Excitons in cuprous oxide
Fishman, Dmitry
Chapter 2

Paraexcitons versus Orthoexcitons
in a quest for Bose-Einstein condensation

In order to see whether one can make an excitonic Bose-Einstein condensate, one firstly needs to have a look at the statistical gas parameters. As an example, the lifetime is considered to be an extremely important parameter. It should be long enough to keep a sufficient density while at the same time thermalization with the lattice should occur fast enough to reach the critical quantum density. Since both types of excitons discussed in Chapter 1 reveal bosonic behavior, both of them can theoretically form a condensate. In this chapter we discuss which one is the best candidate.

In this chapter we present a few experiments aiming at the determination of 1s orthoexciton and paraexciton gas parameters. We focus mainly on the determination of important parameters as the gas temperature, the chemical potential and the population dynamics. In addition, the reader will be introduced to the principles of ultrafast time-resolved spectroscopy and time-resolved luminescence spectroscopy.
2.1. Orthoexciton gas.

Since the orthoexciton transition from the 1s excited state to the ground state is quadrupole allowed, it is relatively easy to study this gas using luminescence spectroscopic techniques. Due to this, orthoexcitons have been studied intensively over the past few decades [1, 2]. In this section we will discuss the results of the one of the recent optical studies, more fully described in K. Karpinska et al., [3]. The main goal of this investigation was to establish the statistical gas parameters and to obtain some information on the temporal evolution of the orthoexciton gas after initial excitation using time-resolved experiments. Some of the experimental techniques are discussed later on in section 2.2. Here we focus mainly on the results with only brief references to the key experimental parameters.

2.1.1. Time evolution of the orthoexciton gas.

Karpinska et al. [3] performed time-resolved experiments using a traveling wave optical parametric amplifier pumped by 1kHz, 1.55 eV, 120 fs pulses produced by an amplified Ti:Sapphire laser system to excite the excitons. The 150 fs excitation pulses (1.4 – 2.5 eV) were focused on a sample with a spot size of about 100 μm. The exciton emission was detected by a Hamamatsu streak camera system operating in photon counting mode with a temporal resolution of 10 ps. The experimental spectral resolution function is measured to be of a Gaussian type with a full width at half height \( \Gamma = 0.37 \) nm.

Figure 2.1 shows the time evolution orthoexciton luminescence spectrum after excitation with a 150 fs pulse of 1.4 eV energy at \( T = 7 \) K. Initially, a broad spectrum is observed dominated by the phonon-assisted transitions reflecting the occupation of the excitons in the higher levels. Despite the fact that the excitation was to a higher lying band, [3], which is a rather indirect way of excitation, no initial growth of the luminescence has been observed, and the exciton creation appears to be instantaneous upon excitation within the experimental resolution of 10 ps. As time progresses both the shape and the integrated intensity of the emission change. The former reflects the cooling of the exciton gas and thus the relaxation of the distribution of occupied states, whereas the latter reflects the temporal decay of the total exciton population. The direct and phonon-assisted peaks become well resolved for delay times longer than 200 ps, and show similar long time decay dynamics.
Fig. 2.1. Time evolution of the orthoexciton emission spectrum after two-photon excitation with 1.4 eV photons. Cu$_2$O crystal of [100] orientation. The lattice temperature is $T = 7$ K, [3].

As described in Chapter 3, one can determine the statistical gas parameters by fitting the phonon-assisted emission line with Eq. 1.18. The parameters resulting from the fitting of this function to the time-resolved spectra are shown in Fig. 2.2. The cooling of the gas, shown in Fig. 2.2a, shows a bi-exponential behavior with decay times $\tau \sim 0.2$ ns and $\tau \sim 6$ ns. The initial, fast, cooling occurs via optical phonon emission and down-conversion to the paraexciton state, [3]. Once the kinetic energy of the excitons becomes too low for this process, the relaxation occurs via acoustical phonon emission with a relatively long decay time. The chemical potential, shown in Fig. 2.2b, decays faster than the temperature, with a time constant $\tau \sim 1$ ns. This decay is essentially due to the loss of particles. Consistently, the integrated intensity (Fig. 2.3) of the luminescence shows a similar decay time ($\tau \sim 1.4$ ns).
Fig. 2.2. The time dependence of the exciton gas temperature (a) and the chemical potential (b) as obtained from an analysis of the phonon-assisted emission line, depicted in Fig. 2.1, using Eq. 1.18 [3].

Fig. 2.3. Temporal decay of the integrated intensities of the total, direct (DI), and phonon-assisted (PA) luminescence. The solid line is a fit to a single exponential decay. Excitation energy 1.4 eV, $T = 7$ K [3].
The \((n,T)\) phase diagram is shown in Fig. 2.4. The line represents the phase boundary, whereas the symbols represent the experimental data from Fig. 4.2 a,b (using Eq. 1.18 to determine the density). Unfortunately, the state of the gas follows the Bose-Einstein condensation phase boundary without ever crossing it. A similar result was observed in [4].

![Phase Diagram](image)

**Fig. 2.4. \((n, T)\) phase diagram. The solid line is the Bose-Einstein condensation boundary. \(n\) is calculated using Eq (1.18).**

Different explanations have been proposed for this so-called *quantum saturation* effect. In [5] it has been suggested that the quantum saturation phenomenon originates from the fact that the orthoexciton gas is not in an equilibrium state so that the number of particles is not well defined. The results discussed here do not support this conclusion. The kinetic energy distribution of the orthoexciton gas can be described with a very good accuracy by the Bose distribution, and, moreover, the decay of the chemical potential coincides with the particle decay obtained independently from the experiment. Therefore, one may conclude that the orthoexciton gas is in fact in quasi-equilibrium, and the particle density is indeed a well defined number. A few other explanations have also been suggested: dominant Auger recombination and/or strong spatial inhomogeneity, [6]. Both these effects are expected to have only a marginal influence on the decay kinetics. Finally, Ell *et al.* [7] presented an analysis of the orthoexciton relaxation including polaritonic effects. The main conclusion of that analysis is that the so-called polaritonic ‘bottle-neck’ effect prevents formation of an
orthoexcitonic Bose-Einstein condensate at \( k=0 \). However, as pointed out in [8] the authors assumed in their model an infinite volume and it is not clear to what extend their conclusions would change when the finite volume relevant to experiments is taken into account.

Independent of the origin, the experiments clearly show that the gas adjusts its quantum properties to the density and temperature and that it is in quasi-equilibrium. Apparently the particle decay is faster than the cooling rate, which inhibits a BEC transition. The eager reader may find more discussion, and a comparison to the paraexciton density evolution at the end of the current chapter.

### 2.1.2. Mechanisms of orthoexciton loss.

Several mechanisms of exciton loss were proposed in literature [3, 9, 10]. It is important where the exciton gas was investigated, in the bulk or near the surface. Since the cubic symmetry near the surface is broken, one may expect additional mechanisms of particle decay. The loss processes described in this paragraph consider bulk excitons only. Some of the described mechanisms work for both types of excitons. However, here we mainly focus on orthoexciton gas. Some additional mechanisms relevant to paraexcitons are described in paragraph 2.2.

Figure 2.5 depicts several processes which may influence the orthoexciton and paraexciton population: transition to the ground state with the emission of photon (panel 1), phonon-assisted orthoexciton down-conversion (panel 2), Auger processes for ortho- and paraexcitons (panel 3) and spin-flip scattering ortho→paraexciton conversion (panel 4).

Since the optical transition (Fig. 2.5, panel 1) to the ground state is only quadruple allowed, the transition rate is quite small, which means that the time constant should be longer than the one observed from experiment, [11]. The dominant relaxation channel is the phonon-assisted ortho→para conversion (Fig. 2.5, panel 2).

The Auger mechanism (Fig. 2.5, panel 3), in which the scattering of two excitons causes one to recombine and the other to excite to a higher lying level, was initially proposed by Hulin et al. [12] and is also discussed in for instance [13]. For an exciton-gas density \( n \), the rate of decay is \( A \) times \( n \), where \( A \) is the Auger constant. Considering only these mechanisms and assuming a spatially uniform gas density, the initial decay rate of orthoexcitons is given by:

\[
\frac{dn_0}{dt} = -\frac{n_0}{\tau_i} - An^2 - Dn_0, \quad (2.1)
\]
Fig. 2.5. Schematic diagram of ortho and paraexciton state interaction – possible processes of exciton losses. 1 – optical transition to the ground stat; 2 – phonon-assisted down-conversion process; 3 – Auger process; 4 – spin-flip scattering ortho→paraexciton conversion;
where $\tau_i$ is the exciton lifetime due to recombination at impurities and $D=1.2$ ns$^{-1}$ is the phonon-assisted down-conversion rate into paraexcitons, which has been measured at low gas density [14]. Moreover, one must take into account the re-generation of ortho and paraexcitons by the same process. In general, due to the different spin states of 1s excitons, there are actually three possible Auger constants, corresponding to various collisions between ortho and paraexcitons. We can write these ‘spin-dependent’ Auger constants as $A_{oo}$, $A_{op}$, and $A_{pp}$. For simplicity we will assume that these are all equal. The rate equations for the ortho ($n_o$) and para ($n_p$) densities are given by:

$$\frac{dn_o}{dt} = -\frac{n_o}{\tau_i} - 2An_o + \frac{3}{4}An^2 - Dn_o,$$  \hspace{1cm}  (2.2)

$$\frac{dn_p}{dt} = -\frac{n_p}{\tau_i} - 2An_p + \frac{1}{4}An^2 + Dn_o,$$  \hspace{1cm}  (2.3)

where the total exciton density is $n=n_o+n_p$. On the right-hand side of each equation the second term represents pure Auger decay, and the third term represents re-generation of excitons from ionized e–h pairs. The factors 3/4 and 1/4 originate from the ortho and para degeneracies.

The value of the Auger constant reported in literature varies widely, ranging from $10^{-16}$ to $10^{-22}$ cm$^3$/ns [6, 9, 15-19]. To elucidate the influence of the presence of Auger processes at high density on the orthoexciton decay we have performed luminescence experiments using intense cw excitation at 532 nm. Fig. 2.6 shows the power dependence of the integrated phonon assisted luminescence as function of the excitation power [20]. The intensity shows a sub-linear growth upon increasing excitation power, and finally saturates for powers exceeding 30 mW. The behavior prior to saturation is well described by a square root of the excitation power dependence (solid line in Fig. 2.6). Since the particles produced by the Auger process reform into both orthoexcitons and paraexcitons one should expect such a nonlinear behavior (see also Eq. 2.1). The same result was observed in [1, 21]: the intensity increases by the square root of the orthoexciton population.
Recently, Kavoulakis and Mysyrowicz [11] have suggested that orthoexcitons at high densities primarily decay by a spin–flip processes (Fig. 2.5, panel 5) rather than by Auger processes. In this case, two orthoexcitons scatter and exchange an electron or a hole, producing two paraexcitons that subsequently release their excess kinetic energy by phonon emission. The decay of orthoexcitons by this ‘spin–flip scattering’ process (plus phonon-assisted down-conversion) is given by:

$$\frac{dn_O}{dt} = -2Bn_O^2 - Dn_O, \quad (2.4)$$

where B is the spin–flip constant. Two main factors distinguish this process from the Auger mechanism. First, this is a ‘one-way process’, because two relaxed paraexcitons do not have sufficient energy to produce two orthoexcitons. Second, the total exciton number is conserved. Kavoulakis and Mysyrowicz predicted the ortho-para spin-flip conversion scattering rate being $B = 1.5 \cdot 10^{-16}$ cm$^3$/ns [11]. The ortho and para rate equations for spin–flip scattering are given by:

$$\frac{dn_O}{dt} = -\frac{n_O}{\tau} - 2Bn_O^2 - Dn_O, \quad (2.5)$$
where we have again included the defect-induced nonradiative recombination time, $\tau_i$, which in natural-grown crystals is typically about 300 ns [14, 22]. Adding the two equations indeed shows that this process conserves the total exciton density ($n_O + n_P$) if one neglects the slow recombination at impurities. The relevance of spin-flip processes has been discussed by Kubouchi et al. [23] using mid-IR absorption experiments: the paraexciton buildup rate increased with excitation power, suggesting a spin–flip constant $B=2.8 \cdot 10^{-15}$ cm$^3$/ns.

Finally, there is a possibility that two orthoexcitons can combine to form an excitonic molecule, so-called bi-exciton. The four-particle bi-exciton (two electrons and two holes) would have a much shorter Auger lifetime than excitons in the relatively dilute gas. However, bi-excitons have not been spectroscopically observed in Cu$_2$O [24], [25].

In conclusion, we discussed several mechanisms of orthoexciton loss (Fig. 2.5). Mainly, the orthoexciton population decay is driven by down-conversion to the paraexcitons at early times. The spin-flip scattering of orthoexcitons may be also effective at early times (few ns). The orthoexciton decay due to the Auger process of orthoexcitons should occur on a time scale of hundreds of ns. However, in the present relatively low density experiments, the Auger process does not seem to play an important role. In addition, paraexciton Auger processes could explain the re-generation of orthoexcitons at late times. However, the experimentally determined constants for this process are orders of magnitude below than predicted by theory.
2.2. Paraexciton lifetime: observation of an unobservable

As already mentioned in Chapter 3, the transition from the 1s paraexciton excited state to the ground state is forbidden for all orders of perturbation. This circumstance makes paraexcitons highly interesting from the solid state physicist’s point of view: the lifetime should now be long enough for sufficient gas cooling. On the other hand, it is highly unpleasant from the optical spectroscopist’s point: the detection of particles tends to be more difficult, since optical transition to the ground state is forbidden.

A method to make the 1s paraexcitons optically active is to break the symmetry. These kind of experiments are interesting, since the luminescence spectrum yields direct information on the statistical distribution of occupied states. There are several methods to break the cubic symmetry in cuprous oxide. The most ‘popular’ and well-studied method is the application of external pressure [26-28]. Such measurements have played an important role in the study of Cu$_2$O. Gross and Kaplyanskii’s observation in 1960 [29] of the polarization of the stress-split components of the 1s yellow state established its quadruple character and provided the experimental basis for Elliot’s 1961 band assignment, [30]. However, the paraexciton lifetime, determined from these experiments can not be named intrinsic in the sense that the system was substantially changed and, as a consequence, the lifetime was reduced. The symmetry can also be broken by the application of the electric fields. Some experiments, as well as electronic band structure calculations in the presence of electric field were presented in [31, 32].

Finally, also an applied magnetic field breaks the symmetry [33-35]. In this case, the optically forbidden paraexciton state $|S>$ mixes with the quadruple allowed $m_J=0$ orthoexciton state $|T_0>$, This leads to a weak, field tunable emission from the paraexciton state, proportional to $(g_e - g_h)^2 B^2$, while the radiative lifetime of the particles becomes inverse proportional to the $B^2$. More details are given in Chapter 1.

Below we discuss a few methods for the determination of the paraexciton lifetime in an unperturbed medium, using a novel experimental technique. After a short introduction to the experimental idea and details, we discuss how one can obtain statistical gas parameters from the measured optical response and introduce the early time dynamics of a paraexciton gas.
2.2.1. Intraexcitonic transitions

As suggested by Haken [36] and Nikitine [37], it should be possible to detect transitions between the ground state of the exciton with principle quantum number \( n=1 \) and higher lying levels in excitonic series. This type of absorption, which changes the angular momentum of the relative electron-hole wave motion from \( l=0 \) (s) state to \( l=1 \) (p) states (Fig. 2.7), is the equivalent to the absorption lines in atomic hydrogen known as the Lyman series. The line profile for the interexcitonic transitions has been recently calculated by Johnsen and Kavoulakis [38]. These authors were the first to point out that the absorption profile should provide direct information on the energy distribution of excitons occupying the \( n=1 \) state. In particular, in the presence of a Bose-Einstein condensation of excitons, the 1s-2p line should undergo a characteristic narrowing. This is a particularly valuable feature because these transitions are also allowed for paraexcitons [39].

A schematic picture of intraexcitonic transitions for the yellow series is presented in Fig. 2.7. The nominal transition energies of dipole allowed intraexcitonic and interexcitonic transitions for \( T=10K \) are shown in Table 2.1. 1s ortho- np energies are extracted from linear absorption and luminescence data, while 1s para – np energies are calculated by assuming a 1s ortho-para splitting of 12 meV, [40]. In addition to the intra-excitonic transitions in the yellow series, some of the yellow-green [41-43] and yellow-blue [44] transitions are also listed in the lower part of Table 2.1. Transitions to the indigo series are not included since they are higher in energy.

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Fig. 2.7. Schematic drawing of intraxcitonic transitions.
Initial state | Final state | Series transition | ΔE, meV
---|---|---|---
1s ortho | 2p ortho | y-y | 115,6
1s ortho | 3p ortho | y-y | 129,0
1s ortho | ∞ | y-y | 139,1
1s para | 2p para | y-y | 128,0
1s para | 3p para | y-y | 140,5
1s para | ∞ | y-y | 151,1
1s ortho | 2p ortho | y-y | 235,0
1s para | 2p para | y-g | 247,0
1s ortho | 1s ortho | y-b | 547,0
1s para | 2p para | y-g | 141,0

Table 2.1. Nominal transitions energies for inter- and intraexcitonic transitions at T=10K, [45].

![Graph](image)

Fig. 2.8. Induced-absorption spectrum due to the 1s-2p paraexciton transition obtained by Fourier spectroscopy technique. Cu$_2$O crystal of [100] orientation. Excitation energy 1.55 eV, T=4.2K, [44].

One of the first attempts to measure intraexcitonic transitions in cuprous oxide have been made by Goppert et. al. [46]. The Cu$_2$O sample was irradiated with a cw laser in order to create a population of n=1 excitons. The difference in the absorption spectrum of the irradiated sample with respect to a dark sample was measured with an infrared Fourier transform spectrometer. However, they did not succeed in observing a signal that might be attributed to the paraexcitons. More successful measurements using pulsed laser excitation
were reported out in [39, 44, 47]. For the experiment carried out in [44] a 120 fs, 1.55 eV pump pulse was used to excite the excitons. As expected, the presence of excitons causes an additional absorption which manifests itself as a decrease of the intensity of the transmitted light around 129 meV. The induced absorption spectrum, measured in [44], is presented in Fig. 2.8. In this experiment the repetition rate of the pump-laser in use was varied in order to estimate the lifetime of the 1s paraexcitons. It was found that the value is around 3 ms, which was in fact predicted by Jolk et al. [48]. However, as one can see from the Fig. 2.8, the width of the line is very narrow. Since the excitons will have some kinetic energy distribution at the measured temperatures, the induced absorption line should be much broader than the observed width of around 1 meV. This circumstance is giving a doubt to trust the presented result and it can be ruled out that the absorption line is due to an defect related absorption at the same energy as the paraexciton 1s-2p transition.

A different approach to detect the paraexcitons was taken in [22, 23]. In these experiments two colour time-resolved pump-probe spectroscopy was used to first excite the excitons by a high energy optical pulse in visible range and subsequently detect the intraexcitonic transitions with a mid-infrared pulse. Before turning to these kind of experiments we will first introduce the principles of pump-probe spectroscopy and give a description how to produce such pulses.

2.2.1.1. Principles of the ultrafast pump-probe experiment

In general, an experimental investigation aims to provide a data set with sufficient accuracy to ensure that all the relevant features of the system under investigation have been captured, [49]. In particular, time-resolved techniques focus on obtaining a high temporal resolution, which allows monitoring some of the fastest processes that occur in nature [50]. The limiting factor is the duration of the interaction between the investigated system and the measuring tool. For instance, observing a flying bullet that changes its position in less than a millisecond requires a photographic camera which can take a picture on this time scale. The trajectory of the bullet can be subsequently reconstructed from a series of successive snapshots. For example, typical motions on the molecular scale occur with speeds of about 1 kilometer per second, which implies that following movements of atoms over the length of a chemical bond (~$10^{-10}$ m) requires a shutter time of about one tenth of a picosecond (1 ps = $10^{-12}$ sec) [51].

Similarly to photography, in spectroscopy a system is investigated by analyzing its interaction with light. When a good time resolution is desired, or in other words when the goal is to obtain a “snapshot” of the system time evolution, the light-matter interaction must be reduced to a very short period of time. The most efficient way to realize this is by using
a flash of light instead of a continuous source. The system is thus observed only for the
duration of the light pulse. From a succession of such “snapshots”, the system’s dynamics
that occur on a timescale slower than the duration of the light burst can be reconstructed.

In general, for a large statistical ensemble in equilibrium, the average properties are not
time dependent. Therefore, in order to observe dynamical processes, a non-equilibrium
situation must be created initially. In other words, a sub-ensemble should be
instantaneously “marked” so that its time evolution can be observed separately from the rest
of the system. Fortunately, ultrashort laser pulses provide also a convenient means for an
impulsive excitation of a system. In this way, an ensemble having certain initial conditions
can be optically labeled and consequently its evolution can be followed separately from that
of the rest of the system.

This is exactly how the optical pump – optical probe experiment works (Fig. 2.9),
which represents one of the most utilized techniques in time-resolved spectroscopy. The
system under investigation is initially prepared in a non-equilibrium state by an interaction
with a first laser pulse, called “pump”. After a certain delay, a second laser pulse, usually
termed “probe”, investigates the current status of the system. By varying the delay between
the pump and the probe, the evolution towards equilibrium is obtained in the form of a
succession of snapshots. It is worth mentioning here that usually the system dynamics are
not monitored in real time, as they occur to fast to allow varying the time delay and
recording the data. Instead, a single snapshot is collected at a certain time delay, and then
the system is allowed to reach equilibrium, so that a new interaction with the pump would
yield the same effect. After that, a new snapshot is obtained by repeating the experiment for
a different delay between pump and probe.

Figure 2.9 Schematic representation of the pump-probe setup.
To exemplify these ideas, let us consider a practical example, Cu$_2$O. As mentioned in the previous paragraph, it is possible to provide and detect the transition between the n=1 and other terms with higher principal quantum numbers. At time zero, an ultrashort pump pulse (Fig. 2.10), resonant with the orthoexciton energy, promotes a certain amount of particles into the 1s excited state. The orthoexcitons then decay to paraexcitons, via, for example, down-conversion processes discussed in paragraph 2.1. In time, relaxation will take place and the system will return to the equilibrium situation. During this time-window, the initially excited excitons can be interrogated by a second (probe) pulse, exciting them from the 1s to, for instance, the 2p excited level. The observed spectroscopic signal is the difference in transmission of probe pulses without paraexcitons (no pump) and with paraexcitons (pump).

What kind of information can be obtained from this experiment? First of all, the lifetime of the 1s excited state is retrieved directly from the evolution of the pump-probe signal amplitude. Second, this would allow us to measure how fast the two types of excitons interchanged. For instance, the conversion time from 1s ortho to 1s para excited state. Additional information can be obtained by analysis of the transition lineshape, i.e. some statistical parameters like chemical potential and gas temperature.

![Fig. 2.10. Schematic representation of time-resolved experiment on intraexcitonic transitions.](image)
2.2.1.2. Experimental details

A schematic drawing of the pump-probe setup is shown in Fig. 2.11. The time difference between the pulses is provided by a mechanical computer-controlled delay stage. Both pump and probe pulses are focused on the sample to a diameter of 1mm and 0.3 mm respectively. The large spot size of the pump pulse ensures a better spatial overlap with the probe pulse and a more homogeneous probe region. The transmitted infrared light is collected using a commercial monochromator (Oriel) and then registered with a MCT detector cooled with liquid nitrogen.

The pump and probe photons needs to be of certain energy: pump in the visible range (1.5-2.5 eV) and probe in mid-infrared (100-150 meV). To produce such photons, a widely adopted method is based on optical parametric generation that uses some non-linear medium. In optical parametric generation a photon of certain frequency is split in to two photons of lower frequencies. It is based on a second order nonlinear optical process - three photon parametric interaction in non-centrosymmetric crystals, [52]. According to energy conservation, the frequency matching condition that need to be satisfied is $\omega_3=\omega_1+\omega_2$, where the subscripts 3, 1 and 2 corresponds to the pump pulse, and two parametric waves, which are called the signal and the idler, respectively. The parametric light converters can be tuned over wide frequency range.

Momentum conservation dictates that a pair of signal and idler waves can only be amplified efficiently when the phase-matching condition $n_3\omega_3=n_1\omega_1+n_2\omega_2$ is satisfied, simultaneously with frequency matching condition. The frequency of the idler and the signal can be tuned continuously through changing the indices $n_1, n_2$ and $n_3$ by controlling the crystal.

Fig. 2.11. Time-resolved pump-probe experimental setup.
orientation, it’s temperature, pressure or electric field applied to the crystal. The energy values of the signal and the idler are in the near-infrared region. In order to produce pulses in the visible range one needs to play with the signal and idler pulses: making their summation frequency or second harmonic generation. When one needs mid-infrared pulses around 100 meV, difference frequency generation can be used. This is, as well, a parametric process with the phase-matching conditions \( \omega_{DF} = \omega_S - \omega_I \) and \( k_{DF} = k_S - k_I \).

In our experiment two commercial parametric amplifiers (Topas, Light Conversion Ltd.) were used to produce pump and probe pulses. The optical scheme of a TOPAS in the horizontal and in the vertical plane is presented in the Fig. 2.12. From the figure one can easily notice that the input beam passes the nonlinear crystal five times. In the first pass (A1-M1) the diameter of the input pump beam is reduced by telescope system and further focused by a cylindrical lens in order to generate superfluorescence in the nonlinear crystal. The iris aperture A1 controls the intensity of the pump beam. The beam splitters BS1 and BS2 couple the beam to the fourth and the fifth pass. In the second pass the weak superfluorescence signal is amplified by several orders. These two stages act as preamplifiers and shape the beam. In the third pass (BS2-M3-M3’-M4-GP-M5-NC-DG-M7) a fresh pump-beam coming from BS2 passes through the nonlinear crystal and is incident on the grating. The grating selects the parametric signal in the fourth pass. The fifth pass starts from the beam splitter BS1 and forms the parametric seed beam for the power amplifier. This parametric seed beam is overlapped in space and time with the fresh pump beam on the mirror M11.

A commercial Ti:Sapphire amplified femtosecond laser system (Hurricane, Spectraphysics) is used as an initial pulse source for both optical parametric amplifiers (Fig. 2.13). Typically the output of such system delivers output pulses of 120 fs (1 mJ per pulse) at 1 kHz repetition rate, with a center wavelength of 800 nm.

The regenerative amplifier is designed to amplify individual pulses from a mode-locked Ti:Sapphire laser using a quasi-continuous high power Nd:YLF laser as pump source (Evolution, Spectraphysics). This laser system consists of a diode-pumped Nd:YLF laser head, optical resonator, acousto-optical Q-switch (© SpectraPhysics) and a LBO (Lithium triborate) frequency doubling crystal. Nd:YLF (Nd:LiYF₄) is used as a working laser medium. This compound has two laser transitions at 1053 nm and 1047 nm of different polarizations. Usually the 1047 nm radiation is utilized due to a higher gain cross section. Such a system is capable of producing pulses with an average power of about 7.5 W at 523.5 nm at a repetition rate of 1 kHz. The Q-switcher (© SpectraPhysics) can be described as follows. A special designed piezo-electric transducer generates an ultrasonic stationary wave in a transparent medium. The photo-elastically generated periodicity of high and low refractive indexes works as an optical phase grating.
Fig. 2.12. Schematic drawing of the optical parametric amplifier. A: iris aperture; Bs – beam splitter, L – lens, Cl – cylindrical lens, M – mirror, Cm – cylindrical mirror, NC – nonlinear crystal, TD – time delay, DG – diffraction grating, GP – path compensation glass plate.
Before entering the regenerative amplifier, femtosecond pulses are stretched in order to avoid damage of the optics inside the amplifier cavity due to self-focusing. When a pulse is stretched its peak power is distributed in time and hence its power density is lowered. The stretcher is based on dispersion by diffraction gratings.

The source of the femtosecond pulses (MaiTai, Spectraphysics) is the mode-locked Ti:Sapphire resonator pumped with a diode laser. The cw diode-pumped laser (Millenia, Spectraphysics) emits 532 nm light with an output power of about 5W. Since Ti:Sapphire has a broad absorption band in the blue and green region the output of the 532 nm cw-laser acts as an ideal pump. This system delivers continuously tunable pulsed output at 80 MHz repetition rate over a range of near infrared wavelengths from 790 - 810 nm with a pulse width of about 80 fs.

The described system can be operated essentially as a ‘black box device’.

For these experiments described, we used a [100] platelet sample of Cu$_2$O with a thickness of 200 μm, cut from a crystal which has been grown by a floating zone technique. The samples was kindly provided by A.Revcolevschi (University of Paris IV) The sample was polished and mounted in a continuous flow cryostat (Cryovac) (base temperature 1,2 K).
2.2.2. Thermally-induced up-conversion

Here we describe another method of probing the 1s paraexciton excited state. This method is based on a thermally induced up-conversion process, partially described in section 2.1.

2.2.2.1. Principle of the experiment

As mentioned in section 2.1, there are a few processes which influence the ortho and paraexciton population. One process involves paraexcitons which are ‘converted’ into orthoexcitons via a thermally induced spin-flip (Fig. 2.14). The energy gap of the exchange splitting is around 12 meV, which is in the order of 140K. If the gas temperature is low enough, at late times, when all ‘normal’ orthoexcitons already decayed, we can detect a weak luminescence from the orthoexcitons, which result from paraexciton up-conversion. Moreover, at high temperatures the particles will have high kinetic energy, increasing the probability of the up-conversion through an Auger process.

![Fig. 2.14. Schematic representation of the time-resolved luminescence experiment. Since the orthoexciton 1s level is populated from paraexciton level, the detected luminescence reflects the amount of paraexcitons.](image)

This experiment can be done in a time-resolved fashion. The temporal dynamics is achieved by triggering the excitation source and detection system. Once the system ‘knows’ when the sample was excited it can activate the detection system at any time after the researcher prefer. This technique has, not surprisingly, worse resolution than the pump-
The probe experiment described in the proceeding paragraph, it is limited by the response time of the detection system, the shape of the excitation ‘pulse’ and the response time of the attendant electronics. But it is useful to measure a signal at long time up to \(ms\) with minimum resolution of few tens of ns. If one would like to provide such times in pump-probe experiments, one needs to construct a delay line with a distance from Groningen to Amsterdam.

It is important to note that in such experiments we do not detect the paraexciton gas by itself. We cannot estimate its temperature or other statistical parameters. Moreover, the lifetime of the excitons at 100K differs from the lifetime at 4K, due to the changes of the diffusion coefficient, for example.

The below described experiments were performed at Gonokami’s Group by M.Otter, N.Naka and K.Yoshioka at University of Tokyo [53] and are more fully described in [54].

### 2.2.2.2. Experimental details

The experimental setup is shown in Fig. 2.15. All measurements were done at a sample temperature of about 77 K. At this temperature the para-to-ortho conversion is efficient enough to see the luminescence (Fig. 2.4 part 4). At 77 K the transition rate is \(10^8\) higher than for the temperatures of 4 K.

A continuous wave argon ion laser (5W, 514 nm, Millennia - Spectra Physics) is used as a pump for the mode-locked Ti-Sapphire system (Mira 900 laser, Spectra Physics). The optical cavity is specifically designed to utilize changes in the spatial profile of the beam.

![Diagram](image)

**Fig. 2.15. Time-resolved luminescence experimental setup.**
produced by self-focusing in the Ti:Sapphire crystal. The output pulses (200 fs, 800 nm, repetition rate of 76 MHz), are fed into a compact regenerative amplifier system (RegA 9000, Coherent Inc.). The diode laser (Verdi, Coherent Inc.) operated at 10 W is used as a pump source.

The excitation pulse is focused on the sample by a lens (f=10 cm). The sample is placed in a continuous flow cryostat with a base temperature of 77 K. The emitted light is collected into a photomultiplier (R 636-10, Hamamatsu). A filter (XB106, Omega optical) cuts all the wavelengths except for the range 605 to 615 nm. The integrated luminescence intensity temporal dynamic, averaged over a few hundred pulse periods, is was recorded with a digital oscilloscope (Textronix TDS 744A).

For the thermally-induced up-conversion experiments we used few [100] platelet samples of Cu₂O of different crystal qualities with a thickness of around 200 μm, cut from a crystal which has been grown by a floating zone technique. The samples was partially provided by A.Revcolevschi (University of Paris IV) and M.Gonokami (University of Tokyo).
2.2.3. Lifetime and discussion of exciton loss processes.

The transient changes of the transmission in the vicinity of the intra-excitonic transitions after one-photon excitation ($E_p=2.07\text{eV}$) are presented in Fig. 2.16. The presence of excitons causes additional absorption bands, manifested as a decrease of the intensity of the transmitted probe beam near the intra-excitonic absorption energies. A summary of the dipole active intraexcitonic transitions is presented in Table 2.1.

![Fig. 2.16. Transient induced transmission spectrum originating from the presence of excitons in Cu$_2$O ([100] crystallographic orientation). Excitation energy 2.1 eV, bath temperature $T = 10 \text{K}$.](image)

The spectral width of the probe pulse is around 30 meV. As a result, one may expect to observe several intraexcitonic transitions within the probe energy range. As a matter of fact, the probe pulse spectrally covers 1s-2p orthoexciton transition, 1s-2p paraexciton and 1s-3p orthoexciton transitions (Fig. 2.16, Table 2.1). The energies of 1s-2p paraexciton and 1s-3p orthoexciton transitions are lying close to each other ($\Delta=1 \text{ meV}$). As was mentioned in §2.2.2.2., the spectral resolution of our detection system is about 0.3 meV. However, we can not resolve these two lines, since each line is thermally broadened: the width of the line at $T=8\text{K}$ is around 1.6 meV, [40] (see also §3.3).

The 1s-3p paraexciton transition line would definitely be preferable for investigation. However, there is an additional strong absorption band at those frequencies (Fig. 2.17), making experiments in this energy range more difficult.
The origin of this band is a topic of discussion. In [55-58] it was assigned to a transition between two different sets of excitons, i.e. between yellow and green exciton series. In [59] this band was assigned to a fundamental lattice vibration, though no indications of such a high-frequency fundamental vibration are available from inelastic neutron scattering studies [60] and lattice dynamics calculations [61]. Another possible explanation was given in [62], where it was assigned to silicon defect states. In [63] it was argued that this band is due to a multiphonon process. However, in [64] a comparative study of the temperature dependencies of the peak frequency and the band width on one hand and those of infrared and Raman active fundamental vibrations on the other hand showed the one-particle nature of this band. Finally, in [65] it was proposed that the 144 meV feature originates from a bound bi-phonon state split off from the two-phonon band $\omega(k)+\omega(-k)$.

Independent of the origin of the 144 meV band, it is obvious that the study on paraexcitons from 1s-3p transition is hampered by its presence. We therefore focus on lower energy para 1s-2p transition. Fig. 2.18 shows a few shots from the temporal dynamics of intraexcitonic transition lines at T=8K. First, the 1s-2p orthoexciton transition near 115 meV builds up in a few tens of picoseconds. After this, the 1s-2p ortho-
Fig. 2.18. Induced changes in the intra-exciton transmission spectrum at various times after excitation by one-photon absorption at 2.07 eV (~700 μJ/cm²). The thick black solid lines schematically indicate the paraexciton part. T=8 K. Cu₂O of [100] orientation (provided by A. Revcolevschi, University of Paris IV).

Fig. 2.19. Shift of the center of mass of the 1s-2p para / 1s-3p ortho transition line as a function of time due to the orthoexciton decay.
exciton band decays exponentially with a time constant of about 1.5 ns. This is indeed what one expects for the orthoexcitons, based on numerous fluorescence studies, [20, 66, 67] (and references therein). In the vicinity of the paraexciton 1s-2p transition, we also observe an induced absorption band with a similar build-up time. As time evolves, the centre of mass of this band shifts to lower energy (Fig. 2.19). This shifting saturates after about 1.5 ns. The origin of this shift lies in the near coincidence of the ortho 1s-3p and para 1s-2p energy levels (see Table 4.1). Also there is a shift of the paraexciton line itself; discussed in detail in §2.2.4. The ortho 1s-3p band has the same time dynamics as the 1s-2p ortho transition at 115 meV. As it was discussed above, the formation of the paraexciton occurs through an ortho-para down conversion process, and thus takes a longer time to

Fig. 2.20. Time dynamics of spectral changes induced with one-photon excitation at 2.07 eV and T=8K. The result was obtained by surveying $\Delta T/T$ values at certain parts of the spectrum (gate window width 0.5 meV): circles – 128 meV line (1s-2p para), triangles – 129 meV line (1s-3p ortho), grey line – 115.6 meV line (1s-2p ortho). Inset: 1s-2p paraexciton transition (semi-logarithmic scale). Cu$_2$O of [100] orientation (provided by A. Revcolevschi, University of Paris IV).
build up (general overview in Fig. 2.20). The observed time constant for the down conversion process is about 300 ps [22], which is consistent with earlier experiments, [39]. Since the 1s-2p paraexciton energy is slightly below the 1s-3p ortho energy, these two effects lead to a gradual shift of the observed band. Once the orthoexciton has decayed, the induced absorption around 130 meV is solely due to the 1s-2p para transitions.

The overview of the observed early time dynamics is shown in Fig. 2.20. From the inset in Fig. 2.20, it is clear that paraexciton decay has a double exponential behavior. The initial fast exponential decay ($\tau_1=1.5$ ns) is partly due to small contributions of the nearby 1s-3p orthoexcitonic transition and partly due to the up-conversion of hot paraexcitons back to the 1s orthoexciton state, which may subsequently decay radiatively.

The time constant for the decay of the para-exciton absorption after 1.5 ns can not be reliably determined from the present data, the only indication the data gives is that the lifetime is at best in order of a few tens of ns. This observation is contradicting expectations. As discussed above, the paraexciton lifetime should be extremely long (not ns), since the transition is forbidden in all orders of perturbation. Let us now discuss it somewhat more detailed.

### 2.2.4. Mechanisms of paraexciton losses.

The processes which influence the orthoexciton population are mentioned in paragraph 2.1.2 (Fig. 2.4). The processes for paraexciton decay are also partially discussed there. As one can see, some of the mechanisms for orthoexcitons are applicable for paraexcitons. Fig. 2.21 depicts the most important decay processes for paraexcitons: thermally induced up-conversion (panel 1), Auger recombination (panel 2) and paraexciton trapping by the crystal imperfections (panel 3).

One of the intrinsic decay processes is the thermally induced up-conversion of the paraexciton to the orthoexciton (Fig. 2.21, panel 1). The transition probability of such conversion is strongly temperature dependent and may be expressed by:

$$\rho_{P\to O} \propto e^{-\frac{\Delta}{k_B T}},$$

where $\Delta$ is the energy difference between the ortho and paraexciton states (12 meV). At elevated temperatures one can use this decay channel to indirectly observe the para-exciton decay by monitoring the luminescence from the upconverted ortho-excitons [54], as discussed in §2.2.2. At low temperatures, however, the transition probability is so low that this process can be neglected.
The Auger processes mentioned in §2.1.2 for the orthoexcitons could also limit the lifetime of the paraexcitons. From a study of the phonon-assisted emission of orthoexcitons, O'Hara et al. [6] came to the conclusion that the coefficient of Auger recombination process for ortho-excitons is as large as $A=7\times10^{-17}$ cm$^3$/ns.

![Schematic diagram of ortho and paraexciton state interaction – possible processes of paraexciton losses. 1 – thermally induced up-conversion; 2 – Auger recombination, 3 – trapping by impurities.](image)

**Fig. 2.21.** Schematic diagram of ortho and paraexciton state interaction – possible processes of paraexciton losses. 1 – thermally induced up-conversion; 2 – Auger recombination, 3 – trapping by impurities.
This channel should be equally effective for paraexcitons. The value reported by Wolfe et al. [67, 68] was about $10^{-16}$ cm$^3$/ns. On the other hand, Jolk et al. [48] have claimed, based on a pump-probe measurements involving the higher Rydberg series in the visible region, that the Auger coefficient is smaller by several orders of magnitude. Recent calculations [11] have also shown that the Auger process recombination rate should indeed be negligible given the long paraexciton lifetime.

In general, the Auger recombination of paraexcitons should be highly dependent on the density of the excitons as well as any decay process involving two particles. As an example, in Fig. 2.22, the time decay of the paraexcitons due to the is shown for different pump energy densities. Since the initial density of the excitons is different for different powers, one may consequently expect a higher contribution from the Auger process for the highest pump densities. However, the decay curves do not depend on the pump power density, showing that Auger processes are indeed irrelevant for the pump power densities used.

Fig. 2.22. Decay curve of the paraexciton population for different excitation powers. Results obtained from time-resolved luminescence experiment at 77K on the sample with high defect concentration. Excitation wavelength 800 nm, Cu$_2$O of [100] orientation. These experiments have been carried out at University of Tokyo by M.Otter, N.Naka, K. Yoshioko, M.Gonokami, [53], [54].
There is another process, which is not presented in Fig. 4.21, but which might be important. Since the sample has a different symmetry near the surface one can expect additional mechanisms of exciton loss. It is possible to check this experimentally. One may carry out the described above pump-probe experiment on 1s-2p paraexciton transition using for excitation photons of different energies. Since photons with different energies have a different penetration depth in the sample, one can vary the relative contribution from the surface. For example, the creation of the yellow electron–hole pair (C₁-V₁) by one-photon absorption (2.07 eV) leads to creation of excitons in the vicinity of the surface (penetration depth ~30 μm, [Katarzyna]). In contrast, two-photon absorption using 1.55 eV photons (penetration depth ~1 mm) primarily excites excitons in the bulk, [66]. In this latter case blue electron-hole pairs (C₁-V₂) are initially created with subsequent relaxation to the yellow series. Fig. 2.23a shows the induced absorption spectra of intraexcitonic transitions at different times after creation of the exciton gas using two-photon excitation. The normalized dynamics of the integrated spectra of the 1s-2p transition for both excitation methods are shown in Fig. 2.23b. The average excitation power was the same in both of the experiments.

![Fig. 2.23. (a) Induced changes in probe spectrum versus time using two-photon absorption excitation method with 1.55 eV (~200μJ/cm²), T=8K. (b) Early time dynamics of 1s-2p paraexciton transition. One-photon excitation at 2.07 eV – open circles, two-photon excitation with 1.55 eV – filled circles. T=8K, pump density ~200μJ/cm² in both experiments. Cu₂O of [100] orientation (provided by A. Revcolevschi, University of Paris IV).]
Since there is no difference for this sample in decay time constant for the gas created near the surface and in the bulk one can conclude that there is no additional observable process which contributes to the exciton losses due to the presence of the surface.

Furthermore, the presented result (Fig. 2.23b) again shows that Auger recombination does not play a significant role. The volume, where the exciton gas is created is different for discussed excitation methods. As it will be shown later on in §2.2.4, with one-photon absorption (2.07 eV photons) one may achieve densities of around $10^{18}$ cm$^{-3}$, while with two-photon absorption (2x1.55 eV) the density of the 1s excited paraexcitons is around $10^{17}$ cm$^{-3}$. Since the densities differ by an order of magnitude, one would expect a faster decay in the one-photon excitation case when Auger process would be important. This is clearly not observed.

In Fig.2.21 (panel 3) one more mechanism is presented which is based on the exciton trapping by crystal imperfections. Since the excitons diffuse in the crystal, there is some finite probability for them to be trapped by impurities. This process can definitely shorten the lifetime and, in particular for Cu$_2$O, it is extremely important since the paraexcitons exhibit a surprisingly high diffusion constant. Trauericht et al. [69] investigated the paraexciton gas in a potential trap and observed a tremendously high diffusivity. The value of diffusivity was much higher than it was predicted by standard deformation-potential analysis. As an illustration of the extreme diffusivity, Fig. 2.24 shows two spatial and time-resolved images of exciton luminescence, taken from the work by Trauernicht et al. [61]. The expansion of the cross-sectional area of the paraexciton cloud corresponds to a diffusion constant of 600 cm$^2$/s at 2K.

![Fig. 2.24. Time-resolved images of the paraexciton luminescence in Cu$_2$O at T=2K. The time difference between a) and b) is 400 ns. The dashed lines represents the spatial resolution. (Figure reproduced from [69] with permission).](image)
In order to investigate the influence of defects and impurities on the paraexciton lifetime we carried out time-resolved experiments (§2.2.2) for two samples of different qualities, named L sample (the sample was provided by M. Gonokami’s group, University of Tokyo) and S (the sample was provided by A. Revcolevschi’s group, University of Paris IV) sample for simplicity. Also luminescence spectra for L- and S-samples were measured: as it was mentioned in Chapter 1, the amount of impurities, i.e. sample quality, can be evaluated from photoluminescence experiments, [70]. The exact spectral structure and assignments of the lines lying inside band-gap are discussed in §3.3. The luminescence spectra for samples L and S are shown in Fig. 2.23a1 and Fig. 2.23b1. It is clear, that the paraexciton lifetime created in sample L is much longer (2 μs) than for the particles created in sample S (10 ns), (Fig. 2.25 a2,b2).

Fig. 2.25. **Left panels:** Luminescence spectra measured under identical experimental conditions for S–sample (a1) (sample provided by A.Revcolevschi’s group, University of Paris) and L-sample (b1) (sample provided by M.Gonokami’s Group, University of Tokyo). Excitation wavelength 532 nm, T=77K. **Right panels:** Paraexciton population time decay for S-sample (a2) and L-sample (b2) at 77K, measured by time-resolved luminescence technique. Excitation wavelength 800 nm. These experiments have been carried out at University of Tokyo by M.Otter, N.Naka, K. Yoshioko, M.Gonokami, [53], [54].
The amount of the impurities can be qualitatively evaluated from the comparison of the defect line strength with respect to the exciton luminescence line. Form panel a1 and b1 of Fig. 2.25 one may easily see, that samples L and S are different in the amount of oxygen and copper vacancies.

Fig. 2.25 shows that the ratio of the oxygen peak intensity to the exciton peak intensity for both oxygen peaks increases by about one order of magnitude when the lifetime decreases from the order of μs to ns, indicating that the oxygen vacancy concentration might influence the lifetime. More strikingly, however, is the difference in Cu vacancy concentration. For sample S, where the paraexciton lifetime is short, the ratio of copper vacancy intensity to exciton intensity is in order of $10^4$, whereas for sample L the ratio is in order of $10^{-1}$. The correlation of this ratio with the lifetimes strongly suggests that the main mechanism for paraexciton loss is trapping by Cu vacancy.

2.2.4. Exciton trapping by the crystal imperfections.

Exciton trapping by impurities in solids have been investigated theoretically and experimentally by several authors [12, 36, 61, 71-82]. Some models for capture into deep levels were proposed, namely multiphonon capture [83], cascade capture [84, 85] or Auger capture of free carriers [86-90]. None of these mechanisms can account for the experimental facts in Cu$_2$O, [91]. Another concept, Auger recombination of exciton via a deep defect level, was proposed in [91]. In this model the capture of an electron into a deep level may occur when a free exciton meets the defect. The electron from the exciton is captured by the defect, and the excess energy is transferred to the hole which is thereby highly excited into the valence band. Processes like this are known in scattering theory as rearrangement collisions. Such a capture of an electron by an defect is quite similar to the scattering of a proton by a hydrogen atom where the electron is picked up by the incident proton. Analogously, a hole may be captured into a deep level thereby exciting the electron into the conduction band. Using the general conclusion from [91], the coefficient for electron or hole capture depends on the bands from which the defect wave function is mostly composed.

In general, impurities in Cu$_2$O, as well as in other semiconductors, can form either charged or neutral potential traps. The excitonic capture, theoretically studied in [91] is based on the idea that when a free exciton approaches an defect, one of the electronic particles of the exciton is attracted by the ionized defect. If this particle (electron or hole) is captured by the defect, the excess energy is transferred to the other particle of the free exciton, which then is excited into the continuum in an Auger-like process. This basic process is illustrated in Fig. 2.26a for the case of a free exciton interacting with an ionized
defect. In our case the ionized acceptor is the vacancy state, formed by taking a copper ion \( \text{Cu}^+ \) out from the crystal (see also Chapter 1). Since this vacancy carries a negative charge, the hole of the free exciton can be attracted.

\[
W = \frac{2\pi}{\hbar} \int d^3k |M(k)|^2 \delta(E_i - E_f) D(k), \quad (2.10)
\]

**Fig. 2.26.** a) Illustration of the exciton trapping by the ionized defect. b) Interactions between the particles participating in the hole capture process.
Here $M(k)$ is the transition matrix element, $D(k)$ is the density of states in $k$ space of the final state. The $\delta$ function between the initial energy $E_i$ and the final energy $E_f$ enforces energy conservation. Assuming parabolic energy bands and an isotopic matrix element one can obtain:

$$ W = \frac{2mk}{\pi\hbar^3} |M(k)|^2, \quad (2.11) $$

The complete Hamiltonian that describes the electron, the hole, and the defect contains a background term $H_0$ plus the three interaction terms shown as well schematically in Fig. 4.26b:

$$ H = (H_0 + U_E) + (V_1 + V_2), \quad (2.12) $$

In our calculation the hole-defect interaction has been considered as a perturbation causing the transition, meaning that we have to calculate the matrix element of $V_2$. The transition matrix element in the Born approximation may be written as follow:

$$ M = \langle x^K_i | V_1 | y^\kappa_k \rangle, \quad (2.13) $$

where $|x^K_i\rangle$ is the eigenstate ($H_0 + U_E$) of the free exciton and $|y^\kappa_k\rangle$ is the eigenstate of the hole bound to the defect plus the highly excited electron ($H_0 + V_1$). The next step, of course is to give the explicit wave functions for the $|x^K_i\rangle$ and $|y^\kappa_k\rangle$. The eigenstates of a free exciton with a momentum $K$ are expanded in terms of eigenstates of the crystal with a lattice of $L$ sites [92]:

$$ |x^K_i\rangle = \psi^i(r_1, r_2) u_{c, K, \beta} (r_1) u_{v, k_2} (r_2) = $$

$$ = \frac{1}{L^{1/2}} \sum_{\beta} A'_{K, \beta} e^{i \beta \cdot \mathbf{k}} e^{i (K - \beta) \cdot r_2} u_{c, \beta} (r_1) u_{v, K - \beta} (r_2), \quad (2.14) $$

Here $u_{c, \beta}(r_1)$ and $u_{v, \beta}(r_2)$ are the periodic parts of the electron and hole Bloch functions, and $A'_{K, \beta}$ is the Fourier transform of the internal wave function $\psi(r_1, r_2)$ of the exciton. The final state $|y^\kappa_k\rangle$ is described by a product of the wave functions of the hole bound to the defect and that of a highly excited electron. In general, the wave function of a hole bound to the defect is again a superposition of Bloch functions [93];
whereas the highly excited electron with momentum $\kappa$ is described by:

$$\phi(r_2) = e^{i\kappa_2} u_{c,\kappa}(r_2), \quad (2.16)$$

Finally, the interaction potential between the particles are of the form (screened Coulomb interaction):

$$V(r) = \frac{e^2}{\varepsilon r} e^{-k_s r}, \quad (2.17)$$

In order to take into account many-particle effects in a simple approximation, here the inverse screening length $k_s$ was added since there is a screening of the Coulomb interaction. Now we have all the prerequisites to calculate the transition matrix element $M$. By inserting the wave functions from Eq. 2.14, 2.15, 2.16 as well as the interaction (Eq. 2.17) into the Eq. 2.13 for the matrix element we get for the leading term:

$$M = \frac{1}{L} \int d^3 r_1 d^3 r_2 \sum_{n,\beta'} C^*_{n,\beta'} \sum_{n,\beta} C_{n,\beta} e^{-i\beta_1 r_1} u^*_{n,\beta}(r_1) e^{-i\kappa_2 r_2} u_{c,\kappa}(r_2) \cdot \frac{e^2}{\varepsilon r_2} e^{-k_s r_2} \left( \sum_{\beta} A_{K,\beta} e^{i\beta_1} u_{v,\beta}(r_1) e^{i(K-\beta)r_2} u_{c,K-\beta}(r_2) \right), \quad (2.18)$$

Now we exchange the integrations over $r$ and $\beta$, getting:

$$M = \frac{1}{L} \sum_{n,\beta} \sum_{\beta'} C^*_{n,\beta'} A_{K,\beta} \int d^3 r_1 d^3 r_2 e^{-i\beta_1 r_1} u^*_{n,\beta}(r_1) e^{-i\kappa_2 r_2} u_{c,\kappa}(r_2) \cdot \frac{e^2}{\varepsilon r_2} e^{-k_s r_2} e^{i\beta_1} u_{v,\beta}(r_1) e^{i(K-\beta)r_2} u_{c,K-\beta}(r_2), \quad (2.19)$$
First, the integral over $r_1$ can be executed immediately, yielding:

\[
M = \frac{1}{L} \sum_{n,\beta} \sum_{\beta} \int d^3 r_2 C^*_n A_{k,\beta} \delta_{n,\beta} e^{-ikr_2} u^*_k(r_2) .
\]

\[
e^{-k_ir_2} u_{v\beta}(r_i) e^{i(K-\beta)r_2} u_{e,K-\beta}(r_2), \quad (2.20)
\]

In order to calculate the remaining integral over $r_2$, the Bloch factors $u_{ck}$ are expressed by a Fourier series:

\[
u_{ck}(r) = \sum_{Q} B_{cQ}(k) e^{iqr}, \quad (2.21)
\]

Now allowing for the calculation of the final integral I over $r_2$:

\[
I = \sum_{Q,Q'} B^*_{cQ}(\kappa) B_{cQ'}(K-\beta) \frac{4\pi e^2}{\varepsilon} \frac{1}{k_s^2 + (K-\beta-K-Q-Q')^2}, \quad (2.21)
\]

The main contribution to this sum comes from the first Brillouin zone [94], i.e. $Q=Q'=0$, getting:

\[
M = \langle \chi^*_i | V | \chi^*_k \rangle = -\frac{4\pi e^2}{\varepsilon L} \sum_{\beta} \frac{A_{k,\beta} F_{vv} C_{c,K-\beta}}{k_s^2 + (K-\kappa-\beta)^2}, \quad (2.22)
\]

Here $F_{vv}$ is the overlap integral, which can be written as:

\[
F_{vv} = \frac{1}{L} \int d^3 r u^*_c(r) u_{v,K-\beta}(r), \quad (2.23)
\]

For the case of a ground exciton state (1s) some simplifications can be made. For instance, the overlap integrals containing functions of the same band are equal to unity.
$F_{v_r} = \delta_{v_r}$, whereas those with functions of different bands vanish, [95]. Furthermore, for isotropic parabolic bands the exciton wave function in real space may be written as:

$$\psi^{1s}(R, \rho) = e^{iKR} \left( \frac{a^3}{\pi} \right)^{1/2} e^{-a\rho}, \quad (2.24)$$

where $R$ is the center of mass coordinate, $\rho$ is the coordinate of relative motion and $a$ is the reciprocal excitonic Bohr radius.

The most difficult problem remaining now is to get some realistic simple approximation for the wave function of the hole bound to the defect. Since the a priori calculation of the defect wave function is beyond the scope of the present investigations, we will use one of the models frequently employed in literature, [93, 96-99]. It appears to be the fact that for the impurities there is no direct relation between the energetic position of the defect level and the spatial localization of the defect wave function [91]. For instance, we can use the effective-mass and $\delta$-potential model of Lucovsky [100], meaning that the localized defect potential is approximated by a $\delta$-function. The respective wave function with the localization parameter $\gamma$ for $\delta$-potential [100] and effective-mass 1s hydrogen-like wave function [88, 89] read as:

$$\psi^{1s}(r) = \left( \frac{\gamma}{2\pi} \right)^{1/2} e^{-\gamma r}$$

$$\psi^{\delta}(r) = \left( \frac{\gamma}{2\pi} \right)^{1/2} \frac{1}{r} e^{-\gamma r}, \quad (2.25)$$

The Fourier coefficients of the 1s exciton wave function and the defect wave function are given by, [88, 89, 100]:

$$A_{K, \beta} = \left( \frac{\alpha^3}{\pi} \right)^{1/2} \frac{8\pi \alpha}{\left( \alpha^2 + (K - \beta)^2 \right)^{3/2}}$$

$$C^{1s}(\beta) = \left( \frac{\gamma}{2\pi} \right)^{1/2} \frac{4\pi}{\gamma^2 + \beta^2}, \quad (2.26)$$
Some theoretical estimations of the capture coefficient for a 1s excited state are already done in literature [88, 89, 91, 93, 96-98, 100]: using the effective-mass defect wave function with localization from 0.5 to 4 lattice constants, the absolute value of the capture coefficient varies between $10^{-18} \text{cm}^3/\text{ns}$ and $10^{-14} \text{cm}^3/\text{ns}$. We are not going to repeat here this long and difficult calculation, but we do want to point out some of the conclusions arising from them. The transition probability happens to be strongly dependent on the localization parameter and the excitonic Bohr radius:

$$W \propto \frac{1}{\gamma^3 a_0^3}, \quad (2.26)$$

From qualitative considerations one expects that stronger localization causes a larger extension of the wavefunctions in $k$ space, which in turn should lead to an increased transition probability. In contrast, from Eq. 2.26 it follows the transition probability decreases with increasing localization. The reason for this surprising result is that for the scattering process the localization of the electron and hole within the exciton also plays an important role. The transition matrix element (Eq. 2.21) contains a product of the Fourier transforms $A_{K,\beta}$ and $C_{\nu\beta}$ of the hole and defect wave functions, whose shape is governed by the least localized one of the wave functions (the exciton). The defect wave function, which is more localized and has less variation in $k$ space, merely enters with its amplitude at $k=0$ which decreases with increasing localization.

Next conclusion is that the transition probability increases with the decrease of the excitonic Bohr radius (Eq. 2.26). Therefore, large capture coefficients are expected in a case of 1s paraexcitons in view of their extremely small free exciton Bohr radius of 0.7 nm.

The model we have discussed above contains the idea of a “single-shot” trap: once it traps the exciton it is not able to trap another one. In this case, we should be able to “switch-off” all impurities by the certain amount of excitons. In other words, if the exciton density is higher than some “critical” value, which depends on the defect concentration and on the quenching probability, the lifetime should increase. This actually strongly contradicts with the experimental results on L sample (the sample was provided by M.Gonokami’s group from University of Tokyo) presented in Fig. 2.27. For the simple calculation of the exciton gas density we can assume, that the probability of the absorption of the photon and the consequent creation of the exciton is $P=1$. For the pump energy densities used in the present experiment (Fig.2.27) we can achieve an exciton gas density up to $\sim 10^{19} \text{cm}^{-3}$, almost $10^4$ times higher, than the estimated defect concentration (see also Fig. 2.29). Apparently, we are not able to saturate the defect levels.
In order to explain the experimental results, we here propose a chain model of exciton trapping Fig. 2.28. The initial state of this process can be imagined as an ionized vacancy $V_{\text{Cu}}$ and a free exciton (Fig. 2.28a). Then a hole from the exciton will be captured by the ionized vacancy and the excess energy is transferred to the electron, which is excited into the continuum (Fig. 2.28b). Then, few processes can take place. For example, the acceptor hole and an excited electron form a bound exciton state (Fig. 2.28c). Recently, bound excitons were observed by Jang et al., [101]. Alternatively, recombination with another exciton at the same acceptor can take place Fig. 2.28e. This process can be described as a two-hole transition, [102]. Also, after process b, the defect can be again ionized upon simple recombination of an electron and hole (Fig. 2.28d). The copper vacancy, while it is still in an ionized state, can after all attract a second free exciton and repeat the process (Fig. 2.28a). Thus, once the procedure is initialized, it can continue in a kind of chain reaction (Fig.2.28).

![Excitation energy density](image)

**Fig. 2.27.** Paraexciton lifetime at 77K for different excitation powers. Results obtained from time-resolved luminescence experiment on the sample with high defect concentration. Excitation wavelength 800 nm, Cu$_2$O of [100] orientation These experiments have been carried out at University of Tokyo by M.Otter, N.Naka, K. Yoshioko, M.Gonokami, [53], [54].
Fig. 2.28. Illustration of the “chain reaction” exciton trapping.
For the present model of highly mobile excitons in a system containing traps, we can estimate the lifetime of the free excitons as a function of the defect density, assuming the diffusion coefficient is a known parameter. Random walks of a particle on a lattice that includes traps have been studied in [72, 76, 103-105]. Also for paraexcitons in Cu$_2$O some simulations are already done, [40], where the values of the diffusion coefficient vary from 0.5 to 20 cm$^2$/s. We also calculated the survival probability of an exciton diffusing with a coefficient $D$ in a matrix of quenching sites. The distance between these quenching sites is approximated by a Poisson distribution with average distance $L$. In the limit of a high density or at long times the temporal dynamics can be described by, [106]:

$$I(t) = I(0) \left( \frac{t}{\tau_{\text{diff}}} \right)^{\frac{1}{2}} \exp \left( - \frac{t^\beta}{\tau_{\text{diff}}^{\beta}} \right) \exp \left( - \frac{t}{\tau_0} \right), \quad (2.28a)$$

$$\tau_{\text{diff}} = \left[ 2\pi^2 (3/2)^3 D n_{1D} \right]^{-1}, \quad (2.28b)$$

Here $\tau_{\text{diff}}$ is a characteristic diffusion time and $n_{1D} = (n_{3D})^{1/3}$ or $n_{1D} = 1/L$ is the one-dimensional density of quenching centers. The first term is related to the movement of a particle in the matrix of quenching sites as was calculated by Balagurov et al., [106]. The exponent $\beta$ comes from the dimensionality of the process and equals $1/3$, $1/2$ and $3/5$ for diffusion in 1D, 2D and 3D, respectively. The time dependence of the exciton lifetime $\tau_0$ accounts for the decrease in intensity when no trapping occurs. Eq. 2.27 is correct only for times which fulfill the condition:

$$t >> \frac{L^2}{\pi^2 D}, \quad (2.29)$$

It is not difficult to understand this condition from the physical point of view: the time should be bigger than the average time needed for an exciton to travel the average distance between traps.

The examples of fitting the experimental data with the described function (Eq. 2.28) are presented in Fig. 2.29 for samples S (samples was provided by A. Revcolevschi, University of Paris IV) and L (sample was provided by M. Gonokami, University of Tokyo) (see also Fig. 2.25). The fitting parameter was one-dimensional density of quenching centers $n_{1D}$, while the diffusion coefficient was chosen being a fixed parameter $D=0.5$ cm$^2$/s. As a result, for sample S we suggested the defect concentration of $10^{15}$ cm$^{-3}$ and for sample L – $10^{11}$ cm$^{-3}$. Also, from these fits, we can conclude, that at long time, the lifetime behavior can be well described using a single exponential function, while at early times the non-exponential part $\sim t^{1/2}$ (Eq. 2.28) contributes.
Fig. 2.29. Fitting of paraexciton population time decay with Eq. 2.28: (a) sample S (sample was provided by A. Revcolevschi, University of Paris IV), (b) sample L (sample was provided by M. Gonokami, University of Tokyo). Experimental data was obtained at $T=77K$. These experiments have been carried out at University of Tokyo by M.Otter, N.Naka, K. Yoshioko, M.Gonokami, [53], [54]. Excitation wavelength 800 nm. One-dimensional defect density $n_{1D}$ was a fitting parameter ($10^5$ cm$^{-1}$ for sample S and $10^4$ cm$^{-1}$ for sample L).

Fig. 2.30. Numerical simulation of exciton lifetime using Eq. 2.28. Simulation parameters: $D=0.5$ cm$^2$/s, $\tau_0=3$ ms. Black curve – numerical simulation; dots was obtained from the calculation of $I_{Cu}/I_{Exciton}$ ratio for the S samples (close dots, samples was provided by A.Revcolevschi, University of Paris) and L samples (open dots, samples was provided by M.Gonokami, University of Tokyo).
For samples of different quality it has been measured the lifetime of the paraexciton gas and the defect luminescence spectra by M. Otter, N. Naka, K. Yoshioka, M. Gonokami at University of Tokyo, [53], [54]. By looking at the ratio of $I_{\text{Cu}}/I_{\text{exc}}$ for each vacancy spectrum measured we can relate this ratio to a vacancy concentration. Here we assume that the luminescence intensity linearly depends on the amount of impurities. This is shown in Fig. 2.30. The simulation fits the measured ratio quite well. Evidently, the copper vacancy concentration is directly related to the exciton lifetime.

2.2.5. Time evolution of paraexciton gas statistical parameters

As discussed in Chapter 1 and §2.1 luminescence spectra can give direct information about the statistical exciton gas parameters, i.e. temperature, chemical potential and density. As one can already guess, the statistical parameters of the exciton gas can not be determined through the time-resolved luminescence experiment via the orthoexciton state (§2.2.2). However, the pump-probe experiment of intraexcitonic transition is quite a powerful tool. As we will show in the following, the line shape and strength of the induced absorption (Fig.2.16) depends crucially on the statistical parameters. First, we will focus on a line shape analysis and will try to extract from the experimental results the chemical potential and the temperature of the exciton gas. Then we will connect analytically the strength of the absorption transition line and the gas density.

Consider two dispersion curves for the $1s$ and $np$ states as depicted in Fig. 2.31. Since the effective exciton mass in the $1s$ state is larger than in the $np$ states ($m_{1s}>m_{np}$) the energy gap $E_{1s-np}(k)$ between this levels increases with $k$:

$$E_{1s-np}(k) = E_{k=0} + \frac{\hbar^2 k^2}{2} \left( \frac{1}{m_{np}} - \frac{1}{m_{1s}} \right), \quad (2.29)$$

The transition rate $W_{1s-np}$ can directly be written by applying Fermi’s Golden Rule:

$$W_{1s-np} = \frac{2\pi}{\hbar} \int |\mu_i|^2 f_{1s}(\vec{k}) \left[ 1 + f_{np}(\vec{k}) \right] \delta \left[ E_{1s-np}(\vec{k}) - E \right] d^3\vec{k}, \quad (2.30)$$

Here $\mu_i$ is the transition matrix element, $f_{1s}, f_{np}$ are the distribution functions of the $1s$ excitons, np excitons and $E$ is an energy of the incident photon. From this point we need to
make some assumptions. First of all we suppose that the transition matrix element $\mu_i$ is $k$-independent. Second, since the transitions in a cubic lattice are direction independent we can write:

$$d^3k = 4\pi k^2 dk, \quad (2.31)$$

Finally, we assume that the $np$ levels are not occupied at all. In this case we can derive the line shape of the induced absorption as:

$$\alpha_{\text{ind}}(E) \propto \int k^2 f_{1s}(k)\delta(E_{1s-np} - E) dk, \quad (2.32)$$

Eq. 2.32 can be transferred into an integral over $E_{1s-np}$ by using Eq. 2.29:

$$\alpha_{\text{ind}}(E) \propto \int f_{1s}(k)\sqrt{E_{1s-np} - E_{k=0}}\delta(E_{1s-np} - E) dE_{1s-np}, \quad (2.33)$$

For a small gas density we can use the Boltzmann approximation for the thermal distribution within the 1s band. Such an approach is used in [40, 107]. Higher exciton densities will require the use of the Bose distribution function. Qualitatively, however it is clear that when the chemical potential approaches zero, the line shape will increasingly narrow, [38].

![Fig. 2.31. Schematic drawing of the dispersion of the generalized 1s and np states.](image-url)
Finally, the analytical solution for the induced absorption line shape using the Bose
distribution (Chapter 1) reads as:

\[ \alpha_{ind}(E) \propto \frac{\sqrt{E_{1s-np} - E_{k=0}}}{E_{1s-np} - E_{k=0} - \frac{\mu}{k_B T} \left( \frac{m_{1s}-1}{m_{np}} \right) k_B T - 1}, \]  

(4.34)

As already clear from Fig. 2.31, the line shape should broaden with increasing
temperature as well as with an increasing effective mass ratio. When the masses are equal
the lineshape reduces to a \( \delta \)-function at \( E=E_{k=0} \). For the data analysis we used effective
masses of \( m_{1s}=2.7 \) and \( m_{np}=2.1 \), [44].

In the last step before presenting experimental data, homogeneous line broadening is
discussed. This additional broadening can be neglected in the case of a \( 1s \) state since the
linewidth is already in order of \( k_B T \). In order to estimate the homogeneous broadening of
para np levels, we can compare to the broadening, observed in absorption spectra of the
 Corresponding orthoexciton levels (Chapter 1, Fig. 2.4). There is no particular reason why it
should be different for the paraexciton band, since the dephasing mechanism is phonon
scattering which is not sensitive to the spin. Based on it, the final Eq. 4.34 needs to be
convoluted with the usual thermal broadening Lorentzian function.

Fig. 2.32 shows a number of spectra of the induced 1s-2p paraexciton absorption at
different bath temperatures (left panels) and at different times after the excitation pulse
(right panels, bath temperature \( T=1.3 \) K) for Cu2O crystal in [100] orientation, provided by
A. Revcolevschi (University of Paris IV). These spectra were measured after two-photon
absorption at a fixed time delay of 3 ns after excitation. A convolution of a Lorentzian
thermal broadening with Eq. 2.34 was fitted to the data, where the fitting parameters are the
transition line position \( E_{k=0} \), temperature \( T \) and chemical potential \( \mu \).

We start with the analysis of the temperature dependence, presented at Fig. 2.32a. First
of all, the transition shifts toward higher energy with increasing temperature (Fig. 2.33).
Apparently, the involved levels do not shift with the bath temperature in a similar fashion.
The origin of this is the decrease in the binding energy of the \( 1s \) level. Whereas both levels
shift as a result of the reduction of the band-gap, the \( 1s \) level experiences an additional shift
due to a reduction of the central cell correction energy.
Fig. 2.32. Normalized induced absorption due to the 1s-2p paraexciton transition. Excitation via two-photon absorption using photons of 1.55 eV energy (2 mJ/cm\(^2\)). The black line is a fitting function—which is the result of the convolution of Eq. 2.34 (light grey) and the Lorentz broadening function (grey). The left plots (a) represents the results at different bath temperatures but fixed delay time at 3 ns. Right plots (b) represents the results at different time delays, but at a fixed bath temperature of 1.3 K. The Cu\(_2\)O sample of [100] orientation was provided by A.Revcolevschi, University of Paris IV.
Fig. 2.33. $1s-2p$ paraexciton transition energy as a function of temperature.

Fig. 2.34. Time dependence of (a) the exciton temperature and (b) chemical potential from the fitting analysis of the experimental results by Eq. 2.34.

Fig. 4.35. (a) Time dependence of the exciton density, calculated using Eq. 1.18 And results from Fig. 2.34 (solid line is the guide for an eye). (b) $n,T$ phase diagram (solid line is the phase transition boundary).
This is in a good agreement with the absorption and luminescence experiments [40] on orthoexciton states, assuming the splitting of the ortho and para states is temperature independent.

The gas temperature resulting from fitting the convoluted Eq. 2.34 to time-resolved spectra (Fig. 2.32) of excitonic transitions are shown in Fig. 2.34a. With respect to the orthoexcitons dynamics the cooling of the gas occurs with a relatively long decay time of 7 ns. The decay of the chemical potential in time, shown in Fig. 2.34b, is also found to be slower than for the orthoexcitons (Fig. 2.3), resulting in a time constant of 9 ns. Similar to the orthoexciton case, we can calculate the density of the paraexciton gas using the Eq. 1.18. The result is shown in Fig. 2.35. The state of the gas is approaching the BEC boundary, but the lifetime of the particles is still not sufficient to cross the boundary. Actually, Kavoulakis [10] has argued that the above mentioned fitting-based-analysis which was used to extract the exciton temperature and, therefore, density is misleading since the gas is in a classical regime. In general, the condition of which model, classical or quantum, should be considered as correct is based on the relation between the thermal de Broglie wavelength $\lambda$ of the particles and average distance between them $l=n^{1/3}$, where $n$ is the gas density [108]. We can establish the transition condition from classical to the quantum case as:

$$a << l \text{ for classical regime}$$

$$a >> l \text{ for quantum regime}$$

The border equation will determine the “transition” concentration:

$$n_{Q} = \left( \frac{\langle P \rangle}{\hbar} \right)^{3} = g \left( \frac{mk_{B}T}{2\pi\hbar^{2}} \right)^{3/2}, \quad (2.35)$$

This, so called quantum density corresponds to one particle in a cube with sides equal to the average de Broglie wavelength. The estimated value (Fig. 2.35 a,b) is around the quantum density for a paraexciton gas with a particle density of $10^{-18}$ cm$^{-3}$ at 7K. This means that we can already consider our gas being in the quantum regime.

The above obtained result can even be easily checked using a different method of density estimation. This analytical method is based on the direct connection of the induced absorption with oscillator strength. By calculating the Einstein coefficients, the dielectric function and relating these to the oscillator strength, it can be shown [109], that the oscillator strength is given by:
\[ f_i = \frac{2m \Delta E}{\hbar^2 e^2} |\mu_i|^2, \quad (2.36) \]

where \( \Delta E \) is the transition energy and \( \mu = 2.6 \cdot 10^{-29} \) C·m is a dipole matrix element, [44]. From the dielectric function with simultaneous laser excitation we take the additional imaginary part \( \varepsilon^* \), since it determines the induced absorption [39, 40]:

\[ \varepsilon_2^* = \text{Im}[\varepsilon(E) - \varepsilon^*(E)] = \text{Im}\left[ \sum_i \chi_i \right], \quad (2.37) \]

\[ \chi_i(E) = \frac{n_{1s} \hbar^2 e^2}{m \varepsilon_0} \frac{f_i}{\Delta E^2 - E^2 - i\hbar \Gamma E} \]

where \( \Gamma \) is the damping and \( n_{1s} \) is the density of the 1s excited state. Now the induced absorption can be written as:

\[ \alpha_{\text{ind},i}(E) = \frac{\varepsilon_2^*(E)E}{\hbar cn} \approx \frac{\text{Im}[\chi_i(E)]E}{\hbar c \sqrt{\varepsilon_B}} = \frac{2E_i n_{1s} |\mu_i|^2}{\hbar c \varepsilon_0 \sqrt{\varepsilon_B}} \frac{\hbar \Gamma}{\left( \Delta E - E \right)^2 + \left( \hbar \Gamma \right)^2}, \quad (2.38) \]

Here \( c \) is the light velocity and the index of the refraction is approximated by \( \varepsilon_B = 7.1 \), [40, 45]. The ratio on the right hand side describes a normalized Lorentzian with an integrated area of \( \pi/2 \) Integration of the Eq. 2.38, assuming that \( \hbar \Gamma \ll \Delta E \), yields the connection between the density of the 1s excited state and the area of the induced absorption (Fig. 2.18, 2.21a):

\[ n_{1s} = \frac{\hbar c \varepsilon_0 \sqrt{\varepsilon_B} A_i}{\pi |\mu_i|^2 \Delta E} \]

where \( A_i = \int \alpha_{\text{ind},i}(E)dE, \quad (2.38) \)

Because the 1s exciton differs from the hydrogen model, the matrix dipole element needs to be calculated specially, taking into account the wave functions of the 1s and 2p excited states. The exact value of the dipole matrix element was taken from [39, 40].
By applying the described above method to the experimental data (Fig. 2.23), the early time dynamics of the exciton density of the paraexciton gas can be determined. The resulting time dependence of the density is presented in Fig. 2.36 for two cases: exciton gas created via two-photon absorption into the blue series and direct one-photon absorption to the 1s yellow orthoexciton level. It is obvious, that these results agree well with one discussed above and presented in Fig. 2.35a. Also, as discussed in Chapter 1, different methods of excitation may excite different excitonic states, with different efficiencies. Besides the difference in the exciton creation mechanism the penetration depth differs: 30 μm for 2.07 eV excitation and the whole bulk in a case of 1.55 eV. It is obvious, that one can reach much higher excitation densities via one-photon absorption, which very well agrees with the experimental results (Fig. 2.36).

Moreover, we can make an additional conclusion from Fig. 2.36. Since the creation of the exciton gas via two-photon excitation with 1.55 eV pulses is going through the blue series, one may expect that the 1s paraexciton state can be created via decay to the yellow series. For one-photon absorption of 2.07 eV pulses the only possibility to populate the paraexciton state is the spin-flip down-conversion from the orthoexciton state. The present experimental results (Fig. 2.36) are showing that despite the excitation method, 1s paraexcitons are primarily created via down-conversion from the 1s orthoexciton state.
2.2.6. Paraexciton gas parameters evolution in \((\mu Tn)\)-space.

Above we established the ways how to determine exciton gas statistical parameters. Now we will discuss question: “Can we reach the condensed state for paraexcitons?” In a case of non-condensed gas, the chemical potential, temperature and density are connected:

\[
n(\mu, T) = A \int_0^\infty dEf_{BE}(E, \mu, T)D(E)
\]

where \(f_{BE}\) is the Bose-Einstein distribution function, \(D(E)\) is the density of states. Therefore, the possible states of a boson gas form a surface in \(\mu Tn\)-space (Fig. 2.37): knowing two parameters, one can easily predict the third. In the experiment, we initially create a hot exciton gas of high density. In time, the gas temperature will decay toward the lattice temperature, leading, in principle, to a decrease of the chemical potential. If the density of the gas stays sufficiently high, the exciton gas will reach the condensate state: the surface \((n,T)_{\mu=0}\) determines the Bose-Einstein condensation boundary.

Fig. 2.37. The dynamics of the paraexciton gas statistical parameters. Light grey trace – calculated dynamics (lifetime 1\(\mu s\)); dark grey – dynamics obtained from the described above experiments.
The dark grey trace in Fig. 2.37 shows the real dynamics of the exciton gas statistical parameters as determined from the experiments described in §2.2.4. At early times, the exciton temperature and chemical potential decay providing a “movement” toward the transition boundary. However, in these experiments the lifetime of the paraexcitons was relatively small (10 ns), leading to fast density decay and a chemical potential which “moves” toward larger negative values. As a result, the trace of exciton gas state is slowly turning away from the condensation boundary. For comparison, we did a theoretical calculation for a long-lived paraexciton gas (light grey trace in Fig. 2.37). The lifetime of the particles was assumed to be 1 μs, while the gas cooling time was chosen to be the same as obtained from the present experiment. The result of the calculation does show, that for such a gas condensation may occur (in this case after 1000 ns), if the initial exciton gas density is high enough.

2.3. Conclusions.

In conclusion, we investigated two types of excitons in cuprous oxide and discussed the ideas and results of the experiments aimed at determining the exciton gas parameters and their time evolution. It was shown that the lifetime is one of the most critical parameters determining whether a condensate state may occur.

For the orthoexcitons, it was shown that the gas adjusts its quantum properties to the density and temperature and that it is in quasi-equilibrium. Apparently the particle decay is faster than the cooling rate, which inhibits a BEC transition.

Further, the ways of direct and in-direct probing of the optically inactive paraexcitons were presented and described. Based on the results of the experiments and analysis of the experimental data, we discussed the processes which may contribute to paraexciton losses. The most important conclusion is that at the currently achieved densities (~10^{18} cm^{-3}) the main paraexciton loss process is trapping by crystal imperfections. It was concluded, that the lifetime is strongly depends on amount of copper impurities and a mechanism of exciton trapping by copper impurities was proposed.

The presented experiments were carried out using quite impure samples: the cooling rate was not sufficient to overcome the particle loss. However, under the proper experimental conditions, it is possible for the paraexcitons to achieve a condensate state: low bath temperature (1.2K for densities ~10^{17} cm^{-3}), low concentration of crystal defects, one-photon excitation method for a smaller excitation volume and intense enough excitation source.
References

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