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TIME RESOLVED RESONANT TWO-PHOTON ABSORPTION SPECTROSCOPY IN Cu_2O

A. Mysyrowicz, D.Hulin
Groupe de Physique des Solides, Ecole Normale Supérieure
Tour 23, 2, place Jussieu, 75005 Paris - France
and
A.Migus, J.L. Martin, R. Astier, A. Antonetti
Laboratoire d'Optique Appliquée, Ecole Polytechnique-ENSTA
91120 Palaiseau - France

Resonant two-photon absorption is studied in Cu_2O with subpicosecond resolution. It is possible to distinguish between true two-photon transition and two-step processes.

With available pulsed light sources of subpicosecond duration, it is possible to measure dynamical processes on a fast time scale, of the order of 10^{-12} sec. The purpose of this paper is to present an experimental study concerning time-resolved measurements of a two-photon process in a semiconductor. A situation will be examined, in which the system is continuously tuned from the case of a pure two-photon absorption (for which both incident light frequencies ω_1 and ω_2 do not fall in a linear absorption region of the crystal) to a resonant one (when ω_1 corresponds to a strong linear absorption of the medium).

Cu_2O has several advantages for such a study[1]. Its lowest intrinsic absorption of electronic origin lies in the region of emission of mode-locked Rh 6 G lasers. Tuning of the incident laser frequency ω_1 inside the resonance is obtained here by changing the crystal temperature (thereby shifting the absorption of the crystal) rather than by changing ω_1. In this way, use can be made of the high performances of the passively mode-locked dye laser, (pulse duration $t_p \sim 0.5$ ps) operating under optimal conditions. Further, the resonant intermediate state has two interesting aspects for dynamical studies on a fast time scale : on one hand, the absorption has a broad spectral width, larger than that of the pump beam ($\Delta\omega \gtrsim 2\pi/t_p$ corresponding to ~ 20 Å), so that no distorsion of the response is introduced at resonance. On the other hand, the intermediate state is well defined and isolated from other electronic transitions. Thereby the system is well defined in view of its relative simplicity. The intermediate state is the n = 1 term of the exciton yellow series of Cu_2O, with a binding energy B = 0.13 eV. The creation of the n = 1 exciton occurs predominantly with emission or absorption of parity conserving optical phonon Γ_{12}^-. Therefore, the lowest absorption edge in this direct gap material is similar to that observed in crystals with indirect gap.

The principle of the measurement is shown in Fig. 1. The pump pulse ω_1 (wavelength around 613 nm, duration $t_p \gtrsim 0.5$ ps) is obtained by cavity dumping from a passively mode-locked Rh 6 G laser and amplified in a three stage dye amplifier to an energy $E \sim 1$ mJ[2]. Part of the pulse irradiates a Cu_2O single crystal, of thickness ~ 0.5 mm held at different temperatures. The rest of the pump beam is focused in a cell filled with H_2O or D_2O, generating a broad band continuum of subpicosecond duration, used as a weak probe beam. The induced absorption $\Delta\alpha$ of the probe beam ω_2 (we used only the wavelengths below the band gap) is measured in function of ω_2

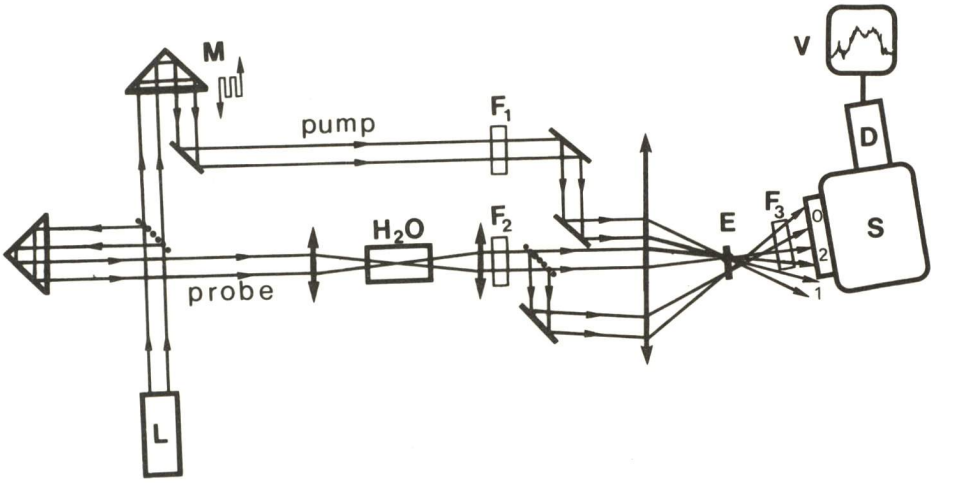

Fig.1 Experimental setup : L is the output of an amplifier of subpicosecond pulses (0.5 ps, 1 mJ, 10 Hz), M a step motor, F1, F2, F3 optical densities and colored filters. The beam 1, the pump, is focused on the sample E in a spatial coincidence with the white probe beam 2. Beams 2 and 0 (reference white pulse) enter in the spectrometer S and the OSA D. Induced absorption spectrum appears on display V.

and Δt, the time delay between pump and probe pulses.

In Fig.2 we show the phonon-assisted absorption band to the 1 S exciton of Cu_2O together with the pump beam spectrum.

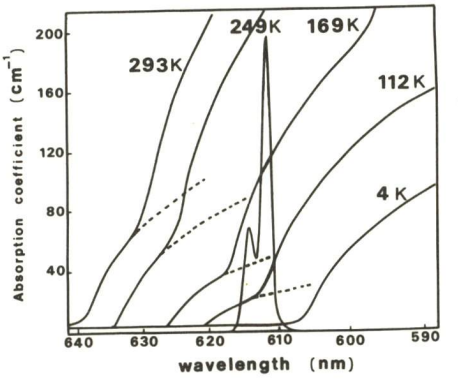

Fig.2 Absorption coefficient of Cu_2O at different temperatures after ref. [1]: Also shown is the spectrum of the pump beam.

Since the pulse duration is of the order of one cycle of the phonon involved in the transition ($\hbar\omega_0$ = 13.5 meV)we have compared, in a preliminary experiment, the absorption of Cu_2O measured with cw white light and the subpicosecond probe continuum. The spectral dependence of α and its change with T were found similar in both cases. In all measurements presented here, care was taken to keep the pump intensity below 10^{12} W/cm^2, so that the maximum exciton density estimated from the linear losses at ω_1 did not reach the Mott dissociation limit $n_M \sim 10^{20}$ cm^{-3}.

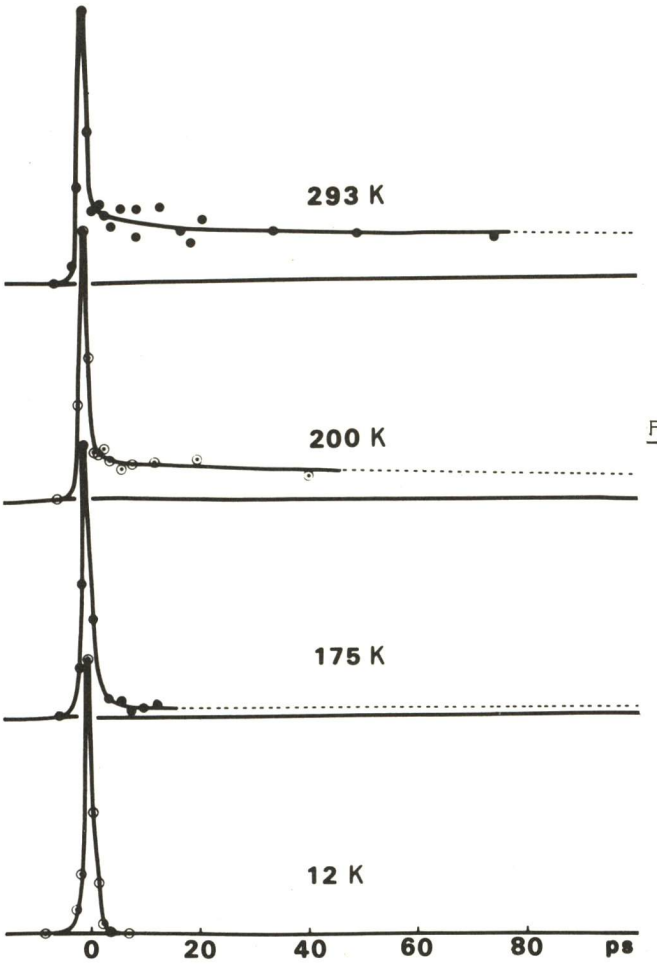

Fig. 3 Induced absorption of the probe beam as a function of delay between pump and probe pulses: The peaks have been normalized.

In Fig. 3, the induced absorption $\Delta\alpha$ at different temperatures is shown in function of Δt for a total energy $\hbar (\omega_1 + \omega_2) = 3.8$ eV. The value of $\Delta\alpha$, taken at $\Delta t = + 5$ ps, does not change between $\hbar \omega_2 \cong 1.4$ eV and $\hbar \omega_2 = 1.8$ eV. We have also measured the self attenuation of the pump beam ω_1 at $T \cong 15$ K where no linear losses exist, as a function of input intensity I_o. The ratio I_o / I_t (I_t is the transmitted intensity) is well expressed by the relation $I_o / I_t = 1 + a I_o$, indicating that higher order terms than two-photon may be neglected.

From the time behaviour of $\Delta\alpha$, shown in Fig.3 the pure two-photon absorption may be distinguished from the two-step excitation process: two-photon(ω_1 and ω_2) absorption is instantaneous and is the only contribution left at low T, where there is no linear losses at ω_1. The observed fast signal then corresponds to the correlation of the pump and probe pulses. Two-step absorption involves the real creation of excitons as the first step, and the probe beam completes the transition towards a continuum of electron-hole pairs. Due to the large spectral width of the pump beam, a superposition of exciton states with different k vectors within the n = 1 kinetic energy band are formed at t = 0. The second step

in the transition has a smooth spectral dependence so that the total exciton population lifetime is measured from the time dependence of the amplitude of the slow component , rather than the relaxation time of an exciton with a particular k vector to other exciton states [3]. The population lifetime of excitons at 300 K, as deduced from our results, is in excess of 10^{-10} sec. Measurements performed at low T with nanosecond pulsed excitation indicate very long exciton lifetime $\tau \sim 10^{-6}$ sec at temperatures up to 100 K [4]. Finally, we consider the ratio of the amplitude of the fast and slow absorption components at high T. Taking a simplified model, in which only linear and two-photon terms are considered, it can be shown [5] that this ratio should be of the form : $\Delta\alpha$ (t =0)/ $\Delta\alpha$ (t > 5 ps) = $\exp[\alpha_1 \int^{\ell} I\, dZ]$ where α_1 is the two-photon absorption coefficient, Z the propagation axis, I the pump intensity and ℓ the crystal thickness. From the measured ratio at 300 K, we estimate $\alpha_1 \sim 5\times10^{-9}$ cm/W to be compared with the value $\alpha_1 \simeq 2\times10^{-10}$ cm/W obtained for the pump beam at 15 K when ω_1 is not at resonance. The ratio of these two values may have some significance although the absolute magnitudes of α_1 are subject to uncertainty (estimated not to exceed 10 X) due to errors in measuring spot size and beam power.

In conclusion, true two-photon absorption can be distinguished from two-step processes by time-resolved measurements on a picosecond time-scale,using high intensity excitation.

1) see a review by S. Nikitine in " Optical properties of Solids" edited by SS. Nitra and S. Nudelman (Plenum, N.Y. 1969).

2) A. Migus, J.L. Martin, R. Astier and A. Orszag. Proceeding of the Topical Meeting on Picosecond Phenomena, Cap Code, Mass, USA (1980).

3) This is to be contrasted with resonant Raman scattering. See for example P.Y.Yu, Y.R. Shen, Y. Petroff, L.M. Falicov, Phys. Rev. Lett. 30, 283 (1973)

4) A. Mysyrowicz, D. Hulin, A. Antonetti: Phys. Rev. Lett. 43, 1123 (1919) and unpublished results.

5) **A. Mysyrowicz, D. Hulin and A. Antonetti: to be published.**