cuprous oxide at low temperatures is \( c_v \rho = 36T^3 \text{ J m}^{-3} \text{ K}^{-4} \) [Gregor, 1962] so the local lattice temperature can be found by setting the local density of absorbed energy equal to \( \int c_v \rho \, dT = 8.9T^4 \text{ J m}^{-3} \text{ K}^{-4} \). The resulting curves of lattice temperature versus laser power appear in figure 27. These curves give an upper limit to the local lattice heating; e.g., over a 10ns period ballistic phonons would travel 40μm, greatly lowering the energy density.

The band gap of Cu₂O decreases with elevated lattice temperature. (Lattice expansion cannot explain the band gap shift because the coefficient of thermal expansion of cuprite is tiny, and negative, below 100K.) The corresponding decrease in the exciton energy was thoroughly studied by Grun et al. [1961] over the temperature range of 4 to 300K. The expression \( \Delta E = 0.0014T^2 \text{ meV K}^{-2} \) approximates the shift in exciton energy below 100K. An increase in local lattice temperature to 10K would produce a shift of 0.14meV, which would be observable in the direct orthoexciton luminescence line. In the experiments considered here, no shift this large is seen, but there is sometimes a low-energy tail of about this width on the direct line (see figure 36 on page 73).
Additional evidence that the energy released by Auger decay events heats the exciton gas comes from the strain-well experiments that will be presented in section 5.4. These experiments use the phonon-assisted orthoexciton absorption to produce excitons with near 100% efficiency, creating as a by product only one optical phonon per exciton produced. Still, the exciton gas temperature rises above that of the lattice at higher excitation densities.

5.2 Definitions

We define the Auger constant $A$ such that $A n^2$ is the number of decay events per unit volume in a gas of excitons of density $n$. The lifetime of an exciton against Auger decay is then $(A n)^{-1}$.

We use the constant $A$, rather than a cross-section, because we do not expect the rate to have the form $n \sigma_A v$. There is no reason to expect the rate to be proportional to the relative velocity of the colliding excitons. Auger decay is different from elastic scattering in that the density of final states is not proportional to the initial velocity of the particles. The ionized electron and hole can reach a large volume of phase space because they share an amount of kinetic energy equal to the band gap. The Auger decay rate, and thus $A$, may still be proportional to some power of the relative velocity for some other reason. We make the simplest working assumption that $A$ is constant.\footnote{Even if $A$ is finite for excitons at rest, we should expect the momentum-dependence of $A$ to show structure when the relative momentum reaches $\hbar/c_0$, corresponding to an exciton energy of about 25meV, \textit{i.e.} 300K.}

There are two spin states for the 1s excitons in cuprite, the orthoexciton and the paraexciton, and different experiments measure the Auger decay constant in gasses with different mixes of these states. Conceptually, there are three distinct Auger decay constants, one for each choice of spin states of the colliding excitons. Under the assumption that free electrons and holes form excitons with randomly distributed spin states, three orthoexcitons for each paraexciton, the coupled population equations for the orthoexciton density $o$, and paraexciton density $p$ are

$$\frac{d o}{d t} = \frac{3}{4} G - 2 A^{oo} o^2 - 2 A^{op} op + \frac{3}{4} \eta (A^{oo} o^2 + 2A^{op} op + A^{pp} p^2) - B o + 3Be^{-\Delta/kT} p$$

$$\frac{d p}{d t} = \frac{1}{4} G - 2 A^{op} op - 2 A^{pp} p^2 + \frac{1}{4} \eta (A^{oo} o^2 + 2A^{op} op + A^{pp} p^2) + B o - 3Be^{-\Delta/kT} p$$

where $B$ is the rate for interconversion, and $\Delta$ the splitting, between orthoexcitons and paraexcitons. The rate of destruction of excitons is $2An^2$ (with $n=0+p$ and taking $A = A^{oo} = A^{op} = A^{pp}$: generalization is straightforward). This is consistent with our initial definition of $A$ because each Auger collision removes \textit{two} excitons, one electron-hole pair recombines and the other is ionized. The factor $\eta$ is the fraction of those ionized electron-hole pairs which bind to form new excitons. Thus the \textit{net} loss of excitons due to Auger decay is $(2-\eta)An^2$.\footnote{Even if $A$ is finite for excitons at rest, we should expect the momentum-dependence of $A$ to show structure when the relative momentum reaches $\hbar/c_0$, corresponding to an exciton energy of about 25meV, \textit{i.e.} 300K.}
I neglect the possibility of Auger recombination events involving an exciton and a free carrier in the initial state, and one hot free carrier in the final state. Conservation of energy and momentum is difficult, unless a phonon is created during the recombination. The effect of this type of decay on the population equations above is to add a term describing how many recombination events can be caused by the electron and hole liberated in each exciton-exciton Auger decay. If the free carrier lifetime is independent of density the new term would be proportional to the number of free carriers recently generated, and to the number of excitons a free carrier can reach in its lifetime. The added term would involve $n^3$; I do not believe I am seeing a recombination mechanism proportional to $n^3$. If on the other hand the free carrier lifetime were limited by electron-hole rebinding, and thus shorter at higher density, the additional term in the population equation would be proportional to $n^2$ and equivalent to an increased $A$.

5.3 Previous estimates of the rate

We review seven experimental estimates of the Auger decay rate constant $A$. The first three measurements were made with steady state excitation. These experiments produced gasses consisting mainly of paraexcitons because the orthoexciton-to-paraexciton conversion rate is fast on the scale of the paraexciton lifetime.

The first experimental measurement of the Auger decay rate of excitons in Cu$_2$O was by Mysyrowicz et al. [1981] who found that as they increased the excitation density, the paraexciton luminescence increased more slowly than the orthoexciton luminescence. By assuming that at low power the paraexciton density was the excitation density times the paraexciton lifetime of 10µs, in a crystal at 12K, they extracted an Auger rate constant for the paraexcitons $(2-\eta)A_{pp} = 2 \times 10^{-19} \text{cm}^3/\text{ns}$. Diffusion of the excitons was neglected, as the unusually high diffusivity of paraexcitons [Trauernicht, 1986a] had not yet been reported. The diffusivity at 12K would allow the paraexcitons to travel about 1mm within their lifetime, so the non-radiative decay observed by Mysyrowicz et al. most likely took place in a gas with volume much larger than the excitation volume. The resulting overestimate of the gas density would have lead to a severe underestimate of $A$.

Trauernicht et al. [1986b] report the Auger constant based on a measurement of the number of paraexcitons in a strain well versus steady-state excitation density. In this experiment, with the crystal at 2K, the dye laser beam was positioned to produce excitons within a small volume near the strain well. The excitons diffused from the creation region into the well. The yield curve shows a break from linear to fourth-root behavior (in contrast to the square-root seen in figure 25a) as Auger decay becomes the dominant exciton decay process in the two regions. Trauernicht et al. report the quantity $2(2-\eta)A_{pp}/\Omega = 0.05/\text{s}$, where $\Omega$ is the effective average volume of the two regions. The volume of the exciton cloud in the strain well was measured and reported as $V_{\text{FWHM}}$ (the volume at which the density is greater than half its maximum) equal to
$5 \times 10^{-7}$ cm$^3$. The effective volume appropriate to Auger decay is derived in the next section to be $\Omega = 6.5 \times V_{\text{FWHM}}$. If we assume that the effective volume of the excitation region was similar to that of the strain well, we extract $(2-\eta)A_{\text{PP}} = 0.8 \times 10^{-16}$ cm$^3$/ns, for paraexcitons in a strain well at about 3.6 kbar uniaxial stress along [100].

An earlier experiment by Trauernicht et al. [1983] measured paraexciton number as a function of laser power $P$ absorbed, exciting the strain well directly. The absolute number of paraexcitons $N_{\text{para}}$ was determined using the measured exciton lifetimes, which included all decay mechanisms, from a separate time-resolved experiment. They found

$$\frac{N_{\text{para}}}{V_{\text{FWHM}}} = 6 \times 10^{14} \text{ cm}^3 \sqrt{\frac{P}{\text{mW}}}.$$ 

Each photon absorbed created one exciton, so the generation rate is $G = P/(\Omega \hbar \omega)$ where $\Omega$ is again the correct effective volume for two-body decay. Trauernicht et al. report that the exciton cloud in the well has a full-width at half-maximum of 145 μm, so $\Omega = 1.0 \times 10^{-5}$ cm$^3$. Letting $p$ denote the appropriate average paraexciton density,

$$p = \frac{N_{\text{para}}}{\Omega} = \frac{6 \times 10^{14}}{6.5} \sqrt{\frac{P}{\text{mW}}} = \sqrt{\frac{G}{4 \times 10^{-17} \text{ cm}^3/\text{ns}}} ,$$

which is the steady-state solution to the population equation with $(2-\eta)A_{\text{PP}} = 0.4 \times 10^{-16}$ cm$^3$/ns. Again this rate applies to a crystal at 2K under approximately 3.6 kbar uniaxial [100] stress. Trauernicht et al. did interpret this result as due to Auger decay but chose not to report any numerical Auger constant.

The first determination of the Auger constant through direct observation of the exciton decay rate was made by Snoke and Wolfe [1990c]. In a crystal at 2K, Snoke and Wolfe measured the lifetime of the orthoexciton luminescence following an intense 100 ps laser pulse. Using the spectral fits to a Bose distribution to infer the exciton density, they reported an Auger rate constant of $10^{-18}$ cm$^3$/ns for orthoexcitons, with the caveat that part of the observed decay rate may have been due to conversion of orthoexcitons to paraexcitons.

Lin and Wolfe [1993] presented measurements of a paraexciton gas having a 100 ns lifetime in a crystal at 2K under 0.3 kbar uniform uniaxial [100] stress. Based largely on spectral fits of the coexisting orthoexciton gas to equilibrium Bose distributions, they estimated the paraexciton gas density to be nearly constant at $10^{19}$/cm$^3$. While Lin and Wolfe did not interpret this result in terms of an Auger rate, their claim does imply that $A_{\text{PP}}$ is less than $10^{-21}$ cm$^3$/ns, and this result has been used in further research [Kavoulakis, 1996a, 1996b].

O'Hara et al. [1999b] measured the decay in orthoexciton luminescence in a 2K crystal after a 0.5 ns laser pulse. We estimated the instantaneous number of orthoexcitons using the method described in chapter 3. We used micro-imaging of the time-resolved luminescence to determine the shape of the exciton cloud in the plane of the crystal face that was excited, but had to assume
that it had the same shape in the third dimension, depth into the crystal. Both orthoexcitons and paraexcitons were present in this experiment, but we were able to analyze only the orthoexciton luminescence. In the paper we report the value of an effective Auger constant for the mixed gas, 
\[(2-\eta)A = 0.7\times10^{-16} \text{ cm}^3/\text{ns},\]
and argue that \(A^{oo}\) alone contributes between 75% and 100% of this value \(A\).

The experimental challenge in measuring the Auger constant using time-resolved luminescence is to separate the decay rate \(\dot{A}\) from: 1) the ortho-para conversion rate, 2) the time-resolution limits of the laser pulse and photon detection, 3) the single-exciton lifetime, and 4) the rate at which the exciton cloud density decays due to exciton diffusion.

Experiments in progress by Warren et al. [1999] in the MRL Laser Laboratory solve these problems by holding the crystal at 70K. At this higher temperature, the exciton diffusivity is 30 times slower than at 2K, so exciton motion is less of a problem. The rate of interconversion between orthoexcitons and paraexcitons is quite fast, extrapolation from figure 22b predicts 10/ns. Warren et al. watch the exciton density fall through the range in which the Auger decay rate is slower than ortho-para interconversion, but faster than the single-exciton decay rate. They control the volume by making the excitation volume large on the scale of the diffusion length, and measure the exciton number using the method of section 3.7.

Since conversion between orthoexcitons and paraexcitons is fast at 70K, the fraction of excitons in each spin state remains very close to the equilibrium values, \(o = 0.29n\) and \(p = 0.71n\). Warren et al. are measuring the effective Auger constant
\[\dot{A} = \frac{o^2}{n^2} A^{oo} + 2 \frac{op}{n^2} A^{op} + \frac{p^2}{n^2} A^{pp}\]

\[= 0.08 A^{oo} + 0.41 A^{op} + 0.51 A^{pp}.\]

Currently, it appears that the result will be \(\dot{A} = (0.6\pm0.1)\times10^{-16} \text{ cm}^3/\text{ns}\), measured in a strain-free crystal at 70K.

To summarize, those experiments making reliable measurements of the exciton density find both \(A^{oo}\) and \(A^{pp}\) to be on the order of \(10^{-16} \text{ cm}^3/\text{ns}\).

The first theoretical estimate of the Auger decay rate seems to be that by Čulík [1966]. He treated the Coulomb interaction between the individual electrons and holes in two Wannier excitons to first-order. From Fermi's Golden Rule he finds the transition rate from a pair of excitons to a free electron and hole. He finds a rate of zero for 1s excitons in cuprous oxide. (For 2p excitons in cuprite he quotes \(A = 10^{-14} \text{ cm}^3/\text{ns}\), averaging over spin states.)

Kavoulakis and Baym [1996] treated the same problem, also to first order in the Coulomb interaction, but more completely with respect to the initial relative velocity of the excitons. For
orthoexcitons in Cu$_2$O they find the tiny Auger constant $A^{00} = 4 \times 10^{-21} T \text{cm}^3 \text{ns}^{-1} \text{K}^{-1}$ where $T$ is the temperature of the orthoexciton gas.

Kavoulakis and Baym [1996] also considered phonon-assisted Auger decay processes, with an optical phonon accompanying the electron and hole in the final state. They report $A^{00} = 0.8 \times 10^{-18} \text{cm}^3/\text{ns}$, $A^{\text{op}}$ half as large, and $A^{\text{pp}}$ negligibly small. However, in calculating the Auger rate, Kavoulakis and Baym used observed exciton lifetimes to estimate the phonon-assisted luminescence rate$^3$ as $\gamma_{12} = 4 \times 10^7/\text{s}$. Adjusting their results using $\gamma_{12} = 7 \times 10^4/\text{s}$ from section 3.4 reduces the predicted Auger rate to the minuscule value $A^{00} = 10^{-21} \text{cm}^3/\text{ns}$ for their proposed phonon-assisted mechanism.

To date, theoretical calculations of the Auger constant for 1s excitons in Cu$_2$O predict $A$ to be below $10^{-20} \text{cm}^3/\text{ns}$ — four orders of magnitude below the observed value.

**5.4 Measurement of the rate in a strain well**

We confine the excitons to a strain well so that diffusion does not reduce the density of the exciton cloud. Then we can observe Auger decay of thermalized excitons on a microsecond time scale. This has been done before [Trauernicht, 1986b] but this time I am using a calibrated optical system to measure the exciton density and thus the Auger decay constant.

Figure 28 shows a time-resolved luminescence spectrum from a strain well in a crystal held at 2K. The strain well was formed by pressing a lens with radius of curvature 8.15mm onto a (001) face of Cu$_2$O with a force of 340N. At the bottom of the well, the orthoexciton energy is 2014.9meV; the paraexciton energy was 2009.3meV.

We measure $o$ and $p$ using the technique section 3.7, correcting for the polarization and anisotropy of the luminescence from the lower stress-split orthoexciton level (appendix A). We assume that the phonon-assisted radiative rates are the same in the strain well (1% strain) as in a strain-free crystal.

This assumption has been verified for the orthoexciton luminescence, as the corresponding absorption strengths have been measured in stressed crystals [Gross, 1961; Agekeyan, 1977]. The orthoexciton phonon-assisted absorption bands are seen to split and become polarization-dependent as described by the theory in appendix A, but the total absorption strength of each multiplet is not noticeably changed by experimentally attainable strain. Note that in the strain-well spectrum of figure 28, the various orthoexciton phonon-assisted luminescence lines have the same relative intensities as they have in a strain-free crystal.

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$^3$As one of those given access to the paper before publication, and thanked for "helpful comments". I have to accept some of the blame for this error.
Figure 28: Luminescence spectrum recorded 1000ns after a 10ns dye laser pulse tuned 0.5meV above the onset of the phonon-assisted orthoexciton absorption band. 10^8 photons were absorbed in the well from each pulse. Luminescence is collected along [100], perpendicular to the direction of compression. The relative intensities of the phonon-assisted luminescence lines are found to be the same as in a strain-free crystal. The spectral features are fit to the appropriate Mavellian distributions [Trauericht, 1986b] and from their integrals we determine the numbers of orthoexcitons (1×10^4) and paraexcitons (2×10^6) using the method of section 3.7.

Paraexciton $\Gamma_{25}$ phonon-assisted luminescence is a more subtle process because it requires flipping an electron spin (appendix A). This luminescence process depends on the size of the spin-orbit splitting of a deep valence band (which provides the intermediate state for the hole). This splitting may be changed, by a substantial fraction of its size, under the 1% strain used to create these strain wells. It must be borne in mind that the paraexciton $\Gamma_{25}$ phonon-assisted luminescence rate has not been measured as a function of strain. I work under the assumption that the luminescence rate is unchanged by strain, but make independent estimates of the paraexciton density whenever possible.

This experiment was analyzed under the assumption that the Auger constant does not depend on the spin states of the colliding excitons; that is, $A^{oo}=A^{pp}=A^{op}=A$. Adding the population equations from section 5.2, we get an equation for the total number of excitons $n=o+p$:

$$\frac{dn}{dt} = G - (2-\eta)A n^2 - n/\tau$$

where we include the term $n/\tau$ to describe the slow eventual non-radiative decay of the excitons.

In this experiment we observe the total number of excitons, the spatial integral of a cloud with non-uniform density. The integral of the population equation over space,

$$\frac{d}{dt} \int n \, d^3r = \int G \, d^3r - (2-\eta)A \int n^2 \, d^3r - \int n \, d^3r /\tau$$

$$\frac{dN}{dt} = I - (2-\eta)A \int n^2 \, d^3r - N /\tau,$$
involves the observable total number of excitons \( N = \int n \, d^3r \) and total number of photons absorbed \( I = \int G \, d^3r \), but also \( \int n^2 \, d^3r \), which is not directly observable. If we assume that the spatial distribution of particles in the well is the equilibrium distribution in the potential \( V = \alpha r^2 \), then \( n \propto \exp(-V/k_B T) = \exp(\alpha r^2/k_B T) \). We define the ‘effective volume’,

\[
\Omega = \left( \frac{\int n \, d^3r}{\int n^2 \, d^3r} \right)^2 = \left( \frac{\exp(-\alpha \frac{r^2}{k_B T}) \, d^3r}{\exp(-2 \alpha \frac{r^2}{k_B T}) \, d^3r} \right)^2 = \left( \frac{2\pi \frac{k_B T}{\alpha}}{\alpha} \right)^{3/2},
\]

so that \( \int n^2 \, d^3r = N^2/\Omega \). In terms of the Gaussian standard deviation, \( \Omega = (4\pi)^{3/2} \sigma^3 \). In terms of the full-width at half-maximum, \( \Omega = (\pi / \log 4)^{3/2} \) (FWHM)^3.

The paraexciton cloud was measured to have a Gaussian width \( \sigma \) (standard deviation) of 50±5μm in the transverse direction, determined from the phonon-assisted luminescence. Another exciton cloud at the same lattice temperature in a strain well of the same depth was measured in both directions, and found to be 20% smaller along the stress axis. Thus we expect the extent of this exciton cloud along the stress axis is \( \sigma_z = 40 \mu m \). For the present experiment, \( \Omega = (4\pi)^{3/2} \times 40 \times 50 \times 50 \mu m^3 = (4.5 \pm 1.3) \times 10^{-6} \) cm^3.

Using the effective volume, the population equation becomes

\[
\frac{dN}{dt} = I - (2-\eta)A \frac{N^2}{\Omega} - \frac{N}{\tau}
\]

This equation has a free solution, when \( I = 0 \), of the form presented earlier,

\[
N(t) = \frac{N_0 \, e^{-t/\tau}}{1 + (2-\eta)(A/\Omega)N_0 \tau \left( 1 - e^{-t/\tau} \right)}.
\]

For this experiment, the monochromator entrance slit was set at 100μm for good spectral resolution, accepting only the central 19μm of the exciton cloud. This entrance slit accepted luminescence from only 15% of the excitons in the well, based on the measured \( \sigma_x = 50 \mu m \) transverse width of the exciton cloud. Figure 29 fits the observed number of excitons to 15% times \( N(t) \) above.

Thus we extract \( (2-\eta)A = 0.43/s \times 4.5 \times 10^{-6} \) cm^3 = 19×10^{-16} cm^3/ns, which is thirty times the value reported by O'Hara et al. [1999b] and that now being obtained by Warren et al. One source of error is the uncertainty in the measurement of the absolute number of excitons \( N_0 \). At the date of this experiment, I estimated the possible error in the determination of exciton numbers based on spectral fits as a factor of two in either direction. The time-dependence of the exciton luminescence depends only on \( AN_0/\Omega \), so if \( N \) is underestimated due to unanticipated loss of luminescence on its way to the photomultiplier tube, \( A \) is overestimated by the same factor.

We can independently estimate \( N_0 \), the initial number of excitons in the well, based on the number of laser photons absorbed in the strain well. The dye laser was tuned to 2028.9meV, which is 0.4meV above the threshold for simultaneous creation of orthoexcitons and \( \Gamma_{12} \) optical phonons. The absorption curve in figure 8 of section 3.2 is locally shifted to lower energies, as
the orthoexciton energy is shifted in the strain well. Assume the orthoexciton energy varies as $\alpha x^2$ along the path of the laser beam. Based on the measured transverse width of the exciton cloud and measured exciton gas temperature, $\alpha=40\text{meV/mm}^2$, and in this experiment the absorption band threshold was below the laser photon energy for a path length of 200$\mu$m. The fraction of photons absorbed is the average absorption coefficient, 4$\text{cm}^{-1}$, times 200$\mu$m, which comes to 8%. This was confirmed by measuring the transmitted laser power as the laser beam was moved on and off the strain well; this test indicated that about 10% of the laser power was absorbed.

Each laser pulse contained $1.3\times10^9$ photons as it passed the strain well. I estimate $10^8$ were absorbed in the well. Due to the absorption mechanism, each absorbed photon created one exciton. The initial number of excitons $N_0$ should have been $10^8$ — four times larger than the number inferred from the luminescence intensity. With more confidence we can bound the Auger decay constant between two limits,

$$5\times10^{-16}\text{cm}^3/\text{ns} < (2-\eta)A < 19\times10^{-16}\text{cm}^3/\text{ns}.$$  

The lower limit is obtained by estimating exciton density from the number of laser photons we sent into the well; the upper from how many luminescence photons we collected from the well. Still, the Auger decay constant derived from this experiment is approximately ten times that derived from other experiments.

Several hundred nanoseconds after the laser pulse, in a crystal at 2K, virtually all the orthoexcitons have converted to the lower paraexciton spin state. The relatively large number of orthoexcitons observed in figure 29a must have been freshly created from the electron-hole pairs resulting from Auger decay of the paraexcitons. Balancing the rate of creation of orthoexcitons
with their decay by down-conversion, we have \( \frac{3}{4} \eta A p n^2 = B o \), where again \( n = o + p \). One can solve for the rebinding efficiency \( \eta \) in terms of the experimentally measurable ratio \( o/n^2 \). This is plotted in figure 30, where we find that the ratio we expect to yield \( \eta \) is much greater than one.

There are more orthoe excitons present than can be explained as the rebound electrons and holes released by Auger recombination. On can check directly from figure 29 that the number of exciton decay events, times the 3.5ns lifetime of the orthoe exciton against down-conversion, is not nearly as large as the observed number of orthoe excitons. For example, at 1000ns, about 200 excitons decay each nanosecond, but there are significantly more than 200/ns \( \times \) 3.5ns = 700 orthoe excitons present at that time.

Figure 30: Ratio of observed number of orthoe excitons to the number that would be seen if each e-h pair released by Auger decay produced one new exciton.

(If the paraexciton phonon-assisted luminescence rate were smaller under strain than in a strain-free crystal, a possibility we considered at the beginning of this section, then part of the discrepancy could be blamed on an experimental underestimate of \( p \) and thus of \( n \). However, we can be sure that we have not underestimated \( p \) by more than a factor of four, because the number of excitons can be no greater than the number of photons absorbed. The ratio in figure 30 cannot be reduced below 10 under this hypothesis.)

The source of this large number of orthoe excitons at late times is hard to imagine. One explanation is that each electron-hole pair released in an Auger event flips 50 spins of individual carriers in paraexcitons, converting those 50 paraexcitons to orthoe excitons. This would use up 600meV of the 1870meV of kinetic energy that these liberated carriers absorbed in the Auger event. The question of the extra orthoe excitons has not been answered, and the effect is not included in the model I use in chapter 6.

Repeating the strain well experiment with ten times higher laser power produces the time-traces in figure 31. The effect of Auger decay is more apparent in the curvature of these time-traces, but the inferred Auger constant is not as large. Specifically, the fit parameter \( A/\Omega \) is only one third as large as that found using low laser power. The discrepancy between photons
Figure 31: a) Numbers of orthoexcitons and paraexcitons, within a 19μm-
wide observation region in the strain well, following a 10-ns dye laser pulse
from which 10⁹ photons were absorbed in the well. b) The total number of
exciton in view, fit to the solution of the population equation, assuming 15%
of the excitons in the well are in view. The best fit parameters are \( N_0 = (12±2) \times 10^7, (2-\eta)(A/\Omega) = 0.14±0.01/s, \tau = 780±50\)ns.
absorbed and exciton luminescence is greater in the high-power experiment — a factor of eight
as opposed to four before.

The apparent gas temperature was also higher, peaking at 3.4K around 400ns after the pulse,
while in the previous experiment it reached only 2.5K. Since the equilibrium volume of the
exciton cloud increases as \( T^{3/2} \), we should expect \( \Omega \) to be 40% larger than before. Unfortunately,
the cloud was not measured at this excitation density. Using the same analysis as for the low
power experiment, but a 40% larger volume, we bound the Auger constant in the range:
\( 1 \times 10^{16} \text{ cm}^3/\text{ns} < (2-\eta)A < 9 \times 10^{16} \text{ cm}^3/\text{ns} \). One would expect these values to underestimate \( A \)
because in this experiment the effective volume \( \Omega \) is larger than its thermal equilibrium value.
Nevertheless, this measurement of \( A \) is larger than the more recent measurements from this
group, which were made in strain-free crystals.

The analysis above assumed that the exciton cloud shape was the thermal equilibrium
distribution in a parabolic potential well. There is an additional effect which makes the spatial
distribution of excitons different from its equilibrium distribution in this experiment. Auger
decay selectively removes excitons at the center of the potential well, and the exciton gas must
recover its shape through diffusion. Mathematically,
\[
\frac{\partial n}{\partial t} = -A n^2 - D \nabla^2 n + \nabla \cdot (n \mu \nabla V)
\]
where \( V = \alpha r^2 \) is the local potential energy for excitons and \( \mu = D/k_B T \) is the exciton mobility.

The linear terms in this equation have the steady-state solution \( \exp(-\alpha r^2/k_B T) = \exp(-r^2/2\sigma^2) \)
where \( \sigma \) denotes the equilibrium standard deviation. Exciton diffusion repairs distortions of the
steady-state distribution with a relaxation time of \( \sigma^2/2D \), found by normal mode analysis of the
linear terms. Trauernicht and Wolfe [1986a] measured the diffusivity of paraexcitons under strain, and at 3.2kbar stress (the condition near the center of this strain well) they find that $D$ is about $200\,\text{cm}^2/\text{s}$ at $2\,\text{K}$. The relaxation time for the spatial distribution is then $(50\mu\text{m})^2 / (2\times20\mu\text{m}^2/\text{ns}) = 60\,\text{ns}$.

The initial slopes of figures 29 and 31 indicate lifetimes of 90ns and 60ns respectively (and those excitons at the center of the well have lifetimes $2\sqrt{2}$ times shorter). Therefore, Auger decay did affect the spatial distributions of excitons in this strain well experiment. At this point it is clear that in order to measure $A$ quantitatively using this method, the size of the exciton cloud must be monitored throughout the time-resolved experiment. Also, use of a smaller strain well would shorten the diffusion time and improve the experiment. We began efforts in this direction, but since the experiment required time-resolved micro-imaging of the exciton cloud we decided that the strain well was of little use and measured $A$ in a strain free crystal as is described in the paper by OHara et al. [1999b].

5.5 Auger collisions between excitons in different spin states

The previous two sections quoted several widely varying measurements of the Auger decay constant. Those with reliable measurements of the exciton density report $A$ on the order of $10^{-16}\,\text{cm}^3/\text{ns}$ regardless of the spin states of the colliding excitons. Most of the evidence concerning $A_{\text{pp}}$ comes from strain wells, however. The possibility remains that in strain-free Cu$_2$O Auger recombination involving two paraexcitons is forbidden, as is indicated by the results of Lin and Wolfe [1993].

I address this question using results from the type of experiment which I will be modeling in the next chapter. In figure 32 we see the numbers of orthoexcitons and paraexcitons resulting from surface excitation using pulsed argon ion laser light, and a $50\mu\text{m}$ aperture on the surface of the sample in a $2\,\text{K}$ helium bath. When the excitation-density was increased by a factor of 100, the paraexciton intensity increased by less than a factor of 10. In view of figure 26, one must realize that the paraexciton density increased even less than the intensity. From this result we conclude that paraexcitons are not immune to Auger decay. At least $A_{\text{op}}$ is comparable to $A_{\text{oo}}$.

The relative numbers of ortho- and paraexcitons shown as the upper data of figure 32a are quite different from what has been reported by Lin and Wolfe. I have never seen the paraexciton number exceed the peak orthoexciton number after pulsed excitation intensities from about $10^{13}$ photons per $\text{cm}^2$ to my highest controlled excitation density of $10^{16}$ photons absorbed per $\text{cm}^2$. In contrast, the data of Lin and Wolfe indicates that, at the very high excitation density of $7\times10^{16}$ incident photons per $\text{cm}^2$, the paraexciton density increases during the laser pulse to three times that of the orthoexcitons and remains there for tens of nanoseconds after the pulse.
The tempting possibility remains that, if $A_{pp}$ is zero, under very strong excitation, the paraexciton density could overcome the losses to Auger decay with orthoexcitons and exceed the critical density for Bose condensation. The remainder of this section investigates the plausibility of this scenario.

![Graph](image)

Figure 32: a) Areal densities of orthoexcitons (lines) and paraexcitons (circles) following a 10-ns argon-ion laser pulses depositing $9 \times 10^{11}$ (lower data) and $9 \times 10^{13}$ (upper data) photons per cm$^2$ in the crystal. b) The same experiment using 0.5-ns laser pulses depositing $9 \times 10^{11}$ and $9 \times 10^{13}$ photons per cm$^2$ in the crystal. (Error bars that would extend to the bottom of the plot were omitted for clarity.)

![Graph](image)

Figure 33: Some free ($G=0$) solutions of the coupled population equations for the orthoexciton and paraexciton densities, $o$ and $p$, with $o$ divided by three for clarity. Dashed lines are the orthoexciton density divided by three; solid lines are the paraexciton density. I took $A=0.3 \times 10^{16}$ cm$^{-3}$/ns and $B=0.3$/ns to get the units shown on the axis labels. a) The case $A_{oo} = A_{pp} = A_{op} = A$, and rebinding efficiency $\eta = 0$. b) The case $A_{oo} = A_{pp} = A_{op} = A$, and rebinding efficiency $\eta = 1$. c) The case $A_{oo} = A, A_{pp} = 0, A_{op} = \frac{1}{2}A$, and rebinding efficiency $\eta = 0$. d) The case $A_{oo} = A, A_{pp} = 0, A_{op} = \frac{1}{2}A$, and rebinding efficiency $\eta = 1$. 

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Figure 33 plots numerical solutions to the coupled population equations

\[
\frac{d\sigma}{dt} = \frac{3}{4} G - 2 A^{\infty} \sigma^2 - 2 A^{\text{op}} \sigma p + \frac{3}{4} \eta (A^{\infty} \sigma^2 + 2 A^{\text{op}} \sigma p + A^{\text{pp}} p^2) - B \sigma + 3 Be^{-\Delta/T} p
\]

\[
\frac{dp}{dt} = \frac{1}{4} G - 2 A^{\text{op}} \sigma p - 2 A^{\text{pp}} p^2 + \frac{1}{4} \eta (A^{\infty} \sigma^2 + 2 A^{\text{op}} \sigma p + A^{\text{pp}} p^2) + B \sigma - 3 Be^{-\Delta/T} p
\]

for the case of \( G \) a \( \delta \)-function in time, and ignoring the final terms because \( \exp(-\Delta/T) \) is less than \( 10^{-30} \) when \( T = 2K \). I assume the above-bandgap laser light produces excitons in random spin states, and choose initial conditions satisfying \( \sigma = 3p \).

Figure 33a takes the Auger probability to be independent of the initial spin states; only the down-conversion rate \( B \) breaks the symmetry between orthoexcitons and paraexcitons. In this case, the paraexciton density has a limiting curve. Allowing re-binding of the electron-hole pairs released by Auger decay, as in figure 33b, does not change the qualitative results. If \( A^{\text{pp}} \) is zero, we see in figure 33c that at high excitation levels, the paraexciton density breaks free of Auger decay. For initial exciton densities above \( 10^{19} \), the final paraexciton density is 5% the total density of excitons (ortho- and para-) initially created.

However, when we consider a finite-width pulse, and again assume that \( A^{\text{pp}} = 0 \) but that \( A^{\text{op}} \) and \( A^{\infty} \) are on the order of \( 10^{-16} \text{ cm}^3/\text{ns} \), the paraexcitons cannot escape Auger decay. Figure 34 plots solutions to the populations equations, now with the generation function \( G \) a Gaussian in time 10ns wide. The orthoexcitons produced during the trailing edge of this pulse are always sufficient to destroy most of the paraexcitons through \( A^{\text{op}} \).

![Graph showing solutions of coupled population equations](image)

Figure 34: Solutions of the coupled population equations with the generation rate \( G \) a Gaussian in time, under the assumption that paraexciton-paraexciton collisions cannot result in Auger decay. Specifically, \( A^{\text{pp}} = 0 \), and \( A^{\text{op}} = \frac{1}{2} A^{\infty} = 0.3 \times 10^{16} \text{ cm}^3/\text{ns} \).
I am unable to reconcile the result of Lin and Wolfe with my own observations, such as figure 32,\textsuperscript{4} which indicate that paraexcitons are just as susceptible to Auger decay as are orthoexcitons. In the model presented in the next chapter, I take the Auger decay mechanism to be independent of initial exciton spin states.

5.6 Elastic scattering

The interaction potential between excitons should show itself in the luminescence spectra in two ways: lifetime broadening due to interruption of the luminescence by elastic scattering, and a mean-field shift in the position of the direct line. Both effects have been reported [Snoke, 1990b; Lin, 1993] and interpreted in terms of exciton interactions [Snoke, 1995]. In this section I review the evidence for interactions in light of our recent direct measurements of the exciton density.

Some theoretical predictions regarding exciton-exciton scattering are available. These are generally expressed in terms of a scattering length $a_s$ which is related to the cross-section through $\sigma = 4\pi a_s^2$. In the first Born approximation, the direct Coulomb interaction between the individual electrons and holes gives zero contribution to the scattering length, but the exchange terms are non-zero. For spin-aligned orthoexcitons, the scattering length is [Hanamura, 1977]

$$a_s = \frac{13}{6} \frac{ma_o^3}{\hbar^2} E_{\text{binding}} = \frac{13}{12} \frac{(m_e+m_h)^2}{m_em_h} a_o = 4.6a_o$$

using $E_{\text{binding}} = \hbar^2/(2m_{\text{red}}a_o^2)$ and the mass ratio for cuprous oxide, $m_e/m_h = 0.6$. Elkomoss and Munschly [1981] numerically solve for the wavefunction describing the relative motion of two excitons, but make the internal structure of each exciton immutable. Their calculations result in a scattering length around $0.05a_o$ for excitons in a semiconductor with electron-hole mass ratio 0.5. The nature of this calculation precludes exchange of individual electrons or holes. John Shumway is using diffusion-Monte-Carlo techniques to find the scattering wavefunctions for the constituent electrons and holes. His calculations will appear in his Ph.D. thesis in this department; they indicate scattering lengths near $3a_o$, thus a cross-section on the order of $\sigma \approx 50 \text{ nm}^2$.

A Lorentzian line shape occurs when emission of radiation is interrupted. In atomic spectra, collisions between the atoms lead to a Lorentzian line shape,

$$\frac{\Gamma/2\pi}{\hbar^2(\omega-\omega_o)^2 + \Gamma^2/4},$$

\textsuperscript{4}The comparison between orthoexciton number and paraexciton number depends on the relative luminescence rates, but Lin and Wolfe used moderate (0.3 to 1.0 kbar) compressive stress along the [110] axis which, as we considered in section 5.4, could change the paraexciton phonon-assisted luminescence rate. However, I have found that application of 0.7 kbar compressive stress along [110] results in exciton numbers qualitatively similar to those in figure 32a.
where $\Gamma$ is the full-width at half-maximum intensity. The line width $\Gamma = \hbar \gamma + 2\hbar/\tau_c$ where $\gamma$ is the inverse lifetime of the excited state and $\tau_c$ is the mean time between collisions [White, 1934, chapter 21]. The theory of the width of exciton absorption lines [Toyozawa, 1958; Dexter, 1965, chapter 4] sets $\Gamma$ equal to the exciton-phonon scattering rate. The luminescence rate $\gamma$ clearly does not contribute to the exciton luminescence line width, because the low-temperature absorption and luminescence line widths in cuprous oxide are less than $\hbar \gamma = 0.15 \text{meV}$, the direct luminescence rate derived in section 3.5. (We do not need to consider Doppler broadening because the energies released in the luminescent recombinations are specified in the rest frame of the crystal, which is at rest in the lab.) In an experiment in Cu$_2$O using intense argon-ion laser excitation, we have a density $n \approx 10^{16} \text{cm}^3$ and a mean exciton velocity $v \approx 2 \times 10^6 \text{cm/s}$ so if the cross section for elastic scattering were $\sigma \approx 50 \text{nm}^2$ we would expect $\Gamma = 2\hbar n \sigma v = 2\hbar 10/\text{ns} = 0.013 \text{meV}$.

When extracting Lorentzian linewidths from experimental data, I restricted myself to those luminescence spectra which were collected from the same side of the sample as was illuminated, because reabsorption of the direct orthoexciton luminescence as it passes through a 1mm sample will significantly distort the line shape. Also, I restricted myself to those spectra collected using narrow slits on the monochromator to produce a spectral resolution function no wider than 0.1meV at half maximum. Larger Lorentzian linewidths are often observed in high excitation-density experiments which do not meet these criteria.

![Figure 35: Orthoexciton luminescence during an intense 10ns pulse focused on the surface of Cu$_2$O at 2K. The collection geometry minimized the effects of re-absorption of luminescence by the crystal. The fit is a Bose distribution and a 0.08meV-wide triangle, both convoluted with a 0.06meV wide Lorentzian.](image)
Figure 35 shows a spectrum collected during a 10ns argon-ion laser pulse which was tightly focused onto a sample of Cu$_2$O at 2K. The density of excitons was not measured directly because the excitation and observation volumes were not controlled. (The observed exciton kinetic energy distributions match those seen using a controlled excitation density between $10^{15}$ and $10^{16}$ photons absorbed per cm$^2$.) The direct line at 2033meV is fit to the spectrometer resolution function, a triangle with full-width at half maximum 0.08meV, convoluted with a Lorentzian. The phonon-assisted luminescence is fit to a Bose distribution (used only because it fits the data very well) convoluted with the same Lorentzian. The best-fit $\Gamma$ is plotted as a function of time in figure 36, along with the best-fit $\Gamma$ obtained from an experiment using one hundred times less intensity. Also shown in figure 36 are results of 0.5ns pulses.

Figure 36: a) The open circles are best-fit Lorentzian width for the time-resolved spectrum from which figure 35 was taken. The solid circles are from fits to an experiment using one hundredth the laser power.

b) Apparent exciton gas temperature from the same experiment. The apparent scatter is due to the modulation of the laser intensity at 779MHz by our two-pass cavity dumper. The weak ‘echo’ at 20ns is due to an unwanted extra laser pulse, $10^{-3}$ the intensity of the main pulse.

c) The position of the centroid of the direct orthoexciton luminescence line. The temporary red-shift at 20ns is due to a low-energy tail which appears at that time.

d-f) The same quantities as in parts a-c, but derived from an experiment using 0.4ns pulses and a micro-channel plate photomultiplier having 90ps timing resolution.
The line widths under intense excitation are significantly larger than the natural line width. The true width of the orthoexciton direct absorption line is often obscured by small shifts in the orthoexciton energy due to residual strains in a large sample. My absorption curve in section 3.2, measured in a 2mm thick sample at 2K, shows a direct absorption line with width at half-maximum near 0.1meV. Other authors have seen absorption lines as narrow as 0.06meV [Bloch, 1979] and 0.016meV [Kreingol'd, 1975] in thin, carefully chosen samples. Luminescence from a localized exciton cloud shows less inhomogeneous broadening. At low excitation density and at 2K, the direct orthoexciton luminescence from our crystals is no more than 0.02meV wide.

The absorption line width measured in good samples increases nearly linearly with temperature, reaching 0.15meV at 70K [Kreingol'd 1975]. In our samples, under low-intensity excitation at 70K, the luminescence line width is 0.15meV. A temporary increase in local lattice temperature to 25K, seen to be possible in section 5.1, would explain the line widths in figure 36a. However, the spectrum remains significantly broadened even as the exciton gas temperature falls to 5K, and we assume the gas is not colder than the lattice. Also, the line widths resulting from short-pulse excitation (figure 36d) are greater than can be explained by lattice heating.

The Lorentzian width is correlated with the exciton density $n$ and mean exciton velocity $v$. However, the width does not vary as quickly with $n$ and $v$ as does the scattering rate $n \sigma v$ for a constant cross-section $\sigma$. This observation was made by Snook et al. [1990b] who tentatively interpreted the width as partially due to collision broadening, and partially due to interactions with Bose-condensed excitons. I am most interested in the exciton kinetic energy distributions which resemble a saturated Bose distribution with gas temperature 50K. Under these conditions the Lorentzian width is about 0.06meV. This width, if due to elastic collisions, indicates a mean time between collisions of $2\hbar/(0.06\text{meV}) = 20\text{ps}$, or a collision rate of 50/ns.

Our laboratory has performed one experiment to try to observe elastic scattering directly. Jeremy Warren created a gas of orthoexcitons, density on the order of $10^{14}/\text{cm}^3$, using a 5ps dye laser pulse tuned 3meV above the threshold of the orthoexciton phonon-assisted absorption band. The orthoexciton velocities are all $2 \times 10^6$ cm/s in magnitude, but uniformly distributed in direction. No elastic scattering was observed within the 30ps phonon emission time of these excitons. Specifically, no change in the shape of the time-resolved spectra was seen when the exciton density was changed by a factor of two. This null result indicates that the elastic scattering cross-section is less than 10,000 nm$^2$. The experiment could be made much more

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5The line width predicted using Toyozawa's theory can account for some of the observed width. From chapter 4, the rate of scattering out of the zero-momentum state is $\gamma_{LA}(0) + \gamma_{TA}(0) = 1.5 \text{ ns}^{-1} \text{K}^{-1} \times T$, where I have taken the high temperature ($T>8K$) limit of the phonon occupation numbers. At $T=70K$, $\hbar \gamma_{LA} + \hbar \gamma_{TA} = 0.07\text{meV}$. 

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sensitive to smaller cross-sections. It was a mistake for me to suggest using the picosecond lasers of the MRL Laser Lab for this experiment, because pulses as short as 5ps (width of the intensity autocorrelation) created an exciton kinetic energy distribution nearly 1meV wide.  

Another probe of the interaction between excitons is the position of the direct luminescence line. If we characterize the exciton-exciton interaction potential by an s-wave scattering length \( \alpha \), then within certain approximations\(^7\) the energy of an exciton in the mean field of a gas of excitons with density \( n \) is

\[
V = \frac{2\pi \hbar^2}{m} n \alpha_s = (3 \times 10^{-19} \text{meV-cm}^3/\text{nm}) \times n \alpha_s.
\]

In the direct luminescence process, the photon carries away all the energy of the exciton, including its mean-field interaction with its neighbors. If the excitons have a scattering length \( \alpha_s = +2\text{nm} \), and a peak density \( 10^{17}/\text{cm}^3 \) during the laser pulse, we should see a blue shift of 0.06meV. It is possible that the scattering lengths between different exciton spin states have different algebraic signs, so that the mean field shift would be less than this prediction due to partial cancellations (though John Shumway’s results indicate that all the scattering lengths are non-negative.) The observed shifts plotted in figure 36 are less than 0.05meV, and it is clear that there are other factors besides exciton-exciton interaction influencing the direct line position. Based on the small magnitude of the observed shifts in the direct line position, we can infer that a scattering length of greater than 2nm is unlikely.

An elastic scattering cross-section for excitons on the order of 50 nm\(^2\) is predicted by theory and not inconsistent with experimental results to date. At the exciton density (\( 10^{16}/\text{cm}^3 \)) and mean exciton velocity (\( 10^6 \text{ cm/s} \)) with which I am concerned, such a cross-section would result in an elastic scattering rate on the order of 5/ns. The LA-phonon emission rate from chapter 4, \( 11/\text{ns} \times \epsilon/\text{meV} \), is equal to 10/ns for a typical exciton under the same conditions. Therefore we can justify neither the neglect of elastic collisions, nor the assumption that elastic collisions establish an effective temperature in the exciton gas.

\( ^6 \)The time-energy product of the measured full-widths is 5ps-meV = 7\( \hbar \). For a pair of transform-related Gaussians the product of the standard deviations would be \( \hbar/2 \). However, the autocorrelation is \( \sqrt{2} \) times as wide as the intensity, and the product of the full-widths, which are 2.35 = \( \sqrt{\log 256} \) times the standard deviations, is 3.9\( \hbar \).

\( ^7 \)This result follows from using the Born approximation on the scattering potential, or by replacing the real potential with one giving the same scattering length \( \alpha \) but for which the Born approximation is valid. Alternatively, if a particle is constrained to lie within a sphere centered on another particle with which it has scattering length \( \alpha \), the interaction raises the ground state energy by this amount.
In section 3.8 I concluded that the observed luminescence spectra cannot be explained in terms of an inhomogeneous gas of excitons which has established a local temperature. In the next chapter, I show that the observed spectra can be reproduced in a model in which elastic scattering is ignored. A complete treatment of elastic scattering is beyond the scope of this thesis. However, model results including elastic scattering with a constant cross section of $\sigma = 50 \text{ nm}^2 = 4\pi(2\text{nm})^2$ are included in Appendix B.

5.7 Summary

The existence of a two-exciton non-radiative decay mechanism called Auger recombination [Hulin, 1980] is indicated by the fact that exciton luminescence becomes sub-linear in excitation strength. The cross-over from linear to sub-linear behavior occurs near $10^{13}$ photons absorbed per cm$^2$ for photoexcitation with the commonly used 514.5nm green argon-ion laser line. Auger decay limits exciton density during photoexcitation to $\sqrt{G/A}$ where $G$ is the exciton generation rate and $A$ is the Auger decay constant.

Coincident with the sub-linear exciton yield at high excitation intensity, one notices an increase in the mean exciton kinetic energy above that expected for excitons in equilibrium at the bath temperature. The amount of the increase is greater than could be explained by local heating of the lattice by the laser pulses, and it is postulated that a large fraction of the bandgap energy released in each Auger decay event appears as kinetic energy in the exciton gas. This effect of Auger heating in cuprous oxide was first reported by Mysyrowicz et. al. [1981]. (The effect is, of course, more easily observed at lower lattice temperatures, below around 30K.)

We define the Auger rate constant $A$ such that defined so that the lifetime of an individual exciton against Auger recombination is $(A\ n)^{-1}$. The most reliable measurements of $A$ place it near $10^{-16}$ cm$^3$/ns. While this rate constant could in principle depend on the spin states (ortho- or para-) of the excitons involved, the assumption that $A$ is independent of exciton spin is consistent with my experimental observations.

I am aware of no observation of elastic scattering between 1s excitons in Cu$_2$O. The Lorentzian broadening of the luminescence lines has in the past been partially attributed to elastic scattering [Snoke, 1990b] but the Lorentzian width is too large to be reasonably attributed to elastic scattering between excitons, given the measured exciton gas density. The exciton-exciton interaction should also be observable as a mean-field shift in the position of the orthoexciton direct luminescence line. Shifts of up to 0.05meV have been observed in the experiments discussed in this thesis, but the time of appearance of these shifts relative the excitation pulse is not consistent with a mean-field exciton interaction energy. A very recent theoretical calculation, by John Shumway in our department, estimates the elastic scattering cross-section to be

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\( \sigma \approx 50 \text{ nm}^2 \), after averaging over exciton spin states. A cross-section of this size is barely consistent with our failure to observe elastic scattering experimentally.

Returning to the main point of this chapter, the magnitude of the Auger decay rate in Cu_2O, coupled with the degree of heating apparently caused by Auger decay, prevents the formation of a Bose-Einstein condensate of excitons in Cu_2O.

First, we consider the possibility that excitons exchange energy quickly through elastic collisions, as would be the case in experiments using higher excitation intensities than the experiments reported in this thesis. We apply an argument due to Kavoulakis et al. [1996a] to evaluate the effects of Auger heating. Each Auger decay event deposits energy \( E_A \) into the exciton gas, where \( E_A \) appears to be at least several meV. The Auger heating per exciton is then

\[ \frac{\partial \epsilon}{\partial t} = A n E_A \cdot \]

Phonon emission removes energy at a rate

\[ \frac{\partial \epsilon}{\partial t} = -2 \sqrt{2} \frac{\Xi_o^2 m^{5/2}}{\pi \rho \hbar^4} \epsilon^{3/2} \]

from section 4.3. Balancing the heating and cooling rates gives a mean exciton energy of

\[ \langle \epsilon \rangle \approx \frac{\hbar^2}{2m} n^{2/3} \left[ \frac{E_A \pi \hbar A \rho}{\Xi_o^2 m} \right]^{2/3} \]

The quantity in square brackets is on the order of 1000 for \( E_A = 10 \text{ meV} \). On the other hand, Bose-Einstein condensation requires the energy to be low enough that the thermal deBroglie wavelength becomes comparable to the inter-particle spacing. That is,

\[ \langle \epsilon \rangle = \frac{\hbar^2}{2m} \frac{1}{\lambda^2} < \frac{\hbar^2}{2m} n^{2/3} \]

is required for Bose-Einstein condensation. Auger heating keeps the mean exciton energy well above the level required for Bose condensation.

Under the alternative assumption that excitons move completely independently of one another, we can compare the rate at which excitons would drop into the ground state through phonon emission with the Auger recombination rate. Assuming a zero-point lattice, these processes change the ground state occupation number \( g_o \) at a rate

\[ \frac{dg_o}{dt} = \frac{\Xi_o^2 m^3 s_L}{4 \pi \rho \hbar^4} 16 g_p (1 + g_o) - A n \]

where \( g_p \) is the occupation number of those exciton eigenstates that are connected to the ground state through LA-phonon emission; such states have momentum \( 2ms_L \). Let us imagine an initial distribution in which the occupation numbers are equal to \( g_p \) within a sphere in momentum space

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8The phonon scattering rate does increase with lattice temperature, through the \((1+f)\) enhancement for stimulated phonon emission. However, the inverse process of phonon absorption scatters excitons out of the ground state exactly fast enough to cancel any advantage.
just large enough to include the states \( p \), and are zero outside that sphere. The density of excitons in this case is found by counting states inside the sphere: 
\[
n = (4m^3s_L^3 / 3\pi^2\hbar^3) \, g_p.
\]
The rate of increase in \( g_0 \) is then
\[
\frac{dg_0}{dt} = \frac{3\pi \Xi_0^2}{\hbar \rho s_L^2} (1+g_0) n - A \, n
\]
\[
= [5 \times 10^{-17} \, \text{cm}^3/\text{ns} (1+g_0) - A ] \, n.
\]
By coincidence, the numerical factor derived from the phonon emission rate is very close to our best estimates of \( A \). Unless the condensate has been 'seeded' by some other means, the ground state occupation number \( g_0 \) is initially small compared with one. We see that even under the rather favorable conditions of this thought experiment, exciton relaxation cannot populate the ground state faster than Auger decay depletes it.\(^9\)

In summary, Auger decay precludes the formation, through thermalization processes, of a Bose-Einstein condensate in an exciton gas in Cu\(_2\)O. More forceful methods could succeed, such as filling the ground state directly through resonant excitation, or creating excitons at an energy from which they can enter the ground state through emission one LA phonon. Such methods would still be defeated by Auger heating if they are attempted at such a high exciton densities that elastic collisions re-distribute the energy released by Auger recombinations.

\(^9\)In Appendix B we find that, even if there were no Auger decay, phonon emission alone builds a condensate only very slowly.
6. MODELING THE RELAXATION KINETICS OF EXCITONS

6.1 The Boltzmann equation

Hot excitons are created near the crystal surface, suffer Auger recombination, cool through phonon emission, relax to the lower spin state, and migrate into the crystal. For each of these processes we have a model based on observations of each process individually. What kinetic energy distributions will result when these processes act simultaneously? We write a Boltzmann equation to describe how the distribution of excitons develops with time.

The Boltzmann equation [Aschroft, 1976, chapter 16] describes the evolution of the particle occupation number \( g(x,k) \) as a function of both position and particle momentum. For motion free of external forces, the Boltzmann equation has the form\(^1\)

\[
\frac{\partial g(x,k)}{\partial t} + \frac{k \cdot \nabla g(x,k)}{m} = \frac{1}{(2\pi \hbar)^3} \int \left\{ W_{p \rightarrow k} g(x,p) [1+g(x,k)] - W_{k \rightarrow p} g(x,k) [1+g(x,p)] \right\} d^3p
\]

where the gradient operator indicates the gradient in \( x \), and \( W \) is a scattering kernel. We will actually consider the right hand side as the sum of several scattering integrals, one for each interaction. Since we are investigating ways in which a low-density gas may mimic the spectrum of a degenerate Bose gas, for clarity of purpose I omit the \([1+g]\) factors in the simulations in this chapter. The occupation numbers \( g \) were monitored, and did not exceed 0.03 in simulations of realistic experiments.

The approximations implicit in the Boltzmann equation should not affect this application. First, the concept of an occupation number \( g(x,k) \) specified in terms of both position and momentum must break down at small scales \( \delta x \cdot \delta k < 2\pi \hbar \). We are interested in effects on a coarser scale. In fact, the simulations presented here were done on a grid of coarseness \( \Delta x \cdot \Delta k \approx 10\pi \hbar \).

Second, only the occupation numbers of single-particle states are stored, not any coherence between these states. In terms of the many-body wavefunction, only the diagonal elements of the single-particle density matrix are stored (diagonal in a wave packet basis that partially specifies both position and momentum). This approximation will neglect any quantum interference effects between spatially separated parts of the exciton gas, or between different energy states. I do not expect such interference to be important in a gas far below the quantum density.

We can reduce the number of independent variables in \( g(x,k) \). We want to describe experiments that create excitons using surface excitation with light having an absorption length near 2.5\( \mu \)m, and which use an aperture to excite uniformly over a 50\( \mu \)m-diameter disk. Within

\(^1\)In this chapter, \( \mathbf{k} \) and \( \mathbf{q} \) denote momenta, not wavevectors, to reduce the number of \( \hbar \)'s. Note that the units of \( W \) are \( m^3/s \).
the disk the exciton density depends only on one spatial dimension — depth into the crystal. We can ignore diffusion across the disk within the 10ns period of interest, but the excitons can diffuse several microns into the crystal within this amount of time. (The exciton diffusivity at 2K is 60μm²/ns [Trauernicht, 1986a]). In my numerical integrations, I store the exciton occupation number \( g(z, k, \cos \theta) \) as a function of distance \( z \) from the crystal surface, the magnitude \( k \) of the exciton momentum, and the angle \( \theta \) between the exciton momentum and the surface normal.

Above-bandgap excitation produces free electrons and holes, which most likely form excitons in random spin states, uniformly distributed in momentum space. Integrating the Boltzmann equation on a computer, I can represent only a small sphere in momentum space. In obtaining the results in this chapter, I followed the occupation numbers \( g(k) \) for exciton velocities up to 15 times the longitudinal sound velocity, corresponding to a kinetic energy of 39meV (450K). Excitons at this kinetic energy emit phonons at the rate of 500/ns so the occupation numbers are never very large at the upper velocity limit. Those excitons formed in higher-energy states would emit phonons, on a time scale faster than I wish to follow, and soon land in one of the represented states. I distribute all the initially created excitons uniformly throughout the sphere of momentum space that is represented in the computer.

Acoustic phonon emission was treated in section 4.3. The expression we obtained from Fermi’s Golden rule, when expressed in terms of a scattering integral, yields

\[
W_{p \rightarrow k} = \frac{\pi \Xi_o^2 |k-p|^2}{\hbar \rho s_L} \left[ \delta(p^2/2m + s_L |k-p| - k^2/2m) f_{|k-p|} + \delta(p^2/2m - s_L |k-p| - k^2/2m)(1+f_{|k-p|}) \right]
\]

where the deformation potential \( \Xi_o = 1.7eV \) from hydrostatic pressure experiments [Riemann, 1989], and the \( f \)'s are phonon occupation numbers. The phonon occupation numbers could be calculated (which would require a model of thermal diffusion) or assumed to be the thermal distribution at the local lattice temperature.

In section 5.1, we saw that there is the possibility of local temporary heating of the lattice from the ambient 2K to around 25K at the excitation densities that produce the interesting exciton spectra. No direct evidence of lattice heating has been seen, however, and 10ns after the laser pulse, the exciton gas temperature is seen to fall to 3K. Therefore this model will assume that the lattice is a perfect bath at 2K, so the phonon occupation numbers \( f_q \) are given by the Planck function \( f_q = [\exp(s_L q / 2K) - 1]^{-1} \).

Emission of transverse acoustic phonons is possible for the orthoexcitons only, and it is considerably slower than LA phonon emission. It becomes relatively important only for the cooling of orthoexcitons with kinetic energy less than 2K, for which LA phonon emission is impossible. I use the deformation potentials \( \Xi_{zz} = -0.29eV \), and \( \Xi_{xy} = 0.18eV \) determined from my fits of the static strain experiments by Waters et al. [1980].
Optical phonon emission has only been observed for orthoexcitons. In these simulations I do not allow optical phonon emission by paraexcitons. If paraexcitons do emit optical phonons, then I have underestimated their cooling rate for the first 100ps of their existence. However, the conclusions of this chapter depend only on the fact that the paraexcitons can be expected to reach a narrow distribution after several nanoseconds, and this is found to be the case with or without the help of optical phonon emission.

There are three optical phonon energies below 40meV, the eight modes \(3\Gamma_{25}^+, 2\Gamma_{12}^+, 3\Gamma_{15}^+\), which I model with one mode at an average energy \(E_{\text{op}}=15\text{meV}\). Having only one optical phonon energy in the model makes the effects of optical phonon emission more visible in the numerical results, for example by putting a small kink in the distributions at 15meV. The total emission rate of these modes was estimated in section 4.7 from experimental results:

\[
\gamma_{\text{op}} = 2\text{ ns}^{-1}\text{ meV}^{-3/2}(2\varepsilon-E_{\text{op}})^{1/2},
\]

The corresponding scattering kernel, using a deformation potential model, is

\[
W_{p\to k} = \frac{8\pi C^2 (k-p)^2}{\hbar \rho E_{\text{op}}} (\delta(p^2/2m+E_{\text{op}}-k^2/2m) f_{\text{op}} + \delta(p^2/2m-E_{\text{op}}-k^2/2m) (1+f_{\text{op}}))
\]

where the effective optical phonon deformation potential\(^2\) is \(D_{\text{op}} = C|k-p|\), where \(C \approx 1\text{eV}\) fits the observed emission rates.

When we developed the deformation potential model for longitudinal acoustic phonon emission in chapter 4, we implicitly treated the exciton as a point particle moving in a potential \(\Xi_0 \nabla \cdot \mathbf{u}\). In reality, the electron and the hole feel the deformation of the lattice independently. This fact becomes important when the electron-hole separation is comparable to the phonon wavelength. The correction [Toyozawa, 1958] is to replace the exciton deformation potential, which is the difference between the electron and hole deformation potentials, \(\Xi_0 = a_e - a_h\) by

\[
a_e \left[ 1 + \left( \frac{m_e q \ a_o}{2(m_e+m_h)} \right)^2 \right]^{-2} - a_h \left[ 1 + \left( \frac{m_h q \ a_o}{2(m_e+m_h)} \right)^2 \right]^{-2}.
\]

The phonon wavevector \(q\) is equal, within a factor of two, to that of the exciton that emitted it. Therefore, the correction becomes noticeable (reducing the phonon emission rate by 25\%) when the exciton wavevector is about \(1/a_o\). This corresponds to an exciton energy of about 25meV. Since the electron and hole masses are similar, and the individual deformation potentials are both close to 2eV in magnitude [Ohyama, 1997], I follow Snoke et al. [1991] in replacing \(\Xi_0\) with

\[
\Xi_0 \left[ 1 + (q a_o/4)^2 \right]^{-2}.
\]

\(^2\)The deformation potential interaction favors large momentum changes due to the dependence on the phonon wavevector, \(k-p\); this effect would not follow from a Frölich interaction. But, the mean free path against LA phonon emission is already very short for the high-energy excitons which can emit optical phonons, so the specific choice of exciton-phonon interaction does not affect my results.
The argument above applies equally well to TA and optical phonon emission. I include the factor in each phonon scattering kernel.

For interconversion between orthoexcitons and paraexcitons I use the acoustic-phonon-emission model of Snoke et al. [1990a] except that I take the matrix element to be proportional to the wavevector of the phonon as in channel (1) of section 4.8. Unfortunately, neither of the specific models considered in that section matches both the temperature-dependent rate [Weiner, 1983] and our observed down-conversion rate at 2K, 0.29±0.03/ns. I use the mechanism described as channel (1) in section 4.8, divided by 1.9 so as to match our measured down-conversion rate at 2K.

There are two convenient approximations made in modeling the orthoexciton-paraexciton interconversion. I ignore the energy of the TA phonon absorbed or emitted. When a low-energy orthoexciton becomes a paraexciton, the paraexciton will have either 135K or 145K of kinetic energy, depending on whether a phonon was emitted or absorbed. I take the paraexciton energy to be 140K in this case. In the transition matrix element, I replace the magnitude of the phonon momentum with its minimum value \( Q = \sqrt{2m\Delta} \), where \( \Delta \) is the orthoexciton-paraexciton splitting. With these simplifications, the scattering integral is

\[
W_{\text{ortho,}p \rightarrow \text{para},k} = 0.3/\text{ns} \times \frac{2\pi^2\hbar^3}{Qm} \delta(p^2/2m + \Delta - k^2/2m) [1 + 2 f_Q]
\]

where the prefactor was chosen to match the observed down-conversion rate at 2K. For those orthoexciton-to-paraexciton conversions in which the paraexciton momentum lies outside the range of momenta stored in the computer, I substitute a vertical transition as shown in the figure. In these cases a Boltzmann factor \( \exp[\Delta/k_BT_{\text{lattice}}] \) must be included explicitly in up-conversion scattering integral.

Figure 37: Orthoexciton to paraexciton conversions under a simplified model. The dashed transition goes to a paraexciton state that is not represented, so the vertical transition made in its place.
Elastic scattering demands much more computer time than phonon scattering. The scattering kernel $W_{p\rightarrow k}$ must include all the scattering events of the form $p, q \rightarrow k, p+k-q$. Therefore calculation of the scattering kernel involves an integral over $q$, and the integral involves $g(q)$ so it cannot be done ahead of time. Since we have no experimental measurement of the elastic scattering cross-section, I will consider only two extreme cases, each of which can be calculated quickly. For most of the results of this chapter I take the elastic scattering cross section to be zero. For one case at the end of section 6.3 I will allow assume elastic scattering is very fast and that the gas establishes a local temperature. (Limited numerical results including a reasonable elastic scattering cross section are included in Appendix B.)

Auger decay adds a term to the right hand side of the Boltzmann equation expressing a decay rate $An$ independent of the exciton momentum and spin state;

$$\frac{\partial}{\partial t} g(k) = -(2 - \eta)An \, g(k)$$

where

$$n = \frac{1}{(2\pi\hbar)^3} \int [3 \, g^{\text{ortho}}(p) + g^{\text{para}}(p)] \, d^3p.$$  

One difficult question is: "How much of the bandgap energy released in an Auger recombination is deposited in the exciton gas?" Kavoulakis et al. [1996a] gave this question serious consideration. They argue that the electron and hole liberated by Auger decay shed most of their excess energy into optical phonons. Their argument is based on a comparison of the calculated exciton-electron elastic scattering cross section and the rate of emission of $\Gamma_{15}$ optical phonons through the Frölich interaction. In my model I put all of the excess energy of the free carriers into the lattice. The excitons that form when these carriers rebind are distributed uniformly in momentum space (or rather, that part of momentum space represented in the computer model) in the same way that the initial excitons were distributed.

In a model that ignores all collisions, and assumes a fixed lattice temperature, the only way for Auger decay to increase the average kinetic energy of the exciton gas is by creating new hot excitons from the electrons and holes liberated in each Auger decay event. I take the rebinding efficiency $\eta$ to be one. The complete effect of Auger decay on the exciton occupation numbers is

$$\frac{\partial}{\partial t} g^{\text{ortho}}(k) = -2An \, g^{\text{ortho}}(k) + \frac{1}{4} \, A \, n^2 \times \frac{(2\pi\hbar)^3}{d^3p}$$

$$\frac{\partial}{\partial t} g^{\text{para}}(k) = -2An \, g^{\text{para}}(k) + \frac{1}{4} \, A \, n^2 \times \frac{(2\pi\hbar)^3}{d^3p}$$

where the integrals over $p$ are over the finite volume of momentum space represented in the computer. I use $10^{-16}$ cm$^3$/ns for the Auger constant $A$, a round figure in the midst of the experimental estimates.
6.2 Results for excitons at low density

First we check that the model is in agreement with experiment regarding the behavior of a low-density exciton gas. The phonon emission rates are generally faster than the time resolution of the equipment I use, so I borrow data taken by Jeremy Warren in the Materials Research Laboratory Laser Facility. Figure 38 shows orthoexciton distributions recorded within one nanosecond following a 5ps dye laser pulse, which created orthoexcitons with 3meV kinetic energy. Peaks corresponding to excitons which have emitted zero, one, and two acoustic phonons are apparent in the numerical model, but are not well resolved in the experiment due to the broad band excitation pulse. The figure confirms that excitons in Cu$_2$O cool at approximately the rate incorporated in the model.

![Figure 38: a) Orthoexciton kinetic energy distributions sampled at several times after a 5ps dye laser pulse with photon energy 2050meV. Such photons produce orthoexcitons with 3meV of kinetic energy. The sample was held at 2K. This data was obtained by Jeremy Warren (for a different purpose) with 0.25meV energy resolution and 50ps time resolution. b) Results of integrating the Boltzmann equation forward in time, starting with a monoenergetic distribution of excitons.](image)

We can observe more ‘typical’ kinetic energy distributions by creating the excitons with much higher kinetic energy, though still at low density. The data in figure 39 also, from Jeremy Warren, resulted from a 5ps dye laser pulse at 577nm, for which the absorption length is near 50µm. The exciton distributions resulting from such an experiment have a high-energy tail that appears to be exponential in energy [Snoke, 1990c]. An empirical curve which roughly fits the data is, with parameters $a$ and $b$,

$$n(\varepsilon) = \frac{a \sqrt{\varepsilon}}{\exp(\varepsilon/k_B\Theta)} + b$$

where $\Theta$ is the apparent gas temperature. We do not assume that exciton establishes a real temperature; $\Theta$ is merely one parameter in an empirical description of the observed distributions.
The distributions resulting from the simulation can also be fit, surprisingly well, by this empirical function, though they generally require $b>0$ while the experimental spectra require $b<0$.

Figure 39: a) Orthoexciton luminescence spectra after low-density excitation using a dye laser pulse with photon energy 2148 meV. The crystal was immersed in a 2K bath. Data borrowed from Jeremy Warren. b) Filled circles: apparent orthoexciton temperature. Open circles: average observed orthoexciton kinetic energy.

Figure 40: Simulation of the energy relaxation of a low density (non-interacting) gas of excitons exchanging phonons with a 2K lattice. a) Kinetic energy distributions. b) Apparent temperature and mean exciton kinetic energy. Dashed line: exciton gas temperature given by the theory quoted in the text. Inset: ratio of the mean kinetic energy to apparent temperature versus time.
The average exciton kinetic energy is shown alongside Θ in the following plots. The ratio of apparent temperature to average kinetic energy gives an indication of the shape of the distribution. For a Maxwell-Boltzmann distribution, \( \langle \varepsilon \rangle = (3/2)k_B\Theta \); for a fully saturated Bose distribution, \( \langle \varepsilon \rangle = (3/2)[\zeta(5/2)/\zeta(3/2)]k_B\Theta \approx 0.77k_B\Theta \).

My model slightly overestimates the rate of loss of kinetic energy of the excitons. The model does, however, fill the states with kinetic energy below 1meV at approximately the observed rate. Certainly no adjustments of the static deformation potentials are justified.

The experiment reveals a wider spread in exciton energies than I can explain in terms of acoustic phonon emission. That is, the observed distributions have both a large number of low-energy excitons and a ‘hot’ high-energy tail.

The rate at which hot excitons shed energy through acoustic phonon emission is proportional to \( \varepsilon^{3/2} \) (section 4.3). Each time-step, the hotter excitons lose a greater fraction of their kinetic energy than the cooler ones, tending to make the distribution compact. The fact that excitons can scatter from each initial state into several final states tends to make the distribution spread out. These competing effects result in a non-equilibrium distribution slightly more compact than a Maxwell-Boltzmann, with a ratio of mean kinetic energy to apparent temperature near 2.

Before discussing interactions in exciton gases at higher density, we can compare this model of exciton cooling with a standard result for phonon cooling of carriers in semiconductors. This result applies to carriers which exchange energy among themselves quickly enough that they are always found in a Maxwell-Boltzmann distribution with a well-defined gas temperature. In the limit of low sound velocity or high gas temperature, \( m s_L^2 \ll k_B T_{\text{gas}} \), the rate of change of the gas temperature is [Cornwell, 1967, p122]

\[
\frac{\partial T_{\text{gas}}}{\partial t} = -\frac{64}{3} \sqrt{\frac{2}{\pi}} \frac{\Xi_0^2}{4\pi \rho \hbar^4} \sqrt{m s_L^2} k_B T_{\text{gas}} \left( T_{\text{gas}} - T_{\text{lattice}} \right).
\]

A solution is plotted as the dashed line in figure 40.

Comparing the dashed line to the results of the full model, we see that the inclusion of a finite speed of sound slows the exciton cooling rate significantly, even when the mean exciton kinetic energy is still several times \( m s_L^{2/2} = 0.2\text{meV} \) (2K).

6.3 Results for excitons at high density

Orthoexciton luminescence spectra resulting from high-intensity excitation have been thoroughly studied by Snoke and Wolfe [1990c]. The observed spectra fit nearly saturated Bose-Einstein distributions. In the first part of this section, we find that our model of the relaxation kinetics of excitons predicts similar spectral shapes, assuming classical statistics.

First we consider the exciton distributions at the surface of the crystal where the density was highest. Snoke and Wolfe used 100ps-wide argon-ion laser pulses, providing a peak incident
power density of $10^8$ W/cm$^2$. This would result in $10^{20}$ photons absorbed per cm$^3$ near the sample surface. To simulate this experiment I assume that 30% of the absorbed photons form orthoexcitons and 10% form paraexcitons, consistent with figure 14 of section 3.7 and a random distribution of spin states. I model the laser pulse as a Gaussian, 100ps wide at half maximum intensity. Figure 41 shows the simulated kinetic energy distribution at the surface of the crystal. Compared to the low-density results in the previous figure, the average exciton kinetic energy stays higher for longer, due to the continuous introduction of new hot excitons formed from electrons and holes liberated in Auger recombination events. This effect was observed experimentally by Snoke and Wolfe [1990c] and figures 40-41 and 44 were designed for easy comparison with their paper.

Figure 41: a) Calculated local exciton energy distributions in a region of Cu$_2$O which absorbed $10^{20}$ green photons per cm$^3$, assuming 30% orthoexciton 10% paraexciton production efficiencies, and a Gaussian pulse 100ps wide at half maximum intensity. b) Mean kinetic energies and apparent temperatures as before.

These simulated energy distributions certainly do not suggest Bose statistics; having no particular sharpness near zero-energy. However, they do have a smaller ratio of mean kinetic energy to apparent temperature than in the low-density case. The hot new excitons, recently formed from carriers liberated by Auger decay, add a hot tail to the cold distribution of excitons that have been cooling since their formation by the 100ps generation pulse.

The laser pulse creates excitons deeper in the crystal, in a spatial distribution proportional to $\exp(-z/2.5\mu$m$)$. Figure 42 displays the results of the simulation at various depths $z$, at the time 200ps after the center of the generation pulse. Losses to Auger recombination were more severe near the surface where the density was higher. The surviving excitons are distributed roughly 10\mu$m deep in the crystal — several times the penetration depth of the excitation.
Figure 42: a) Simulation results for the energy distribution of orthoexcitons at discrete depths $z$ into the crystal, ranging from 1$\mu$m to 25$\mu$m in steps of 2$\mu$m. The time is 200ps after absorption of $3 \times 10^{16}$ green photons per cm$^2$ from a 100ps pulse. b) Exciton densities and mean orthoexciton kinetic energy versus depth into the crystal.

The observed luminescence is spatially integrated over the inhomogeneous exciton gas. Figure 43 compares the sum of the distributions in figure 42a with experimental spectra. This experiment of ours was intended to produce conditions similar to those used by Snoke and Wolfe [1990c]. There was no aperture on the crystal in this experiment. Rather, the argon ion laser was focused to a spot which was at most 34$\mu$m wide at half-maximum intensity. Laser pulses containing 12nJ with a 150ps width produced a peak incident power of at least $5 \times 10^6$ W/cm$^2$. While the peak excitation density in this experiment may have been less than the $10^8$ W/cm$^2$ used by Snoke and Wolfe, the experimental luminescence spectra are just as hot. The model does not perfectly reproduce the data; it fails to produce quite as much high-temperature tail and simultaneous low-energy peak as is observed. However, the model does produce a spectrum which is better fit by a degenerate Bose distribution than by a Maxwellian distribution.

In figure 43 and following figures, both experimental and numerical distribution are fit to:

$$
\frac{a \sqrt{\varepsilon}}{\exp(\alpha + \varepsilon/k_B\Theta) - 1}.
$$

This function fits the data well, and allows easy comparison with previously published experimental results because it has the same shape as a Bose distribution with temperature $\Theta$ and chemical potential $-\alpha k_B \Theta$. It is important to note, however, that in this chapter the three parameters are allowed to vary independently; the prefactor $a$ is not determined by the exciton density of states as it would be if we were fitting to a real Bose-Einstein distribution. In fitting the simulation results, the 'zero' of kinetic energy was allowed to shift, as is usually done when fitting luminescence spectra. The magnitude of the shift was never more than 0.05meV and its effect on the fit parameters was minor.
Figure 43: a-b) Our observed orthoexciton luminescence resulting from a focused 150ps pulse, from which at least $10^{15}$ photons were absorbed per cm$^2$. Luminescence is plotted as error bars only; the curves are fits to the empirical function described in the text, with parameters $\Theta$ and $\alpha$, plus a Lorentzian for the direct luminescence line. The luminescence was collected using a micro-channel plate photomultiplier, which was not calibrated, so the vertical axes are in arbitrary units. a) 160ps after pulse center. b) 300ps after pulse center. c-d) The sum over depth $z$ of results of the simulation as in part (a) of the previous figure, c) 160ps after pulse center, d) 300ps after pulse center.

The direct line was added by hand to figures 43c and d. Its integral was based on the numerically determined occupation number at zero kinetic energy and the luminescence rates of chapter 3. Its width was chosen to match the spectral resolution of the corresponding experimental spectra.

The precise meaning of ‘best fit’ requires some explanation. Given a set of measurements $y_i$ corresponding to values $x_i$ of the independent variable, the least-squares fit minimizes

$$\chi^2 = \sum_i \frac{(f(x_i) - y_i)^2}{\sigma_i^2}$$

over a space of fitting functions, where $\sigma_i$ is the uncertainty of the data point $y_i$. The largest source of uncertainty in the points in these luminescence spectra is in the estimation of the luminescence intensity based on counting a finite number of photons. The observed photon count is Poisson-distributed with standard deviation equal to the square root of the expected count. I take the uncertainty in each spectral point to be equal to the square root of the number of photons counted, $\sigma_i = \sqrt{y_i}$, except that I use $\sigma_i = 1$ for those points with zero counts.
The kinetic energy distributions derived from the simulation are fit using the weighting they would have had if they had generated luminescence in an experiment, taking into account the non-uniform sampling in kinetic energy. Each ‘+’ is a sample of the exciton distribution $n(\varepsilon_i)$, and each ‘+’ represents all the excitons $n(\varepsilon_i) \delta \varepsilon_i$ within an energy range $\delta \varepsilon_i$. In a luminescence experiment, the number excitons in this range would be measured with uncertainty proportional to $\sqrt{n(\varepsilon_i) \delta \varepsilon_i}$. Thus, each ‘+’ is treated as a measurement of $n(\varepsilon_i)$ with uncertainty $\sigma_i = \sqrt{n(\varepsilon_i) \delta \varepsilon_i / \delta \varepsilon_i}$.

Figure 44 provides a closer look at the simulation results. The simulated energy distributions are better fit by Bose-shaped distributions than by Maxwell-Boltzmann distributions. However, the fits to the simulation are not quite as good as those to the experimental spectra (seen in the paper by Snoke and Wolfe [1990c]) and the Bose-shaped functions which fit the simulation are not quite as degenerate ($\alpha$ not as small) as those which fit the experiment.

Figure 44: a-c) The sum over $z$ of the calculated orthoexciton distributions at the times indicated, fit to Bose-shaped distributions. The excitation was the same 100ps pulse as for the previous two figures.

d) Apparent temperature and mean orthoexciton energy versus time.
We turn now to the case of somewhat longer 0.5ns excitation pulses. In section 5.5 we presented observations of the numbers of orthoexcitons and paraexcitons following 0.5ns pulses of different intensities, and concluded that the paraexcitons were not immune to Auger decay. We could not conclude directly from those observations whether para-para collisions can result in Auger decay, or if the loss in paraexcitons is entirely due to ortho-para collisions.

Figure 45 presents numerical results under these two assumptions. Part (a) of the figure is the result of my model in the standard configuration, with Auger decay independent of exciton spin. Part (a) is in good agreement with the corresponding experimental result, figure 32b in section 5.5, the only difference being the consistently lower paraexciton yield in the experiment. The alternate assumption of $A_{pp} = 0$ produced figure 45b. Here the paraexciton numbers increase with excitation intensity more than seen in the experiment. This assumption also leads to the prediction that the orthoexciton decay rate at late times (more than 6ns after the pulse) is noticeably enhanced by Auger decay with the abundant paraexcitons; this effect is not seen in experiments. The assumption that the Auger decay rate is essentially independent of the spin states of the colliding excitons is consistent with all the data I have taken.

Figure 45: Simulation of number of ortho- and para-excitons after 0.5ns green laser pulses depositing $10^{12}$ and $10^{14}$ photons per cm$^2$.

a) Auger rates independent of exciton spin; $A^{oo} = A^{op} = A^{pp} = 1 \times 10^{-16}$ cm$^3$/ns.

b) No para-para Auger decay; $A^{oo} = 1 \times 10^{-16}$ cm$^3$/ns, $A^{op} = 0.5 \times 10^{-16}$ cm$^3$/ns, and $A^{pp} = 0$.

Longer, 0.5ns, pulses result in the prediction of more strongly peaked distributions than for the 100ps pulses considered so far. In the simulation, excitons created near the beginning of the pulse have had time to cool to below 1 meV, and coexist with more recently created excitons. The model is in good qualitative agreement with the experimental spectra in figure 46, except that the model does not explain apparent temperatures as high as seen in experiment. Figure 47 compares the same experiment with the model in the time domain. Apart from the lower temperatures, the model describes the behavior of the non-equilibrium exciton gas well.
Figure 46: Luminescence spectra resulting from 0.5ns argon ion laser pulses from which the sample absorbed $1.3 \times 10^{15}$ photons per cm$^2$. a) Spectrum 0.3ns after the center of the laser pulse, b) 0.6ns after the center of the pulse. Experimental time-resolution was 0.4ns. c) and d) Simulation results for the same conditions, assuming that each photon has a 30% chance of creating an orthoexciton and a 10% chance of creating a paraexciton.

Figure 47: a) Apparent temperature and chemical potential from fits to Bose-shaped distributions of the data of the previous figure. b) The same parameters from the simulation results of the previous figure.
Figures 48 and 49 compare experimental and theoretical results at various levels of excitation. The effectiveness of Auger decay in limiting the exciton density is correctly reproduced by the model, but the model underestimates Auger heating at high excitation levels.

At the low excitation levels, the model predicts a higher-than-observed apparent temperature during the excitation. The fault most likely lies with the experiment, which used 0.4ns time resolution. In figure 39, with better time resolution, we saw that the low-density gas cools quite rapidly, but no more rapidly than predicted by our model. At low excitation density, the apparent gas temperature derived from the numerical results falls monotonically from the beginning of the simulation. Therefore in figure 49b we plot the fit temperature at the center of the simulated excitation pulse, to compare with the peak apparent temperatures from experiment.

Figure 48: Number of orthoexcitons versus time after various 0.5ns green laser pulses.  

a) Experimental results of excitation densities ranging from \(5 \times 10^{11}\) through \(1.25 \times 10^{15}\) photons absorbed per cm\(^2\) (the same data as in figure 24b).  

b) Numerical results covering the same range of excitation intensity.

Figure 49: a) Maximum apparent temperature from fits to orthoexciton luminescence obtained in the experiment of figure 48a. b) The fit temperature for simulated orthoexciton kinetic energy distributions taken at the center of the excitation pulse. The horizontal axis is the excitation intensity, number of photons per cm\(^2\): the simulation assumes a 30% production efficiency for orthoexcitons, 10% for paraexcitons.
The Bose-like kinetic energy distributions of orthoexcitons are the result of superposition. First, there is superposition in time: the coexistence of excitons of different ages that have cooled by very different amounts. Auger decay enhances this superposition in time because, even after the laser pulse, each Auger decay event liberates an electron-hole pair.

The second type of superposition is in space. The exciton gas near the surface undergoes faster Auger decay, and contains a relatively higher fraction of new, hot excitons than do the regions of gas further into the crystal. Near the end of chapter 3, we concluded that superposition in space alone could not explain the observed spectra. We finish this section by determining just what kind of distributions would result if the excitons did establish a local temperature.

I simulate perfect local thermal contact between the excitons by calculating, at each \( z \), the local temperature

\[
k_B T = \frac{2}{3} \frac{1}{n} \int \left( 3g^{\text{ortho}} + g^{\text{para}} \right) \left( k^2 / 2m \right) \frac{d^3 k}{(2\pi\hbar)^3}.
\]

and drift momentum

\[
\mathbf{K} = \frac{1}{n} \int \left( 3g^{\text{ortho}} + g^{\text{para}} \right) \mathbf{k} \frac{d^3 k}{(2\pi\hbar)^3}.
\]

In these expressions the total density is

\[
n = n^{\text{ortho}} + n^{\text{para}} = \int \left( 3g^{\text{ortho}} + g^{\text{para}} \right) \frac{d^3 k}{(2\pi\hbar)^3}.
\]

Then the occupation numbers are recalculated from equilibrium distributions at each step through

\[
g^{\text{ortho}} = \frac{1}{3} n^{\text{ortho}} \left[ \frac{2\pi\hbar}{mk_B T} \right]^{3/2} \exp \left[ -\frac{(k-K)^2}{2mk_B T} \right],
\]

and

\[
g^{\text{para}} = n^{\text{para}} \left[ \frac{2\pi\hbar}{mk_B T} \right]^{3/2} \exp \left[ -\frac{(k-K)^2}{2mk_B T} \right].
\]

Figure 50: a) The sum over \( z \) of exciton density predicted by the model at an instant 0.3ns after the center of a 0.5ns simulated pulse that deposited \( 1.3 \times 10^{15} \) photons per cm\(^2\). Perfect local thermalization of excitons was assumed. The fit is to a Bose-shaped distribution. The dashed curve is a Maxwell-Boltzmann distribution with the same temperature. b) Exciton density and gas temperature versus position.

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Numerical results assuming perfect thermalization, and a moderately intense 0.5ns pulse, are shown in figure 50. Local thermalization of the exciton gas removes a good bit of the low-energy weight in the exciton distributions. The spatial inhomogeneity alone results in a distribution which is better fit with a Bose-shaped distribution than by a Maxwell-Boltzmann — though with $\alpha = 1.04$ it is near the Maxwell-Boltzmann limit. Without local thermalization, the conditions of figure 50 resulted in the numerical results shown in figure 46c, which are fit by a Bose-shaped distribution nearer to the fully saturated limit, with $\alpha = 0.10$.

6.4 Results of long laser pulses

Experiments using 10ns pulses have produced the orthoexciton spectra that most closely resemble saturated Bose distributions [Snoke, 1987] and paraexciton spectra that have been interpreted as a fully saturated Bose distribution, plus a Bose condensate [Lin, 1993]. The longer pulses provide ample time for a fraction of the excitons to cool, and the simulation results for the kinetic energy distributions will be fit remarkably well by nearly saturated Bose distributions.

The pulse shape used to produce the data in this section is shown in figure 51. This pulse is obtained by dumping a cavity containing a continuously lasing argon plasma. The ideal pulse shape would be a square, with length equal to the round-trip time for photons in the cavity. The cavity dumper I have used is an acousto-optic modulator which modulates the output at twice its acoustic frequency; the ideal pulse shape would be a square envelope multiplying these beats. The pulse shapes actually produced have rise and fall times of over one nanosecond.

Any pulse shape can be introduced into my model. For the shapes I have tried, their effects on the results are not surprising. The cavity-dumper modulation, for example, produces a corresponding modulation in apparent temperature $\Theta$ and a much smaller modulation in the instantaneous exciton number. For simplicity, all the results in this section use a Gaussian generation profile — with full-width at half-maximum intensity equal to 7.0ns because that is the width of the Gaussian which best-fits my ‘10ns’ pulses.

Figure 51: The laser pulse shape used to produce the data in this section, measured with the same photon counting system that collected the exciton luminescence. The trace shown here is not visibly affected by the transit time spread of the photon collection system. The modulation at 779MHz is due to the use of a two-pass acousto-optic modulator to dump the laser cavity. The dashed curve is a Guassian with 7ns full width.
Figure 52 presents the orthoexciton distributions resulting from the creation of $8 \times 10^{14}$ excitons per cm$^2$ (chosen to match an experiment in which $2 \times 10^{15}$ photons per cm$^2$ were absorbed) in an exponential distribution penetrating 2.5μm deep into cuprous oxide. The distributions shown are for the time 4ns after the center of the generation pulse. Compared to the results for a short pulse, figure 43 in section 6.3, the exciton gas near the surface is hotter because the tail of this wider laser pulse is still producing new excitons and driving fast Auger decay. Also, there has been more time for those excitons that have escaped Auger decay to cool, producing more low-energy weight in the distributions.

Figure 52: a) Simulation results for the energy distribution of orthoexcitons at various depths $z$ into the crystal. The time is 4ns after the center of a 7ns pulse which created $6 \times 10^{14}$ orthoexcitons and $2 \times 10^{14}$ paraexcitons per cm$^2$. b) Exciton densities and mean orthoexciton kinetic energy versus depth into the crystal.

Theory is compared with experiment in figure 53. The experiment used the 50μm aperture on the crystal surface and the calibrated photon counting system. The excitation was the argon ion transition at 514.5nm (2409meV) which has a 2.5μm absorption length in Cu$_2$O.

There is qualitative agreement between theory and experiment regarding the kinetic energy distributions, though the theoretical distribution is not as well fit by the Bose shape as is the experimental data. Note that the difference between the spectra and the Bose fits has the same shape in both theory and experiment. The paraexciton distribution is slightly more narrow than the orthoexciton distribution because the paraexcitons are generally older, and thus cooler. The orthoexciton-to-paraexciton conversion rate is 0.3/ns in a crystal at 2K, so within a 7ns pulse many of the orthoexcitons have become paraexcitons. Both spin states have their lifetimes shortened by Auger decay, but several microns deep in the crystal, where the density is not too high, paraexcitons are the more abundant species, and these paraexcitons have had several nanoseconds in which to cool.
Figure 53: a-c) Spectra recorded 0, 4, 8ns after center of a 10ns laser pulse from which the sample absorbed $2 \times 10^{15}$ photons per cm$^2$.

The luminescence intensity has been converted to an areal density of excitons.

The conversion factor for the paraexciton ($\Gamma_{25}$ phonon assisted) luminescence is 500 times that for the ($\Gamma_{12}$ phonon assisted) orthoexciton luminescence.

In addition the paraexciton spectra have been shifted to higher energies by 9.3meV and raised by about $2 \times 10^{12}$/cm$^2$ for clarity.

d-f) Results from the numerical simulation assuming the creation of $6 \times 10^{14}$ orthoexcitons and $2 \times 10^{14}$ paraexcitons per cm$^2$ by a Gaussian generation pulse with full-width 7ns.

The paraexciton numbers have been raised by $10^{13}$/cm$^2$ for clarity.
Figure 54: a-c) Orthoexciton distributions from the same numerical simulation as shown in the previous figure, and the same fits as in that figure. d) A comparison of orthoexciton and paraexciton distributions, the significance of which is discussed in the text.

Figure 54 presents the same simulation results in semi-logarithmic plots. The fit to Bose-shaped distributions is acceptable down to 1% of the peak in the distributions. The kink in the numerical distributions at 15meV is due to optical phonon emission, which is allowed for excitons above this energy. Cuprite actually has three optical phonon emission thresholds in the range shown, all with comparable emission rates, so we neither expect nor see such a clear kink in experimental spectra. If it were not for optical phonon emission, the distributions would diverge from the Bose fits earlier.

Imagine for the moment that we had reason to believe that the excitons were thermalized among themselves and that the density was nearly homogeneous, but unknown. In that case it would be natural to interpret the orthoexciton spectra as equilibrium spectra from a gas above 85% the critical density for Bose condensation. The critical density for the paraexcitons is one-third that for the orthoexcitons. In figure 54d we have used the fit to the orthoexciton distribution, divided by three, as an approximation to the fully saturated paraexciton distribution. (A fully saturated Bose distribution diverges at zero kinetic energy, but this divergence would be softened by particle interactions and by finite spectral resolution.) The paraexciton distribution
in figure 54d is easily interpreted as a somewhat broadened, fully saturated Bose distribution, plus an extra contribution peaked at about 0.2meV, possibly due to a Bose condensate.

Figure 54d resulted of course from numerical integration of a Boltzmann equation which purposefully ignored Bose statistics. The true explanation of the figure is that the high-energy orthoexcitons and paraexcitons both reside in the hot, dense gas near the crystal surface. The ratio of orthoexcitons to paraexcitons is kept near 3:1 by the randomizing effects of Auger decay. Deeper into the crystal, the density is lower, Auger decay less prevalent, and the lifetime of the excitons is longer. The average age of the excitons is greater deeper into the crystal, and with age comes a lower ratio of orthoexcitons to paraexcitons due to more time to down-convert, and a lower average kinetic energy. The paraexciton-rich low-energy gas seen in the overall distribution resides deep in the sample. Figure 55 shows the orthoexciton and paraexciton distributions at discrete depths up 25μm, at the time used for figure 54d.

![Graphs showing orthoexciton and paraexciton distributions](image)

Figure 55: Simulation results for the same situation as the previous figure. Orthoexciton (a) and paraexciton (b) kinetic energy distributions at discrete depths from the crystal surface, from 1μm through 25μm deep, plotted at 2μm intervals. The time shown is 4ns after the center of the generation pulse.

The following two figures summarize the evolution in time of the exciton distributions. The simulation, figure 56b, predicts that the orthoexciton number breaks from its 3.5ns exponential decay because electrons and holes created in the Auger decay of paraexcitons are rebinding to create new orthoexcitons. The experiment shows no such effect because the exciton density in the experiment is lower than in the theory due to diffusion in the plane of the excitation surface. The diffusion length \( \sqrt{2Dt} \) is 60μm at \( t = 30\text{ns} \), longer than the 50μm diameter excitation area. This particular experiment, at these late times, cannot be modeled with only one spatial dimension. (Diffusion into the crystal is correctly accounted for in the simulation through the terms in the Boltzmann equation describing transport and phonon scattering.)
Figure 56: a) Observed numbers of excitons after a 10ns argon ion laser pulse from which the sample absorbed $2 \times 10^{15}$ photons per cm$^2$. b) Simulated numbers of excitons after generation of $8 \times 10^{14}$ excitons per cm$^2$.

Figure 57: a) Parameters from the best fit to Bose-shaped distributions of the orthoexciton luminescence spectra. The oscillation in apparent temperature is due to the modulation at 389MHz of the excitation light.
b) Parameters from fits to Bose-shaped distributions of the simulated orthoexciton kinetic energy distributions.
(The discontinuity in the best-fit chemical potential is a shift between two locally optimal fits. Before 13ns the globally optimal fit involves a 0.03meV shift in the low-energy edge of the fitting function, and a chemical potential $-1.3$K. After 13ns, it is better to use zero shift and a chemical potential $-2$K.)
Figure 58: a) Simulation results for the number of orthoexcitons versus time after various 10ns green laser pulses. Compare figure 24a from section 5.1. b) Peak orthoexciton areal density versus excitation density. Compare figure 25a. The dashed lines have slopes one, and one-half. The horizontal scale indicates the density of photons absorbed in the corresponding experiment, given our estimated exciton production efficiencies.

Figure 59: a) Peak apparent orthoexciton gas temperature $\Theta$ from fits to Bose-shaped distributions of the data set of figure 24a in section 5.1. (The final data point is to be regarded with caution, because at this excitation intensity a gas bubble formed in the liquid helium bath.) b) Maximum $\Theta$ from fits of orthoexciton distributions from a simulation of the experiments. For the very low-intensity runs, $\Theta$ is maximum very early in the pulse; in these cases the value of $\Theta$ at the center of the generation pulse is plotted.

Figures 58 and 59 compare theory and experiment through the available range of excitation densities. Figure 58 shows the exciton yield crossing over from linear to square-root in excitation intensity. in agreement with the corresponding experimental result in figure 25 on page 54. In figure 59 we see again that the effectiveness of Auger decay in heating the exciton gas is again somewhat underestimated in the model.
The temperatures extracted from the model in figure 59b result from a balance between Auger heating proportional to $A n^2$, and phonon cooling proportional to $n \varepsilon^{3/2}$. The exciton density near the surface during the excitation pulse goes as $\sqrt{G/A}$ where $G$ is the exciton generation rate. Setting the heating and cooling rates equal gives $\langle \varepsilon \rangle \propto (AG)^{1/3}$. As this relation predicts, the peak exciton temperature rises by one order of magnitude from 10K to 100K as the generation rate increases over three orders of magnitude. At higher excitation intensity the increase in exciton temperature slows as the mean exciton energy nears the threshold for optical phonon emission, which provides a faster cooling mechanism.

Finally, we address the question of the importance of exciton motion. Figure 60 presents results from the same simulation as figures 52-57, except that the transport term in the Boltzmann equation was omitted. The ratio of paraexcitons to orthoexcitons is less than in the corresponding simulations including exciton transport, and the paraexciton distribution is less sharp.

These numerical results indicate that exciton diffusion contributes noticeably to the relatively sharp paraexciton peak by allowing a few paraexcitons to escape Auger decay by moving away from the surface. (Compare figures 60b and 52b.) However, we see that exciton motion is not essential to the explanation of the general shapes of the observed exciton distributions produced by 10ns pulses. Experiments using shorter pulses allow less time for the excitons to move while the non-equilibrium distribution persists, so the effects of exciton motion are even less important in experiments using shorter pulses.

Figure 60: Simulation results for the same conditions as figures 52-57, except with no exciton motion. The time is 4ns after the center of a 7ns full-width generation pulse.

a) Orthoexciton and paraexciton energy distributions with a Bose-shaped distribution fit to the orthoexciton distribution, showing a slightly higher temperature and slightly lower degeneracy than that in figure 53e.

b) Exciton densities and mean orthoexciton kinetic energy versus depth into the crystal. There are noticeably fewer paraexcitons deep in the crystal than seen in figure 52b.
In this chapter we have seen how the gross features of the observed transient kinetic energy distributions, both of orthoexcitons and of paraexcitons, are the expected consequences of 1) Auger heating, 2) exciton cooling through phonon emission, and 3) the inhomogeneous distribution in which excitons are created by photoexcitation. The Bose statistics of excitons is not important in explaining the observations, as the occupation numbers of the exciton quantum states — whether determined from experiment or predicted by numerical simulation — can not exceed 0.03.

I am often asked for an explanation of why the exciton distributions fit Bose distributions so well. I have none. The Bose distribution is simply sufficiently flexible to fit the nonequilibrium distributions resulting from the exciton relaxation processes, if the chemical potential and particle density are allowed to vary independently. It is often said that any theory can fit any experiment, given a sufficient number of variable parameters. The lesson from my experience in cuprous oxide is that an experimentalist should reduce the number of independent parameters at every opportunity — and the sooner done the better.
7. CONCLUSION

Cuprous oxide is a long-recognized semiconductor that has enjoyed renewed interest during the past two decades due to its perceived promise as a host for a Bose-Einstein condensate of excitons. My work began as an attempt to provide a firmer basis for claims of Bose-Einstein condensation of excitons in cuprous oxide, which up to this point have depended heavily on luminescence lineshape analysis.

In order to measure the exciton density more directly, I used the absolute brightness of their luminescence. I derived the luminescence rate from the corresponding absorption coefficient, and estimated the collection efficiency of our optical system. The exciton densities measured in this way are two orders of magnitude lower than those derived from lineshape analysis, and well below the densities at which excitons should exhibit their Bose statistics in the shape of their energy distribution.

Other experimental evidence had been presented which indicated that the excitons formed a condensed or nearly condensed Bose gas. One example was the report that the relative intensity of the direct recombination luminescence increased with excitation density, which would indicate large occupation numbers of the low-energy exciton states [Snoke, 1987]. Figure 11 on page 25 records my failure to reproduce this effect, although experimental conditions and spectral lineshapes are similar to those in the experiment I was trying to reproduce. Another report indicated that the paraexcitons were not susceptible to the Auger decay process that limits the orthoexciton numbers [Lin, 1993]. My observations, such as figure 32 on page 69 and figure 56 on page 100, show that the paraexcitons are not immune to Auger decay. (Another piece of evidence seems to indicate that effects of Bose statistics are important for excitons in Cu$_2$O: Snoke et al. [1991a] observe a paraexciton kinetic energy distribution that is narrower than a Maxwell-Boltzmann distribution at the inferred lattice temperature, as would be expected for the equilibrium distribution of a dense Bose gas. I have not repeated this experiment.)

The existence and importance Auger decay had been generally accepted, but estimates of the magnitude of the effect varied widely. The measurement of the Auger rate using a strain well (section 5.4) was important in convincing me that the rate constant $A$ was in fact on the order of $10^{-16}$ cm$^3$/ns — not $10^{-18}$ cm$^3$/ns as had been inferred from experiments that derive the exciton density from lineshape analysis [Snoke, 1990c]. However, this experiment exposed one new puzzle, the source of the large number of orthoexcitons at late times, which is still unsolved. Analysis of the experiment uncovered problems with the experimental design, and the method has been superseded by that used by that used by Warren et al. [1999] in this group.

One important question has not been directly answered: could the Auger rate constant for paraexciton collisions, $A_{PP}$, be zero in a strain free crystal? The method used by Warren et al. is
sensitive to $A_{pp}$ in a strain-free crystal. The measurement that has been done held the crystal at
70K, so 71% of the excitons were paraexcitons, so the experiment measured the combination:

$$(a^2/n^2) A^{oo} + 2 (op/n^2) A^{op} + (op^2/n^2) A^{pp} = 0.08 A^{oo} + 0.41 A^{op} + 0.51 A^{pp}.$$ 

One could distinguish the three Auger constants by repeating the experiment at various crystal
 temperatures near 70K. (Temperatures below the range accessible by using liquid N$_2$, 64K to
77K, would probably be needed to clearly separate $A_{pp}$.)

In the final chapter, I took advantage of the detailed understanding of Cu$_2$O that has been
developed over the years. I developed a numerical model of the excitons in cuprite that includes
their acoustic and optical phonon emission, interconversion between their spin states, their
motion along one spatial dimension, and their Auger decay. The model ignored elastic
scattering, so there was no mechanism by which the excitons could exchange energy directly
among themselves. The transient, non-equilibrium kinetic-energy distributions predicted by the
model agree semi-quantitatively with the observed exciton distributions — including their
similarity to Bose distributions, although the quantum occupation numbers predicted by the
model remain below 0.03. Recently, this model has been extended to include elastic scattering
between excitons (appendix B). Using a theoretical estimate of the cross-section provided by
John Shumway in this department, I find that the qualitative agreement with experiment remains,
though at early times the number of excitons at low energies (i.e., energies on the scale of the
lattice temperature) is generally less than seen in experiment.

Finally, one recent development in cuprite seems to be squarely in the traditional domain of
this group. Benson et al. [1996] observe the motion of a packet of photoexcited excitons across a
2mm sample of cuprite at very near the sound velocity. One can easily picture the excitons
surfing on the thermoelastic wave generated by the same laser pulse that generated the excitons.\(^1\)
We have not made a serious attempt to reproduce these results. On the basis of the experience of
my initial experiments, I would recommend creating excitons in a thin vertical line using the a
10ns dye laser pulse tuned to the orthoexciton phonon-assisted absorption band. Simultaneously
with this pulse, the elastic wave could be created by another laser; preventing exciton production
by this pulse would be helpful, but not necessary.

Cuprous oxide is a great semiconductor in which to study the behavior of excitons, but not a
good semiconductor in which to observe effects of the Bose statistics of excitons.

\(^1\)The required magnitude of the elastic wave can be determined using figure 21b on page 47: the
elastic wave must accelerate the exciton up to the sound velocity within the mean time in which
the exciton scatters an ambient phonon, 5ns in a 2K lattice. This argument leads to the
requirement $\varepsilon/\lambda > 10/m$ for the maximum strain $\varepsilon$ and wavelength $\lambda$ of the elastic wave. A wave
carrying energy density $\varepsilon^2 s L^2 \rho \lambda = 1J/m^2$ in one $\lambda=50\mu$m wavelength meets this requirement.
APPENDIX A: SELECTION RULES FOR EXCITON LUMINESCEENCE

It is possible to work out the optical selection rules for Cu₂O by treating the electronic wavefunctions as if they were at zone center. This approximation ignores any effect the center-of-mass motion of the exciton has on the wavefunction within one unit cell. This is not a serious problem at 2K, where the thermal deBroglie wavelength of an exciton is 50 nm, while the unit cell is 0.427 nm on a side.

Considering only zone-center electronic states simplifies the discussion a great deal. For these states, we can forget that Cu₂O has screw axes and glide planes because the translational part of these operations does not change the phase of the wave function (as it would for a general Bloch state). The point group at zone-center for Cu₂O is O₅, the full point-group of the cube. That is, any rotation in O₅, followed if necessary by a translation, brings the crystal back onto itself, and thus brings a zone-center eigenstate onto either itself or a linear combination of states with which it is degenerate. From group theory we know that there are only a few distinct patterns in which a group of rotations can rearrange a set of degenerate states. One calls these patterns representations of the group and says that a set of eigenstates forms such-and-such representation. The name of the representation that a band forms serves as a useful name for the band, and provides all the necessary information for making arguments based on symmetry.

Uniaxial strain along a four-fold axis reduces the point group at zone-center to D₄h, that of a square prism. Compression along a two-fold axis should reduce the symmetry to that of a rhombic prism, D₂h. (Some authors work under the assumption that the center of inversion may be lost under [110] strain, making the symmetry of the strained crystal C₂v. This assumption leads to a different set of names for the states, but few differences in predictions.)

Table 4 on the next page lists all the representations of each of these point groups. The sets of functions are sample bases for the representations, adapted from Kittel [1987]. The representations below the double line are those formed by states with half integral spin, which behave differently under rotation.

The rows of table 4 are arranged to show how sets of degenerate states split when the symmetry of the crystal is reduced. For example, the Γ₂₃⁹ orthoexciton states split into a doublet and a singlet when the crystal symmetry is reduced to D₄h, but the degeneracy is completely removed if the crystal symmetry is reduced to D₂h.
<table>
<thead>
<tr>
<th>$D_{4h}$</th>
<th>$O_h$</th>
<th>$D_{2h}$</th>
<th>$C_{2v}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_1^+$</td>
<td>1</td>
<td>$\Gamma_1^+$</td>
<td>1</td>
</tr>
<tr>
<td>$M_3^+$</td>
<td>$x^2-y^2$</td>
<td>$\Gamma_2^+$</td>
<td>$(y^2-z^2)(x^2-z^2)(x^2-y^2)$</td>
</tr>
<tr>
<td>$M_1^+$</td>
<td>1</td>
<td>$\Gamma_{12}^+(\Gamma_3^+)$</td>
<td>${ 2z^2-x^2-y^2, x^2-y^2 }$</td>
</tr>
<tr>
<td>$M_3^+$</td>
<td>$x^2-y^2$</td>
<td>$\Gamma_4^+$</td>
<td>${ yz(y^2-z^2), xz(x^2-z^2), xy(x^2-y^2) }$</td>
</tr>
<tr>
<td>$M_2^+$</td>
<td>$xy(x^2-y^2)$</td>
<td>$\Gamma_{15}^+(\Gamma_4^+)$</td>
<td>${ yz(y^2-z^2), xz(x^2-z^2), xy(x^2-y^2) }$</td>
</tr>
<tr>
<td>$M_5^+$</td>
<td>${ yz, xz }$</td>
<td>$\Gamma_{25}^+(\Gamma_5^+)$</td>
<td>${ yz, xz, xy }$</td>
</tr>
<tr>
<td>$M_4^+$</td>
<td>$xy$</td>
<td>$\Gamma_{25}^+(\Gamma_5^+)$</td>
<td>${ yz, xz, xy }$</td>
</tr>
<tr>
<td>$M_5^+$</td>
<td>${ yz, xz }$</td>
<td>$\Gamma_{25}^+(\Gamma_5^+)$</td>
<td>${ yz, xz, xy }$</td>
</tr>
<tr>
<td>$M_1^-$</td>
<td>$xyz(x^2-y^2)$</td>
<td>$\Gamma_{12}^+(\Gamma_3^-)$</td>
<td>${ xyz(2z^2-x^2-y^2), xz(x^2-y^2) }$</td>
</tr>
<tr>
<td>$M_3^-$</td>
<td>$xyz$</td>
<td>$\Gamma_{25}^+(\Gamma_5^-)$</td>
<td>${ x, y, z }$</td>
</tr>
<tr>
<td>$M_2^-$</td>
<td>$z$</td>
<td>$\Gamma_{15}^+(\Gamma_4^-)$</td>
<td>${ x, y, z }$</td>
</tr>
<tr>
<td>$M_5^-$</td>
<td>${ x, y }$</td>
<td>$\Gamma_{25}^+(\Gamma_5^-)$</td>
<td>${ x, y, z }$</td>
</tr>
<tr>
<td>$M_4^-$</td>
<td>$z(x^2-y^2)$</td>
<td>$\Gamma_{25}^+(\Gamma_5^-)$</td>
<td>${ x, y, z }$</td>
</tr>
<tr>
<td>$M_5^-$</td>
<td>${ x, y }$</td>
<td>$\Gamma_{25}^+(\Gamma_5^-)$</td>
<td>${ x, y, z }$</td>
</tr>
<tr>
<td>$M_6^+$</td>
<td>$\Gamma_6^+$ spin-1/2: ${ \uparrow, \downarrow }$</td>
<td>$\Gamma_6^+$ spin-1/2: ${ \uparrow, \downarrow }$</td>
<td>$\Sigma_5^+(\Gamma_5)$</td>
</tr>
<tr>
<td>$M_7^+$</td>
<td>$\Gamma_7^+$ $(y^2-z^2)(x^2-z^2)(x^2-y^2) \times { \uparrow, \downarrow }$</td>
<td>$\Gamma_7^+$ $(y^2-z^2)(x^2-z^2)(x^2-y^2) \times { \uparrow, \downarrow }$</td>
<td>$\Sigma_5^+(\Gamma_5)$</td>
</tr>
<tr>
<td>$M_6^+$</td>
<td>$\Gamma_8^+$ the four spin-3/2 states</td>
<td>$\Gamma_8^+$ the four spin-3/2 states</td>
<td>$\Sigma_5^+(\Gamma_5)$</td>
</tr>
<tr>
<td>$M_7^+$</td>
<td>$\Gamma_8^+$ $(y^2-z^2)(x^2-z^2)(x^2-y^2) \times { \uparrow, \downarrow }$</td>
<td>$\Gamma_8^+$ $(y^2-z^2)(x^2-z^2)(x^2-y^2) \times { \uparrow, \downarrow }$</td>
<td>$\Sigma_5^+(\Gamma_5)$</td>
</tr>
<tr>
<td>$M_6^-$</td>
<td>$\Gamma_6^-$ $(y^2-z^2)(x^2-z^2)(x^2-y^2) \times { \uparrow, \downarrow }$</td>
<td>$\Gamma_6^-$ $(y^2-z^2)(x^2-z^2)(x^2-y^2) \times { \uparrow, \downarrow }$</td>
<td>$\Sigma_5^+(\Gamma_5)$</td>
</tr>
<tr>
<td>$M_7^-$</td>
<td>$\Gamma_7^-$ $xyz \times { \uparrow, \downarrow }$</td>
<td>$\Gamma_7^-$ $xyz \times { \uparrow, \downarrow }$</td>
<td>$\Sigma_5^+(\Gamma_5)$</td>
</tr>
<tr>
<td>$M_6^-$</td>
<td>$\Gamma_8^-$ $(y^2-z^2)(x^2-z^2)(x^2-y^2) \times { \uparrow, \downarrow }$</td>
<td>$\Gamma_8^-$ $(y^2-z^2)(x^2-z^2)(x^2-y^2) \times { \uparrow, \downarrow }$</td>
<td>$\Sigma_5^+(\Gamma_5)$</td>
</tr>
<tr>
<td>$M_7^-$</td>
<td>$\Gamma_8^-$ the four spin-3/2 states</td>
<td>$\Gamma_8^-$ the four spin-3/2 states</td>
<td>$\Sigma_5^+(\Gamma_5)$</td>
</tr>
</tbody>
</table>

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Table 4 (previous page): Representations of four point groups, arranged as a compatibility table. The x, y, and z axes are the fourfold axes of the cubic crystal. The notations for the representations are those of the original papers. When the numbering of the representations in Koster's book [1963] is different, that notation follows in parentheses.

The choice of axes for the sample functions is as follows:

the fourfold axes of $O_{4h}$ are $\hat{x}$, $\hat{y}$, and $\hat{z}$,
the fourfold axis of $D_{4h}$ is $\hat{z}$, (appropriate for compression along $\hat{z}$)
the twofold axes of $D_{2h}$ are $\hat{x}$, $\hat{x}+\hat{y}$ and $\hat{x}-\hat{y}$, in that order, and
the twofold axis of $C_{2v}$ is $\hat{x}+\hat{y}$ (appropriate for compression along $\hat{x}+\hat{y}$).

A few representations are of particular interest here. The three orthoexcitons in Cu$_2$O form a basis for $\Gamma_{25}^+$; the paraexciton transforms as $\Gamma_2^+$. The components of the electric dipole operator transform as $\Gamma_{15}^-$. Magnetic dipoles transform as $\Gamma_{15}^+$. (A magnetic dipole along $\hat{z}$ really does behave like $xy(x^2-y^2)$ under the inversion and the rotations in the cubic group.) Electric quadropoles are $\Gamma_{25}^+$ and $\Gamma_{12}^+$.

**Phonon-assisted luminescence**

Phonon-assisted optical transitions important in Cu$_2$O because, for some phonons, they are dipole-allowed while direct transitions are not. In this second order process emission (or absorption) of an optical phonon converts the exciton into a virtual electronic state which is dipole-allowed and luminesces immediately. If we include excitons and phonons in our system and treat the light as an external field, the matrix elements involved in phonon-assisted luminescence look like

$$\langle \text{exciton, } 0 | H_{\text{electron-phonon}} | i, \text{phonon} \rangle \langle i, \text{phonon} | H_{\text{dipole}} | 0, \text{phonon} \rangle,$$

where $| i \rangle$ is the dipole-allowed intermediate state and '0' denotes a state with no excitations.

The selection rules come quickly using a group multiplication table such as table 5. Any product of states and/or operators belonging to representations A, B, C, ..., can be decomposed into a sum of states and/or operators belonging to the representations contained in the product $A \times B \times C \times \cdots$. Thus $H_{\text{dipole}} | 0 \rangle$ contains only states belonging to $\Gamma_{15}^- \times \Gamma_1^+ = \Gamma_{15}^-$. 

A matrix element is a product of states and operators, so the results above apply. On the other hand, a matrix element is a scalar, invariant under any rotation; it belongs to the representation $\Gamma_1^+$. In order for a matrix element to be non-zero, the product of the representations of its factors must contain $\Gamma_1^+$. 

Furthermore, $\Gamma_1^+$ appears in a product only when a representation multiplies itself as in $axa$. Thus $\langle i | H_{\text{dipole}} | 0 \rangle$ can be non-zero only if $| i \rangle$ belongs to one of the representations contained in $H_{\text{dipole}} | 0 \rangle$. The intermediate state $| i \rangle$ must belong to $\Gamma_{15}^-$. 

$H_{\text{electron-phonon}}$ has the full symmetry of the crystal; it belongs to $\Gamma_1^-$. The matrix element $\langle \text{exciton, } 0 | H_{\text{electron-phonon}} | i, \text{phonon} \rangle$ is non-zero only when the phonon belongs to a
Table 5: Multiplication table for the representations of \( O_d \) as can be found in Koster [1963]. Parities (plus or minus) simply multiply separately.

representation in \( \Gamma_{15} \times \Gamma_1^+ \times A = \Gamma_{15} \times A \) where \( A \) is the representation to which the exciton belongs.

For phonon-assisted orthoexciton recombination the phonon must be one of \( \Gamma_{15} \times \Gamma_2^+ = \Gamma_2^+ + \Gamma_1^2 + \Gamma_{15}^+ + \Gamma_{25}^+ \). This list happens to contain all of the odd parity phonons in \( \text{Cu}_2\text{O} \). Of these, luminescence using the \( \Gamma_{12}^+ \) phonon is brightest by far. Bloch and Schwab [1978] offered an explanation. They point out that the odd-parity intermediate state must have either the electron or the hole in an odd-parity band. In order for the second-order process to be strong, the odd-parity band must be near the bands forming the exciton, otherwise the energy denominator would be large and transition weak. The odd-parity band in \( \text{Cu}_2\text{O} \) closest to the bandgap is the \( \Gamma_{12}^- \) (before spin) conduction band, and it takes a \( \Gamma_{12}^- \) phonon to scatter the exciton's \( \Gamma_1^+ \) electron into that state.

For the paraexciton, \( \Gamma_{15} \times \Gamma_2^- = \Gamma_{25}^- \); only the \( \Gamma_{25}^- \) phonon can help. The nearest band which can provide an intermediate state is a deep \( \Gamma_{15}^- \) valence band. The remoteness of the intermediate state explains the relative weakness of the \( \Gamma_{25}^- \)-assisted luminescence of both orthoexcitons and paraexcitons.

The paraexciton \( \Gamma_{25}^- \)-assisted transition only \( 1/17 \) as strong as the corresponding orthoexciton transition because paraexciton luminescence involves a spin-flip. At first glance, it is not obvious that paraexciton luminescence should be allowed at all. Neither of the steps in the process just described, phonon emission nor electric dipole radiation, flips electron spins.

The process depends on the spin-orbit splitting of the deep \( \Gamma_{15}^- \) valence band, which provides the intermediate state, into two levels at \( \Gamma \). The \( \Gamma_{25}^- \) phonon scatters the hole equally well into both the spin-orbit split states, and both are connected by an electric dipole to the electron in the conduction band. If one writes out second-order scattering amplitude for the phonon-assisted
luminescence, keeping the spin- and spatial parts of the wavefunctions explicit, as in section 2.3, and ignores the energy difference between the intermediate states, one finds that the two luminescence paths destructively interfere. By including the spin-orbit splitting, we see that one intermediate state is favored over the other, due to a smaller energy-denominator, and the destructive interference is no longer perfect.

**Orthoexcitons**

The selection rules that follow have been presented in very compact from by Elliot [1961]. Some are presented in a table in the review article by Agekeyan [1977]. I have found the following simpler presentation of these results useful.

An orthoexciton at rest in Cu$_2$O has no dipole moment. In order to describe the direct transition we have to consider the finite wavevector of the either the photon or the exciton. Either choice leads to the same selection rules. The finite wavevector of the exciton contributes little dipole moment to the exciton, because Cu$_2$O has few odd-parity bands near the bandgap. Imagining a finite wavelength electromagnetic wave interacting with the quadrupole moment of an exciton at rest is more realistic.

To visualize the direct luminescence from the orthoexcitons consider first just one orthoexciton state. The orthoexciton which transforms as $xy$ is connected to the ground state by only one type of electric quadrupole operator, the type associated with a quadrupole moment of the shape $xy$. This quadrupole moment will emit light most strongly along the $x$ and $y$ axes. The intensity falls off away from these axes, reaching zero in the two planes $x = y$ and $x = -y$. All the radiated light is polarized in the $x$-$y$ plane.

Considering all three orthoexcitons, looking along $\hat{x}$ we will see the $xy$ orthoexciton polarized along $\hat{y}$ and the $zx$ orthoexciton polarized along $\hat{z}$. Looking along $\hat{x}+\hat{y}$ we will see the $yz$ and $zx$ orthoexcitons, both polarized along $\hat{z}$, but neither exciton is at full brightness in this direction.

In general, direct orthoexciton luminescence along a $\langle 001 \rangle$ direction is unpolarized, while that along a $\langle 110 \rangle$ direction is polarized with electric field along the perpendicular $\langle 001 \rangle$ direction. The intensity radiated along a $\langle 110 \rangle$ direction is half that in a $\langle 001 \rangle$ direction. In practice, these polarization selection rules are observed much more cleanly in absorption than in luminescence.

The phonon-assisted luminescence in an unstrained crystal is unpolarized and isotropic. The three components of the dipole operator contribute equally, and three electric dipole radiation fields add to give a spherically symmetric sum.

In a strained crystal, we assume that the exciton wave functions and phonon shapes are virtually the same as those in the cubic crystal. (To the extent that the elasticity of the crystal remains linear under strain, the phonon energies no not change at all.) Then the matrix of the
dipole operator between exciton states and phonon states is the same as it would be in a cubic crystal, and can be found in Koster's book [1963] under coupling coefficients for a $\Gamma_{15}$ operator. The most interesting case for Cu$_2$O is the $\Gamma_{12}$ phonon-assisted luminescence of the orthoexciton, the matrix of the dipole operator between the $\Gamma_{25}^-$ excitons and the $\Gamma_{12}^-$ phonons is:

$$p \propto \begin{bmatrix}
-\hat{x} \sqrt{3}/2 & -\hat{z}/2 \\
\hat{y} \sqrt{3}/2 & -\hat{y}/2 \\
0 & \hat{x}
\end{bmatrix} \begin{bmatrix}
ye \\
xz
\end{bmatrix}$$

The intensity of luminescence with polarization vector is $e$ is proportional to the sum over phonon states of the squared matrix elements: $\Sigma |\langle \text{exciton}| e \cdot p |\text{phonon}\rangle|^2$.

<table>
<thead>
<tr>
<th>Strain along:</th>
<th>Ortho state</th>
<th>Ortho shape</th>
<th>$\Gamma_{15}^-\leftarrow \Gamma_{2}^-$</th>
<th>$\Gamma_{12}^-\leftarrow \Gamma_{15}^-, (\text{strong})$</th>
<th>$\Gamma_{25}^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[001]</td>
<td>$M_4^+$</td>
<td>$xy$</td>
<td>$e^2_z$</td>
<td>$\frac{1}{2} e^2_x + \frac{1}{2} e^2_y$</td>
<td>$\frac{1}{2} e^2_x + \frac{1}{2} e^2_y$</td>
</tr>
<tr>
<td></td>
<td>$M_5^+$</td>
<td>${yz, , xz}$</td>
<td>$e^2_x + e^2_y$</td>
<td>$\frac{1}{2} e^2_x + \frac{1}{2} e^2_y + e^2_z$</td>
<td>$e^2_x + e^2_y + e^2_z$</td>
</tr>
<tr>
<td>[110]</td>
<td>$\Sigma_2$ (G$3$)</td>
<td>$z(x-y)$</td>
<td>$e^2_+e^2_\parallel$</td>
<td>$\frac{1}{4} e^2_\parallel + \frac{1}{4} e^2_\perp$</td>
<td>$\frac{1}{2} e^2_\parallel + \frac{1}{2} e^2_\perp$</td>
</tr>
<tr>
<td></td>
<td>$\Sigma_4$ (G$4$)</td>
<td>$z(x+y)$</td>
<td>$e^2_\parallel$</td>
<td>$\frac{1}{2} e^2_\parallel + \frac{1}{2} e^2_\perp$</td>
<td>$\frac{1}{4} e^2_\parallel + \frac{1}{4} e^2_\perp$</td>
</tr>
<tr>
<td></td>
<td>$\Sigma_1$ (G$1$)</td>
<td>$xy$</td>
<td>$e^2_z$</td>
<td>$\frac{1}{2} e^2_\parallel + \frac{1}{2} e^2_\perp$</td>
<td>$\frac{1}{2} e^2_\parallel + \frac{1}{2} e^2_\perp$</td>
</tr>
</tbody>
</table>

Table 6: Orientations of the orthoexciton electric quadrupole seen in direct luminescence, and the electric dipoles seen in phonon-assisted luminescence of orthoexcitons, in cuprite under uniaxial strain. For phonon-assisted luminescence, the sum $\Sigma |\langle \text{exciton}| e \cdot p |\text{phonon}\rangle|^2$ is listed. The $x$, $y$, and $z$ axes are the four-fold axes of the crystal. Exciton states are listed in order of decreasing energy, as one reads down the table, for compressive uniaxial stress. Phonons are listed in order of increasing energy, left to right. For [110] strain, $e_\parallel$ is along [110], and $e_\perp$ is along [110].

Table 6 summarizes the results. For example, suppose we apply [110] strain, and look at the luminescence emitted along [110]. Only the highest-energy state has a quadrupole moment that produces an electric field at points in the $\hat{x} - \hat{y}$ direction, and this field is along $\hat{z}$, that is, [001]. The $\Gamma_{12}^-$-assisted recombination of the lowest-energy state will be polarized along [001]. The other two states have their $\Gamma_{12}^-$-assisted luminescence polarized along [110], with the middle line $\frac{1}{4}$ as bright, and the highest-energy line $\frac{1}{4}$ as bright as the lowest $\Gamma_{12}^-$-assisted line.

A magnetic field splits the orthoexciton line into three. The extreme components of the triplet are separated by 0.1 meV/Tesla, independent of the direction of the field. In this case, the luminescence can be circularly polarized along some directions. The direct transition looks like a radiating quadrupole shaped like the real part of the shape function in table 7, plus one shaped like the imaginary part, one quarter cycle out of phase. Phonon-assisted luminescence will also be (partially) circularly polarized when observed along the direction of the magnetic field, but table 7 below gives only the luminescence intensities in a linear polarization basis.
<table>
<thead>
<tr>
<th>H along:</th>
<th>Ortho energy</th>
<th>Ortho shape</th>
<th>$\Gamma_{15}^{-}$</th>
<th>$\Gamma_{12}^{-}$ (strong)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[001]</td>
<td>+$\mu H$</td>
<td>$yz + ixz$</td>
<td>$\frac{1}{2}e_x^2 + \frac{1}{2}e_y^2 + e_z^2$</td>
<td>$e_x^2 + e_y^2$</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>$xy$</td>
<td>$e_x^2 + e_y^2$</td>
<td>$2e_z^2$</td>
</tr>
<tr>
<td></td>
<td>-$\mu H$</td>
<td>$yz - ixz$</td>
<td>$\frac{1}{2}e_x^2 + \frac{1}{2}e_y^2 + e_z^2$</td>
<td>$e_x^2 + e_y^2$</td>
</tr>
<tr>
<td>[110]</td>
<td>+$\mu H$</td>
<td>$\frac{1}{2}z(x - y) - ix$</td>
<td>$e_z^2 + \frac{1}{2}e_x^2 + \frac{1}{2}e_y^2$</td>
<td>$\frac{3}{4}e_z^2 + \frac{1}{4}e_x^2 + e_z^2$</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>$z(x+y)$</td>
<td>$e_z^2 + e_x^2$</td>
<td>$\frac{1}{2}e_z^2 + \frac{1}{2}e_x^2$</td>
</tr>
<tr>
<td></td>
<td>-$\mu H$</td>
<td>$\frac{1}{2}z(x - y) + ix$</td>
<td>$e_z^2 + \frac{1}{2}e_x^2 + \frac{1}{2}e_y^2$</td>
<td>$\frac{3}{4}e_z^2 + \frac{1}{4}e_x^2 + e_z^2$</td>
</tr>
</tbody>
</table>

Table 7: Orientations of the electric quadrupole, and phonon-assisted electric dipole, luminescence of orthoexcitons in a magnetic field.

Paraexcitons

The paraexciton is non-degenerate, so there are no splittings to consider. The three $\Gamma_{25}^{-}$ phonons which assist in its recombination are capable of creating an electric dipole with the paraexciton in each of three mutually perpendicular directions. so the phonon-assisted line is unpolarized and isotropic, even when the crystal is under strain. There is, however, the possibility of direct recombination.

From the compatibility tables we see that under [001] stress the $\Gamma_{2}^{+}$ paraexciton becomes $M_{3}^{+}$, as do any $\Gamma_{12}^{-}$ electronic states. We should expect the paraexciton to mix with any nearby $\Gamma_{12}^{-}$ states to first order in the strain, picking up an electric quadrupole moment of the shape $x^2 - y^2$. This luminescence will be most visible along [110] and [110], will be polarized with electric field in the x-y plane, and will have intensity proportional to the square of the strain.

Under [110] stress the paraexciton becomes $N_{3}^{+}$ and can again have an $x^2 - y^2$ electric quadrupole. In addition, it can mix with the $\Gamma_{15}^{+}$ state which has a magnetic dipole along the z axis. The observed radiation pattern matches that of the $x^2 - y^2$ electric quadrupole.

If the crystal does lose its center of inversion under [110] strain, and the paraexciton becomes $\Sigma_{3}$, it could pick up an electric dipole moment along $\hat{x} - \hat{y}$. One would expect this to be the most easily noticed of the newly-allowed luminescence mechanisms.

Finally, magnetic fields mix the paraexciton wave function with that of the middle of the three field-split orthoexciton states. The field-induced paraexciton luminescence, both direct and phonon-assisted, mimics that of this middle orthoexciton. The paraexciton luminescence increases as the square of the field.
APPENDIX B: NUMERICAL INTEGRATION TECHNIQUES

Sampling pattern

Although the results of the computer integrations were presented as kinetic-energy distributions, it is advantageous to work with samples of the occupation number \( g(k) \) which are evenly spaced in particle momentum. This puts more sampling points where they are needed to describe the sharper features of the kinetic energy distribution at low kinetic energies. The spacing of the samples in \( k \) is chosen so to divide evenly the longitudinal sound velocity.

Non-uniform sampling in \( z \) would more efficiently represent the strong variation in the exciton gas near the crystal surface, as well as the large volume of cold excitons deeper in the crystal. However, I cannot make a convincing demonstration of the quality of the transport part of the model if I use a non-uniform grid. Specifically, a packet of excitons moving from the surface with uniform velocity spreads out as the sampling grid spreads out. I sample uniformly in \( z \), sacrificing some resolution near the surface and representing less depth of the crystal than I could otherwise.

The dependence of the occupation numbers on the angle \( \theta \) between the particle momentum and the normal to the crystal surface is expanded in Legendre polynomials in \( \cos\theta \).

\[
g(k, \cos\theta, z) = \sum L g_{k,L,z} P_L(\cos\theta).
\]

This representation allows the effects of scattering through small-angles to accumulate, whereas sampling in \( \theta \) could not faithfully represent any cumulative effects of multiple scattering through angles smaller than the sampling interval. More importantly, the angular-dependence of phonon scattering is diagonal in the Legendre polynomial basis.

The standard grid for most of the results in chapter 6 kept the first three Legendre polynomials, up to \( 3\cos^2\theta - 1 \), covered the first 60\( \mu \)m of the crystal with 30 samples in \( z \), and represented exciton velocities up to \( 15s_L \) with 105 samples in \( k \).

Angular dependencies in the scattering integrals

The part of the Boltzmann equation describing the free motion and LA phonon scattering is

\[
\frac{\partial}{\partial t} g(k, \cos\theta, z) + \frac{k \cos\theta}{m} \frac{\partial}{\partial z} g(k, \cos\theta, z) = \frac{\pi a^2}{\hbar \rho s_L (2\pi\hbar)^3} \times
\]

\[
\int \left\{ g(p, \cos\varphi, z) |k-p| \left[ \delta(p^2/2m + s_L |k-p| - k^2/2m) f_{|k-p|} + \delta(p^2/2m - s_L |k-p| - k^2/2m)(1 + f_{|k-p|}) \right] \right. \\
- g(k, \cos\theta, z) |k-p| \left[ \delta(k^2/2m + s_L |k-p| - p^2/2m) f_{|k-p|} + \delta(k^2/2m - s_L |k-p| - p^2/2m)(1 + f_{|k-p|}) \right] \\
\left. \right\} \, d^3p.
\]

Acoustic phonon scattering connects a state \( k \) with a 2-D sheet of states \( p \). Express \( p \) in spherical coordinates \( \alpha \) and \( \beta \) where \( \alpha \) is the angle between \( k \) and \( p \). For each magnitude \( p \), the energy conserving \( \delta \)-function sets the angle \( \alpha \) through the relation
\[
((k^2 - p^2) / 2 m s_L)^2 = |k-p|^2 = k^2 + p^2 - 2 k p \cos \alpha.
\]

The angle \( \phi \) between \( p \) and the \( z \)-axis follows from a law of cosines.

\[
\cos \phi = \cos \theta \cos \alpha + \sin \theta \sin \alpha \cos \beta.
\]

Performing the integral over \( \alpha \), the phonon scattering terms become

\[
\frac{-\pi^2}{8\pi^2 \rho s_L \hbar^4} \int_{|k-2ms|}^{k+2ms} \left\{ |f_q| \int_0^{2\pi} g(p, \cos \theta \cos \alpha + \sin \theta \sin \alpha \cos \beta, z) \, d\beta - |f_{-q}| \int_0^{2\pi} g(k, \cos \theta, z) \right\} \frac{p q^2}{k s_L} \, dp.
\]

where the phonon momentum \( q = (k^2 - p^2)/2ms_L \) and I have used the formal relation \(-f_{-q} = 1 + f_q\) to combine terms.

Using the expansion \( g(k, \cos \theta, z) = \sum_{\ell} g_{k,\ell,z} P_{\ell}(\cos \theta) \), the integral over \( \beta \) simplifies to

\[
\sum_{\ell} g_{p,\ell,z} \int_0^{2\pi} \frac{1}{P_{\ell}(\cos \theta \cos \alpha + \sin \theta \sin \alpha \cos \beta)} \, d\beta = 2\pi \sum_{\ell} g_{p,\ell,z} P_{\ell}(\cos \theta) P_{\ell}(\cos \alpha).
\]

using the addition theorem for spherical harmonics, specifically equations 12.195 and 12.198 in the textbook by Arfken [1985]. Then the Boltzmann equation

\[
\sum_{\ell} \left( \frac{\partial}{\partial t} g_{p,\ell,z} + \frac{k \cos \theta}{m} \frac{\partial}{\partial z} g_{p,\ell,z} \right) P_{\ell}(\cos \theta) = \frac{-\pi^2}{8\pi^2 \rho s_L \hbar^4} \sum_{\ell} P_{\ell}(\cos \theta) \int_{|k-2ms|}^{k+2ms} \left\{ |f_q| \int_0^{2\pi} g_{p,\ell,z} P_{\ell}(\cos \alpha) - |f_{-q}| g_{k,\ell,z} \right\} \frac{p q^2}{k s_L} \, dp
\]

separates into a set of equations if we project out each Legendre component:

\[
\frac{\partial}{\partial t} g_{k,\ell,z} + \frac{\ell+1}{2\ell+3} \frac{k}{m} \frac{\partial}{\partial z} g_{k,\ell+1,z} + \frac{\ell}{2\ell-1} \frac{k}{m} \frac{\partial}{\partial z} g_{k,\ell-1,z} = \frac{-\pi^2 m^3 s_L}{4\pi \rho \hbar^4} \int_{|k-2ms|}^{k+2ms} \left\{ |f_q| \int_0^{2\pi} g_{p,\ell,z} P_{\ell}(\cos \alpha) - |f_{-q}| g_{k,\ell,z} \right\} \frac{p q^2}{k (ms_L)^3} \, dp
\]

where the factor in front of the integral is 0.71/ns and again \( q = (k^2 - p^2)/2ms_L \).

Acoustic phonon emission does not connect components \( g_{k,\ell,z} \) with different \( \ell \), so we can include the angular dependence of exciton-phonon scattering with no penalty in computation time.\(^1\) (That is, no inner sum over \( \ell \) nor integral over \( \theta \) is required.) The equation does not separate so neatly if the identical-particle scattering-enhancement factors \([1 + \sum_m g_{k,m,z} P_{m}(\cos \theta)]\) are retained, but their effect can be treated approximately by including the angle-independent part \([1 + g_{k,0,z}].\)

---

\(^1\)I have since learned that the use of the Legendre polynomial basis is standard [Cornwell, 1967, chapter 5]. Originally I stumbled upon it while following up on a suggestion by Professor Karl Hess.
For optical phonons, the scattering integral is
\[
\int \frac{C^2 (k-p)^2}{\pi^2 \hbar^4 \rho E_{op}} \left[ g(p, \cos \theta_p, z) (1+f_{op}) - g(k, \cos \theta_k, z) f_{op} \right] \delta(p^2/2m - E_{op} - k^2/2m) \, d^3p
\]
\[
+ \int \frac{C^2 (k-p)^2}{\pi^2 \hbar^4 \rho E_{op}} \left[ g(p, \cos \theta_p, z) f_{op} - g(k, \cos \theta_k, z) (1+f_{op}) \right] \delta(p^2/2m + E_{op} - k^2/2m) \, d^3p.
\]
The factor \((p-k)^2 = p^2 + k^2 - 2pk [\cos \theta_k \cos \theta_p + \sin \theta_k \sin \theta_p \cos (\phi_k - \phi_p)]\) simplifies somewhat upon integration over \(\phi_p\); then the integration over \(\theta_p\) leaves \(p^2 + k^2 - (2/3) pk \cos \theta_k\).

Upon integration over \(p\) the scattering integral is
\[
\frac{4C^2 m (2m)^{3/2}}{\pi \hbar^4 E_{op}} \times \left\{ \frac{1}{(2m)^{3/2}} \times \left[ p(p^2+k^2) g_{p,0,0}(1+f_{op}) - \frac{2}{3} kp^2 g_{p,1,0} \cos \theta_k (1+f_{op}) - p(p^2+k^2) \sum \xi g_{k,\xi,\xi} P_{\xi}(\cos \theta_k) f_{op} \right]_{p=\sqrt{k^2+2mE_{op}}}
\]
\[+ \left[ q(q^2+k^2) g_{q,0,0} f_{op} - \frac{2}{3} kq^2 g_{q,1,0} \cos \theta_k f_{op} - q(q^2+k^2) \sum \xi g_{k,\xi,\xi} P_{\xi}(\cos \theta_k) (1+f_{op}) \right]_{q=\sqrt{k^2-2mE_{op}}} \}
\]
where the first factor in front of the brackets must be 2 ns\(^{-1}\) meV\(^{-3/2}\) (and \(C=1.2\text{eV}\)) in order to match the observed emission rates. Again the angular dependence in the scattering integral separates into several terms in the Legendre polynomials in \(\cos \theta_k\). Although they were omitted from these descriptions, factors of \([1 + (|p-k|a/d)^2]^{-4}\) to account for the finite size of the exciton were included in calculation of all the phonon emission rates.

I assume that ortho-para conversion will randomize the direction of the exciton motion so that, with \(p = \sqrt{k^2 + 2m\Delta}\) where \(\Delta\) is the 12meV splitting between spin states,
\[
\frac{\partial}{\partial t} g_{k,\xi,\xi}^{\text{ortho}} = \Gamma_{\text{ortho-para}} \left\{ \delta_{\xi,0} g_{p,\xi,\xi}^{\text{para}} - g_{k,\xi,\xi}^{\text{ortho}} \right\} \left( 1 + 2 f \sqrt{2m\Delta} \right) \sqrt{\frac{k^2}{2m\Delta}} + 1.
\]
For channel (1) of section 4.8, the prefactor which best fits the 2K down-conversion rate is \(\Gamma_{\text{ortho-para}} = 0.3/\text{ns}\). For channel (2), there is an additional factor \(k^2/2m\Delta\), and the prefactor is \(\Gamma_{\text{ortho-para}} = 8/\text{ns}\).

**Stability**

Straightforward finite-differencing of the transport part of the Boltzmann equation is numerically unstable. The solution is to add a diffusion term called the "numerical dissipation". The two-step Lax-Wendroff scheme uses the minimum diffusivity, \(v^2 \Delta t/2\), and is stable for time-steps \(\Delta t < \Delta z / v\). Typically, the maximum exciton velocity followed was 15\(s_L = 15\times4.5\mu\text{m}/\text{ns}\), and the sampling interval in space was 2\(\mu\text{m}\), so stability of the transport terms required the time-step to be less than 30ps.

The phonon scattering rate puts a more stringent limit on the time-step. The acoustic phonon emission rate for excitons moving at 15\(s_L\) is about 500/\(\text{ns}\) so we must use \(\Delta t < 2\text{ps}\) for stability.
Therefore the "numerical dissipation" adds a diffusivity less than \((15\tau_L)^2\) 2ps = 9µm²/ns. For the excitons below 50meV kinetic energy the numerical dissipation is less than 1µm²/ns.

**Elastic scattering**

There are two initial exciton momenta and two final momenta involved, so there is an additional degree of freedom compared with the case of phonon emission or absorption. The scattering rate \(W_{p\to k}\) involves all events in which excitons of momenta \(p\) and \(p_2\) scatter into momenta \(k\) and \(k_2\):

\[
W_{p\to k} = \frac{\sigma}{nm^2} \int \delta \left( \frac{p^2 + p_2^2 - k^2 - k_2^2}{2m} \right) g(p_2) [1 + g(k_2)] \, d^3p_2
\]

where \(k_2 = p + p_2 - k\), and \(\sigma\) is assumed independent of \(|p-k|\). The \(\delta\)-function restricts the integral to those momenta \(p_2\) in the plane \((p_2-k) \cdot (p-k) = 0\). The total scattering rate out of the state \(p\) is, in the limit of small occupation numbers,

\[
\frac{1}{(2\pi\hbar)^3} \int W_{p\to k} \, d^3k = \sigma \int \frac{|p-p_2|}{m} g(p_2) \, d^3p_2.
\]

which is \(n\sigma\overline{v}\) for the appropriate average relative velocity \(\overline{v}\).

If we restricted ourselves to the case of isotropic momentum distributions, we could reduce the scattering kernel to the one-dimensional integral. Integrating over the directions of \(p_2\),

\[
W_{p\to k} = \frac{2\sigma}{m} \int \frac{\Theta(p_2|p-k| > k(|k-p|))}{|p-k|} g(p_2) [1 + g(k_2)] \, dp_2.
\]

where \(k_2 = \sqrt{p^2 + p_2^2 - k^2}\). Then averaging over the angle between \(p\) and \(k\),

if \(p > k\),

\[
W_{p\to k} = \frac{2\sigma}{mk} \left\{ \int_0^k p_2 + \int_0^k k \right\} g(p_2) [1 + g(k_2)] \, dp_2.
\]

if \(k > p\),

\[
W_{p\to k} = \frac{2\sigma}{mk} \left\{ \int_0^k p_2 + \int_0^k k \right\} g(p_2) [1 + g(k_2)] \, dp_2.
\]

The contribution to the Boltzmann equation follows from an integration over \(p\),

\[
\frac{\partial}{\partial t} g_k = \frac{8\pi\sigma}{(2\pi\hbar)^3} \int \int \min\left[\frac{p, p_2, k, k_2}{km}\right] \left\{ g_p g_{p_2} [1 + g_k][1 + g_{k_2}] - g_k g_{k_2} [1 + g_p][1 + g_{p_2}] \right\} \, dp \, dp_2 \, dp_2.
\]

(For purposes of numerical integration it is better to write this last integral in terms of the energy transferred, \(e = p^2 - k^2 = k_2^2 - p_2^2\), and take advantage of the fact for fixed \(e\) and \(p\), \(W_{p\to k}\) depends on \(k\) only through the integration limits.)

The simulation of chapter 6 has been expanded to include elastic scattering —- for the special case of isotropic velocity distributions. The restriction to isotropic velocity distributions precludes net transport of excitons, but exciton transport was seen to have only a minor effect in section 6.4. The following two figures compare simulation results with and without elastic scattering between the excitons. For the elastic scattering cross-section, I used \(\sigma = 50\text{nm}^2 = 4\pi(2\text{nm})^2\) based on preliminary theoretical results from John Shumway in this department. This corresponds to a scattering length three times the exciton Bohr radius.
Figure 61: a-c) Results of the simulation for a 0.5ns pulse including elastic scattering with cross-section $\sigma = 50\text{ nm}^2 = 4\pi(2\text{nm})^2$.
d-f) Results allowing for no elastic scattering between excitons; $\sigma = 0$.
The times are 0, 0.3, and 0.6ns after the center of a 0.5ns generation pulse which created $5\times10^{14}$ excitons per cm$^2$. The fitting function is the one used throughout chapter 6.

Figure 61 presents the results for relatively intense 0.5ns pulses, with conditions identical to those for figure 46 on page 92, except that figure 61 ignores exciton transport. Inclusion of elastic scattering into the model reduces the low-energy peak of the predicted exciton distributions — though not so much as does perfect thermalization as in figure 50 on page 94.
Figure 62: a-c) Results of the simulation for a 7ns pulse including elastic scattering with cross-section \( \sigma = 50\,\text{nm}^2 = 4\pi(2\,\text{nm})^2 \).

d-f) Results allowing for no elastic scattering between excitons; \( \sigma = 0 \).

The times are 0, 4, and 8ns after the center of a 7ns FWHM generation pulse which created \( 8 \times 10^{14} \) excitons per \( \text{cm}^2 \). The fitting function is the one used throughout chapter 6.

Figure 62 presents the results for a relatively intense 10ns generation pulse (with full-width at half maximum equal to 7ns) — conditions identical to those for figure 53 on page 97, except that figure 62 ignores exciton transport. The results are still well-fit by Bose distributions, though with less apparent quantum degeneracy.
Bose condensation

The temptation to simulate the formation of a Bose condensate is irresistible. We need only turn off Auger decay and restore the \([1+g]\) factors in the scattering integrals. Our model is the same as that studied by Inoue and Hanamura [1976] except that we have retained the effect of the finite speed of sound, which prevents excitons below a certain kinetic energy from emitting acoustic phonons. This effect slows the formation of the condensate.

One can estimate the rate of formation of the Bose condensate from an oversaturated gas by considering the phonon scattering integral into the ground state. Taking the limit as \(k \to 0\) of the final equation on page 114,

\[
\frac{d g_0}{dt} = \frac{\Xi_0^2 m^3 s_L}{4 \pi \rho \hbar^4} 16 \left[ (1+f_p) g_p (1+g_0) - f_p (1+g_p) g_0 \right]
\]

where \(p = 2ms_L\) is the momentum of those excitons which can enter the ground state by emitting one LA phonon. The states which are connected to the ground state all have the same energy, \(2ms_L^2 = 8K\). Suppose that the occupation number of these states is close to its equilibrium value, which in a condensed gas is given by the Planck function at that energy just like the phonon occupation number. Then let \(g_p = f_p + \delta g_p\) so that

\[
\frac{d g_0}{dt} = \frac{\Xi_0^2 m^3 s_L}{4 \pi \rho \hbar^4} 16 \left[ (f_p + \delta g_p)(1+f_p) + \delta g_p g_0 \right]
\]

in a 4K crystal,

\[\approx 2.1/\text{ns} + 11/\text{ns} \delta g_p g_0.\]

The ground state occupation number \(g_0\) will increase exponentially with time-constant \(11/\text{ns} \times \delta g_p\), as will the occupation numbers of all other low-lying states. Eventually, the occupation numbers of all the states which can emit phonons will reach their equilibrium values, and all the excess particles (those which will eventually fill the condensate) have momentum below \(2ms_L\).

From this point forward, putting excitons into the condensate becomes more difficult. The 'excess' excitons with energies between zero and 8K must absorb phonons, then some of them must end up in the state with momentum \(p = 2ms_L\), from where they can reach the ground state. The simulation shows that the excess occupation number \(\delta g_p\) becomes very small, and the growth of the condensate nearly linear in time, though faster than the linear increase at 2.1/\text{ns} that would occur for \(\delta g_p = 0\).

The following figures show a simulation of the following thought experiment. Resonantly create a gas of \(10^{18}\) orthoexcitons per \(\text{cm}^3\) (just above the critical density for orthoexcitons) all with kinetic energy \(3\text{meV}\) in a crystal held at 4K in which Auger decay is somehow forbidden. We see that the orthoexcitons fail to form a condensate within their 3\text{ns} lifetime against conversion to paraexcitons. This is in spite of the additional paths to the ground state afforded by TA phonon emission, for which
\[
\frac{dg_{q}}{dt} = \left\{ \frac{8}{15} \Xi_{zz}^{2} + \frac{1}{2} \Xi_{xy}^{2} \right\} m^{3} s T \left\{ \frac{1}{4\pi \phi} \psi^{4} \right\} 16 \left[ (f_{q} + \delta g_{q})(1+f_{q}) + \delta g_{q} g_{q} \right]
\]

in a 4K crystal, 
\[\approx 2.2/\text{ns} + 0.07/\text{ns} \delta g_{q} g_{q}\]

where the TA phonon connects the ground state to momentum \( q = 2ms_{T} \), corresponding to a kinetic energy of 0.7K.

Figure 63: Simulation of the growth of a Bose condensate through phonon emission.
a) Orthoexciton distribution 0.2ns after the initial condition which placed \(10^{18}/\text{cm}^{3}\) orthoexcitons at the kinetic energy 3meV (35K) in a simulated 4K bath.
b) Orthoexciton distribution after 2ns of simulated phonon scattering. The orthoexciton density has decayed through conversion to paraexcitons, and is now \(5 \times 10^{17}/\text{cm}^{3}\). The curve is the best fit Bose distribution, with gas temperature \( T = 3.79 \text{K} \) and chemical potential \( \mu = -0.12 k_{B} T \). (In this fit the integrated density is not a free parameter; it is determined by \( T \) and \( \mu \).)
c) The paraexciton distribution at two times after the start of the simulation. The curve is a saturated Bose distribution. The paraexciton gas is super-saturated, as the critical density for the singly-degenerate paraexcitons, \(2.7 \times 10^{17}/\text{cm}^{3}\) at 4K, is exceeded.
d) The growth of the occupation numbers for the ground states. The paraexciton ground state occupation number grows nearly linearly at approximately 15/\text{ns}.

The singly-degenerate paraexcitons have one-third the critical density of the triply-degenerate orthoexcitons, so the deposited density is over three times that required to form a paraexciton condensate. In figure 63 we see that the excess occupation number \( \delta g_{q} \) is quite small for the states with kinetic energy above 8K, from which excitons can enter the highly-occupied low lying states by LA phonon emission. At late times the paraexciton ground state occupation
number grows only linearly with time, though at a rate faster than the 2.1/ns which would occur if $\delta g_p$ were exactly zero.

The painfully slow formation of the paraexciton condensate is greatly helped by adding elastic scattering with the modest cross section of $\sigma = 0.25 \text{nm}^2 = 0.25 \times 10^{-14} \text{cm}^2$. Taking the limit as $k \rightarrow 0$ in the equation for elastic scattering from the previous section, we find the rate of increase in the ground state occupation number through elastic scattering is

$$
\frac{\partial}{\partial t} g_0 = n_Q \frac{4 \sigma}{2 \pi m} \sqrt{\frac{k_B T}{2 \pi m}} \times \left\{ \int_0^\infty \int_0^\infty g_p g_q \left[ 1 + g_{q'} \right] \frac{d q'^2}{2 m k_B T} \frac{d p^2}{2 m k_B T} + g_0 \int_0^\infty \int_0^\infty \left( g_p g_q \left[ 1 + g_{q'} \right] - g_{q'} \left[ 1 + g_p \right] \left[ 1 + g_{q'} \right] \right) \frac{d q'^2}{2 m k_B T} \frac{d p^2}{2 m k_B T} \right\}
$$

where $(q')^2 = p^2 + q^2$ and $n_Q = (m k_B T/2 \pi \hbar)^{3/2}$ is the quantum density. The quantity in front of the braces is equal to 0.18/ns for the conditions of our thought experiment.

The double integrals in the previous paragraph are potentially divergent. The first term in the curly braces diverges at its lower limits as the occupation numbers $g_k$ approach the fully saturated Bose distribution (i.e., the Planck distribution). The second term has an integrand which goes to zero as the $g_k$ approach a Planck distribution. Based on the numerical integrations, it appears that the quantity in curly braces is of order a few times $g_0$ because the exponential growth rate of the ground state occupation is 3/ns. (The growth rate of growth slows in figure 64c after about 3ns, but this is a numerical artifact which is more pronounced when the sampling of $g_k$ is coarser. The general feature of an exponential increase in $g_0$ is independent of the sampling interval and of the time step.)

The calculations above refer to a homogeneous gas of infinite volume, so the number of particles in the ground state can never reach a finite fraction of the total number of particles (unless the mechanism of filling the ground state leads to kinetics such as $\partial g_0/\partial t \propto g_0^2$, which would cause the ground state occupation number to diverge in finite time). In a finite system, the number of particles in excited states would be depleted by the filling of the ground state, and eventually the system would reach equilibrium. The time required to reach this stage depends on the effective size of the system, but not terribly strongly. For the situation with elastic scattering that we just considered, we found $10^4$ particles in the ground state within 3ns. Assuming the exponential growth continues, in 15 more nanoseconds there would be $10^{23}$ particles in the ground state.

The further formation of true condensate through exciton-exciton collisions is discussed by Kagan et al. [1992]. They conclude that the 'kinematic' steps, cooling and filling the low-energy states to high occupation number, are generally the slowest steps in Bose condensation.
Figure 64: The model of the previous figure, plus elastic scattering with $\sigma = 1\text{nm}^2$.

a) Orthoexciton distribution 0.2ns after the start of the simulation. The sharp peaks, corresponding to orthoexcitons which have emitted zero or one acoustic phonon since their creation, are only slightly reduced by elastic scattering.

b) Orthoexciton distribution after 2ns of simulated phonon scattering. The curve is the best fit Bose distribution, with gas temperature $T = 3.75\text{K}$ and chemical potential $\mu = -0.11 \ k_B T$.

c) The paraexciton distribution at two times after the start of the simulation. The curve is a saturated Bose distribution. Note the convergence at 8K kinetic energy.

d) The growth of the occupation numbers for the ground states. The paraexciton ground state occupation number grows nearly exponentially with an exponential rate near 3/ns. The curvature at 3ns is a numerical artifact related to the discrete sampling in exciton momentum $k$; it moves to later times as the sampling density in $k$ is increased.
APPENDIX C: EXCITON SCATTERING IN THE BORN APPROXIMATION

The Born approximation is not a good approximation for scattering between slowly moving excitons. The Born approximation assumes the particle wavefunctions are nearly undisturbed plane waves through the collision. For one exciton moving through another at 5meV kinetic energy this is not likely to be a good approximation, considering that the exciton binding energy is 150meV.

In Cu₂O we have not been able to directly observe elastic scattering between excitons, yet the presence of Auger decay is obvious. We found this counter-intuitive. The following estimates of scattering cross sections were made in order to get some feel for the possible relative sizes of the elastic and inelastic scattering rates.

Elastic scattering

Consider two excitons interacting through the Coulomb interaction. We ignore band effects, except that we must retain the different electron mass and hole mass in order to see any direct Coulomb interaction between the neutral particles. Let λₑ denote the ratio of the electron mass to the exciton mass and likewise λₕ.

For the initial state let us take one exciton to be at rest, the other with momentum \( \mathbf{p} \). The initial state is

\[
\Psi_i(r_{e1},r_{h1},r_{e2},r_{h2}) = \frac{1}{\Omega} \phi(r_{e1}-r_{h1}) \phi(r_{e2}-r_{h2}) \exp[i \mathbf{p} \cdot (\lambda_e r_{e2} + \lambda_h r_{h2})].
\]

where \( \phi \) is the electron-hole relative wavefunction, a Hydrogen 1s wavefunction \( \phi(\rho) = \exp(\rho/a_0)/\sqrt{\pi a_0^3} \). In the final state momentum \( \mathbf{q} \) has been transferred.

\[
\Psi_f(r_{e1},r_{h1},r_{e2},r_{h2}) = \frac{1}{\Omega} \phi(r_{e1}-r_{h1}) \exp[i \mathbf{q} \cdot (\lambda_e r_{e1} + \lambda_h r_{h1})] \phi(r_{e2}-r_{h2}) \exp[i \mathbf{p} \cdot \mathbf{q}].
\]

For the interaction potential we use the bare Coulomb interaction between each pair of particles, one particle from each exciton, and use SI units:

\[
V = \frac{e^2}{4\pi\varepsilon}[\frac{1}{|r_{e1}-r_{e2}|} + \frac{1}{|r_{h1}-r_{h2}|} + \frac{-1}{|r_{e1}-r_{h1}|} + \frac{-1}{|r_{e1}-r_{h2}|} + \frac{-1}{|r_{e2}-r_{h1}|} + \frac{-1}{|r_{e2}-r_{h2}|}].
\]

We consider first the direct interaction, with no exchange of electrons or holes. This matrix element is then

\[
\langle \Psi_f | V | \Psi_i \rangle = \frac{e^2}{\Omega q^2 \varepsilon} \left[ \frac{1}{[1+(\lambda_e q a_0/2)^2]^4} + \frac{1}{[1+(\lambda_h q a_0/2)^2]^4} - \frac{2}{[1+(\lambda_e q a_0/2)^2][1+(\lambda_h q a_0/2)^2]^2} \right] = \frac{8\pi a_0^3}{\Omega} \frac{1}{(q a_0)^2} \left[ \frac{1}{[1+(\lambda_e q a_0/2)^2]^2} - \frac{1}{[1+(\lambda_h q a_0/2)^2]^2} \right].
\]

where the terms in the brackets come from the Fourier transform of \( \phi^* \phi \), which is \( [1+q^2 a_0^2/4]^{-2} \), and \( E_b = e^2/(8\pi\varepsilon a_0) \) is the exciton binding energy. For either small momentum transfer \( q \), or small mass difference, we can approximate
\[ \langle \Psi_f | V | \Psi_1 \rangle \approx \frac{2\pi E_b a_o^3}{\Omega} \frac{q^2 a_o^2 (\lambda_e - \lambda_h)^2}{(1 + q^2 a_o^2 / 16)^6} \]

The direct Coulomb interaction goes to zero for equal electron and hole masses, or for zero momentum transfer \( q \), and goes to zero as \( q^{-10} \) for large momentum transfer.

The exchange contribution to the scattering matrix element does not go to zero for equal electron and hole masses. Let \( \Psi_1 \) be the wavefunction obtained by exchanging the two electron coordinates \( r_{e1} \) and \( r_{e2} \) in \( \Psi_1 \). Each of the six terms in the potential \( V \) contributes to the matrix element.

\[
\langle \Psi_f | V | \Psi_1' \rangle = \sum_{\alpha \beta} \frac{e^2}{\Omega (\alpha - \beta)^2} \times \]

\[
\{ \Phi_{\alpha - \lambda_e q} \Phi_{\beta - \lambda_h p} [ \Phi_{\alpha - q} \Phi_{\beta - \lambda_e p} - \Phi_{\alpha - q} \Phi_{\beta - \lambda_h p} - \Phi_{\alpha - \lambda_h q} \Phi_{\beta - \lambda_e p} ]
+ \Phi_{\alpha - \lambda_h q} \Phi_{\beta - \lambda_e p} [ \Phi_{\alpha - q} \Phi_{\beta - \lambda_e p} - \Phi_{\alpha - q} \Phi_{\beta - \lambda_h p} - \Phi_{\alpha - \lambda_e q} \Phi_{\beta - \lambda_h p} ] \}
\]

where \( \Phi_q \) is the Fourier transform of the electron-hole relative wave function \( \phi \). Evaluation of the double sum leads to a complicated expression which can be found in the paper by Bobrysheva et al. [1972]. In the limit of zero incident momentum, \( p = q = 0 \), the matrix element is independent of the mass ratio [Hanamura, 1977]:

\[ \langle \Psi_f | V | \Psi_1' \rangle = \frac{26\pi E_b a_o^3}{3 \Omega} \]

The matrix element for non-zero incident momentum is smaller.

Each combination of incident exciton spin states leads to a different combination of exchange terms. For collisions between two orthoexcitons with their spins aligned, the matrix element is exactly \( \langle \Psi_f | V | \Psi_1' \rangle \). Using the Born formula,

\[ \sigma_{o-o} = \frac{(m/2)^2 e^2}{\pi \hbar^4} |\langle \Psi_f | V | \Psi_1' \rangle|^2 = 4\pi \left[ \frac{13}{12} \right] a_o^2 \]

where I have used \( E_b = \hbar^2/(2\lambda_e \lambda_h m a_o^2) \). Using the mass ratio in \( Cu_2O \), the scattering length is \( 4.6a_o \). Within the same model, the interaction energy of a gas of spin-polarized orthoexcitons is

\[ \langle \Psi_f | V | \Psi_1' \rangle \Omega n_o = \frac{13\pi}{3} E_b n_o a_o^3 \approx 10^{-18} \text{ meV cm}^3 n_o \]

Kavoulakis et al. [1996a] have evaluated the elastic scattering cross-section in the limit of high incident momenta to be

\[ \sigma = \frac{33}{35 \lambda_e \lambda_h \hbar^2 p^2/2m} \pi a_o^2 \]

Auger decay

The motivation for this calculation was my observation that the calculations published both by Čulík [1966] and by Kavoulakis and Baym [1996] make the approximation that the matrix element of the dipole operator between two bands, say \( \langle u_{ck} | V | u_{vk} \rangle \), is independent of the
wavevector \( k \). A result of this approximation is the prediction that the Coulomb interaction cause negligible Auger decay in a gas of excitons at rest.

As an experimentalist, I was acutely aware that there is no dipole matrix element between the conduction and valence bands of cuprite at zone center (because the recombination luminescence is weak) but that there is a dipole moment between these bands at other points in the Brillouin zone (because the absorption length for green light is a couple of microns). Therefore, I adjusted the previous calculations of the Auger rate to include a dipole matrix element consistent with experiment. In the end, I still find quite a small Auger decay constant.

This is a simplification of what Čulik [1966] called “exchange collisions” and what Kavoulakis and Baym [1996b] called “process B”. We consider two excitons at rest. For this calculation we can ignore the difference between the electron and hole masses, but we need to differentiate the Bloch functions from different bands, as Auger decay involves an interband transition.

The initial state can be same as in the previous calculation, but here it is easier to us the momentum representation from the beginning. Letting \( u_{\alpha} \) denote the periodic part of the Bloch function for state with momentum \( \alpha \) in the conduction band, we have

\[
\Psi_1(\mathbf{r}_{e1}, \mathbf{r}_{h1}, \mathbf{r}_{e2}, \mathbf{r}_{h2}) = \frac{1}{\Omega} \sum_{\alpha} \frac{(4\pi a_0^3)^{3/2}}{\pi(1+\alpha^2 a_0^2)^2} u_{\alpha}(\mathbf{r}_{e1}) u_{\alpha}(\mathbf{r}_{h1}) e^{i\alpha(\mathbf{r}_{e1}+\mathbf{r}_{h1})} \\
\times \sum_{\beta} \frac{(4\pi a_0^3)^{3/2}}{\pi(1+\beta^2 a_0^2)^2} u_{\beta}(\mathbf{r}_{e2}) u_{\beta}(\mathbf{r}_{h2}) e^{i\beta(\mathbf{r}_{e2}+\mathbf{r}_{h2})}
\]

where the first factor in each sum is the Fourier transform of the relative electron-hole wavefunction. The final state is not an exciton, but rather a free electron and hole:

\[
\Psi_F(\mathbf{r}_{e1}, \mathbf{r}_{h2}) = u_{\alpha} e^{i\alpha(\mathbf{r}_{e1}+\mathbf{r}_{h2})}.
\]

The final state momentum \( k \) is determined by energy conservation, \( \hbar^2 k^2/2m_{\text{red}} = E_{\text{gap}} \).

\[
\begin{array}{c}
\alpha & e1 & \kappa \\
-\alpha & h1 \\
\beta & e2 \\
-\beta & h2
\end{array}
\]

\[
\begin{array}{c}
\alpha & e1 & \kappa \\
-\alpha & h1 \\
\beta & e2 \\
-\beta & h2
\end{array}
\]

Figure 65: Diagrams for the two terms of the Coulomb interaction which can produce this Auger decay. Time increases left to right. The solid lines are electrons and holes, with their momenta shown on the ends of the lines. The dashed line is the photon.

Only two of the terms in the potential make independent contributions to this Auger process; we may take only

\[
V = \frac{e^2}{4\pi \varepsilon} \left[ \frac{1}{r_{e1}-r_{e2}} - \frac{1}{r_{h2}-r_{e2}} \right].
\]

This has a matrix element between the initial and final states of (ignoring Umklapp terms)
\[ \langle \Psi_F | V | \Psi_I \rangle = \frac{(4\pi a_0)^3 \varepsilon^2}{\Omega^2 e} \sum_\alpha \langle u_{ck} | u_{ca} \rangle \langle u_{vk} | u_{ck} \rangle - \langle u_{vk} | u_{ca} \rangle \langle u_{vk} | u_{va} \rangle \]

The interband overlaps such as \( \langle u_{va} | u_{ck} \rangle \) must be zero when \( \alpha = k \) because Bloch functions of a given wavevector but different bands are orthogonal. The factor \((k-\alpha)^2\) in the denominator makes the points \( \alpha \) near \( k \) most important. For small \((\alpha-k)\) we can expand around \( k \) using \( k \cdot p \) perturbation theory:

\[ |u_{ca}\rangle = |u_{ck}\rangle + \frac{\hbar^2}{m_0} \frac{(\alpha-k)}{E_{ck} - E_{vk}} \langle u_{vk} | \nabla | u_{ck} \rangle |u_{vk}\rangle + \text{other bands.} \]

Thus the inner product is

\[ \langle u_{vk} | u_{ca} \rangle \approx \frac{\hbar^2}{m_0} \frac{(\alpha-k)}{E_{ck} - E_{vk}} \langle u_{vk} | \nabla | u_{ck} \rangle \]

There are two intraband overlaps in the matrix element which, for small \((\alpha-k)\) will be near one. We have

\[ \langle \Psi_F | V | \Psi_I \rangle = \frac{(4\pi a_0)^3 \varepsilon^2}{\pi^2 \Omega^2 e} 2 \sum_\alpha \frac{\hbar^2/m_0}{(E_{ck} - E_{vk}) (k-\alpha)^2 (1+\alpha^2 a_0^2)^2 (1+k^2 a_0^2)^2} \cdot \]

The sum must be approximated. There are two regions of \( \alpha \) which may make large contributions.

First, the summand is large for \( \alpha \) near \( k \), where there is an integrable singularity. To estimate the sum we expand the remainder of the summand to first order in \((\alpha-k)\). We assume that this expansion will hold over the entire Brillouin zone, all \( \Omega/a^3 \) terms in the sum where \( a \) is the lattice constant. Using the estimate of the matrix element of \( \nabla \) from the section 2.2,

\[
\langle \Psi_F | V | \Psi_I \rangle \approx \frac{(4\pi a_0)^3 \varepsilon^2}{\pi^2 \Omega^2 e} \frac{2\Omega}{a^3} \frac{(\hbar^2/m_0) k \langle u_{vk} | \nabla | u_{ck} \rangle}{(E_{ck} - E_{vk}) (1+k^2 a_0^2)^5} \frac{2a_0^2}{(1+\alpha^2 a_0^2)^2} \frac{a_0^3}{\Omega} \frac{0.2 \hbar^2/m_0 k^2}{2E_{gap}} \frac{e^2}{4\pi e a_0} \frac{1}{2a_0^2} \frac{1}{(1+k^2 a_0^2)^3} \]

\[
= 0.001 \frac{a_0^3}{\Omega} E_b. \]

The major reason the matrix element is so small is the large power of \( ka_0=5 \) in the denominator.

Second, the factor \((1+\alpha^2 a_0^2)^2\) in the denominator suppresses the terms with large \( \alpha \), so the part of the sum with \( \alpha \) near zero may dominate. Taking \( \alpha=0 \) in every factor except \((1+\alpha^2 a_0^2)^2\),

\[ \langle \Psi_F | V | \Psi_I \rangle \approx \frac{(4\pi a_0)^3 \varepsilon^2}{\pi^2 \Omega^2 e} \frac{2\Omega}{a^3} \frac{(\hbar^2/m_0) k \langle u_{vk} | \nabla | u_{ck} \rangle}{(E_{ck} - E_{vk}) k^2 (1+k^2 a_0^2)^2} \frac{2a_0^2}{(1+\alpha^2 a_0^2)^2} \frac{a_0^3}{\Omega} \frac{0.2 \hbar^2/m_0 k^2}{2E_{gap}} \frac{e^2}{4\pi e a_0} \frac{1}{2a_0^2} \frac{1}{(1+k^2 a_0^2)^3} \]

\[ = 0.005 \frac{a_0^3}{\Omega} E_b. \]

Regardless of the approximation scheme, it is clear the matrix element is no more than one percent of \((a_0^3/\Omega) E_b\).
The rate of Auger decay from Fermi’s Golden Rule is

\[
\Gamma = \frac{2\pi}{\hbar} \frac{\Omega}{(2\pi)^3} \int |\langle \Psi_F | V | \Psi_I \rangle|^2 \frac{m_{\text{red}}}{\hbar^2 q} \delta(q - k) \, 4\pi \, q^2 \, dq
\]

\[
= \frac{\Omega m_{\text{red}}}{\pi \hbar^3} |\langle \Psi_F | V | \Psi_I \rangle|^2.
\]

This rate \(\Gamma\) is the decay rate for an exciton in the presence of a density of excitons equal to one exciton per volume \(\Omega\). This is related to the Auger constant \(A\) by \(\Gamma = A \, \Omega^{-1}\) so

\[
A = \frac{\Omega^2 m_{\text{red}} k}{\pi \hbar^3} |\langle F | V | I \rangle|^2
\]

\[
\approx 3 \times 10^{-5} 10^{-4} \frac{ka_o}{2\pi \hbar} \frac{E_b}{a_o^3}
\]

\[
= 5/\text{ns} \, a_o^3 = 2 \times 10^{-21} \text{cm}^3/\text{ns}.
\]

This is nearly the same as the estimate by Kavoulakis and Baym for this process, who used very different approximations.

**Comparison of the rates**

We have simple calculations of elastic and inelastic scattering within the same model. Using parameters appropriate to Cu_2O, the elastic scattering cross-section is \(\sigma \approx 4\pi(3\text{nm})^2\) and the Auger constant is \(A \approx 10^{-21}\text{cm}^3/\text{ns}\). In the model, elastic scattering is faster than Auger decay whenever the mean exciton velocity is greater than about 1 cm/s. In this sense, this appendix provides no insight into the situation in real cuprite.

On the other hand, we have seen how the Auger rate could have been much larger. The greatest limit to the calculated Auger rate was the large power of \(ka_o\) in the denominator of the matrix element. The reason for this factor was that in our model the interaction touches only one carrier in each exciton. In order for the other carrier to have the necessary final state momentum, \(k\), that momentum must be present in the electron hole relative wavefunction of the incident excitons. In a hypothetical semiconductor for which the Born approximation of these rates is good, and in which the excitons are more tightly bound (smaller \(a_o\)) and in which the band gap is smaller than in cuprous oxide (smaller energy carried away by the carriers, thus smaller \(k\)) we would have an explanation for an Auger rate which is faster than the elastic scattering rate.
APPENDIX D: CROSS-REFERENCE FOR FIGURES

The following table summarizes the experimental conditions for each of the figures which presents results. Figures of an explanatory nature have been omitted.

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<td>57</td>
<td>Time Evolution</td>
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<td>Luminescence Spectrum</td>
<td>Experimental</td>
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<td>10^8</td>
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<td>strain well, late time shown</td>
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<td>29, 65, 30</td>
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<td>10ns</td>
<td>10^8</td>
<td>2K</td>
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<td>10^9</td>
<td>2K</td>
<td>strain well</td>
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<td>Pulse width</td>
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<td>Time-resolved Spectra</td>
<td>Experimental,</td>
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<td>$5 \times 10^{11} / \text{cm}^2$ - $1 \times 10^{15} / \text{cm}^2$</td>
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<td>Power Dependence</td>
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<td>2K</td>
<td>no exciton motion</td>
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<td>Numerical</td>
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<td>elastic scattering $\sigma = 50 \text{nm}^2$</td>
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<td>Numerical</td>
<td>0.5ns</td>
<td>$1.3 \times 10^{15} / \text{cm}^2$</td>
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<td>elastic scattering $\sigma = 50 \text{nm}^2$</td>
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<td>Numerical</td>
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<tr>
<td>64</td>
<td>122</td>
<td>Time-resolved Spectra</td>
<td>Numerical</td>
<td>5ps</td>
<td>$2.5 \times 10^{18} / \text{cm}^3$</td>
<td>4K</td>
<td>no Auger decay, $\sigma = 0.25 \text{nm}^2$</td>
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Assuming that in this paper ‘log’ means to base ten reconciles the figures with the text.


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