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TIME-RESOLVED HOT LUMINESCENCE AND RESONANT RAMAN SCATTERING: Cu_2O REVISITED

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Abstract

Time-resolved resonant scattering of both one-phonon and two-phonon Raman modes at the 1s ortho-exciton state of the yellow series in Cu_2O is reported. From the time dependence of the one-phonon mode we determine the scattering rate among the triply degenerate ortho-exciton states to be $2.5 \times 10^8 sec^{-1}$. From the two-phonon modes we directly determine the exciton lifetime as a function of its kinetic energy.

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Resonant Raman Scattering (RRS) with tunable continuous wave (cw) lasers is a well established technique for studying electronic and vibrational excitations in various materials, ranging from semiconductors to hemoglobin.[1,2] It has been suggested that time-resolved RRS will give information about the dynamics of relaxation processes not provided by cw RRS measurements.[3] There has also been considerable debate in the literature[3-9] about whether RRS, a one-step coherent process, is distinguishable from hot luminescence (HL), a two-step absorption-emission process. It is now generally agreed that the two processes cannot be distinguished by cw experiments but may be distinguished by their temporal behavior after pulsed excitation.

So far, few time-resolved RRS experiments have been reported in the literature.[8,9] In this letter we report the first time-resolved RRS study in a semiconductor where considerable numbers of cw RRS measurements have been made.[10,11] We show that, indeed, time-resolved RRS can provide direct and new information about relaxation of the resonant intermediate states not obtainable from cw measurements. We show that HL can be responsible for the breakdown of Raman selection rules at resonance. Breakdown in Raman selection rules in cw RRS has generally been attributed to wave-vector dependent scattering.[12] However, in light of our result, re-examination of cw RRS of longitudinal optical phonons in many semiconductors may be necessary.

Some of the confusion in the debate over whether RRS and HL are equivalent is due to terminology. We will follow Shen's[5] definitions of HL and RRS. Raman scattering is a coherent process in which scattered photons are radiated by a polarization at frequency ω_s induced in the

medium by incident photons with frequency ω_i. When the incident radiation is turned off the scattered radiation decays at the rate at which the phase coherence of the induced polarization disappears. This phase relaxation time is denoted by T_2. HL results from the radiative decay of the population in the intermediate state excited by the incident photons. HL will therefore decay with the population relaxation time T_1. Since T_2 depends both on dephasing and population decay processes, T_2 is smaller or equal to T_1. In principle, when $T_1 > T_2$, the two processes can be distinguished by their different temporal behavior.

For our resonant intermediate state we have selected the 1s yellow exciton in Cu_2O. This exciton is split by the electron-hole exchange interaction into a Γ_{25}^+ ortho-exciton (ω_o = 16397 cm^{-1}) and a Γ_2^+ para-exciton (ω_p = 16301 cm^{-1}). The Γ_{25}^+ ortho-exciton is electric dipole forbidden but quadrupole allowed.

One-phonon Raman scattering in Cu_2O, as shown in the inset of Fig. 1 (a), involves the excitation of zone center ortho-exctions by electric quadrupole (EQ) transitions and emission of photons via phonon-assisted electric dipole (ED) transitions. The important points to note are that: (i) only the zone-center ortho-exciton is excited resonantly; (ii) the EQ transition is strongly polarized for radiation incident on the [110] surface of Cu_2O, in spite of the fact that Cu_2O has cubic symmetry[13]; and (iii) the one-phonon RRS is strongly polarized.[14] The two-phonon RRS process in Cu_2O, as shown schematically in the inset of Fig. 1(b), involves excitation of ortho-excitons by phonon-assisted ED transitions. Because of phonon participation, excitons with non-zero quasi-momentum can be

excited. Their kinetic energy is given by $\Delta(\hbar\omega) = \hbar(\omega_i - \omega_o - \omega_{12})$, where ω_{12} is the Γ_{12}^- phonon frequency.

The experiments were performed in a back-scattering geometry with a melt-grown single crystal of Cu_2O at $\sim 2^\circ K$. The ortho-exciton EQ absorbtion and emission show considerable polarization, indicating that the sample surface is probably oriented close to the [110] direction.[13] A synchronously pumped, modelocked dye laser was used to excite the sample. The laser pulses were $\sim$ 10 psec long with a linewidth of $\lesssim 1$ cm^{-1}. The ortho-exciton absorption linewidth is ~ 0.4 cm^{-1}. The scattered radiation was time-resolved with a time-delayed coincidence photon counting system.[15] The time response of this system to the incident laser pulses is shown in Fig. 2. The measured time-decays are deconvoluted with this system response to obtain the emission decay time. Although enhancement of several one-phonon and two-phonon Raman modes have been reported in Cu_2O, we will concentrate in this article on the strongest Γ_{12}^- and $2\Gamma_{12}^-$ modes.

Figure 1(a) and (b) show the time-integrated Γ_{12}^- and $2\Gamma_{12}^-$ RRS spectra of our Cu_2O sample. The spectra reproduce well the cw spectra reported previously.[10,11] Each spectrum consists of a sharp Raman peak superimposed on a broader background due to thermalized luminescence. In the two-phonon spectra the strengths of the Raman peaks are comparable to the background, so care must be used to determine their decay times.

Figure 2 shows the time-dependence of the resonantly excited Γ_{12}^- Raman mode for two different polarization geometries: (i) incident laser polarization is approximately along the (001) direction while that of the scattered radiation is perpendicular to it ($\hat{e}_i \perp \hat{e}_s$); and (ii) ($\hat{e}_i \parallel \hat{e}_s$). According to the Raman selection rules calculated by Birman[4] the Γ_{12}^- mode

is allowed in the $\hat{e}_i \perp \hat{e}_s$ geometry but forbidden in the $\hat{e}_i \parallel \hat{e}_s$ geometry. We found the ratio of the time integrated intensities for these two geometries to be ~0.76. A smaller value of ~ 0.52 was found in the cw experiment of Genack et al.[10] who attributed this breakdown in the observed Raman selection rule to imperfections in their sample.

By deconvolution with the system response we found that the emission in curve (ii) of Fig. 2 decays as: e^{-t/τ_a} where the decay time $\tau_a = 1.5$ nsec is the same as the ortho-exciton population lifetime (T_1) obtained in Ref. 16. On the other hand, curve (i) can only be fitted by the sum of two exponentials: $\alpha e^{-t/\tau_a} + \beta e^{-t/\tau_b}$ where τ_a again equals 1.5 nsec and τ_b = 0.7 nsec. If we subtract curve (ii) from curve (i) then the resultant curve (iii) in Fig. 2 represents the degree of polarization of the emission, which decays exponentially with time constant τ_b. Therefore we identify τ_b as the depolarization time T_{depol}, since the emission becomes unpolarized for times >> T_{depol}. We expect that the ratio of intensities in the allowed and forbidden geometries to be $\geq T_{depol}/T_1 = \frac{0.7}{1.5} \simeq 0.47$.

The decay curves can be understood qualitatively in terms of the model shown in the inset of Figure 2. The triply degenerate Γ_{25}^+ ortho-exciton states are labelled 1, 2, and 3. W represents the cross relaxation rate which equalizes the population in the three sublevels. The incident photons generate a non-uniform population distribution among the three sublevels plus a Raman polarization at ω_s. The selection rule allowed geometry $\hat{e}_i \perp \hat{e}_s$ can in principle contain up to 3 time dependent decay components: (a) a RRS component with decay time T_2 due to dephasing of the polarization at ω_s; (b) a HL component with decay time 1/3W due to cross

relaxation; and (c) a HL component with decay time T_1 due to decay of the total population in all three levels. In the forbidden geometry ($\hat{e}_i \| \hat{e}_s$) the intensity is entirely due to HL and should decay with the population lifetime T_1 only. Based on this model we attribute the depolarization of the Raman mode to cross relaxation and identify T_{depol} = 0.7 nsec as equal to $(3W+\frac{1}{T_1})^{-1}$, from which we calculate the cross relaxation rate $W = 2.5 \times 10^8 sec^{-1}$. We did not observe any component in curve (i) decaying with a time constant shorter than 0.7 nsec which we can identify as RRS. Hence, we conclude that either $T_2 = T_{depol}$ so that RRS = HL and the two cannot be distinguished by even time-resolved measurement or else RRS<<HL so that the RRS component is below our detection sensitivity. In both cases the time-integrated emission is dominated by HL. In the second case we can set limits on T_2 as $\sim$ 10 psec$<T_2<$0.7 nsec. The lower limit on T_2 is determined from the linewidth of the ortho-exciton absorption peak assuming homogeneous broadening.

Our $2\Gamma_{12}^-$ Raman mode is unpolarized so only the time dependences of the $\hat{e}_i \| \hat{e}_s$ component are shown in Fig. 3. We therefore expect the time-resolved RRS to show at most two decay times, corresponding to T_1 and T_2. We found that the curves in Fig. 3 show one or two decay components, depending on the ortho-exciton kinetic energy $\Delta(\hbar\omega)$. For $\Delta\omega \simeq 1$ cm^{-1} the Raman mode decays as e^{-t/T_1}, i.e., it is dominated by HL. For curves (ii) and (iii), however, there are two components to the decay. The slower component in both curves has time constant T_1 and is due to the decay of the luminescence background. The faster component with decay time $\tau_{ac}(\Delta\omega)$ depends on $\Delta\omega$, becoming faster as $\Delta\omega$ increases. We associate the faster component with the Raman peak. The variation in τ_{ac} with

$\Delta\omega$ can be explained by the dependence of the ortho-exciton lifetime on exciton energy. Yu and Shen[11] concluded from the cw two-phonon RRS in Cu_2O that the ortho-exciton lifetime is limited by acoustic phonon scattering. Using the model and parameters given in Ref. 17, we have calculated the acoustic phonon scattering rates for $\Delta\omega$=4 and 7 cm^{-1} to be $(1.0\pm0.4)\times10^{+9}sec^{-1}$ and $(2.8\pm0.7)\times10^{+9}sec^{-1}$ respectively. These values are in fair agreement with the values of $(1.8\pm0.6)\times10^{+9}sec^{-1}$ and $(3.3\pm1)\times10^{+9}sec^{-1}$ deduced from curves (ii) and (iii). For $\Delta\omega$=1 cm^{-1} the calculated scattering rate is less than the ortho- to para-exciton decay rate. Therefore, in curve (i) the decay of both the Raman signal and the luminescence background are dominated by ortho- to para-exciton decay so that the decay curve appears to be a single exponential. In summary, we have been able to resolve at most one decay component in the $2\Gamma_{12}^{-}$ Raman mode and the decay times we deduced are consistent with the lifetime of the exciton intermediate states due to acoustic phonon scattering. This result is consistent with the conclusion of the cw RRS result that either HL=RRS in the two-phonon mode or else HL>>RRS.

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Figure Captions

Figure 1: Time-integrated Raman spectra of Cu_2O at $\sim 2^\circ K$. The dotted line represents the thermalized luminescence background. (a) One-phonon Raman spectrum. (b) Two-phonon Raman spectrum for $\Delta\omega=4cm^{-1}$. The insets in (a) and (b) are respectively the schematic diagrams of one-phonon and two-phonon Raman scattering processes discussed in the text.

Figure 2: Time-dependence of one-phonon Raman scattering in Cu_2O. The scattering configurations were: (i) $(\hat{e}_s \perp \hat{e}_i)$ and (ii) $(\hat{e}_s \| \hat{e}_i)$. Curve (iii) was obtained by taking the difference between curves (i) and (ii). Curve (iv) represents the system's response to a $\sim$ 10psec long dye laser pulse. The inset represents the three-level model discussed in the text.

Figure 3: Time-dependence of two-phonon RRS in Cu_2O for incident laser frequencies corresponding to $\Delta\omega = \omega_i - \omega_o - \omega_{12}$ equal to (i) $1cm^{-1}$, (ii) $4cm^{-1}$, and (iii) $7cm^{-1}$ respectively. The dotted curve superimposed on (iii) represents a typical fit to the experimental curves by convolution of the system response with a decay function of the form: $0.126e^{-t/1.5ns} + e^{-t/0.26ns}$.

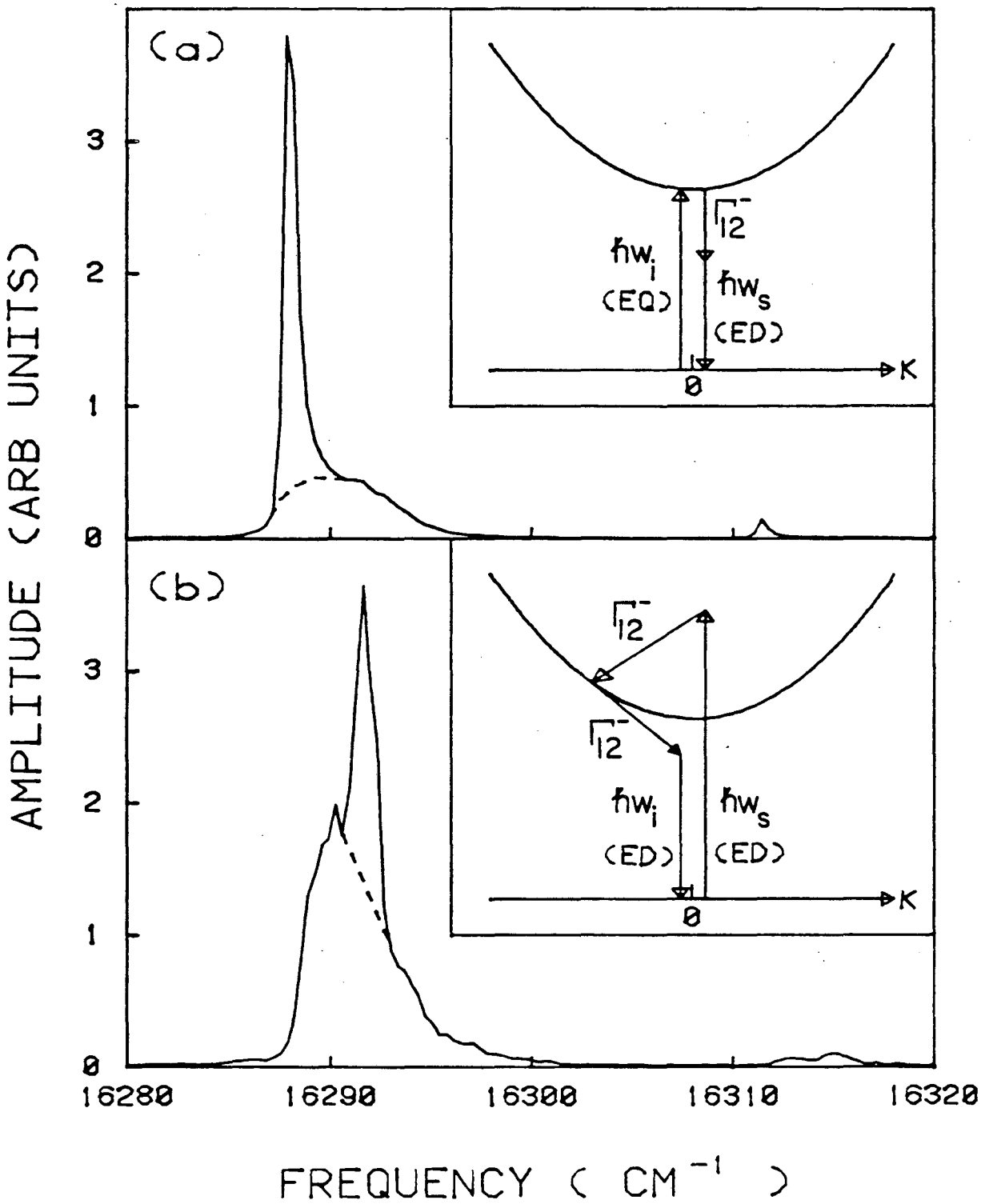

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Fig. 1

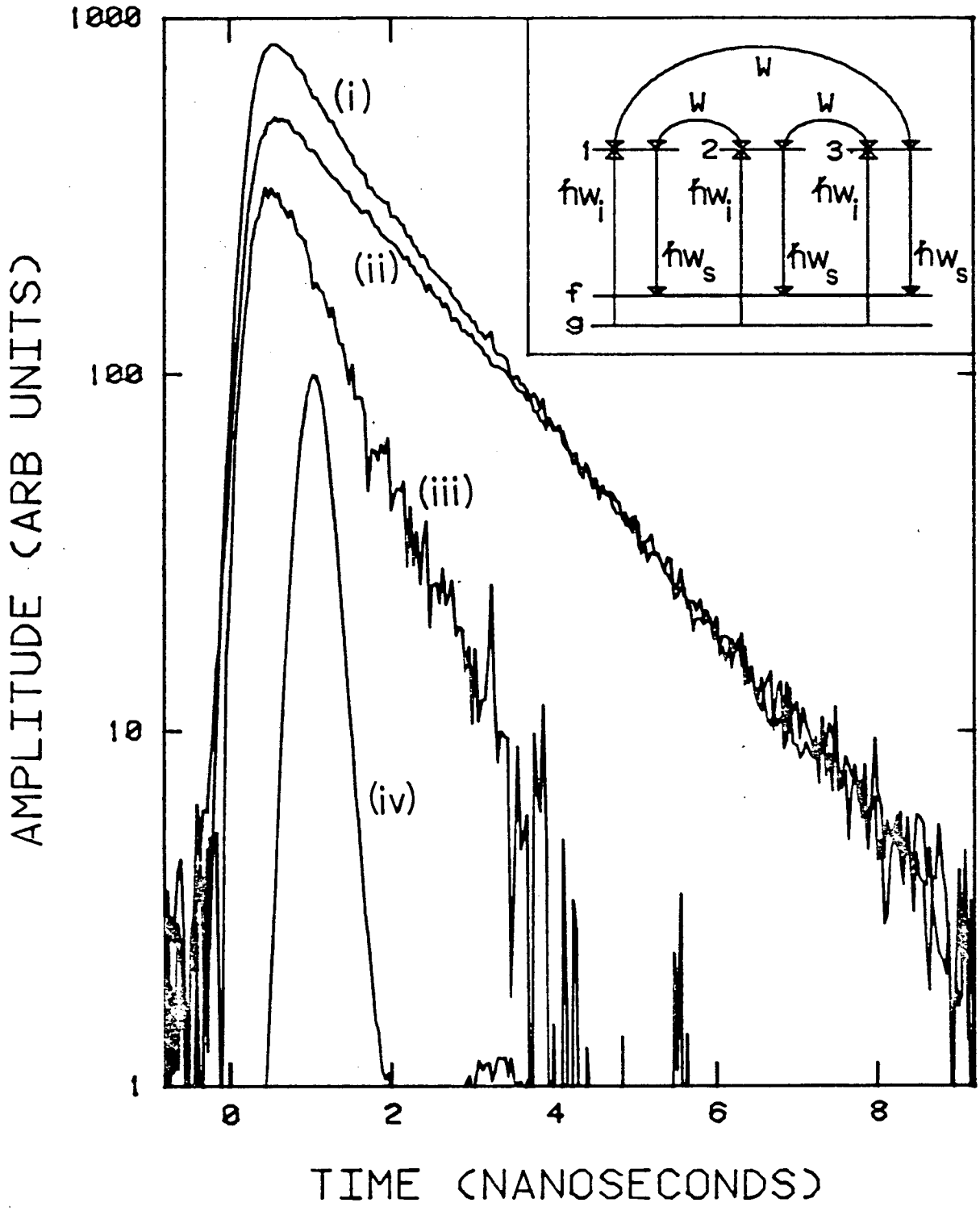

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Fig. 2

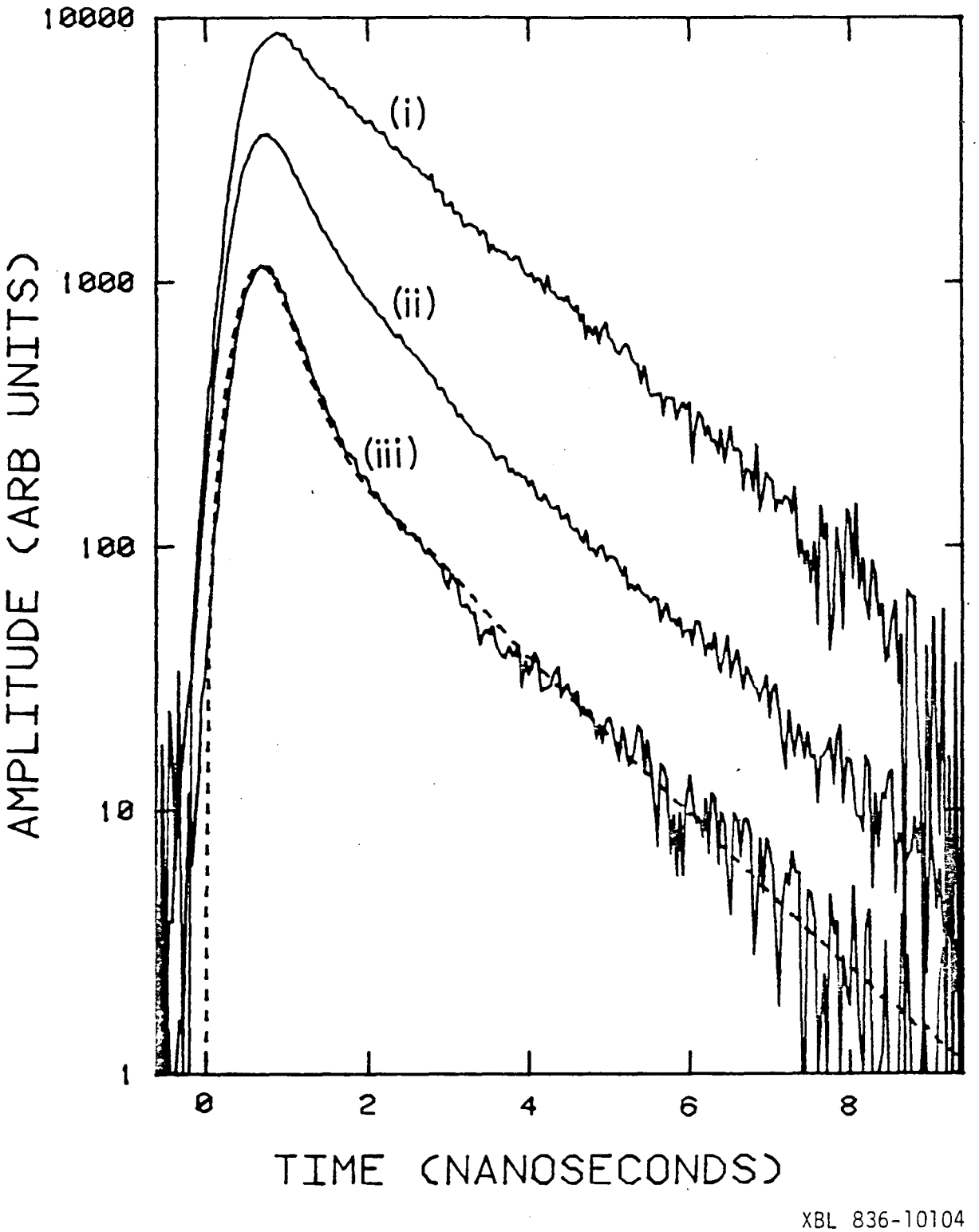
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Fig. 3

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