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High resolution spectroscopy of yellow 1S excitons in Cu_2O

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Abstract

The 1S *ortho*- and *para*-exciton of the yellow series in Cu_2O are studied by high resolution spectroscopy. We observe that the 3-fold *ortho*-exciton (Γ_5^+-symmetry) is not degenerate. For a general **k**-direction there are three resonances with line width down to 1 μeV. The splitting is quantitatively explained by taking into account the long range and short range exchange interaction. The group velocity of the quadrupole polariton is directly determined with use of 20 ns pulses with still high spectral resolution ($\Delta E \approx 0.1$ μeV). Group velocities down to 4×10^4 m/s are quantitatively described by a one-oscillator quadrupole polariton model. The *para*-exciton (Γ_2^+-symmetry) is seen in absorption in magnetic fields down to 1 T. In selected crystals it shows a line width of 0.2 μeV.

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1. Introduction

Cu_2O is praised as the most favorable 3-D system to search for Bose–Einstein condensation (BEC) of excitons. For literature we refer to the critical discussion of possible BEC of excitons by Snoke [1]. There have been many attempts to observe high density effects in the lowest excitons of Cu_2O. In order to achieve high populations, pulsed lasers were used. We report on a different approach. With use of a single frequency dye laser (line width 2 neV) and high quality crystals we investigate the yellow 1S *ortho*- and *para*-exciton. The lowest exciton of the yellow series, the *para*-exciton is a pure spin-triplet state of Γ_2^+-symmetry and thus forbidden for direct excitation without external perturbation. Nevertheless, it can be populated by phonon emission from the threefold singlet-triplet-mixed state of Γ_5^+-symmetry (*ortho*-exciton) which is split off by 12.11 meV to higher energy by electron-hole exchange interaction. The *ortho*-exciton is one-photon quadrupole and two-photon dipole allowed. It can thus be pumped directly, but because of its fast relaxation to the *para*-exciton it is no longer considered as a favorite candidate for BEC. In addition the *ortho*-exciton has to be considered for any optically allowed condition as a polariton. As discussed by Ell et al. [2] there is a criterion for the oscillator strength of a polariton to allow for an effective occupation of the modes at $k \approx 0$.

As recently shown by high-resolution spectroscopy [3], the Γ_5^+ excitons are not anymore degenerate for $k \neq 0$. Because of **k**-dependent exchange terms, the threefold degeneracy is fully lifted for low symmetry directions such as [110] and [112], as shown in Fig. 1. The detailed

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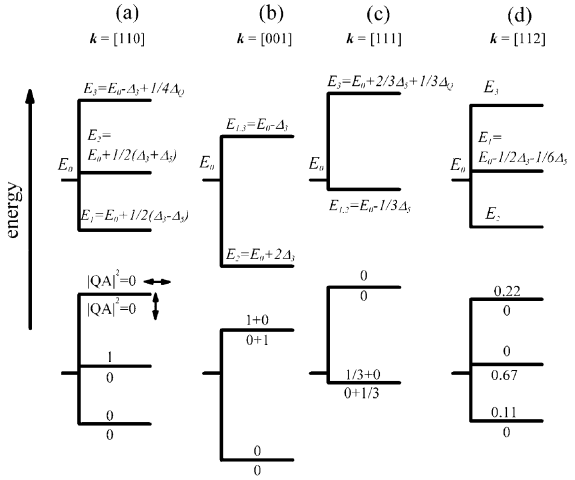

Fig. 1. Energy level diagram of the exciton fine structure of Cu_2O. E_0 gives the *ortho*-exciton energy including the exchange shifts Δ_0 and Δ_1. Panels (a), (b), (c), and (d) give the energy schemes for $k=$ [110], [001], [111], and [112], respectively ($\Delta_Q=5$ μeV, $\Delta_3=-1.3$ μeV, $\Delta_5=2$ μeV). In the upper schemes the analytic expressions for the exchange energy are indicated. In the lower half the oscillator strengths are given for each level. The upper and lower numbers correspond to horizontal and vertical polarization, respectively. In all cases the vertical axis is [−110].

knowledge of the *ortho*-exciton fine structure $E_i(\mathbf{k})$ ($i=1, 2, 3$) and the quadrupole selection rules allow to distinguish *ortho*-excitons with different oscillator strength and *ortho*-exciton dark states, e.g. E_2 ($\mathbf{k}=[001]$) and E_1, E_3 ($\mathbf{k}=[-110]$), which do not couple as a one-photon transition to the ground state. These states gain oscillator strength, if the crystal is turned by an angle ϕ, e.g. around a [111] direction as shown for $\mathbf{k}=[-110]$ in Refs. [3,4]. The *para*-exciton, however, being optically forbidden, remains a dark state, as long as it is not coupled to an optically allowed state by an external perturbation like a magnetic field.

In this contribution we will first discuss in detail the *ortho*-exciton polariton including the fine structure due to the **k**-dependent exchange splitting. After some remarks on the experimental setup we will present measurements of the group velocity, which are very well fitted to the polariton dispersion with use of only one parameter. By application of a magnetic field, the *para*-exciton gains quadrupole oscillator strength from the *ortho*-exciton. This allows to directly excite the *para*-exciton [5]. We present absorption measurements on the *para*-exciton. The polariton character can then be tuned by the field strength ($f_p=f_o\times A\times B^2$), where f_p and f_o are the oscillator strength of the *para*- and *ortho*-exciton, respectively, and A is given by the coupling matrix element. It is then a quantitative question, how much polariton character the *para*-exciton gains, which might hamper BEC [2]. The measurements of the *para*-exciton in a magnetic field up to 7 T yield an accurate value for the *ortho–para*-exciton splitting of $\Delta E_{o-p}=E_o-E_p=12.11$ meV.

2. The quadrupole polariton

We will now derive an expression for the quadrupole polariton, which includes the k-dependent exchange terms. In this simple picture of the polariton without damping we will calculate the excitation intensity around the resonance. In a one-oscillator model the dielectric function for a quadrupole polariton is given by [6]:

$$\varepsilon(\mathbf{k},\omega)=\left(\frac{c\mathbf{k}}{\omega}\right)^2=\varepsilon_b+\frac{f_i(\mathbf{k},\mathbf{e})\hbar^2c^2k^2}{(\hbar\omega_0+\Delta E_i(\mathbf{k}))^2-\hbar^2\omega^2} \tag{1}$$

where $\varepsilon_b=6.5$ is the background dielectric constant, $\hbar\omega_0=E_0=2.032223$ eV the 1S-exciton energy at $k=0$ and $T=1.6$ K, $f_i(\mathbf{k},\mathbf{e})$ stands for the quadrupole oscillator strength of the exciton component $i=1, 2, 3$, which depends on the wave vector **k** and polarization vector **e**. $\Delta E_i(\mathbf{k})$ includes the k^2 -dependent exchange terms and the kinetic energy term $\hbar^2k^2/2M$. The exchange terms $\Delta_3=-1.3$ μeV, $\Delta_5=2$ μeV, $\Delta_Q=5$ μeV are determined for k_0 with $\hbar ck_0/\sqrt{\varepsilon_b}=E_0+\Delta E_i(k_0)$. For convenience we introduce $x=\hbar ck/\sqrt{\varepsilon_b}$ (eV) instead of the wave number k (m^{-1}). Eq. (1) is then rewritten as:

$$\frac{x^2}{E^2}=1+\frac{f_i(\mathbf{k},\mathbf{e})x^2}{(E_0+A_i(\mathbf{k})x^2)^2-E^2} \tag{2}$$

For the quadrupole allowed states in the main symmetry directions the parameters $A_i(\mathbf{k})$ are determined by the exchange parameters Δ_3 and Δ_5 and the isotropic effective mass $M=3.5m_e$, which includes the isotropic k^2-exchange term, as discussed in detail in Ref. [4]:

$$\begin{aligned}
&\mathbf{k}=[001]:\\
&A_{1,3}=\frac{\varepsilon_\mathbf{b}}{2Mc^2}-\frac{\Delta_3}{x_0^2}=2.12\times10^{-6}\ \mathrm{eV}^{-1}\\
&\mathbf{k}=[110]:\\
&A_2=\frac{\varepsilon_\mathbf{b}}{2Mc^2}+\frac{\Delta_3+\Delta_5}{2x_0^2}=1.89\times10^{-6}\ \mathrm{eV}^{-1}\\
&\mathbf{k}=[111]:\\
&A_{1,2}=\frac{\varepsilon_b}{2Mc^2}-\frac{\Delta_5}{3x_0^2}=1.64\times10^{-6}\ \mathrm{eV}^{-1}
\end{aligned} \tag{3}$$

Eq. (2) is biquadratic in E and can thus be solved analytically for the two polariton branches. In Fig. 2 we present for $\mathbf{k}=[001]$ the polariton and exciton dispersion for the allowed states $E_{1,3}$ and the exciton dispersion for the forbidden state E_2, which is split off at x_0 by $3\Delta_3=-3.9$ μeV. From the solutions for $E^2(x)$ one can easily calculate the group velocity v_g for both polariton branches:

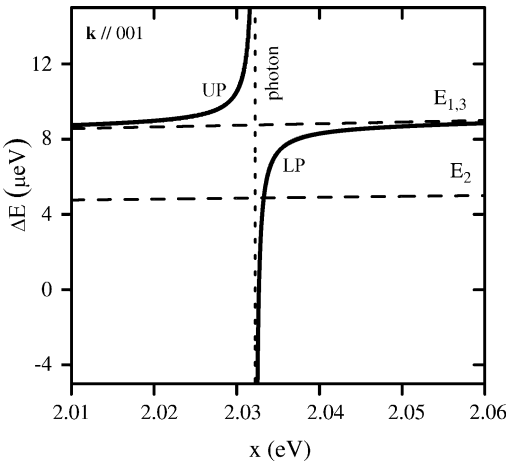

Fig. 2. Upper (UP) and lower (LP) polariton dispersion for allowed states $E_{1,3}$ (solid lines), exciton dispersion for $E_{1,3}$ and forbidden E_2 states (dashed lines) for $\mathbf{k}=[001]$. Wave number k is given in units of $x(\mathrm{eV})=\hbar ck/\sqrt{\varepsilon_b}$. $\Delta E=0$ refers to $E_0=2.032223$ eV. The photon dispersion with background dielectric constant ε_b is shown as dotted line ($\Delta E=(x-E_0)\times 10^6$).

$$v_g=\frac{d\omega}{dk}=\frac{c}{\sqrt{\varepsilon_b}}\frac{1}{2E}\frac{dE^2}{dx} \tag{4}$$

Due to the high spectral resolution ($\Delta E\approx 2$ neV) we can excite a very narrow spectral region within the polariton resonance. Since the polariton excitation intensity depends on the group velocity, we expect a pronounced energy dependence of the polariton density.

3. Experimental setup

For the transmission measurements we use a frequency stabilized ring dye laser (Coherent 899-21) pumped by a frequency doubled Nd:YVO_4-laser, as shown in Fig. 3.

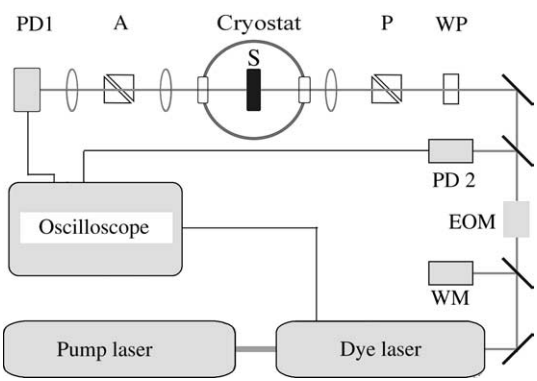

Fig. 3. Schematic setup for high resolution spectroscopy: A, analyzer; P, polarizer; PD, photodiode; EOM, electro–optical modulator; S, sample; WM, wavelength meter; WP, half or quarter wave plate.

Polarizing optics allow to set any polarization. A reference diode is used to compensate for fluctuations of the laser intensity. For the measurements of the group velocity we use an electro-optical modulator to create 20 ns pulses. The measurements were done in an immersion cryostat or a split-coil magnet which allows experiments in Faraday or Voigt configuration in fields up to 8 T.

4. Experimental results

In Fig. 4 we present our measurements of the group velocity for the quadrupole polariton for $\mathbf{k}=[110]$. Since in experiments the photon energy E is tuned, we plot $v_g(E)$. Group velocities as low as 40 km/s were measured. A good agreement between the experimental results and the polariton dispersion is obtained with an oscillator strength $f_2[110]=3.9\times 10^{-9}$ instead of 3.6×10^{-9} from Ref. [6]. In Fig. 4 we have included the velocity values for the LA and TA phonons. It would certainly be a challenge to measure the polariton group velocity down to the velocity of sound. As seen in Fig. 4, there are some indications, that v_g does not decrease going further into the resonance. In our polariton model (Eq. (1)) we have not taken into account any damping. A microscopic damping would have to include phonon scattering which leads to a population of the *para*-exciton.

In a magnetic field the *para*-exciton can be directly excited through the admixture of the $M=0$ component of the *ortho*-exciton [5]. For $\mathbf{k}=[110]$ and $\mathbf{e}=[001]$, the *ortho*-exciton state ($\Gamma_{5x}^{+}+\Gamma_{5y}^{+}$) ($M=0$ component in Faraday configuration) is mixed into the *para*-exciton Γ_2^{+}, as can be derived by group theory [7]. Because of the large exchange splitting of $\Delta E_{o-p}=12.11$ meV, the admixture is rather

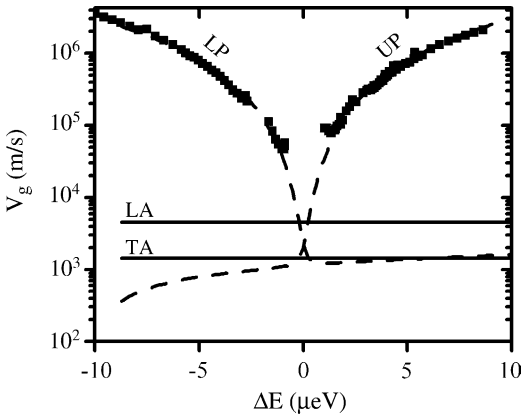

Fig. 4. Group velocity v_g for upper (UP) and lower (LP) polariton branches for $\mathbf{k}=[110]$ as function of photon energy ΔE. Experimental data are given by full squares. Dashed lines are a fit of Eq. (4) to the data with an oscillator strength $f_o=3.9\times 10^{-9}$. Continuous lines represent the sound velocity of the longitudinal (LA) and transverse (TA) acoustic phonons.

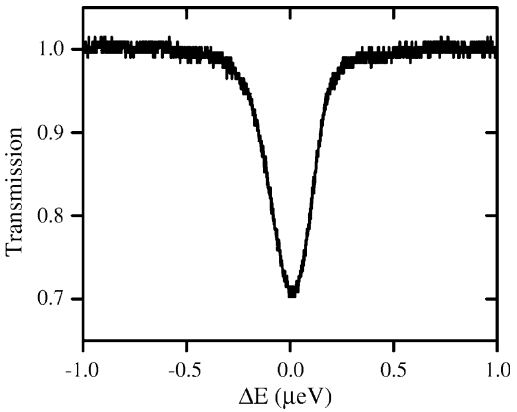

Fig. 5. Transmission spectrum of the *para*-exciton at $B=7$ T and 1.6 K as function of detuning $\Delta E=E-E_p$ from the *para*-exciton resonance $E_p=2.02012$ eV.

small and proportional to B^2. For 7 T the oscillator strength of the *para*-exciton f_p is about $4\times10^{-3}\times f_o$, as derived from the parameters of Ref. [5]. Through this admixture the *para*-exciton becomes a polariton. In Fig. 5 we show the *para*-exciton resonance. The line width of about 0.2 μeV is only achieved by a strain-free mounting of the high quality crystal [4]. From the extrapolation of the field dependence to $B=0$ we get an accurate value for the exchange splitting $\Delta E_{o-p}=12.11$ meV. The detailed field dependence shows the expected B^2-repulsion of the *para*- and $M=0$ *ortho*-exciton.

5. Discussion

The detailed consideration of the polariton and dark state properties of the *ortho*-exciton fine structure and the *para*-exciton together with high resolution experiments opens many new possibilities to study high excitation phenomena in Cu_2O. We will present a simple estimate of the density as function of excitation energy. For a laser beam of d (μm) diameter we get for a laser power of P (mW) a photon flux of $F=4\times10^{21}$. P/d^2 ($cm^{-2}\,s^{-1}$) at a photon energy of 2 eV. The polariton density $n(E)$ (cm^{-3}) neglecting reflection losses is given by $F/v_g(E)$. For $d=10$ μm and $P=100$ mW and a group velocity of 4×10^4 ms^{-1} (Fig. 4) we get already a polariton density of 10^{17} cm^{-3}, which should increase drastically if we tune further into the resonance. For a weakly interacting Bose gas the critical temperature T_c for a density n (cm^{-3}), a degeneracy g and a mass $M=3m_e$, is given by $T_c=(n/g)^{2/3}\times10^{-11}$ [1]. For $n=10^{17}$ cm^{-3} and $g=1$ we get $T_c=2.15$ K.

With high resolution spectroscopy, one could select a non-degenerate state (e.g. E_2 for $\mathbf{k}=[110]$, Fig. 1). As shown in Ref. [2], for excitation of states with sufficiently low oscillator strength (kinetic energy E_{kin} $(k_0)\gg$ Rabi energy $\hbar\Omega_c$) an effective occupation of $k\approx0$ states may be possible and thus lead to BEC. As discussed in Ref. [2], this condition is certainly not fulfilled for the quadrupole allowed *ortho*-excitons in Cu_2O, since the kinetic energy is about 9 μeV for $\mathbf{k}=[001]$ and the Rabi energy is 127 μeV for $f_o=3.9\times10^{-9}$. The *para*-exciton in a magnetic field, however, is a good candidate, since its Rabi energy is $\hbar\Omega_p=\hbar\Omega_0\sqrt{f_p/f_o}$. From the data of Ref. [5] we get for 1 T a Rabi energy $\hbar\Omega_p=1.1$ μeV, which is less than the kinetic energy by a factor of 8. Besides the *para*-exciton in a magnetic field, the *ortho*-exciton dark state E_2 in $\mathbf{k}=[001]$ (Fig. 1) studied by two-photon absorption would be a good candidate. For laser polarization $\mathbf{e}=[110]$ one can excite the quadrupole forbidden Γ_{5z}^+ state, which is the lowest Γ_5^+ *ortho*-exciton (Fig. 1). It should, however, be kept in mind that the Γ_{5x}^+ *ortho*-exciton has then to be considered as a two-photon polariton, where the oscillator strength is determined by the two-photon transition probability, which depends on the laser intensity.

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