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TWO-PHOTON SPECTROSCOPY ON EVEN PARITY EXCITONS

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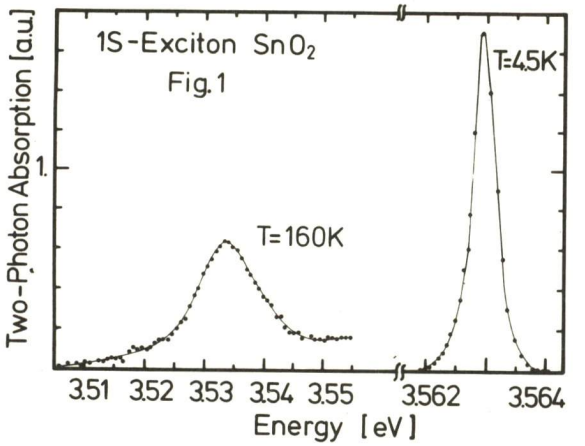
We present two-photon data of materials with a direct forbidden bandgap (SnO_2,Cu_2O). In SnO_2 we study exciton-phonon interaction by a line-width analysis. The detailed exciton fine structure in Cu_2O is explained by an exact diagonalization of the effective-mass Hamiltonian in the spherical approximation.

Direct forbidden band to band transitions and their accompanying excitons are specially suited to be studied by two-photon absorption (TPA). Though this is well appreciated since a theoretical paper by Loudon [1] almost 20 years ago, reliable experimental results are just beginning to drop in [2][3]. Besides the possibility to get reliable symmetry assignments by TPA experiments with polarized light [2] this nonlinear technique is superior to linear absorption in studying the temperature dependence of the exciton linewidth as was shown for CuCl by Kalm and Uihlein [4]. The theory for the exciton-phonon interaction and its influence on the linewidth was worked out by Toyozawa many years ago [5]. In Fig. (1) and (2) we present our results on the temperature dependence of the 1S exciton in SnO_2. As indicated in Fig. (2) the fit can be achieved by a linear term at low temperatures and a Bose function at higher temperatures. The high temperature fit yields a mean phonon energy of $\bar{E}$ = 40 meV which is close to the known optical phonons at 34 meV and 46 meV.



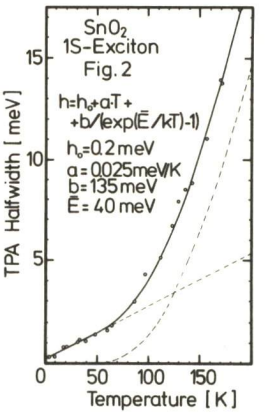


Fig. 1 Experimental results for 4.5K and 160K: Note change in energy scale

Fig. 2 Halfwidth of 1S-exciton in SnO_2 as function of temperature: Solid line results from fit by a Bose function and a linear temperature dependence

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The linear term at low temperatures can be accounted for by assuming that accoustical phonons are responsible for the scattering processes. The Lorentzian line shape points to the case of weak exciton-phonon coupling.

In the second part of this paper we will turn to the most famous candidate for parity forbidden excitons namely Cu_2O, which was first studied in one-photon absorption (OPA) by Hayashi and Katsuki [6] 30 years ago. In Fig. (3) we present a comparison of OPA and TPA. For the discussion on the controversal assignment of quantum numbers we refer to our recent paper [3] and literature cited therein.

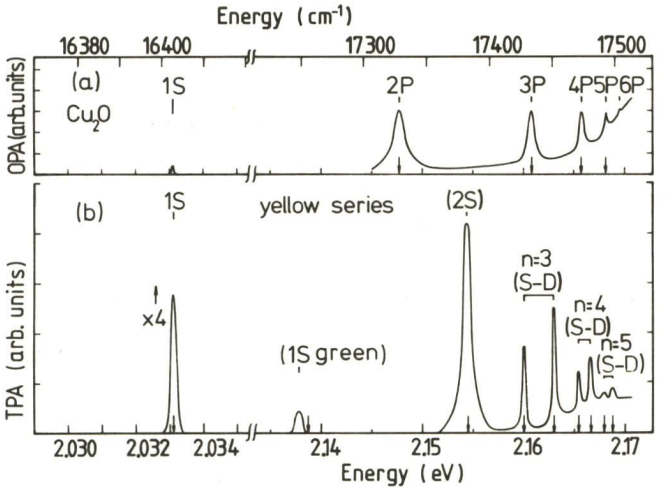

Fig. 3
One- and two-photon spectra of Cu_2O: arrows indicate calculated values

(a) One-photon data (OPA) at 4.2K
(b) Two-photon data (TPA) at 4.5K; the 1S line 2.033 eV was measured at 20K

The main features of the even exciton states are:
1. strong deviations from a hydrogen-like series;
2. occurance of S-D mixed doublets for $n \geq 3$;
3. anomalous exchange-splitting.

The different behavior of even and odd parity states originates from the fact that the 1S exciton of the green series is very close to the higher members of the yellow series. As parity is a good quantum number, this has no consequence for the odd parity states but leads in the case of the even parity states to a strong interseries mixing caused by the H_d term and electron hole exchange interaction.

All the details of the exciton spectra in Cu_2O are quantitatively described by the Hamiltonian

$$H = (1/\hbar^2)p^2 - \frac{2}{r} - \bar{V}_0\delta(\vec{r}) + (2/3)\bar{\Delta}(1+\vec{I}\cdot\vec{\sigma}_h) - (\mu/3\hbar^2)(P^{(2)}\cdot I^{(2)}) + \bar{J}_0(1/4-\vec{\sigma}_e\cdot\vec{\sigma}_h)\delta(\vec{r})$$

$$R_0 = \frac{e^4 m_0}{2\hbar^2\varepsilon_0^2(\gamma_1+\gamma_e)} \qquad a_0 = \frac{\hbar^2\varepsilon_0(\gamma_1+\gamma_e)}{e^2 m_0}$$

which is given here in reduced units R_0 and a_0 with zero energy at the $(\Gamma_7^+ \rightarrow \Gamma_6^+)$ band gap. The first two terms represent the usual hydrogenlike effective mass Hamiltonian followed by a central cell correction term, which is introduced to account for short range deviations from a screened Coulomb potential. Next follow an effective spin-orbit interaction term, the d-like kinetic energy term associated with the Γ_5^+ - valence band (given here in the spherical approximation of Baldereschi and Lipari [7]) and the electron-hole exchange interaction. The different terms of the Hamiltonian have the following effects:

1. Spin-orbit interaction splits the Γ_5^+ -valence band, thus giving rise to the yellow and green exciton series. The different series can be assigned by the effective hole spin $\vec{J} = \vec{I} + \vec{\sigma}_h$, J = 1/2 referring to the Γ_7^+ and J = 3/2 to the Γ_8^+ valence band.

2. The H_d term couples the effective hole spin J with the angular momentum L of the envelope state, which leads to a fine-structure splitting. Exciton states have to be assigned in addition by the quantum number $\vec{F} = \vec{L}+\vec{J}$. States belonging to different L and different J are mixed (strong mixture between 1S-green and yellow D excitons).
3. Exchange interaction splits states having an S envelope admixture into ortho- and paracomponents. States have to be assigned in addition by the quantum number $\vec{F}_{tot} = \vec{F}+\vec{\sigma}_e$. S excitons belonging to different J are mixed (mixture between 1S green and the yellow S excitons).

Applying the technique of Baldereschi and Lipari we end up with a set of differential equations for the eigenvalues and eigenfunctions, which are then solved by means of the finite element method as was done by Mattausch and Uihlein for CuBr [8]. The agreement of the calculated energies and the experimental results is excellent (deviations in most cases much less than 1 meV).

Additional lines, predicted by our theory, show up in a magnetic field of 7 T. We have chosen a Faraday configuration with magnetic field along [100]. This configuration allows only the excitation of states with magnetic quantum number M=0. The energy positions of the various exciton states (see Fig.(4))agree very well with theoretical values, despite of a slight diamagnetic shift towards higher energies. The different states are assigned in Fig. (4) by the atomic notation $^{2J+1}L_F$(L = S,P,D...).

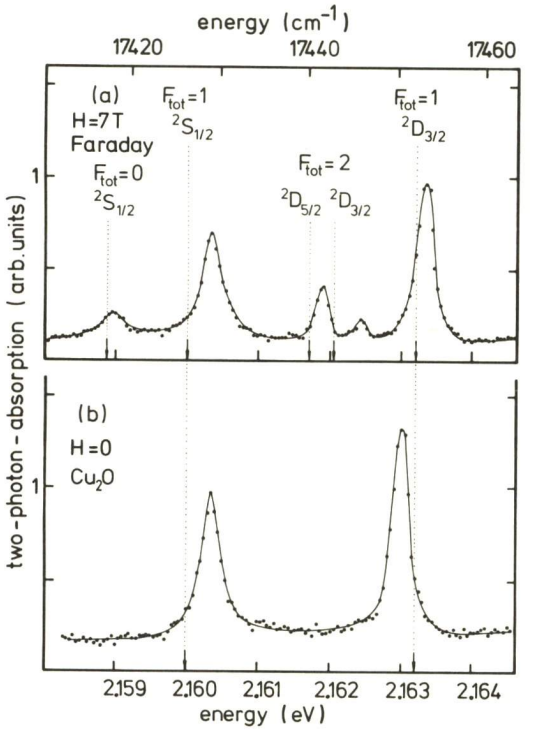

Fig. 4
Two-photon data in n=3 exciton region: Dotted lines indicate theoretical results

(a) Measurements in a magnetic field of 7 T
(b) Measurements without field

The analysis can be extended to the odd parity states. Our theory gives a $^2P_{1/2}$ - and $^2P_{3/2}$-exciton series with a nearly perfect $1/n^2$-dependence. The one-photon allowed $^2P_{3/2}$-exciton series agrees very well with the P exciton series as observed by OPA. The $^2P_{1/2}$ exciton series is dipole forbidden and can therefore not be observed by OPA.

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