

Nonradiative recombination processes of Ni-impurities in CdS and ZnS

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Since d–d transitions are forbidden by Laporte's rule relaxation processes within 3d-impurities commonly are assumed to be essentially nonradiative. These nonradiative processes can be detected by using calorimetric absorption spectroscopy (CAS) which also allows the determination of the quantum efficiency of excited electronic states. In the present work we report on CAS experiments of Ni-doped CdS and ZnS. The determination of the quantum efficiencies of different electronic levels of the Ni²⁺-centre brings up new information on the relaxation and recombination processes within the impurity ion. In both semiconductors the ¹T₂(G) term relaxes completely nonradiatively to the ³T₁(P) level, which exhibit a quantum efficiency of 22% in CdS and 14% in ZnS. Although the quantum efficiency for the ³A₂(F) state is similar in CdS (11%) and ZnS (10%) it has different recombination channels in both systems.

1. Introduction

The optical properties of II–VI semiconductors doped with transition metal impurities are intensively investigated by optical methods like photoluminescence and absorption spectroscopy [1,2]. These techniques allow to attribute the spectral lines to chemical elements and to determine the energy level structure. New experimental techniques like time-resolved photoluminescence and excitation spectroscopy or time resolved saturation spectroscopy yield additional information on the dynamical properties of the impurity centre like the lifetime of excited states or the repopulation time of the ground state [3]. Most methods, however, are only able to detect radiative transitions, whereas nonradiative processes can play a predominant role in the relaxation and recombination processes of 3d-elements. Thus, methods to measure directly nonradiative transitions are of great interest to study the kinetics of recombination processes.

The incorporation of Ni²⁺ ions in CdS and ZnS leads to localized electronic states in the band gap [2,4]. They arise from the 3d-shell of the

Ni²⁺ ion under the action of the surrounding crystal field. They are shown in fig. 2 in a “hole” scheme. The shallow state close to the valence band is an effective mass like state arising from the local potential of the impurity ion. The purpose of this work is to study the nonradiative processes during the relaxation of optical excited Ni²⁺ impurities in CdS and ZnS. We are able to detect directly nonradiative processes by using calorimetric absorption spectroscopy (CAS) which is the measurement of the sample temperature rise in dependence of the excitation wavelength.

2. Experimental technique: calorimetric absorption spectroscopy

To perform CAS the sample is thermally isolated and monochromatically illuminated. By nonradiative processes a fraction of the absorbed light power is dissipated into heat leading to a rise of the sample temperature. A CAS spectrum is taken by tuning the wavelength of the irradiated light and by measuring simultaneously the change of the sample temperature.

Since the sensitivity of CAS increases drastically with decreasing temperature as a consequence of the temperature dependence of the

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specific heat and the increasing sensitivity of the resistance thermometers [5,6] we perform CAS at mK temperatures using a $^3\text{He}/^4\text{He}$ -dilution refrigerator. As light source a tungsten lamp is used in combination with a 1 m double grating spectrometer to decompose the light which is irradiated onto the sample via an optical fiber due to the windowless construction of the dilution cryostat.

Using a very sensitive sample/thermometer arrangement [7] it is possible to measure the heat power produced in the sample (ΔP_{CAS}). One can now determine the quantum efficiency of an excited state if the light power absorbed in the sample $\Delta P_{\text{nr+r}}$ is known. $\Delta P_{\text{nr+r}}$ cannot be measured directly, but can be concluded by a calorimetric measure of the transmitted light power [5]. This is done by putting a black painted copper foil directly behind the sample and by measuring the transmitted light power by a second calorimeter. A detailed description of CAS at mK temperatures is given in ref. [7].

3. Experimental results

In this work we present the determination of the quantum efficiencies of Ni^{2+} states in CdS and ZnS. Quantum efficiency means the ratio of radiative to nonradiative relaxation of an excited system to thermal equilibrium. But if the quantum efficiency of an electronic level is e.g. 40% this does not mean that exactly 40% of the excited charge carriers recombine directly radiatively to the ground state while 60% recombine via the emission of phonons. But one has to take into account the relaxation to or the recombination via lower excited electronic states. Quantum efficiency means the ratio of the sum of all radiative transitions to the sum of all transitions, radiative and nonradiative. So if exactly the recombination and relaxation processes are to be determined, one has to measure the quantum efficiency of each electronic level.

Due to the transmission characteristic of the optical fiber we are able to measure the spectrum only from 0.3 to 1.5 μm . Therefore, the quantum efficiency of the lowest excited state $^3\text{T}_2(\text{F})$ could

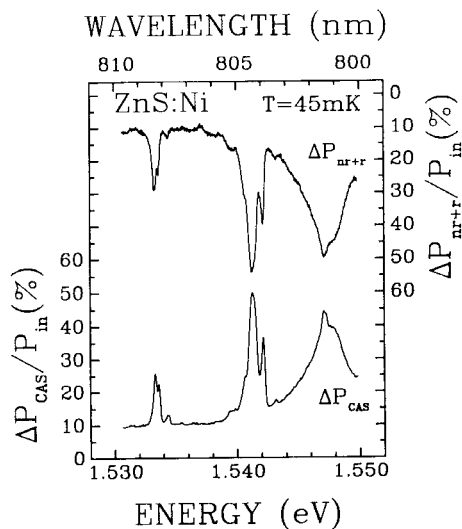


Fig. 1. CAS spectrum of the $^3\text{T}_1(\text{F}) \rightarrow ^3\text{T}_1(\text{P})$ Ni^{2+} absorption in ZnS in comparison to the absorbed light power $\Delta P_{\text{nr+r}}$ calculated from the transmission spectrum.

not directly be determined and the recombination processes cannot completely be given. But nevertheless important information concerning the relaxation between excited states are now available.

3.1. ZnS

In ZnS in addition to the $^3\text{T}_1(\text{P})$ and the $^3\text{A}_2(\text{F})$ also the quantum efficiency of the $^1\text{T}_2(\text{G})$ level can be determined since the oscillator strength of the $^1\text{T}_2(\text{G})$ is much larger in ZnS than in CdS (see below) leading to a clearly detectable resonance in the transmission spectrum. In ZnS at the onset of the charge-transfer band the sharp lines of the shallow-bound state can be detected.

The determination of the quantum efficiency of the $^3\text{T}_1(\text{P})$ level is shown in fig. 1 where the produced heat power within the sample (ΔP_{CAS}) is depicted in comparison to the absorbed light power $\Delta P_{\text{nr+r}}$ calculated from the transmission spectrum. One can see several lines according to the fine structure of the $^3\text{T}_1(\text{P})$ state [8]. The quantum efficiency η follows from the ratio ΔP_{CAS} to $\Delta P_{\text{nr+r}}$ and amounts to 14%. For the $^3\text{A}_2(\text{F})$ level we measured a quantum efficiency η of 11%, and of 9% for $^1\text{T}_2(\text{G})$ term.

That the quantum efficiency of the ${}^3A_2(F)$ is more than zero although no luminescence corresponding to this absorption had yet been observed can be understood by a relaxation process to the ${}^3T_2(F)$ level which decays partly radiatively. Our assumption of a 100% nonradiative relaxation from the ${}^3A_2(F)$ is based on the lack of a luminescence line and is also supported by the small oscillator strength for the ${}^3T_1(F) \leftrightarrow {}^3A_2(F)$ transition and a large FWHM of the absorption lines indicating a very short lifetime of this state. The relaxation process from the ${}^3A_2(F)$ to the ${}^3T_2(F)$ means an energy loss of about 0.5 eV which is completely set free by the emission of phonons. Therefore, from the measured quantum efficiency of 10% for the ${}^3A_2(F)$ the quantum efficiency of the 3T_2 can be roughly estimated to be about 20%.

3.2. CdS

In CdS the quantum efficiency of only the ${}^3T_1(P)$ and the ${}^3A_2(F)$ state can be determined. Since the transitions of the ${}^1T_2(G)$ state and of the Ni-bound exciton (Ni^{2+}, X) are very weak no corresponding resonance in transmission could be detected. Therefore, no ratio of the produced heat power to the absorbed light power could be calculated. But although the absorptions are weak both transitions can be clearly detected in the CAS spectrum. This indicates a very low quantum efficiency, i.e. there will be a predominant nonradiative relaxation via the emission of phonons to a lower excited electronic state. The quantum efficiencies of the inner impurity transitions of Ni^{2+} in CdS amount to 11% for the ${}^3A_2(F)$ state and 22% for the ${}^3T_1(P)$ state.

4. Discussion

In both investigated semiconductors at the onset of the charge-transfer band sharp zero-phonon lines occur. Due to magneto-optical experiments [9] these transitions have been explained by two different models for ZnS and CdS. While in ZnS this shallow state is a hole being deeply bound to a Ni^+ centre (Ni^+, h), in CdS this

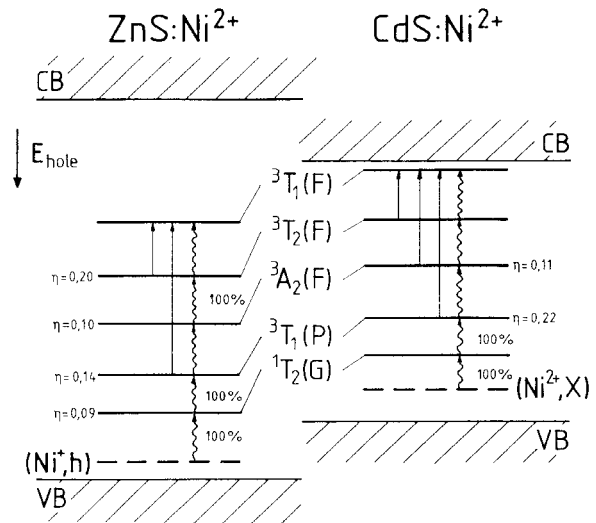


Fig. 2. Relaxation and recombination channels of Ni^{2+} in ZnS and CdS. The quantum efficiency η of different excited electronic states are given, whereas "100%" means a complete nonradiative relaxation to the next lower excited state.

system is better described by an exciton being deeply bound to Ni^{2+} (Ni^{2+}, X). Due to the missing resonance in the transmission spectra no quantum efficiencies can be calculated, but their appearance in the CAS spectra indicate a strong nonradiative recombination. Due to the large binding energy of a few hundred meV their energy is completely transferred to the impurity centre, as it is indicated in excitation spectra of Ni^{2+} luminescence [9]. Even, the Ni-bound exciton (CdS) recombines completely nonradiatively, as it was already assumed by the lack of a corresponding luminescence line. Therefore, in fig. 2 for both systems a 100% nonradiative relaxation is depicted.

For the ${}^1T_2(G)$ level in CdS no quantitative value for the quantum efficiency can be given. The quantum efficiency for this state in ZnS amounts to 9% which is in very good agreement with the value which can be estimated by assuming a 100% nonradiative relaxation to the ${}^3T_1(P)$ state presupposing that after reaching the ${}^3T_1(P)$ state the charge carriers behave the same way the charge carriers being directly excited to the ${}^3T_1(P)$ state do. This relaxation process is connected with an energy loss of about 0.4 eV which is

dissipated into heat leading to the strong CAS signal. This very strong nonradiative relaxation channel for the $^1T_2(G)$ state is also indicated by time resolved photoluminescence experiments where the intracentre relaxation time from the $^1T_2(G)$ to the $^3T_1(P)$ had been determined to be less than 10 ps for both CdS and ZnS [10] which indicates a very strong phonon coupling to the $^1T_2(G)$ state.

In contrast to the $^1T_2(G)$ the $^3T_1(P)$ state recombines partly radiatively leading to a luminescence band with several sharp lines around 1.5 eV according to the $^3T_1(P) \rightarrow ^3T_1(F)$ transition. The quantum efficiency of this level had been determined to be 22% in CdS and 14% in ZnS. The higher quantum efficiency for CdS than for ZnS is in agreement with time resolved luminescence investigations where a shorter lifetime for ZnS has been measured [10] indicating a stronger phonon interaction. But the quantum efficiency of 22(14)% does not mean that exactly 22(14)% of the charge carriers recombine directly radiatively to the ground state. As one can see from typical luminescence spectra for the $^3T_1(P) \rightarrow ^3T_1(F)$ transition [1] the strongest luminescence lines appear at lower energies than the zero-phonon line. This means that the main radiative transitions take place to excited finestructure levels of the ground state followed by nonradiative relaxation to the lowest state which is connected with an energy loss of some tens of meV set free by the emission of phonons. But, of course, this is only an additional factor for the high nonradiative rate of 78(86)%. This value is mainly produced by a nonradiative relaxation from the $^3T_1(P)$ to the $^3A_2(F)$ state which also relaxes further nonradiatively. The value of 14% for the quantum efficiency for the $^3T_1(P)$ level of Ni^{2+} in ZnS has to be seen in comparison to the value for the direct transition $^3T_1(P) \rightarrow ^3T_1(F)$ of $(25 \pm 10)\%$ which has been determined by time-resolved saturation spectroscopy [3]. There might be a discrepancy between both values but still they prove a strong nonradiative relaxation channel for the $^3T_1(P)$ term.

Due to a similar quantum efficiency for the $^3A_2(F)$ state in CdS (11%) and ZnS (10%) one may suppose also similar recombination pro-

cesses. But they are different for both systems as it can already be mentioned by the appearance of a corresponding luminescence in CdS and a lack of such a luminescence in ZnS. Since the absorptions are weak and very broad in ZnS which indicate a very short lifetime of this level and may be explained by the admixture of the $^1T_2(D)$ state [2] leading to a population of the $^3T_2(F)$ level whose quantum efficiency can roughly be estimated from the value of 10% for the $^3A_2(F)$ to be about 20%. In CdS the absorption lines of the $^3A_2(F)$ are stronger than in ZnS and very sharp. Since there is a corresponding luminescence line the $^3A_2(F)$ does not relax completely to the $^3T_2(F)$ but shows a partly radiative decay. Therefore, no quantum efficiency of the $^3T_2(F)$ could be estimated, and the complete relaxation and recombination processes cannot quantitatively be given.

5. Conclusion

We determined the quantum efficiency of some electronic states of the Ni^{2+} impurity in CdS and ZnS. Our results on the relaxation and recombination processes are summarized in fig. 2. The shallow bound state as well as the $^1T_2(G)$ term relaxes completely nonradiatively to the $^3T_1(P)$ level which yield a quantum efficiency η of 22% (CdS) and 14% (ZnS), respectively. The main relaxation channel of the $^3T_1(P)$ is a nonradiative relaxation to $^3A_2(F)$ which further relax 100% nonradiatively in ZnS, but decays partly radiatively in CdS. Using calorimetric absorption spectroscopy it will be possible to determine exactly the relaxation and recombination processes if the quantum efficiency of each electronic level can be measured and photoluminescence experiments are made to determine the radiative transition channels.

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