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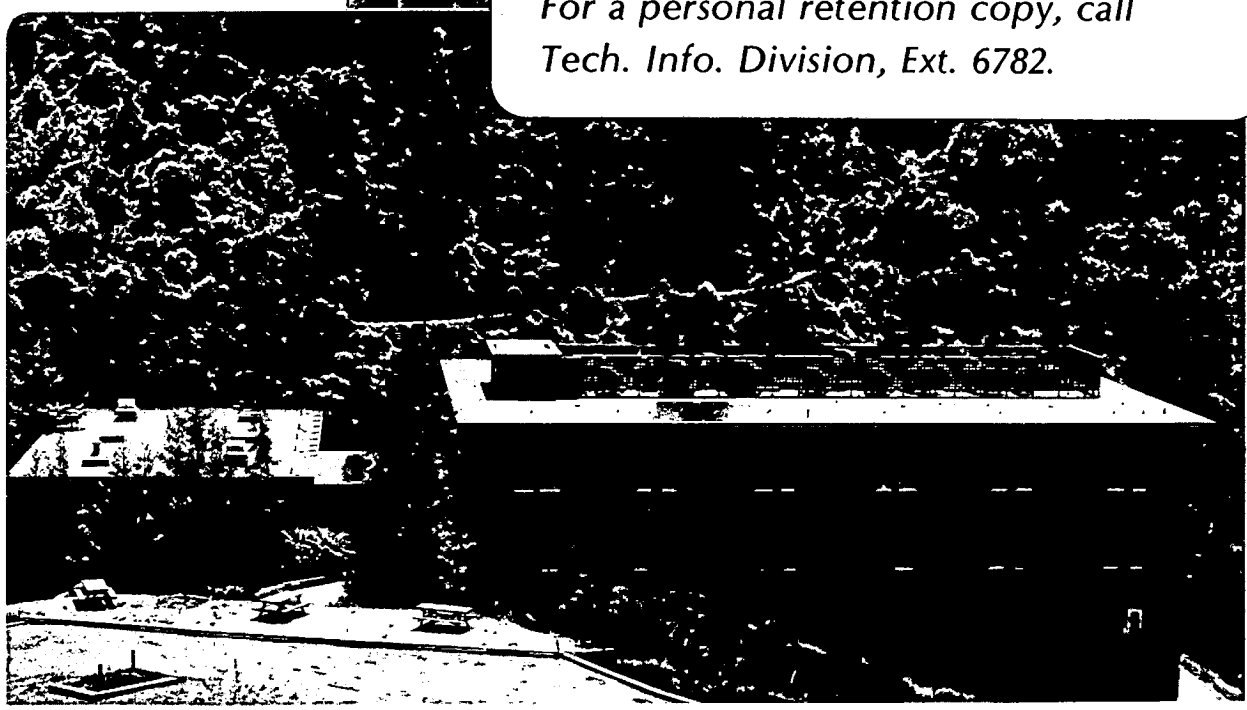

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DISCLAIMER

ORTHO- TO PARA-EXCITON CONVERSION IN Cu_2O: A SUBNANOSECOND TIME-RESOLVED PHOTOLUMINESCENCE STUDY

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The photoluminescence spectra of Cu_2O 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_2O is one of the classic materials for studying properties of excitons in semiconductors.[1] In particular it is well-known that the 1s ground state of the lowest energy exciton in Cu_2O (referred to as the 1s Yellow ortho-exciton in the literature) is electric dipole forbidden.[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.[3,4] Even in the best Cu_2O sample found so far the 1s yellow ortho-exciton lifetime is $\leq$ 3nsec[4]. It has been suggested that the ortho-exciton lifetime is dominated by decay into the para-exciton level.[4]

In this communication we report the first direct determination of the ortho-exciton lifetime in Cu_2O 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_2O.[5,6]

Extensive literature exists on the properties of excitons in Cu_2O.[2] The crystal structure of Cu_2O 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 Γ_{25}^+ triplet and a Γ_2^+ singlet state.[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[2,7] and emission.[8] While only the Γ_{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 O-X, the one with the largest oscillator strength being the Γ_{12}^- (109 cm^{-1}) phonon. In this paper we monitor the decay of the O-X and P-X in Cu_2O 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 O-X and P-X in Cu_2O. For $T>30^\circ K$ they found that the intensity of the Γ_{12}^- phonon-assisted O-X recombination peak increases as $\exp(-\Delta/k_BT)$ with Δ = 12meV. Based on this result they propose that the O-X must be 12meV (or 96 cm^{-1}) above the P-X. Below $30^\circ K$ the O-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 O-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_2O. 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 O-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_2O we utilize a modelocked picosecond dye laser to excite the O-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_2O 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 $E^{\frac{1}{2}}\exp(-E/k_BT)$ 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 O-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 Γ_{12}^- phonon-assisted O-X emission peak and of the Γ_{25}^- phonon-assisted P-X peak at three temperatures. We note that at low temperatures the O-X decays exponentially with a single time constant. At $T \gtrsim 10^\circ K$ 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 $T \gtrsim 50^\circ K$ the slow component dominates over the fast component so the O-X decays again with a single time constant. In contrast to the O-X decay, the P-X decay is independent of temperature. We note that at $T \gtrsim 50^\circ K$ both O-X and P-X decay at the same rate. The results obtained in both Cu_2O samples are qualitatively similar. The main difference lies in the P-X decay rate. In the melt-grown sample the P-X lifetime is ~ 10 nsec while in the high quality natural crystal the P-X lifetime is ~ 13 μsec. The $T \simeq 2.5^\circ K$ lifetime of the O-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 O-X and P-X scatter into each other at the rates D and U which are temperature dependent. N_o, G_o and γ_o are respectively the distribution function, generation rate and recombination rates of the O-X. The corresponding quantities for the P-X are represendted by N_p, G_p and γ_p. $N_o(t)$ and $N_p(t)$ can be obtained by solving the rate equations:

$$g_o\dot{N}_o = -g_oN_oD + g_pN_pU - \gamma_og_oN_o + G_o(t) \quad (1)$$

$$g_p\dot{N}_p = -g_pN_pU + g_oN_oD - \gamma_pg_pN_p + G_p(t) \quad (2)$$

where the degeneracies of the O-X and P-X levels, g_o and g_p, are respectively 3 and 1. By assuming that the generation rates $G_o(t)$ and $G_p(t)$ are both delta-functions and that $U<<(\gamma_o,\gamma_p)< D$, the solutions for $N_o(t)$ and $N_p(t)$ are given approximately by:[13]

$$N_o(t) \simeq C_1 e^{-(D+\gamma_o)t} + \left(\frac{g_p}{g_o}\right)\left(\frac{U}{D}\right) C_2 e^{-\gamma_p t} \qquad (3)$$

$$N_p(t) \simeq -\left(\frac{g_o}{g_p}\right)\frac{D}{D+\gamma_o} C_1 e^{-(D+\gamma_o)t} + C_2 e^{-\gamma_p t} \qquad (4)$$

where C_1 and C_2 are given approximately by $N_o(0)$ and $3N_o(0)+N_p(0)$. Equation (3) explains the origin of the two exponential decay constants observed for the O-X. The first term in $N_o(t)$ 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 $N_o(t)/N_p(t) \simeq \frac{U}{3D} = e^{-\Delta/k_B T}$, 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_o should be given by γ_o+D while the slow decay rate of N_o should be equal to γ_p and should be the same as that of N_p. In practice we found that, for $T \leq 40^\circ K$, N_o 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 γ_o+D and γ_p as adjustable parameters we fit the experimental $N_o(t)$ curves to extract the fast decay rate $D+\gamma_o$ as a function of temperature. The resultant values of $D+\gamma_o$ are plotted as open circles in Fig. (3). The large uncertainty in $D+\gamma_o$ 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 $D+\gamma_o$. Since γ_o 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 γ_p is indeed temperature independent and also that the two samples in spite of their quite different values of γ_p show basically the same temperature dependence in $D+\gamma_o$. 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 $\alpha \approx 4\times10^{8}\text{sec}^{-1}$ and $\beta \approx 0.3\times10^{8}\text{sec}^{-1}(^{\circ}\text{K})^{-3/2}$ 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 O-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 O-X lifetime in Cu_2O 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

1. See for example C. KITTEL, Introduction to Solid State Physics, 5th Edition (J. Wiley & Sons, New York, 1976) p. 341.
2. See for example a review article by S. NIKITINE in Optical Properties of Solids, edited by S. NUDELMAN and S. S. MITRA (Plenum, New York, 1969).
3. R. M. HABIGER and A. COMPAAN, Solid State Communications 18, 1531 (1976).
4. A. MYSYROWICZ, D. HULIN and A. ANTONETTI, Physical Review Letters, 43, 1123 (1979).
5. D. HULIN, A. MYSYROWICZ and C. BENOIT à la GUILLAUME, Physical Review Letters 45, 1970 (1980).
6. A. MYSYROWICZ, D. HULIN and C. BENOIT à la GUILLAUME, in Proceedings of the Luminescence Conference, Berlin, 1981 (to appear in Journal of Luminescence).
7. P. D. BLOCH and C. SCHWAB, Physical Review Letters 41, 514 (1978).
8. E. F. GROSS, F. I. KREINGOL'D and V. L. MAKAROV, Soviet Journal of Experimental and Theoretical Physics Letters 15, 269 (1972); F. I. KREINGOL'D and V. L. MARKAROV, Fiz. Tverd. Tela 15, 3107 (1973) [Sov. Phys.-Solid State 15, 890 (1973).]
9. N. CASWELL and P. Y. YU, Phys. Rev. B 25, 5519 (1982).
10. V. J. KOESTER and R. M. DOWBER, Rev. Sci. Inst. 49, 1186 (1978).
11. Y. PETROFF, P. Y. YU and Y. R. SHEN, Phys. Rev. B 12, 2488 (1975).
12. N. CASWELL, J. S. WEINER and P. Y. YU, Solid State Commun. 40, 843 (1981).
13. Details of this calculation will be published elsewhere.

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Figure Captions

Figure 1 Temperature dependence of the Γ_{12}^{-} phonon-assisted ortho-exciton recombintaion peak in Cu_2O. 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 ~ 10 psec.

Figure 3 The fast decay rate $D + \gamma_o$ 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.

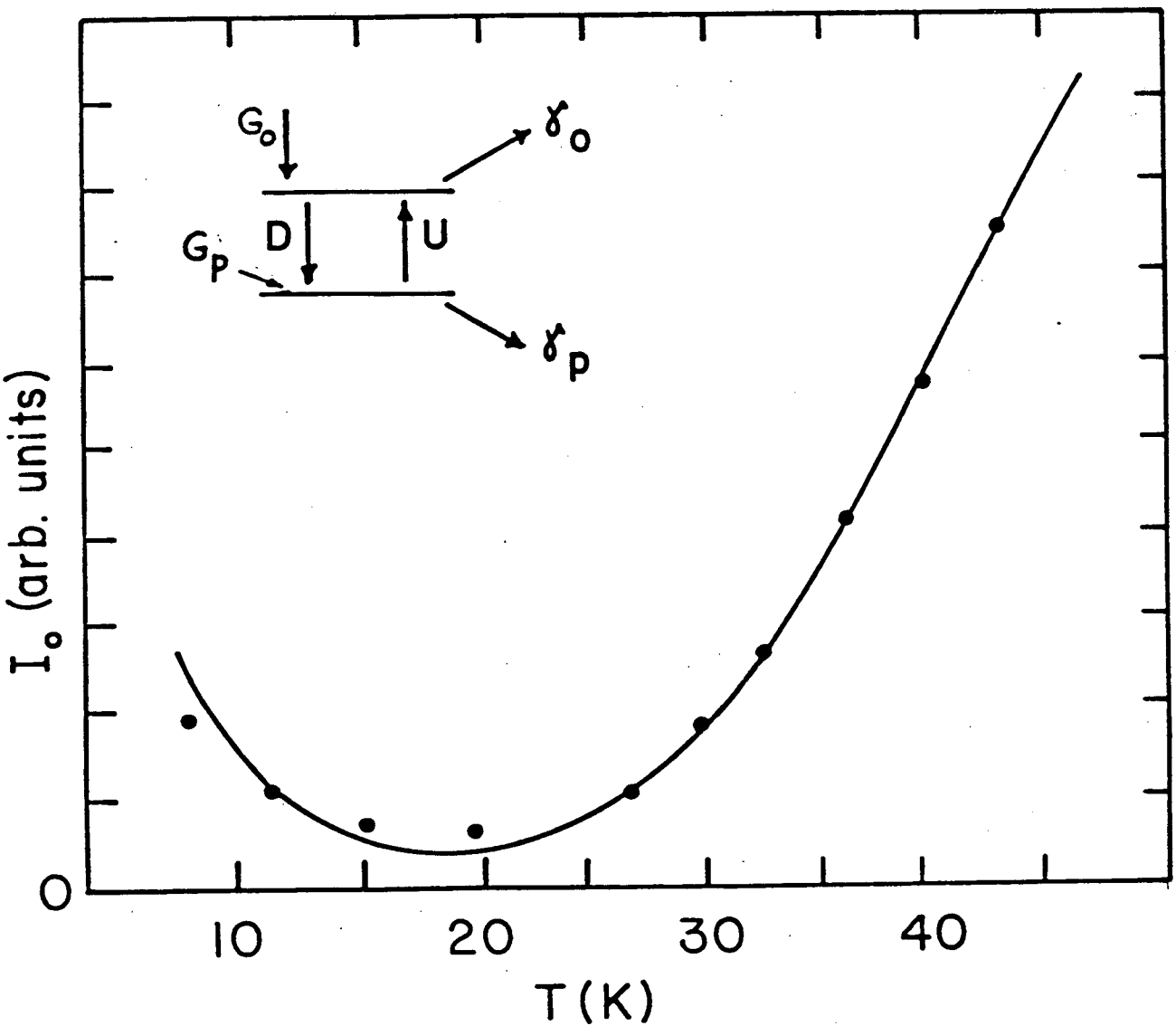

Figure 1

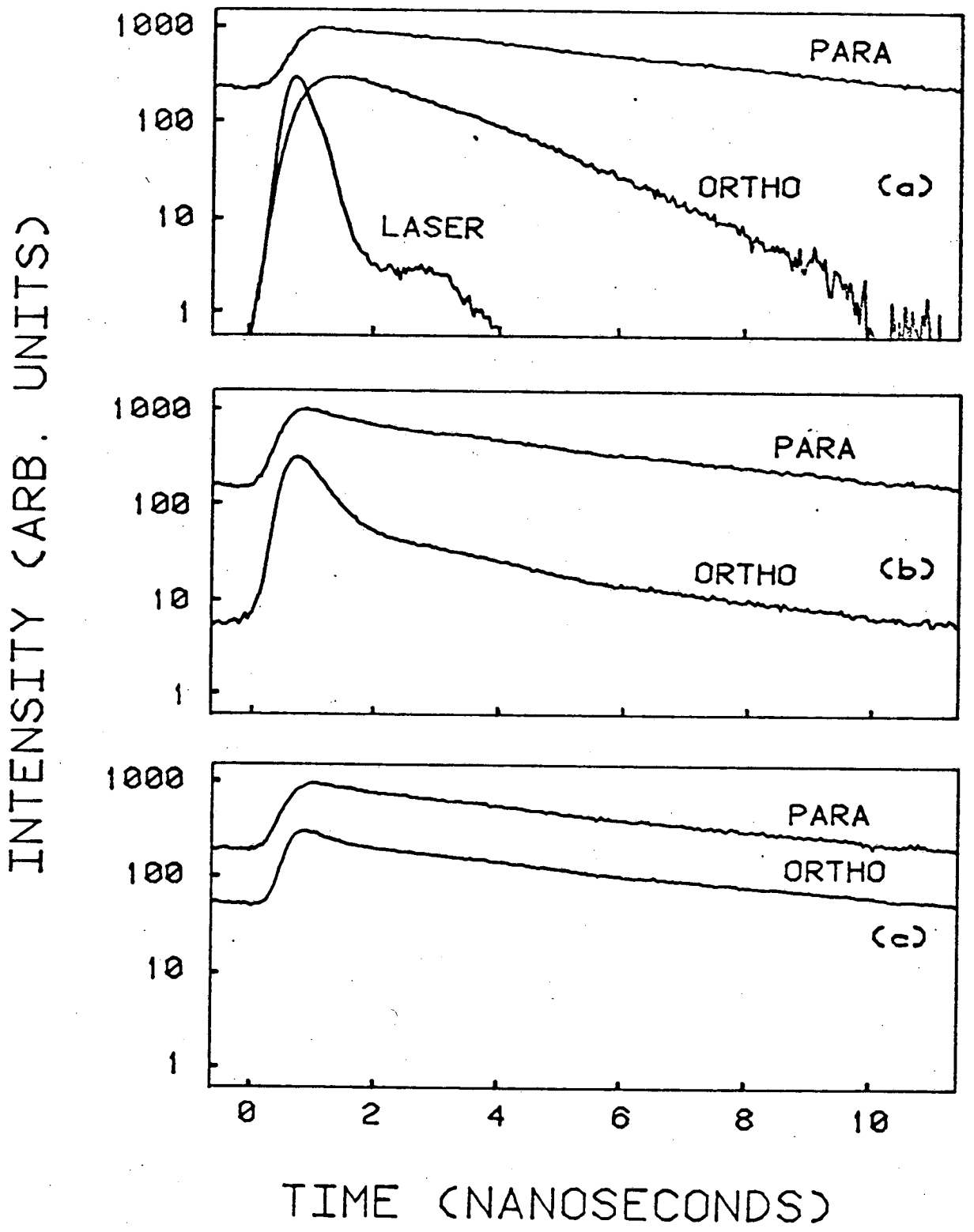
1000
100
10
1
PARA
ORTHO
(a)
LASER
1000
100
10
1
PARA
ORTHO
(b)
1000
100
10
1
PARA
ORTHO
(c)
0
2
4
6
8
10
INTENSITY (ARB. UNITS)
TIME (NANOSECONDS)

Figure 2

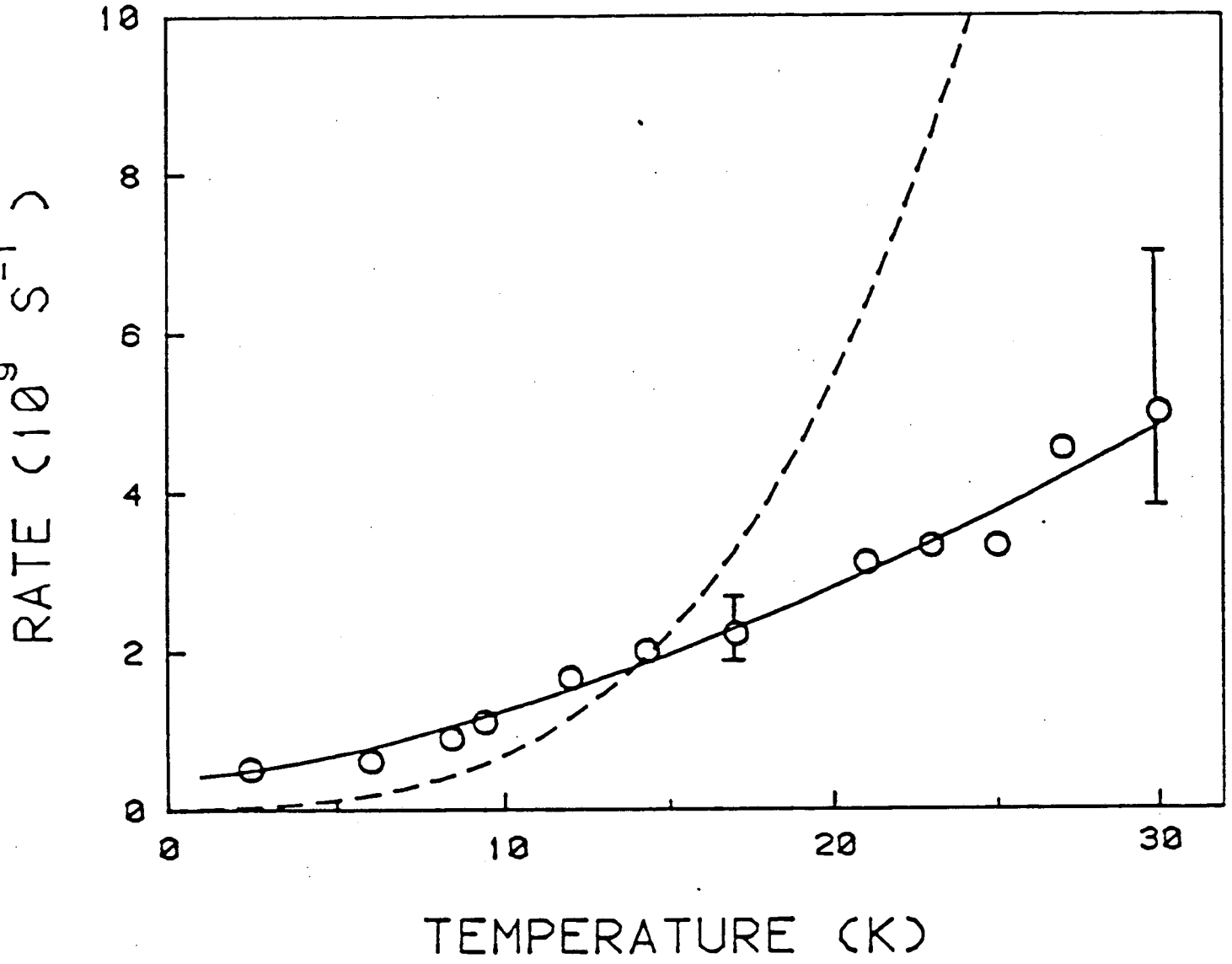

Figure 3

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