



# Calorimetric absorption spectroscopy of copper centers in II–VI semiconductors at mK temperatures

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## Abstract

Calorimetric absorption and transmission spectroscopy at mK-temperatures is the most powerful method to determine quantitatively nonradiative recombination processes. This method is applied to the  $\text{Cu}^{2+}({}^2\text{E}-{}^2\text{T}_2)$  and  $((\text{Cu}^+, \text{h})-\text{Cu}^{2+}({}^2\text{T}_2))$ -transitions in ZnS and ZnO. The obtained quantum yields  $\eta$  explain the drastic differences of the  $\text{Cu}^{2+}$ -luminescence intensities in different II–VI compounds.

## 1. Introduction

Copper is a prominent luminescence activator in II–VI semiconductors and gives rise to various visible and near infrared emission and absorption bands. Although most of these bands have been discussed intensively, the nonradiative recombination processes involved are completely unknown up to now. A well-known copper system is the deep  $\text{Cu}^{2+}$ -acceptor. In the wide gap compounds ZnS, CdS and ZnO it produces two localized d-levels in the band gap [1,2] and a transient shallow acceptor level near the valence band [3–5]. It is a striking fact that the luminescence intensity connected with these levels changes drastically comparing the sulfide compounds with ZnO. In ZnS and CdS an intense infrared  $\text{Cu}^{2+}({}^2\text{E}-{}^2\text{T}_2)$  luminescence and absorption band is observed easily, whereas the  $\text{Cu}^{2+}$  luminescence in ZnO is

extraordinarily weak in spite of a strong absorption band [2,3,6,7]. The aim of this contribution is to elucidate for the first time this open question by measuring the copper related nonradiative relaxation processes using calorimetric absorption spectroscopy (CAS) [8].

## 2. Experimental technique

CAS detects the increase of sample temperature by generation of phonons during the nonradiative relaxation of an excited system to thermal equilibrium. The nonradiative recombination part  $Q$  is given by

$$Q = \frac{P_{\text{CAS}}}{P_{\text{abs}}}, \quad (1)$$

where  $P_{\text{abs}}$  is the light power absorbed by the sample and  $P_{\text{CAS}}$  is that part of  $P_{\text{abs}}$  which is converted into heat.  $P_{\text{abs}}$  and  $P_{\text{CAS}}$  are determined quantitatively by means of calorimetric detection of

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the transmission and of the temperature change of the sample, respectively. We performed our experiments using a  $^3\text{He}/^4\text{He}$ -dilution refrigerator. The experimental setup is described in detail in Ref. [8].

### 3. Experimental results and discussion

#### 3.1. The $\text{Cu}^{2+} (^2\text{E}-^2\text{T}_2)$ -quantum yield

In ZnO and ZnS the copper ion is substituted on a cation site. The tetrahedral crystal field of the four ligands splits the  $^2\text{D}$  state of the free  $\text{Cu}^{2+}$ -ion ( $d^9$ -system) into a  $^2\text{T}_2$ -ground and a  $^2\text{E}$ -excited state. The trigonal crystal field, the spin-orbit interaction as well as the Jahn-Teller effect influence the fine-structure splitting in each material as described elsewhere [2,6,9]. The zero phonon lines (ZPLs) of the  $\text{Cu}^{2+} (^2\text{E}-^2\text{T}_2)$  transition are in the near infrared spectral region at 0.72 eV in ZnO and at 0.86 eV in ZnS. Typical CAS spectra and calorimetric transmission spectra (CTS) of the  $^2\text{T}_2-^2\text{E}$ -transition in ZnO and ZnS are shown in Figs. 1 and 2, respectively. From these spectra the nonradiative recombination part  $Q$  is calculated to be given by  $Q = 75 \pm 3\%$  for ZnO and by  $Q = 52 \pm 3\%$  for ZnS. As  $\text{Cu}^{2+}$  is a simple two-level system,  $Q$  includes only the nonradiative multiphonon relaxation ( $Q_1$ ) and phonons generated in the radiative relaxation ( $Q_2$ )

$$Q = Q_1 + Q_2 = Q_1 + \frac{(1 - Q_1)\Delta}{E}. \quad (2)$$

Here,  $E$  is the energy of the ZPL and  $\Delta$  is the displacement of the center of gravity of the phonon sideband observed in the related emission spectrum.  $Q_1$  is determined using Eq. (2):  $Q_1 = 71 \pm 3\%$  ( $\Delta = 0.10 \pm 0.02$  eV) in ZnO and  $Q_1 = 46 \pm 3\%$  ( $\Delta = 0.10 \pm 0.02$  eV) in ZnS. The quantum yield  $\eta$  of the radiative  $^2\text{E}-^2\text{T}_2$ -transition is given by  $\eta = 1 - Q_1$ . The quantum yields  $\eta$  of the  $\text{Cu}^{2+}$ -luminescence transitions are therefore given by  $\eta = 29 \pm 4\%$  for ZnO and  $\eta = 54 \pm 4\%$  for ZnS. The obtained quantum yields and the measured decay times  $\tau$  of 200 ns for ZnO [7] and 350 ns for ZnS [6] enable us to calculate the radiative as well as the nonradiative transition probabilities  $W_r$

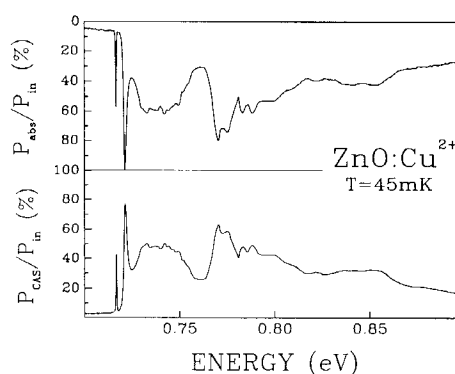


Fig. 1. Calorimetric absorption and transmission spectra of  $\text{Cu}^{2+}$  in ZnO at 45 mK. The calculated quantum yield  $\eta$  is  $29 \pm 4\%$ .

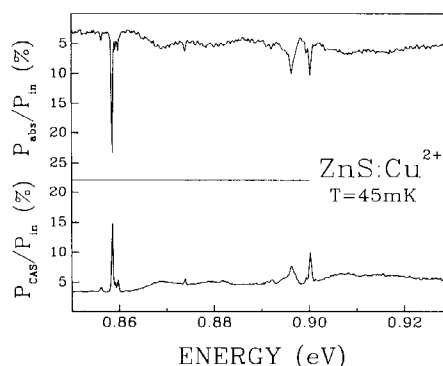


Fig. 2. Calorimetric absorption and transmission spectra of  $\text{Cu}^{2+}$  in a mixed cubic and hexagonal ZnS crystal at 45 mK. The calculated quantum yields  $\eta$  are  $54 \pm 4\%$  for all  $\text{Cu}^{2+}$ -centers.

and  $W_{nr}$  for the  $\text{Cu}^{2+}$ -transition, because  $1/\tau = W_r + W_{nr} = \eta/\tau + (1 - \eta)/\tau$ .  $W_r$  is 1.5 MHz for ZnO and ZnS, indicating the same oscillator strength. Additionally, efficient multiphonon relaxation processes take place, given by  $W_{nr} = 3.6$  MHz for ZnO and 1.3 MHz for ZnS. The  $\text{Cu}^{2+}$  fine structure spectra demonstrate that the  $^2\text{T}_2-^2\text{E}$ -transition has a medium Huang-Rhys factor  $S$ . Thus, the probability of multiphonon relaxation depends on the ratio between the transition and the phonon energy [10]. The lower quantum yield  $\eta$  and the larger  $W_{nr}$  of  $\text{Cu}^{2+}$  in ZnO compared to ZnS can be understood as a

result of the lower transition energy and the larger phonon energy ( $E_{LO(T)} = 72.8$  meV (ZnO), 42.8 meV (ZnS)). Hence, the  $\text{Cu}^{2+}$ -luminescence intensity should be weaker in ZnO, but *still observable*. Indeed, a resonant infrared excitation via the  ${}^2\text{T}_2$ - ${}^2\text{E}$  absorption band leads to the detection of the  $\text{Cu}^{2+}$ -luminescence in ZnO [6]. However, a short wavelength excitation of this luminescence using an  $\text{Ar}^+$ -ion laser or a XBO lamp as excitation source is not successful in ZnO in contrast to ZnS. To elucidate this problem, it is necessary to investigate the different excitation processes and the corresponding transition probabilities in ZnS and ZnO.

### 3.2. The $(\text{Cu}^+, \text{h})$ - $\text{Cu}^{2+} ({}^2\text{T}_2)$ -quantum yield

The different excitation behavior is closely connected with the position of the  $\text{Cu}^{2+}$ -d-states with respect to the valence and conduction bands. The  $\text{Cu}^{2+}$ -acceptor in ZnO is much deeper than in ZnS (Fig. 3).

In the sulfide compounds the  $\text{Cu}^{2+}$ -luminescence can be excited efficiently above 1.2 eV via the  $\text{Cu}^{2+} \rightarrow \text{Cu}^+$  charge transfer process and the subsequent recapture of the free hole [3]. The recombination of the so called “transient shallow acceptor state  $(\text{Cu}^+, \text{h})$ ” into the  $\text{Cu}^{2+} ({}^2\text{E})$ -state is essential for the excitation of the  $\text{Cu}^{2+} ({}^2\text{E}-{}^2\text{T}_2)$ -luminescence. This  $(\text{Cu}^+, \text{h})$ -state is observed in the PL-excitation spectra of  $\text{Cu}^{2+}$  in ZnS [3]. The proposed nonradiative decay of this state is supported by the quantum yield  $\eta$  of the  $((\text{Cu}^+, \text{h})-\text{Cu}^{2+} ({}^2\text{T}_2))$  process determined by means of CAS to  $0 \pm 2\%$ . Furthermore, no  $((\text{Cu}^+, \text{h})-\text{Cu}^{2+} ({}^2\text{T}_2))$ -luminescence is observed in ZnS.

In ZnO the energy difference between the  $(\text{Cu}^+, \text{h})$  and the two  $\text{Cu}^{2+}$ -d-states is much larger than in ZnS (Fig. 3), resulting in a lower multiphonon recombination probability. Thus, the non-radiative recombination part  $Q$  is drastically quenched. In the PL-spectra only the  $((\text{Cu}^+, \text{h})-\text{Cu}^{2+} ({}^2\text{T}_2))$ -luminescence is observed. We have measured a value of  $Q = 10 \pm 4\%$  for this transition. As the mean sideband displacement  $\Delta$  for the green emission band is  $0.33 \pm 0.05$  eV the multiphonon recombination part  $Q_1$  is completely

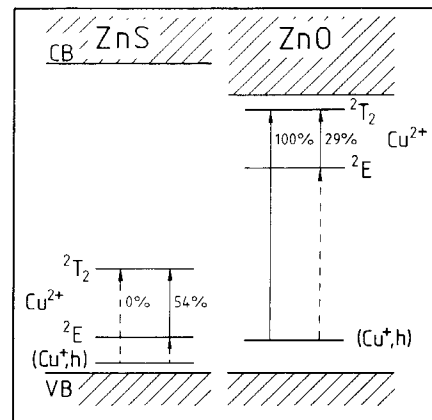


Fig. 3. Schematic hole picture of copper in ZnO and ZnS. The many electron states of  $\text{Cu}^{2+}$  are given by the photoionization process  $\text{Cu}^{2+} \rightarrow \text{Cu}^+ + h_{\text{VB}}$ . The  $\text{Cu}^{2+} ({}^2\text{E}-{}^2\text{T}_2)$ - and the  $((\text{Cu}^+, \text{h})-\text{Cu}^{2+})$ -transitions are represented by arrows. The dashed transitions are not observed in luminescence and the calculated quantum yields  $\eta$  are also indicated.

quenched (Eq. 2) and the heat production in the sample is only due to the phonon assisted radiative recombination process given by  $Q_2 = 10 \pm 4\%$ . Thus, the quantum yield  $\eta$  of the famous green luminescence in ZnO is  $100 \pm 4\%$ . It is proved for the first time, that the  $(\text{Cu}^+, \text{h})$ -state decays pure radiatively leading to no excitation of the  $\text{Cu}^{2+} ({}^2\text{E}-{}^2\text{T}_2)$ -luminescence. However, it should be remarked that the  $\text{Cu}^{2+}$ -luminescence can also be excited with electron irradiation [7] and 3.8 eV laser light [3]. Since, only a thin layer is excited here, reabsorption of the  $\text{Cu}^{2+}$ -luminescence can be neglected, making the detection of the ZPL luminescence possible. A possible excitation channel is the phonon assisted light induced energy transfer from the  $\text{V}^{3+}$ -center to the  $\text{Cu}^{2+} ({}^2\text{E}-{}^2\text{T}_2)$ -absorption band, but this assumption is preliminary up to now.

It can be summarized that the green luminescence is a competing recombination channel to the  $\text{Cu}^{2+}$ -luminescence in ZnO, whereas the decay of the  $((\text{Cu}^+, \text{h})$ -state in ZnS gives rise to an intense  $\text{Cu}^{2+}$ -luminescence. This difference can be explained with the larger binding energy of the ultra-deep Cu-acceptor in ZnO compared to ZnS. A similar behavior as for ZnS is expected for CdS, since the copper acceptor has almost the same position

with respect to the valence band, resulting in analog excitation processes [3].

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