Absolute external photoluminescence quantum efficiency of the 1*s* orthoexciton in Cu_2O

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The photoluminescence quantum efficiency of the yellow series 1*s* orthoexciton in Cu_2O, including its phonon sidebands, was measured in an Ulbricht sphere. The obtained efficiency values between 10^{-4} and 10^{-6} are remarkably low. The nonmonotonous temperature dependence is analyzed.

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I. INTRODUCTION

Cuprous oxide is a semiconductor with a direct gap ($E_g \approx 2.17$ eV at $T=10$ K) at the Γ point. Due to its small Bohr radius, the excitonic ground state $n=1$ is split by electron-hole exchange interaction into the $J=1$ orthoexciton (X_o) and the $J=0$ paraexciton (X_p) which is assumed to lie 12 meV lower in energy.[1,2]

Cu_2O luminescence spectra have been comprehensively discussed in several publications.[3,4] For the paraexciton there exists only one very weak Γ_{25}^- phonon assisted sideband, while its direct radiative recombination is forbidden in all orders. The orthoexciton can either recombine directly in a quadrupole transition, or via a phonon assisted process. Although a X_o replica for each odd-parity optical phonon exists, the PL spectrum is strongly dominated by Γ_{12}^- assisted recombination. The concerned optical phonon has a quite flat dispersion and its absorption/emission is $\vec{k}$ independent in the vicinity of the Γ point. Therefore the line shape of the Γ_{12}^--assisted luminescence directly reflects the energetical distribution of orthoexcitons. For the same reason the integrated intensity of this peak is proportional to the total number of orthoexcitons $n_o(T)$.

Orthoexciton and paraexciton can scatter into each other via a two phonon assisted conversion process, originally proposed by Caswell and Yu[5]

$$\text{up:} \quad X_p + \text{LO} \pm \text{LA} \rightarrow X_o,$$

$$\text{down:} \quad X_o - \text{LO} \pm \text{LA} \rightarrow X_p, \tag{1}$$

where $+/-$ describe the absorption/emission of a phonon. The involved LO phonon is either of symmetry Γ_{12}^- ($E \approx 13.4$ meV) or Γ_{25}^- ($E \approx 11.4$ meV). The energy mismatch is compensated by the LA phonon. The two processes (up and down) can be described by the corresponding transition rates $U(T)$ and $D(T)$. This yields coupled rate equations for the X_o and X_p population, with the steady-state solution

$$n_o = \frac{G_o(U+\gamma_p)}{(U\gamma_o + D\gamma_p + \gamma_o\gamma_p)} \tag{2}$$

for the X_o density.[5] G_o is the generation rate of orthoexcitons, caused by laser excitation. γ_o and γ_p are the loss rates of orthoexcitons/paraexcitons due to other processes such as nonradiative recombination or recombination at defects and are expected to be roughly temperature independent.

II. EXPERIMENTAL RESULTS AND DISCUSSION

We examined a polished, naturally grown sample of high quality with a surface of ≈ 1 mm^2 and a thickness of ≈ 500 μm. The 1*s* excitons were created by excitation with a cw dye-laser at $\hbar\omega = 2.25$ eV in the absorption continuum of the yellow series. Based upon a laser intensity of 1.9 W/cm^2 and assuming a lifetime of several 100 μs for the paraexcitons, we estimate the 1*s* density to be in the range of 10^{16}/cm^3. A spatially integrating sphere (Ulbricht sphere) was mounted in a cryostat to collect the whole luminescence, independent of the angle of emission. With this set-up we are able to determine the external quantum efficiency $\eta_{\text{lum}}(T)$ which is the ratio between the flux of the emitted PL photons and the absorbed laser photons. For details of the experimental set-up and the evaluation procedure see, e.g., Refs. 6,7. Due to the extremely low absorption coefficient of Cu_2O in the spectral region of interest, there occurs almost no self-absorption. Therefore the external quantum efficiency is identical with the internal one.

Figure 1 shows $\eta_{\text{lum}}(T)$ in the range 6 K$\leqslant T \leqslant$90 K, integrated over the whole spectral range of the phonon assisted 1*s* luminescence. The by far dominant contribution comes from the Γ_{12}^- phonon assisted X_o luminescence. The influence of the other PL sidebands is negligible and does not affect the following evaluations.

First we want to call attention to the remarkably low values of η_{lum}, lying between 10^{-4} and 10^{-6}. The Γ_{25}^- assisted X_p luminescence is even weaker by some orders of magni-

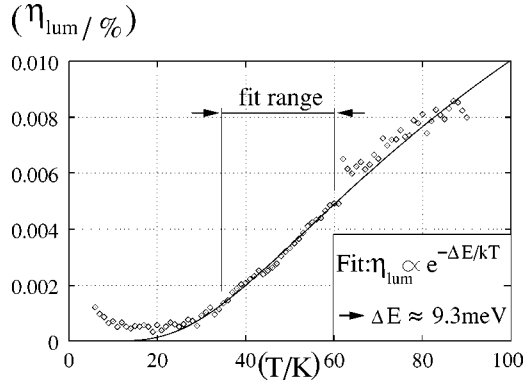

FIG. 1. External quantum efficiency η_{lum}, integrated over the range 1.94–2.07 eV. The solid line shows a fit according to Eq. (3) in the range 35–60 K. Note that the value of η_{lum} is represented in percent.

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tude. This explains why this signal is experimentally hard to measure, especially in a time-resolved manner.

The anomalous temperature dependence, first observed in Ref. 8, can be explained by the $X_p \leftrightarrow X_o$ conversion mechanism discussed before. Starting at $T=0$ K, it is evident that the up-conversion is ''frozen'' ($U=0$) because there are no LO phonons to be absorbed. But also down conversion is reduced for $T \rightarrow 0$ for the following reasons. As already mentioned, two different LO modes (Γ_{25}^- and Γ_{12}^-) come into question to participate at the down-conversion process. The energy of the Γ_{25}^--mode is smaller than the ortho-para splitting. Thus, even at low temperatures, this mechanism works at least under the spontaneous emission of a LA phonon.

Considering the Γ_{12}^--mode the energy of which is ≈ 1.4 meV greater than the ortho-para splitting, the situation changes. If the kinetic energy of the orthoexciton falls below 1.4 meV, this process is only possible by the absorption of an acoustical phonon. Assuming an average kinetic energy of $\frac{3}{2}kT$ one finds a corresponding temperature of ≈ 11 K. A further diminution of temperature reduces the Γ_{12}^- assisted down-conversion channel, caused by the decreasig density of LA phonons. This explains the shape of $\eta_{\mathrm{lum}}(T)$ in the low temperature range ($T<15$ K). Raising the temperature from 6 up to 15 K increases the contribution of Γ_{12}^- assisted down conversion while the up conversion stays negligible. Consequently in this range $\eta_{\mathrm{lum}}(T)$ decreases continously.

Between 15 and 20 K, up-conversion starts and a further increase of temperature repopulates the X_o level. In the range $30 \leqslant T \leqslant 70$ K a thermal quasi-equilibrium is established between the X_o and X_p levels. In this temperature regime ortho- and para-level behave similar to a ''simple'' two-level system and the X_o density should approximately follow

$$n_o(T) \propto \eta_{\mathrm{lum}}(T) \propto \frac{U(T)}{D(T)} \approx \mathrm{e}^{-\Delta E/(k \cdot T)}, \tag{3}$$

where ΔE is the ortho-para splitting. On the one hand our data fulfills the functional relation of Eq. (3) in a convincing manner, on the other hand we find $\Delta E \approx (9.3 \pm 0.2)$ meV, in disagreement with the measurement of Kreingold.[8] Our result should be distinctly more exact than that in Ref. 8, because we used an Ulbricht sphere and much more data points to determine ΔE. Since the ortho-para splitting of $\Delta E \approx 12$ meV has been repeatedly confirmed,[1,2] we do not want to question this value. The slight deviation might be explained by a weak temperature dependence of G_o, γ_o, γ_p [Eq. (2)] or by a strained sample.

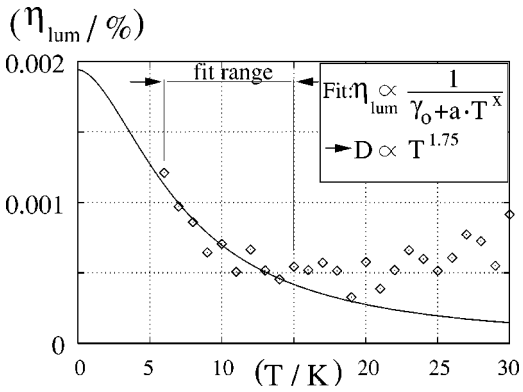

FIG. 2. Determination of the temperature dependence of $D(T)$ in the case of negligible up conversion ($T \leqslant 15$ K) using Eq. (4).

At higher temperatures ($T>80$ K) the large $\vec{k}$ values reduce the probability of direct radiative recombination while the probability of recombination at defects increases. Therefore Eq. (3) is no longer sufficiently fulfilled in this temperature range.

In the limit $T \leqslant 15$ K ($U \approx 0$) Eq. (2) yields

$$\eta_{\mathrm{lum}}(T) \propto n_o(T) \propto 1/[\gamma_o + D(T)]. \tag{4}$$

The theoretical temperature dependence of down-conversion is predicted[9] to be $D(T) \propto T^{3/2}$. Using Eq. 4 and $D(T) = a \cdot T^x$, we find $D(T) \propto T^{1.75}$ (Fig. 2) in good agreement with theory.

III. SUMMARY

We determined the temperature dependent absolute PL quantum efficiency of the yellow series 1s-orthoexciton in Cu_2O. The qualitative temperature dependence found in Ref. 8 was confirmed, but the resulting activation energy slightly deviates. At low temperatures ($T \leqslant 15$ K) the evaluated temperature dependence of the down-conversion rate $D(T)$ is in good agreement with theory.[9]

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