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ORTHO- TO PARA-EXCITON CONVERSION IN CuO:
A SUBNANOSECOND TIME-RESOLVED PHOTOLUMINESCENCE STUDY

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The photoluminescence spectra of Cu$_2$O have been studied as a function of time and temperature. At $T \sim 2.5^\circ$K it was found that the 1s yellow ortho-excitons decay into para-excitons at the rate of $\gtrsim 2.5 \times 10^8$ sec$^{-1}$ while the para-exciton lifetime is much longer and dominated by recombination at defects. As $T$ is raised the rate of conversion of ortho-excitons into para-excitons increases approximately as $T^{3/2}$. None of the existing theories seem to explain this temperature dependence satisfactorily.
Cu$_2$O is one of the classic materials for studying properties of excitons in semiconductors.\textsuperscript{1} In particular it is well-known that the 1s ground state of the lowest energy exciton in Cu$_2$O (referred to as the 1s Yellow ortho-exciton in the literature) is electric dipole forbidden.\textsuperscript{2} As a result its lifetime is expected to be quite long. However, attempts to measure its lifetime with nanosecond laser pulses have not been successful.\textsuperscript{3,4} Even in the best Cu$_2$O sample found so far the 1s yellow ortho-exciton lifetime is $\leq$ 3nsec\textsuperscript{4}. It has been suggested that the ortho-exciton lifetime is dominated by decay into the para-exciton level.\textsuperscript{4}

In this communication we report the first direct determination of the ortho-exciton lifetime in Cu$_2$O using subnanosecond time-resolved photoluminescence spectroscopy. By monitoring both the ortho-exciton and para-exciton decays as a function of time and temperature, we obtain conclusive evidence that the ortho-exciton lifetime at finite temperatures is dominated by its decay into the para-exciton. Furthermore we find that the ortho-para conversion rate increases with temperature approximately as $T^{3/2}$. Our results are important for current efforts to observe Bose-Einstein condensation of excitons in Cu$_2$O.\textsuperscript{5,6}

Extensive literature exists on the properties of excitons in Cu$_2$O.\textsuperscript{2} The crystal structure of Cu$_2$O is cubic and centrosymmetric with two molecules per unit cell. The valence band maximum and conduction band minimum are both non-degenerate and occur at the zone center. Since both bands have even parity, electric dipole transitions between them are forbidden. The exciton formed from these two bands is the yellow exciton relevant to this paper.

Due to exchange interaction its fourfold degenerate 1s state (both the electron and hole have spin degeneracy of two) is split into a $\Gamma_5^+$ triplet and a $\Gamma_5^-$ singlet state.\textsuperscript{4} By analogy with the hydrogen molecule these triplet and singlet excitons are respectively referred to as the ortho-exciton and para-exciton (to be abbreviated in this paper as O-X and P-X respectively).

Although direct electric dipole transitions involving the O-X and P-X are forbidden, weak phonon-assisted dipole transitions involving both have been observed in absorption\textsuperscript{2,7} and emission.\textsuperscript{8} While only the $\Gamma_{25}^-$ (frequency equal to 88 cm$^{-1}$) phonon can assist the excitation of the P-X, several odd-parity phonons can assist
the excitation of the 0-X, the one with the largest oscillator strength being the $\Gamma_{12}$ (109 cm$^{-1}$) phonon. In this paper we monitor the decay of the 0-X and P-X in Cu$_2$O via their phonon-assisted recombination peaks at 16290 and 16220 cm$^{-1}$ respectively. Gross, Kreingold and Makarov$^8$ were the first to estimate the relative ordering of the 0-X and P-X in Cu$_2$O. For $T>30^\circ K$ they found that the intensity of the $\Gamma_{12}$ phonon-assisted 0-X recombination peak increases as $\exp(-\Delta/k_BT)$ with $\Delta = 12\text{meV}$. Based on this result they propose that the 0-X must be 12meV (or 96 cm$^{-1}$) above the P-X. Below 30$^\circ$K the 0-X emission intensity exhibits a minimum at $\sim 20^\circ K$ (their results are reproduced in Fig. 1). They explained this behavior qualitatively by proposing that the 0-X and P-X are not in thermal equilibrium at $T<30^\circ K$. But as $T$ increases above 30$^\circ$K the ortho- to para-exciton conversion rate becomes fast enough for the two to reach thermal equilibrium before recombining. Kreingold and Markarov$^8$ did not offer any theory for the ortho-para conversion mechanism in Cu$_2$O. Recently two temperature dependent models for the ortho-para conversion mechanism have been proposed.$^6$, $^9$ Both are capable of explaining the experimental temperature dependence of the 0-X luminescence intensity. In this paper we present a direct test of these two models by measuring the ortho-para conversion rate as a function of temperature.

To determine the ortho-para conversion rate in Cu$_2$O we utilize a modelocked picosecond dye laser to excite the 0-X and P-X emissions and monitor their decay in real time. A detailed description of our set-up will be presented elsewhere. The sample is excited by a train of dye laser pulses $\sim 10$ psec long and separated from each other by $\sim 12$ nsec. The laser frequency is set at 16800 cm$^{-1}$. The emission from the sample is time-resolved by a delayed coincidence photon counting system.$^{10}$ The response of the detection system to the 10 psec wide laser pulse is a pulse with FWHM equal to $\sim 400$ psec. By deconvoluting the measured time decays with this instrument response, emission decay times shorter than 100 psec can be determined.

It is known that Cu$_2$O samples can be divided into two types by their photoluminescence lineshape.$^{11}$ Those with nonthermalized luminescence presumably contain more defects$^{12}$ so we have performed our measurement on two samples with thermalized lineshape. One is a melt-grown bulk
crystal while the other is a high quality natural single crystal.4 By fitting the time-averaged luminescence lineshape with the expression $E^k \exp(-E/k_BT)$ where $E$ is the exciton energy, $k_B$ is the Boltzmann constant and $T$ is the exciton temperature, we can determine the temperatures of the 0-X and P-X.11 At all temperatures we found that the exciton temperatures are very close to the lattice temperature measured by a calibrated diode thermometer mounted next to the sample. Furthermore, the excitons reach the lattice temperature in less than 100 psec.

Figure 2(a-c) shows the decay in time of the $\Gamma_{12}$ phonon-assisted 0-X emission peak and of the $\Gamma_{25}$ phonon-assisted P-X peak at three temperatures. We note that at low temperatures the 0-X decays exponentially with a single time constant. At $T \geq 10^3$K the decay seems to have two time constants: a slow and a fast one. The amplitude of the fast decaying component, relative to the slow decaying component, becomes smaller with increase in temperature while its decay rate becomes faster. For $T \geq 50^6$K the slow component dominates over the fast component so the 0-X decays again with a single time constant. In contrast to the 0-X decay, the P-X decay is independent of temperature. We note that at $T \geq 50^6$K both 0-X and P-X decay at the same rate. The results obtained in both Cu2O samples are qualitatively similar. The main difference lies in the P-X decay rate. In the melt-grown sample the P-X lifetime is $\sim 10$ nsec while in the high quality natural crystal the P-X lifetime is $\sim 13$ nsec. The $T=2.5^6$K lifetime of the 0-X is about a factor of two longer in the natural crystal than in the melt-grown crystal but this difference disappears at higher temperatures.

These results can be understood in terms of the two-level model shown in the insert of Figure 1. We assumed that the 0-X and P-X scatter into each other at the rates $D$ and $U$ which are temperature dependent. $N_0$, $G_0$ and $\gamma_0$ are respectively the distribution function, generation rate and recombination rates of the 0-X. The corresponding quantities for the P-X are represented by $N_p$, $G_p$ and $\gamma_p$. $N_0(t)$ and $N_p(t)$ can be obtained by solving the rate equations:

$$g_0 \dot{N}_0 = -g_0 N_0 D + g_p N_p U - \gamma_0 g_0 N_0 + G_0(t) \quad (1)$$

$$g_p \dot{N}_p = -g_p N_p U + g_0 N_0 D - \gamma_p g_p N_p + G_p(t) \quad (2)$$
where the degeneracies of the O-X and P-X levels, $g_0$ and $g_p$, are respectively 3 and 1. By assuming that the generation rates $G_0(t)$ and $G_p(t)$ are both delta-functions and that $U < (\gamma_0, \gamma_p) < D$, the solutions for $N_0(t)$ and $N_p(t)$ are given approximately by:

$$N_0(t) = C_1 e^{-(D+\gamma_0)t} + \left(\frac{g_p}{g_0}\right) \frac{U}{D} C_2 e^{-\gamma_p t}$$

$$N_p(t) = \left(\frac{g_0}{g_p}\right) \frac{D}{D+\gamma_0} C_1 e^{-(D+\gamma_0)t} + C_2 e^{-\gamma_p t}$$

where $C_1$ and $C_2$ are given approximately by $N_0(0)$ and $3N_0(0) + N_p(0)$. Equation (3) explains the origin of the two exponential decay constants observed for the O-X. The first term in $N_0(t)$ corresponds to the decay of the excess O-X population into para-excitons. As the para-exciton population builds up, the two excitons will eventually reach thermal equilibrium, with $N_0(t)/N_p(t) = e^{\Delta/k_B T}$, and both levels will decay as $e^{-\gamma_p t}$ for $t \to \infty$. Therefore, according to Eq. (3), the first decay rate of $N_0$ should be given by $\gamma_0 + D$ while the slow decay rate of $N_0$ should be equal to $\gamma_p$ and should be the same as that of $N_p$. In practice we found that, for $T \leq 40^\circ K$, $N_0$ and $N_p$ did not reach thermal equilibrium with each other within the laser pulse separation of $\sim 12$ nsec.

By convoluting Eq. (3) with the instrument response and using $\gamma_0 + D$ and $\gamma_p$ as adjustable parameters we fit the experimental $N_0(t)$ curves to extract the fast decay rate $D+\gamma_0$ as a function of temperature. The resultant values of $D+\gamma_0$ are plotted as open circles in Fig. (3). The large uncertainty in $D+\gamma_0$ at high temperatures is due to the combined effect of the instrument resolution and the smaller amplitude of the fast decaying component at higher temperatures.

The striking result in Fig. (3) is the strong temperature dependence of $D+\gamma_0$. Since $\gamma_0$ is presumably due to recombination of the O-X at defects and hence temperature independent, the strong temperature effect must be attributed to D. This is supported by the fact that $\gamma_p$ is indeed temperature independent and also that the two samples in spite of their quite different values of $\gamma_p$ show basically the same temperature dependence in $D+\gamma_0$. This strong temperature dependence in D was predicted theoretically in order to explain the O-X luminescence intensity behavior$^8$. Caswell and Yu$^9$ recently presented
a physical model for the ortho-para conversion mechanism based on two-phonon scattering. The result of their calculation is compared with our experimental result in Fig.(3). It is clear that their theory predicts a much stronger temperature dependence in D than we observed. The experimental results can be fitted quite well by the expression: \( \alpha + \beta T^{3/2} \) where \( \alpha = 4 \times 10^8 \text{sec}^{-1} \) and \( \beta = 0.3 \times 10^8 \text{sec}^{-1} (\text{K})^{-3/2} \) while the theoretical curve approaches \( T^{7/2} \) instead.

As alternate explanations we have considered the following ortho-para conversion mechanisms: (a) defects such as paramagnetic impurities, (b) combination of phonons and defects and (c) exciton-exciton interaction. Mechanisms (a) and (b) tend to give temperature dependence weaker than \( T^{3/2} \). We have been able to rule out mechanism (c) by varying the excitation intensity. The 0-X lifetime did not show any dependence on excitation intensity although the P-X lifetime decreases with higher intensity.

In conclusion, we have shown that the 0-X lifetime in Cu2O at finite temperatures is determined by its conversion to P-X and that this rate increases with temperature as \( T^{3/2} \). None of the existing theories seem to be able to explain this temperature dependence.

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Footnote

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References

13. Details of this calculation will be published elsewhere.
Figure Captions

Figure 1 Temperature dependence of the $\Gamma_{12}$ phonon-assisted ortho-exciton recombination peak in Cu$_2$O. Experiment points are from Ref. 8. Solid line is the result of a theoretical model calculation presented in Ref. 9. The inset is the schematic diagram of the two-level model discussed in the text.

Figure 2 Time dependent decay of the ortho-and para-exciton luminescence peaks at three different temperatures: (a) 2.5 K, (b) 35 K, and (c) 48 K. The ortho-and para-exciton curves have been displaced from each other for clarity. The curve labelled 'laser' in (a) represents the instrument's response to a dye laser pulse of width $\sim$ 10 psec.

Figure 3 The fast decay rate $D + Y_0$ of the ortho-exciton plotted as a function of temperature. The open circles are experimental points deduced from the luminescence decay curves. The solid line is a plot of the expression $\alpha + \beta T^{3/2}$ while the broken curve is calculated from the two-phonon mechanism proposed in Ref. 9.
Figure 1
Figure 2
Figure 3
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