Journal of Crystal Growth 101 (1990) 532–535
North-Holland

FINE STRUCTURE OF THE Cu^{2+} CENTRE IN CdS

A. HOFFMANN, I. BROSER, P. THURIAN and R. HEITZ

Institut für Festkörperphysik, Technische Universität Berlin, Hardenbergstrasse 36, D-1000 Berlin 12, Germany

High resolution spectroscopy of weakly Cu doped CdS crystals has led in the 1.6 μm spectral region to the detection of general new, very narrow emission and absorption zero-phonon lines (ZPLs). From the temperature behaviour of the ZPLs, we conclude that the ground state is threefold and the excited state twofold splitted. On the basis of Zeeman and uniaxial stress measurements, the complete fine-structured term scheme of the $3d^9$ system can be derived for the first time. The observation of small g-values indicates that for the ground and excited states a strong Jahn–Teller effect has to be taken into account. When excited with the 488 nm Ar-ion laser line, the Cu^{2+} luminescence shows a bistable behaviour at 4.2 K. Possible mechanisms of this non-linear effect will be discussed.

1. Introduction

While in ZnO and ZnS the infrared Cu^{2+} transitions are intensively studied [1–3], the corresponding emission and absorption spectra in CdS [4] have been discussed only scarcely. ZnS crystals have a preferable cubic structure with stacking faults, so that in the absorption and emission spectra different Cu^{2+} transitions in different crystal-field environments occur. Therefore, it is difficult to separate the cubic Cu^{2+} transitions from the polytypic transitions and to find a definite theoretical treatment of the cubic system [5–7]. Furthermore, up to now, the EPR spectrum of an isolated Cu^{2+} centre in ZnS has not been observed [8]. In contrast to these facts, ZnO:Cu absorption spectra and EPR signals have been found by Broser and Schulz [9]. However, no Cu^{2+} luminescence had been detected. For the first time, we are able to present for CdS:Cu the complete zero-phonon transitions of Cu^{2+}. From the newly detected fine structures and their dependence on external fields (magnetic field, uniaxial stress), we obtain knowledge about the electronic structure, the symmetry, and the interaction between the impurity and the host lattice. An observed bistable behaviour of the Cu^{2+} luminescence gives information about the radiationless energy transfer between tightly bound hole states and the Cu^{2+} centre.

2. Experimental results

A typical absorption and emission spectrum of the $Cu^{2+}(^2E-{}^2T_2)$ transitions in CdS is shown in fig. 1. In contrast to earlier measurements [2,4], we observe a richly structured zero-phonon line region. The fine structure of these transitions consists of 5 lines, lines 1 and 5 are perpendicular, line 2 is predominantly parallel polarized and lines 3 and 4 are nonpolarized to the c-axis of the hexagonal CdS crystal. Additionally, we observe lines 1 and 2 in emission and absorption. Emission line 1 thermalizes and is not visible at very low temperatures. The temperature dependence of the zero-phonon emission lines and their first phonon sideband is represented in fig. 2. The given temperature values relate to the helium bath temperature. With increasing temperatures a strong decrease of the emission intensity of line 2 occur, while the emission intensity of line 1 increases. At $T = 20$ K the zero-phonon lines disappear.

Due to these results we are able to propose the following term scheme for a d^9 configuration (see insert in fig. 1). Line 2 corresponds to a transition from the Γ_4 level of the excited ^2E state to the lowest Γ_4 level of the $^2T_2$ ground state, while lines 3 and 4 are transitions from the Γ_4 level of the ^2E states to the excited Γ_4 and $\Gamma_{5,6}$ levels of the ground state. Lines 1 and 5 are transitions from the excited $\Gamma_{5,6}$ level of the ^2E state to the differ-

0022-0248/90/$03.50

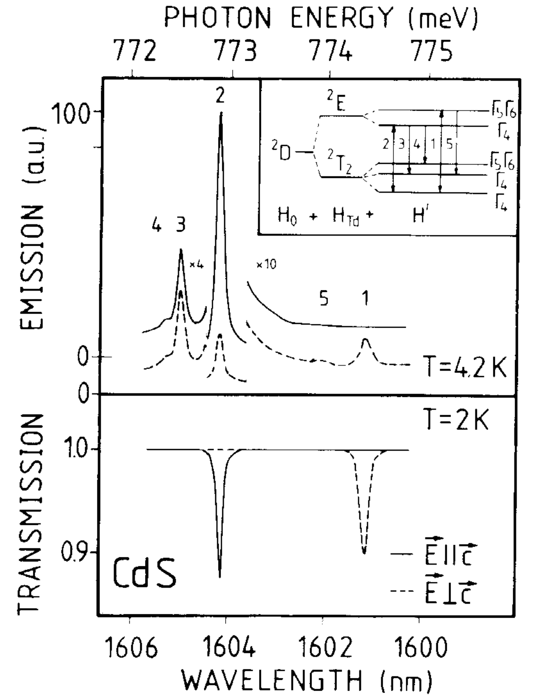

Fig. 1. Polarized emission and absorption spectra of the ZPL region of CdS : Cu. The insert shows the Cu^{2+} term scheme in CdS.

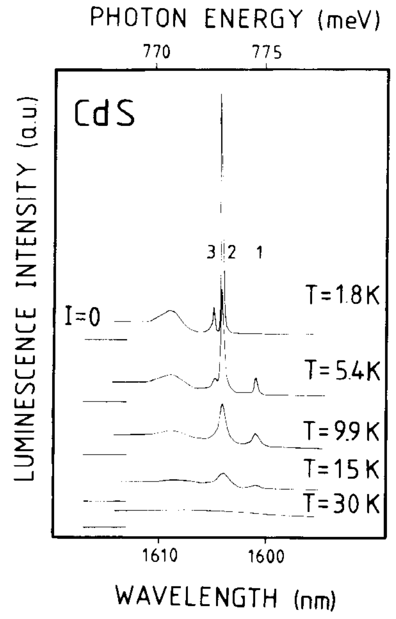

Fig. 2. Temperature dependence of the Cu^{2+} luminescence intensity.

Table 1
The energy differences and the observed g-values ($B > 7$ T) for the electronic states of the Cu^{2+} centre

Electronic state	E (meV)	g-value ($B > 7$ T)	
		$g_{\parallel}$	$g_{\perp}$
^{2}E $\Gamma_{5,6}$	774.40	–	–
Γ_4	772.88	1.55 ± 0.02	0.09 ± 0.03
^{2}T$_2$ $\Gamma_{5,6}$	0.56	1.70 ± 0.10	–
Γ_4	0.41	1.87 ± 0.02	1.15 ± 0.05
Γ_4	0.00	1.93 ± 0.02	0.13 ± 0.03

ent Γ_4 states of the $^2T_2$ ground state. To understand quantitatively the zero-field splittings, we remember that the total Hamilton operator H is composed of the Hamiltonians of the tetragonal crystal field, of the spin–orbit coupling, of the Jahn–Teller effect, and of the trigonal crystal field. From this we are able to deduce the zero-field splitting of the ground and excited states (table 1); the strong quenching of the spin–orbit parameters [14,15] becomes clear. Further evidence that a Jahn–Teller effect works in the ground and excited states is given by uniaxial stress measurements [10]. The dependence of the emission lines 1–5 on uniaxial stress fields parallel to the c-axis shows that the Jahn–Teller interaction in the ground and the excited states will be reduced [10]. This is in contrast to corresponding measurements of $ZnO : Cu^{2+}$ [11].

When a magnetic field is applied parallel or perpendicular to the c-axis, the degeneration of the five Cu^{2+} electronic terms (Kramers doublets) can be lifted (fig. 3). The zero field splittings are small compared to the Zeeman splittings at high magnetic fields (fig. 3, Paschen–Back range). For $B \parallel c$ at high magnetic fields, a linear splitting is found and the different splitting emission components shift mutually parallel, showing that the ground states have the same g-values. For $B \perp c$, the g-value of the lowest ground state level is 0.13 ± 0.03. A linear Zeeman behaviour can be assumed within the margin of errors. The Zeeman splitting of the lowest excited state yields a g-value smaller than 0.1.

When the crystal is rotated from $B \parallel c$ to $B \perp c$ [10], additional information about the Zeeman

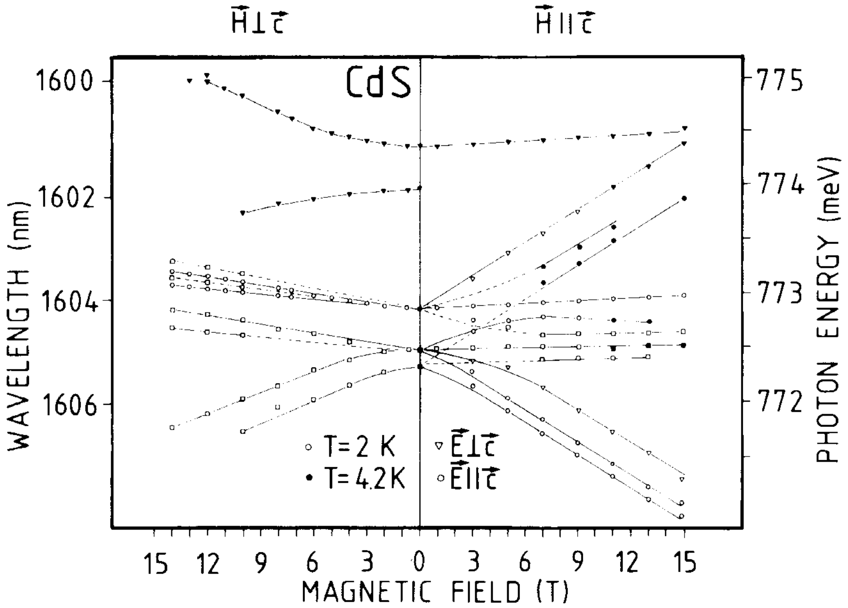

Fig. 3. Zeeman pattern of the whole ZPL region for the magnetic field orientation $H \parallel c$ and $H \perp c$ at $T = 2$ K (open symbols) and $T = 4.2$ K (filled symbols).

behaviour at low magnetic fields can be obtained. A possible linear splitting behaviour of all energy levels at low magnetic fields can be excluded. We observe a term interaction between levels of the same symmetry. This is further proof that all five zero phonon lines belong to the same impurity centre.

By exciting the samples with the 488 nm cw Ar-ion laser line, we observe a bistable behaviour at 4.2 K (see fig. 4). The switch-down of the Cu^{2+} luminescence intensity occurs at power densities of 5.7 W/cm^2, whereas the switch-up effect happens at power densities of 4 W/cm^2. The absolute values of these power densities depends sensitively on the crystal geometry. The switching time is in the order of some ms. While exciting the Cu^{2+} luminescence at $T < 2$ K or with the 476.5 nm or 514.5 nm Ar-laser lines, we observe no bistable behaviour. We detect similar bistable processes for the Ni^{2+} centre and the V^{3+} centre [13], but not for shallow bound excitons.

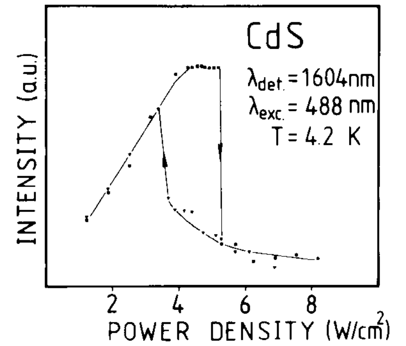

Fig. 4. Bistable behaviour of the Cu^{2+} luminescence at $T = 4.2$ K exciting with the 488 nm cw line of the Ar$^+$ laser.

3. Discussion

The observation of the different fine structures and their behaviour in magnetic and stress fields call for a Jahn–Teller effect in the ground and excited states of the Cu^{2+} centre. We found a reduction of the spin–orbit parameter by a factor of 320. The g-values which are given in table 1 correspond to values at high magnetic fields. Data from EPR measurements [9] cannot be compared with our data quantitatively, because these g-factors are values detected at weak magnetic fields. As the zero-field splittings of the Cu^{2+} states in

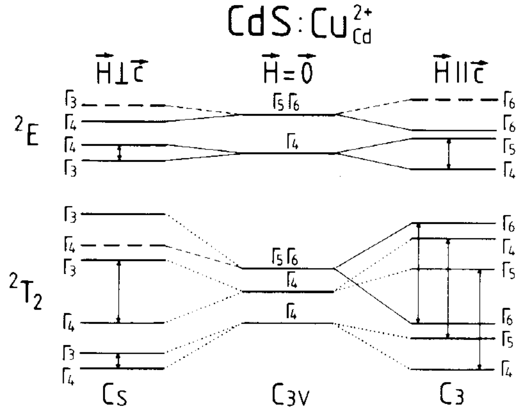

Fig. 5. Term scheme of the Cu^{2+} centre in CdS for the configuration $H \perp c$, $H = 0$ and $H \parallel c$. Term interaction between terms of the same symmetry at low magnetic fields is represented through dotted lines. Electronic states which are not observed are represented through dashed lines. The g-values, which are listed in table 1, are drawn as arrows.

CdS are small compared to the Zeeman splittings, we have to consider a term interaction to explain the nonlinear behaviour at low magnetic fields. Terms of the same symmetry in a centre are not allowed to cross and show repulsion. The repulsion of terms of the same symmetry is weaker in the excited ^2E state than in the $^2T_2$ ground state. This results from the Jahn–Teller interaction, which is weaker in the excited ^2E state than in the ground state. Figs. 3 and 5 illustrate the term interaction effects.

The bistable behaviour of the Cu^{2+} luminescence is a direct consequence of the temperature behaviour of the luminescence. With increasing excitation power densities, the Cu^{2+} emission intensity increases linearly. The crystal temperature changes drastically when the crystal, which is immersed in liquid He, is heaten by the exciting laser light so far that evaporated He forms a thin gas film on the surface of the crystal. This leads to a strong decrease of the luminescence intensity (see fig. 2). When the excitation power densities decrease, the crystal temperature will be stable until the temperature is low enough to destroy the film. Then the luminescence intensity switches. Since this bistable behaviour of the Cu^{2+} luminescence cannot be observed for the excitation wavelengths of 476.5 nm and 514.5 nm, it depends on the excitation mechanism. Excitation spectroscopy of the Cu^{2+} emissions, irradiating the CdS crystal with light near the band edge, yields an excitation band where shallow hole states bound to a negatively charged Cu^{+} are involved. Exciting with the 488 nm Ar-ion laser line, we get an effective energy transfer from the shallow bound hole states to the Cu^{2+} centre [12]. The main feature for this so-called bistable behaviour of the luminescence is the strong temperature dependence. In our opinion this type of thermally induced bistability for low excitation densities has been observed for the first time.

Acknowledgements

This paper has been supported by the Deutsche Forschungsgemeinschaft. The authors wish to thank Dr. R. Broser for supplying the crystals.

References

[1] R.E. Dietz, H. Kamimura, M.D. Sturge and A. Yariv, Phys. Rev. 132 (1963) 1559.
[2] H.A. Weakliem, J. Chem. Phys. 36 (1962) 2117.
[3] G.F.J. Garlick and M.J. Dumbleton, Proc. Phys. Soc. (London) B67 (1954) 442.
[4] I. Broser, H. Maier and H.J. Schulz, Phys. Rev. A140 (1965) 2135.
[5] B. Clerjaud and A. Gelineau, Phys. Rev. B9 (1974) 2832.
[6] C.M. Weinert and U. Scherz, Phys. Status Solidi (b) 124 (1984) 287.
[7] B. Clerjaud, Acta Phys. Polon. A73 (1988) 909.
[8] W.C. Holton, M. de Witt, R.K. Watts, T.L. Estle and J. Schneider, J. Phys. Chem. Solids 30 (1969) 963.
[9] I. Broser and M. Schulz, Solid State Commun. 7 (1969) 651.
[10] A. Hoffmann, I. Broser, P. Thurian and R. Heitz, to be published.
[11] H. Heinze, Thesis, Technische Universität, Berlin (1975).
[12] A. Hoffmann, R. Heitz and I. Broser, to be published.
[13] D. Buhmann, H.J. Schulz and M. Thiede, Phys. Rev. B19 (1979) 5360.
[14] U. Scherz, J. Phys. Chem. Solids 30 (1969) 2077.
[15] U. Scherz, J. Phys. Chem. Solids 31 (1970) 995.