

## THE NATURE OF RECOMBINATION CENTRES IN SILVER- AND CHLORINE-DOPED CdS PHOSPHORS

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**Abstract**—The intensity of photoluminescence (PL) emission bands in CdS:Ag:Cl depends on the added Ag ( $10^{16}$ – $10^{20}$  cm $^{-3}$ ) and Cl ( $10^{16}$ – $10^{19}$  cm $^{-3}$ ) concentration and the partial pressure of Cd or S is measured. It is shown that the intensity of PL bands is a power function of the silver and chlorine concentration and the partial pressure of the components. The comparison between the experimental and theoretical curves permits one to determine the nature of the radiative and non-radiative recombination centres of Ag and Cl in CdS:Ag:Cl.

**Keywords:** Photoluminescence, radiative and non-radiative recombination centres, quasichemical defect formation reactions, CdS.

### 1. INTRODUCTION

The photoelectric characteristics of semiconductor materials are studied by investigating the chemical nature and physico-chemical processes involved in forming point defects that act as recombination centres in a crystal lattice. In our previous papers a new physico-chemical method based on luminescence emission measurements as a function of the impurity content and the partial pressure of the components was proposed in order to identify the recombination centres with crystal lattice defects in wide bandgap semiconductor compounds [1, 2]. Using the proposed method the chemical nature of the  $r$ -,  $k$ -, and  $s$ -centres in CdS:Cu:Cl [2, 3], ZnSe:Cu:Cl [4] and ZnS:Cu:Cl [5] phosphors was determined. At the same time this method has not yet been used for determining the nature of the recombination centres in A<sup>II</sup>B<sup>VI</sup> compounds doped with silver as an activator, although silver-doped materials based on A<sup>II</sup>B<sup>VI</sup> compounds also have good photoelectrical and luminescence characteristics. Moreover, in our previous papers A<sup>II</sup>B<sup>VI</sup> compound phosphors were prepared under a minimum pressure of the components, that is in the condition of free evaporation [1–5], whereas the increase of the component pressure leads to a change or modification of the crystal lattice defect structure [6, 7]. The purpose of the present paper is to clarify the nature of the radiative and non-radiative recombination centres and the predominant impurity defects in CdS:Ag:Cl prepared under different partial pressures of the components.

### 2. EXPERIMENTS AND RESULTS

The initial material used was CdS powder containing metallic impurities at the following concentrations—aluminium:  $4 \times 10^{15}$  cm $^{-3}$ , copper:

$2 \times 10^{15}$  cm $^{-3}$ , silver:  $2 \times 10^{15}$  cm $^{-3}$ . The oxygen content was  $1.2 \times 10^{18}$  cm $^{-3}$ , and the chlorine concentration was not known. The starting powder was purified from chlorine and oxygen for 8 h in H<sub>2</sub>S flow at 800°C. Silver acquired from AgNO<sub>3</sub> aqueous solution was added to CdS on conditions analogous to the afore-mentioned purification. Chlorine acquired from CdCl<sub>2</sub> aqueous solution was added to CdS in evacuated and wedged-up quartz ampoules at 1050°C for 24 h. After this the thermodynamic equilibrium of the defects in CdS:Ag:Cl was obtained by keeping the sample at 850°C in a two-zone quartz ampoule for 4 h. The first temperature zone was used for the CdS:Ag:Cl powder, the second one for producing the component partial pressure by placing there a piece of cadmium or sulphur. The partial pressures of cadmium and sulphur were determined by the temperature of the component evaporation in the second zone [8]. After the high-temperature firing treatment the powder samples were rapidly cooled to room temperature in order to freeze in the high-temperature atomic defect concentrations. The silver content in the samples was determined by the atom absorption method and the chlorine one by potentiometric titration with an accuracy of 5%. The concentration of added impurities was about an order of magnitude or more larger than the concentration of the residual impurities so that any noticeable effect of these impurities was not detected.

The photoluminescence emission spectra measurements were performed at 77 K using the standard apparatus described in [2]. The luminescence was excited with the monochromatic UV light ( $\lambda = 365$  nm) from a 250 W high-pressure mercury lamp. The excitation intensity was estimated to be  $10^{15}$  photons cm $^{-2}$  s and was kept constant during the whole experiment.

The photoluminescence emission spectra shown in Fig. 1 were decomposed into a green edge emission band centred at  $h\nu = 2.4$  eV (*G*-band), an orange emission band centred at  $h\nu = 2.0$  eV (*O*-band), and a red emission band centred at  $h\nu = 1.7$  eV (*R*-band) by a modified Gaussian analysis [9]. Using this analysis we could also determine the integral intensities  $\Phi$  of the *G*, *O*, *R* emission bands, which turned out to be a power function of the total Ag or Cl concentration and the partial vapour pressure of Cd (Figs 2-5).

$$\Phi_i \sim N_{\text{Cl}}^{\bar{\alpha}_i} N_{\text{Ag}}^{\beta_i} p_{\text{Cd}}^{\bar{\gamma}_i}, \quad (1)$$

where  $i = G, O, R$ ;  $N_{\text{Ag}}, N_{\text{Cl}}$ —total Ag and Cl concentration in CdS;  $p_{\text{Cd}}$ —partial vapour pressure of cadmium.

3. DISCUSSION

It has been shown by one of the authors [1, 4] that in the case of a predominantly non-radiative recombination in  $A^{II}B^{VI}$  compounds at quite high excitation

levels, where the main charge defects under electro-neutrality condition (ENC) are free electrons and holes,  $n \approx p$ , the intensity of the  $i$ -emission band is expressed as

$$\Phi_i = \frac{aG^*u_iN_i}{\sum u_m N_m}, \quad (2)$$

where  $i = G, O, R$ ;  $m = G, O, R, s$ ;  $s$  denotes the rapid non-radiative recombination centres in CdS-type semiconductors [10];  $a$  is a coefficient,  $G^*$  is the electron-hole pair generation rate.

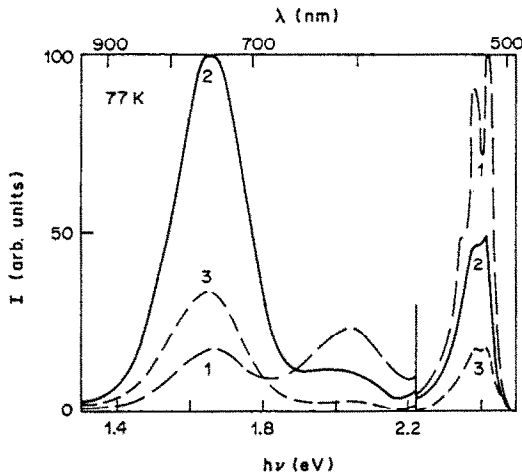


Fig. 1. Emission spectra of CdS:Ag:Cl ( $N_{\text{Ag}} = 10^{17} \text{ cm}^{-3}$ ) at 77 K. (1)  $N_{\text{Cl}} = 10^{16} \text{ cm}^{-3}$ ; (2)  $N_{\text{Cl}} = 10^{17} \text{ cm}^{-3}$ ; (3)  $N_{\text{Cl}} = 3 \times 10^{18} \text{ cm}^{-3}$ .

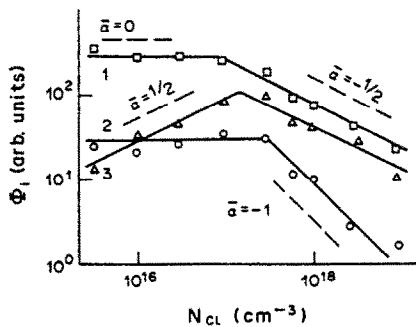


Fig. 2. Intensity dependence of *G*, *O*, *R* emission bands of CdS:Ag:Cl on the concentration of chlorine ( $N_{\text{Ag}} = 3 \times 10^{17} \text{ cm}^{-3}$ ,  $p_{\text{Cd}} = p_{\text{min}}$ ): (1) *G*-band; (2) *O*-band; (3) *R*-band.

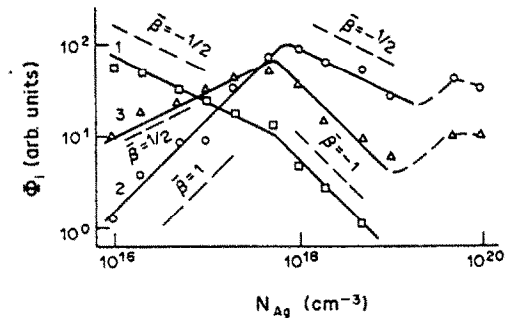


Fig. 3. Intensity dependence of *G*, *O*, *R* emission bands of CdS:Ag:Cl on the concentration of silver ( $N_{\text{Cl}} = 10^{18} \text{ cm}^{-3}$ ,  $p_{\text{Cd}} = p_{\text{min}}$ ): (1) *G*-band; (2) *O*-band; (3) *R*-band.

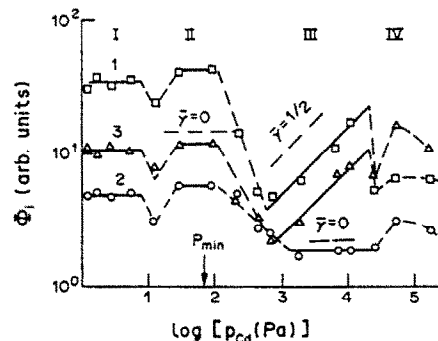


Fig. 4. Intensity dependence of *G*, *O*, *R* emission bands of CdS:Ag:Cl on the cadmium vapour pressure ( $N_{\text{Ag}} = 10^{16} \text{ cm}^{-3}$ ,  $N_{\text{Cl}} = 3 \times 10^{17} \text{ cm}^{-3}$ ): (1) *G*-band; (2) *O*-band; (3) *R*-band.

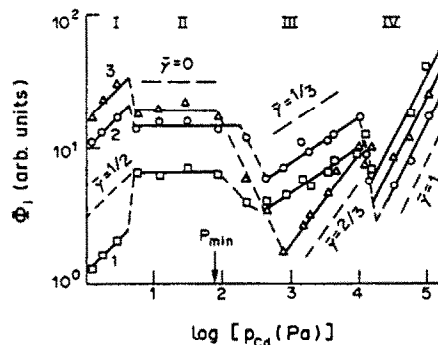


Fig. 5. Intensity dependence of *G*, *O*, *R* emission bands of CdS:Ag:Cl on cadmium vapour pressure ( $N_{\text{Ag}} = 10^{19} \text{ cm}^{-3}$ ,  $N_{\text{Cl}} = 3 \times 10^{16} \text{ cm}^{-3}$ ): (1) *G*-band; (2) *O*-band; (3) *R*-band.

Here,

$$u_i = \frac{C_{ni} C_{pi}}{C_{ni} + C_{pi}} \quad (3)$$

$C_{ni}$  and  $C_{pi}$  are electron and hole capture probabilities on the  $i$ -centre,  $u_i$  is expressed analogous to eqn (3). The coefficient  $u_i$  may be treated as the recombination rate through the  $i$ -channel of recombination.  $C_{ni} = VS_{ni}$  and  $C_{pi} = VS_{pi}$ , where  $V$  is the average thermal velocity of free charge carriers, and  $S_{ni}$  and  $S_{pi}$  are effective electron and hole capture cross-sections of the  $i$ -centre.

As has been shown in [2] the power law dependence (1) over a wide range of  $N_{Ag}$ ,  $N_{Cl}$  and  $p_{Cd}$  values is theoretically possible if: (1) the Brouwer approximation [6] is applicable in the case of the high-temperature equilibrium of defects not only under ENC, but also under the equations of material balance (EMB) of silver and chlorine; (2) at the rapid cooling of the material the high-temperature atomic defects are frozen in; (3) under the conditions of high-temperature defect equilibrium for the given type of defects with different charge states in the EMB one term is predominant; (4) the formula connecting  $\Phi_i$  with the recombination centre concentration  $N_i$  is approximated by products or quotients of the concentrations of different recombination centres not containing their algebraic sum.

The application of item (4) to (2) means that the main recombination current goes through one of the  $s$ -centres and we may leave only one term in the denominator (2). In this case the emission band intensity is at  $G^* = \text{const}$  proportional to the quotient of the concentrations of the emission and  $s$ -centres:

$$\Phi_i \sim \frac{N_i}{N_s} \quad (4)$$

The accuracy of eqn (4) results from the fact that for CdS  $u_s \gg u_i$  [10, 11].

To obtain the dependence of  $N_i$  and  $N_s$  on  $N_{Cl}$ ,  $N_{Ag}$  and  $p_{Cd}$ , it is necessary to compose a system of equations based on the quasichemical defect formation equilibrium reactions (QCDFR) in CdS:Ag:Cl (Table 1) and to solve the system in different Brouwer approximations for ENC and EMB of Ag and Cl. Table 2 illustrates one of the solutions at ENC  $[Ag_{Cd}^+][Cl_s^-] = [Cl_s^-]$ , EMB on Cl  $N_{Cl} = 2[V_{Cd}^{2+}(Cl_s^-)_2]$  and EMB on Ag  $N_{Ag} = 2[Ag_{Cd}^+ Ag_i^-]$ . As follows from Table 2, the dependence of the high-temperature equilibrium defect concentration  $[X]$  upon  $N_{Cl}$ ,  $N_{Ag}$  and  $p_{Cd}$  is a power function

$$[X] \sim N_{Cl}^\alpha N_{Ag}^\beta p_{Cd}^\gamma \quad (5)$$

The power indices  $\alpha$ ,  $\beta$  and  $\gamma$  can be treated as the quasichemical coefficients of the  $X$ -type point defect. Formula (5) is applicable for all crystal lattice point defect concentrations, in particular for defects acting as recombination centres. Substituting eqn (5) in eqn (4) we obtain

$$\Phi_i \sim \frac{N_i}{N_s} = \frac{[X_i]}{[X_s]} \sim \frac{N_{Cl}^{\alpha_i} N_{Ag}^{\beta_i} p_{Cd}^{\gamma_i}}{N_{Cl}^{\alpha_s} N_{Ag}^{\beta_s} p_{Cd}^{\gamma_s}} \quad (6)$$

By comparing the theoretical dependence (6) with the experimental one (1) we can identify the  $G$ -,  $O$ -,  $R$ - and  $s$ -centres with the crystal lattice defects of CdS:Ag:Cl which guarantee the coincidence of the power indices in (6) with the corresponding indices in (1), i.e.

$$\bar{\alpha}_i = \alpha_i - \alpha_s, \quad (7)$$

$$\bar{\beta}_i = \beta_i - \beta_s, \quad (8)$$

$$\bar{\gamma}_i = \gamma_i - \gamma_s. \quad (9)$$

Theoretical values of  $\alpha$ ,  $\beta$ ,  $\gamma$  were found by resolving the system of equations, which consists of the mass action law equations of QCDFR (Table 1),

Table 1. QCDFR for CdS:Ag:Cl and the corresponding mass action relations

No.	QCDFR		Mass action relation
1	$Cd(g) = V_s^{2+} + 2e' + Cd_{Cd}^0$	$H_1$	$K_1 = [V_s^{2+}]n^2 p_{Cd}^1$
2	$O = V_s^{2+} + V_{Cd}^{2-}$	$H_2$	$K_2 = [V_s^{2+}][V_{Cd}^{2-}]$
2a	$S_s^{2-} = V_s^{2+} + S_i^{2-}$	$H_{2a}$	$K_{2a} = [V_s^{2+}][S_i^{2-}]$
3	$V_s = V_s^{2+} + e'$	$E_3$	$K_3 = [V_s^{2+}]n[V_s]^{-1}$
4	$V_{Cd}^{2-} = V_{Cd}^{2-} + e'$	$E_4$	$K_4 = [V_{Cd}^{2-}]n[V_{Cd}^{2-}]^{-1}$
4a	$S_i^{2-} = S_i^{2-} + e'$	$E_{4a}$	$K_{4a} = [S_i^{2-}]n[S_i^{2-}]^{-1}$
5	$2Cd_{Cd}^0 + S_s^{2-} = S_{Cd}^{2-} + e' + 2Cd(g)$	$H_5$	$K_5 = [S_{Cd}^{2-}]n p_{Cd}^2$
6	$Cl_s^- + V_{Cd}^{2-} = V_{Cd}^{2-} Cl_s^-$	$H_6$	$K_6 = [V_{Cd}^{2-} Cl_s^-][Cl_s^-]^{-1}[V_{Cd}^{2-}]^{-1}$
7	$Cl_s^- + V_{Cd}^{2-} Cl_s^- = V_{Cd}^{2-} (Cl_s^-)_2$	$H_7$	$K_7 = [V_{Cd}^{2-} (Cl_s^-)_2][Cl_s^-]^{-1}[V_{Cd}^{2-} Cl_s^-]^{-1}$
8	$Ag_{Cd}^+ = V_{Cd}^{2-} + Ag_i^-$	$H_8$	$K_8 = [V_{Cd}^{2-}][Ag_i^-][Ag_{Cd}^+]^{-1}$
9	$2Ag_{Cd}^+ = (Ag_{Cd}^+)_2$	$H_9$	$K_9 = [(Ag_{Cd}^+)_2][Ag_{Cd}^+]^{-2}$
10	$Ag_{Cd}^+ + Cl_s^- = Ag_{Cd}^+ Cl_s^-$	$H_{10}$	$K_{10} = [Ag_{Cd}^+ Cl_s^-][Ag_{Cd}^+]^{-1}[Cl_s^-]^{-1}$
11	$2Ag_{Cd}^+ Cl_s^- = (Ag_{Cd}^+ Cl_s^-)_2$	$H_{11}$	$K_{11} = [(Ag_{Cd}^+ Cl_s^-)_2][Ag_{Cd}^+ Cl_s^-]^{-2}$
12	$e' + Ag_i^- + V_{Cd}^{2-} + S_{Cd}^{2-} = (Ag_{Cd}^+ S_{Cd}^{2-})'$	$H_{12}$	$K_{12} = [(Ag_{Cd}^+ S_{Cd}^{2-})']n^{-1}[Ag_i^-]^{-1}[V_{Cd}^{2-}]^{-1}[S_{Cd}^{2-}]^{-1}$
13	$Ag_{Cd}^+ + V_s = Ag_{Cd}^+ V_s$	$H_{13}$	$K_{13} = [Ag_{Cd}^+ V_s][Ag_{Cd}^+]^{-1}[V_s]^{-1}$
14	$Ag_{Cd}^+ + Ag_i^- = Ag_{Cd}^+ Ag_i^-$	$H_{14}$	$K_{14} = [Ag_{Cd}^+ Ag_i^-][Ag_{Cd}^+]^{-1}[Ag_i^-]^{-1}$
15	$2Ag_{Cd}^+ Ag_i^- = (Ag_{Cd}^+ Ag_i^-)_2$	$H_{15}$	$K_{15} = [(Ag_{Cd}^+ Ag_i^-)_2][Ag_{Cd}^+ Ag_i^-]^{-2}$

Table 2. Defect concentration as power function of  $N_{Cl}$ ,  $N_{Ag}$  and  $p_{Cd}$  under the conditions:  $N_{Ag} = 2[Ag'_{Cd}Ag'_i]$ ,  $N_{Cl} = 2[V''_{Cd}(Cl'_s)_2]$ ,  $[Ag'_{Cd}] = [Cl'_s]$ 

No.	Defect	Expression for defect concentration	$\alpha$	$\beta$	$\gamma$
1	$V''_S$	$K_7 K_8^{1/2} K_2^{1/2} K_8^{-1/2} K_8^{-1/2} N_{Cl}^{-1/2} N_{Ag}^{1/2}$	-1/2	1/2	0
2	$V''_{Cd}$	$K_6^{-1/2} K_7^{-1/2} K_8^{1/2} K_8^{1/2} N_{Cl}^{1/2} N_{Ag}^{-1/2}$	1/2	-1/2	0
3	$S''_i$	$K_{2a} K_6^{-1/2} K_7^{-1/2} K_8^{1/2} K_8^{1/2} N_{Cl}^{1/2} N_{Ag}^{-1/2}$	1/2	-1/2	0
4	$V''_{Cd}$	$K_1^{-1/2} K_2^{1/2} K_4 K_5^{-1/4} K_7^{-1/4} K_8^{1/4} K_8^{1/4} N_{Cl}^{1/4} N_{Ag}^{-1/4} p_{Cd}^{-1/2}$	1/4	-1/4	-1/2
5	$S''_i$	$K_1^{-1/2} K_2^{1/2} K_{2a} K_{4a} K_6^{-1/4} K_7^{-1/4} K_8^{1/4} K_8^{1/4} N_{Cl}^{1/4} N_{Ag}^{-1/4} p_{Cd}^{-1/2}$	1/4	-1/4	-1/2
6	$n$	$K_1^{1/2} K_2^{-1/2} K_6^{-1/4} K_7^{-1/4} K_8^{1/4} K_8^{1/4} N_{Cl}^{1/4} N_{Ag}^{-1/4} p_{Cd}^{1/2}$	1/4	-1/4	1/2
7	$V''_S$	$K_1^{1/2} K_2^{1/2} K_3^{-1} K_6^{1/4} K_7^{1/4} K_8^{-1/4} K_8^{-1/4} N_{Cl}^{-1/4} N_{Ag}^{1/4} p_{Cd}^{1/2}$	-1/4	1/4	1/2
8	$S''_{Cd}$	$K_1^{-1/2} K_2^{1/2} K_3 K_6^{1/4} K_7^{1/4} K_8^{-1/4} K_8^{-1/4} N_{Cl}^{-1/4} N_{Ag}^{1/4} p_{Cd}^{-3/2}$	-1/4	1/4	-5/2
9	$Cl'_s$	$2^{-1/2} K_6^{-1/4} K_7^{-1/4} K_8^{1/4} K_8^{1/4} N_{Cl}^{1/4} N_{Ag}^{-1/4}$	1/4	1/4	0
10	$V''_{Cd} Cl'_s$	$2^{-1/2} K_6^{1/4} K_7^{-3/4} K_8^{1/4} K_8^{1/4} N_{Cl}^{-1/4} N_{Ag}^{-1/4}$	3/4	-1/4	0
11	$V''_{Cd} (Cl'_s)_2$	$2^{-1} N_{Cl}$	1	0	0
12	$Ag'_{Cd}$	$2^{-1/2} K_6^{-1/4} K_7^{-1/4} K_8^{-1/4} K_8^{-1/4} N_{Cl}^{1/4} N_{Ag}^{1/4}$	1/4	1/4	0
13	$Ag'_i$	$2^{-1/2} K_6^{1/4} K_7^{1/4} K_8^{1/4} K_8^{-3/4} N_{Cl}^{1/4} N_{Ag}^{-1/4}$	-1/4	3/4	0
14	$Ag'_{Cd} Ag'_i$	$2^{-1} N_{Ag}$	0	1	0
15	$Ag'_{Cd} Cl'_s$	$2^{-1} K_6^{-1/2} K_2^{-1/2} K_8^{-1/2} K_8^{-1/2} K_{10} K_{14}^{-1/2} N_{Cl}^{1/2} N_{Ag}^{1/2}$	1/2	1/2	0
16	$(Ag'_{Cd} Cl'_s)_2$	$2^{-2} K_6^{-1} K_7^{-1} K_8^{-1} K_{10}^2 K_{14}^{-1} N_{Cl} N_{Ag}$	1	1	0
17	$(Ag'_{Cd})_2$	$2^{-1} K_6^{-1/2} K_7^{-1/2} K_8^{-1/2} K_8^{-1/2} K_9 K_{14}^{-1/2} N_{Cl}^{1/2} N_{Ag}^{1/2}$	1/2	1/2	0
18	$(Ag'_{Cd} S''_{Cd})'$	$2^{-1/2} K_3 K_6^{-1/4} K_7^{-1/4} K_8^{3/4} K_{12} K_{14}^{-1/2} N_{Cl}^{1/4} N_{Ag}^{1/4} p_{Cd}^{-2}$	1/4	1/4	-2
19	$Ag'_{Cd} V''_S$	$2^{-1/2} K_1^{1/2} K_2^{1/2} K_3^{-1/2} K_7^{-1/2} K_{13} K_{14}^{1/2} N_{Cl}^{1/2} N_{Ag}^{1/2} p_{Cd}^{-1}$	0	1/2	1/2
20	$(Ag'_{Cd} Ag'_i)_2$	$2^{-2} K_{15} N_{Ag}^2$	0	2	0

a simplified electroneutrality condition (ENC) and the equation of matter balance (EMB) on Ag and Cl (Brouwer approximation [6]).

Experimental values of  $\bar{\alpha}$ ,  $\bar{\beta}$ ,  $\bar{\gamma}$  were found from Figs 2–5. Samples of CdS having different concentrations of dopants Ag and Cl (Figs 2 and 3) were prepared at a fixed cadmium vapour pressure  $p_{Cd} \approx p_{min}$  corresponding to region II on Figs 4 and 5. In this Brouwer region of cadmium vapour pressure,  $\bar{\gamma} = 0$  for all measured emission bands of CdS:Ag:Cl, i.e.

$$\bar{\gamma}_G = \bar{\gamma}_O = \bar{\gamma}_R = 0 \quad (N_{Cl} \leq N_{Ag}). \quad (10)$$

As was mentioned above, the quasichemical approximation is applicable if one of the dopants predominates, i.e.  $N_{Ag} > N_{Cl}$  or  $N_{Cl} > N_{Ag}$ . This situation also follows from Figs 2 and 3: the power dependence  $\Phi(N_{Ag, Cl})$  with power indices of different values is replaced by a curve of mathematically indefinite form in a narrow region around the concentration point  $N_{Cl} = N_{Ag}$ . Therefore it is reasonable to examine the above-mentioned Ag and Cl concentration regions separately: (i)  $N_{Cl} > N_{Ag}$  and (ii)  $N_{Ag} > N_{Cl}$ :

(i)  $N_{Cl} > N_{Ag}$

$$\begin{aligned} \bar{\alpha}_G &= -1/2; & \bar{\alpha}_O &= -1; \\ \bar{\alpha}_R &= -1/2 \text{ (Fig. 2);} \end{aligned} \quad (11)$$

$$\begin{aligned} \bar{\beta}_G &= -1/2; & \bar{\beta}_O &= 1; \\ \bar{\beta}_R &= 1/2 \text{ (Fig. 3).} \end{aligned} \quad (12)$$

(ii)  $N_{Ag} > N_{Cl}$

$$\begin{aligned} \bar{\alpha}_G &= 0; & \bar{\alpha}_O &= 0; \\ \bar{\alpha}_R &= 1/2 \text{ (Fig. 2);} \end{aligned} \quad (13)$$

$$\bar{\beta}_G = -1; \quad \bar{\beta}_O = -1/2;$$

$$\bar{\beta}_R = -1 \text{ (Fig. 3).} \quad (14)$$

Substituting the values  $\bar{\alpha}$ ,  $\bar{\beta}$ ,  $\bar{\gamma}$  (10)–(14) in the left-hand side of eqns (7)–(9), respectively, and using in the right-hand side of these equations one by one the calculated  $\alpha$ ,  $\beta$ ,  $\gamma$  of the point defects (Table 3) appropriate to the  $G$ -,  $R$ -,  $O$ - or  $s$ -centres, we obtain the following results:  $V''_{Cd}$ ,  $S''_i$  as  $G$ -centre,  $Ag'_{Cd} Ag'_i$  as the  $O$ -centre,  $Ag'_{Cd} Cl'_s$  as the  $R$ -centre and  $V''_{Cd} (Cl'_s)_2$  ( $N_{Cl} > N_{Ag}$ ) or  $(Ag'_{Cd} Ag'_i)_2$  ( $N_{Ag} > N_{Cl}$ ) as the  $s$ -centre (see also Table 3). Table 3 also indicates the predominant charge defects:  $Ag'_{Cd}$  and  $Cl'_s$  ( $N_{Cl} > N_{Ag}$ );  $Ag'_{Cd}$  and  $Ag'_i$  ( $N_{Ag} > N_{Cl}$ ); impurity defects:  $Ag'_{Cd} Ag'_i$  (Ag) and  $V''_{Cd} (Cl'_s)_2$  (Cl) at  $N_{Cl} > N_{Ag}$ ;  $(Ag'_{Cd} Ag'_i)_2$  (Ag) and  $(Ag'_{Cd} Cl'_s)_2$  (Cl) at  $N_{Ag} > N_{Cl}$ . Comparing the nature of recombination centres with the predominant impurity defects, it can be concluded that the predominant impurity defects act as non-radiative recombination  $s$ -centres. This result is in accordance with the previous papers dealing with investigations of CdS:Cl [12] and CdS:Cu:Cl [2]. Similar to our results are the findings obtained in [11, 13, 14] about the nature of  $O$ - and  $R$ -centres. It is necessary to mention that the  $R$ -centre in CdS:Ag:Cl has an analogous centre in CdS:Cu:Cl—the  $r$ -centre  $Cu'_{Cd} Cl'_s$ , responsible for the emission band in the infrared spectral region ( $\lambda_{max} \approx 1030$  nm) [2].

Other independent series of luminescent measurements were made using materials of CdS:Ag:Cl (fixed  $N_{Ag}$  and  $N_{Cl}$ ), prepared under an abundant pressure of cadmium ( $p_{Cd} > p_{min}$ ) or sulphur ( $p_{Cd} < p_{min}$ ) vapour, see Figs 4 and 5. The observed dependences in Figs 4 and 5 can be divided into four regions. The III Brouwer region in Figs 4 and 5 is more suitable for quasichemical analysis due to different values of  $\bar{\gamma}$  for different emission bands. The equality of  $\bar{\gamma}$  for

Table 3. Values of  $\alpha$ ,  $\beta$  and  $\gamma$  in defects of CdS:Ag:Cl in region II (Figs 4 and 5)

EMB for Ag: EMB for Cl: ENC:		$N_{Cl} > N_{Ag}$ $N_{Ag} = 2[Ag'_{Cd} Ag'_i]$ $N_{Cl} = 2[V'_{Cd} (Cl'_S)_2]$ $[Ag'_{Cd}] = [Cl'_S]$			$N_{Ag} > N_{Cl}$ $N_{Ag} = 4[(Ag'_{Cd} Ag'_i)_2]$ $N_{Cl} = 2[Ag'_{Cd} (Cl'_S)_2]$ $[Ag'_{Cd}] = [Ag'_i]$				
No.	Defect	$\alpha$	$\beta$	$\gamma$	Centre	$\alpha$	$\beta$	$\gamma$	Centre
1	$V''_S$	-1/2	1/2	0		0	0	0	
2	$V''_{Cd}, S''_i$	1/2	-1/2	0	<i>G</i>	0	0	0	<i>G</i>
3	$V'_S$	-1/4	1/4	1/2		0	0	1/2	
4	<i>n</i>	1/4	-1/4	1/2		0	0	1/2	
5	$S'_{Cd}$	-1/4	1/4	-5/2		0	0	-5/2	
6	$V'_{Cd}, S'_i$	1/4	-1/4	-1/2		0	0	-1/2	
7	$Cl'_S$	1/4	1/4	0		1/2	-1/4	0	
8	$V''_{Cd} Cl'_S$	3/4	-1/4	0		1/2	-1/4	0	
9	$V''_{Cd} (Cl'_S)_2$	1	0	0	<i>s</i>	1	-1/2	0	
10	$Ag'_{Cd}$	1/4	1/4	0		0	1/4	0	
11	$Ag'_i$	-1/4	3/4	0		0	1/4	0	
12	$Ag'_{Cd} Ag'_i$	0	1	0	<i>O</i>	0	1/2	0	<i>O</i>
13	$Ag'_{Cd} Cl'_S$	1/2	1/2	0	<i>R</i>	1/2	0	0	<i>R</i>
14	$(Ag'_{Cd} Cl'_S)_2$	1	1	0		1	0	0	
15	$(Ag'_{Cd})_2$	1/2	1/2	0		0	1/2	0	
16	$(Ag'_{Cd} S'_{Cd})'$	1/4	1/4	-2		0	1/4	-2	
17	$Ag'_{Cd} V'_S$	0	1/2	1/2		0	1/4	1/2	
18	$(Ag'_{Cd} Ag'_i)_2$	0	2	0		0	1	0	<i>s</i>

all emission bands in the I, II and IV Brouwer regions leads to the ineffectiveness of the quasicheical luminescence method for the identification of recombination centres with crystal lattice point defects as proposed in [2]. It follows from the III Brouwer regions, Figs 4 and 5:

$$\begin{aligned} \bar{\gamma}_G &= 1/2, & \bar{\gamma}_O &= 0 \\ \bar{\gamma}_R &= 1/2 \quad (N_{Cl} > N_{Ag}) \end{aligned} \quad (15)$$

$$\begin{aligned} \bar{\gamma}_G &= 1/3, & \bar{\gamma}_O &= 1/3 \\ \bar{\gamma}_R &= 2/3 \quad (N_{Ag} > N_{Cl}). \end{aligned} \quad (16)$$

Substituting eqns (15) and (16) and the calculated values of  $\gamma$  for the point defects in different simplified

expressions for ENC and EMB (Table 4) in eqn (9) we obtain: *G*-centre— $V''_{Cd}, S''_i$ ; *O*-centre— $Ag'_{Cd} Ag'_i$ ; *R*-centre— $Ag'_{Cd} Cl'_S$ ; *s*-centre— $(Ag'_{Cd} Cl'_S)_2$  ( $N_{Cl} > N_{Ag}$ ) or  $(Ag'_{Cd} Ag'_i)_2$  ( $N_{Ag} > N_{Cl}$ ).

Comparing the results based on eqns (11)–(14) with (15) and (16) it is seen (Tables 3 and 4) that the transition from the II Brouwer region to the III one is caused by changes in the defect concentration. In particular, the predominant Ag defect in the II region  $Ag'_{Cd} Ag'_i$  is replaced by  $Ag'_{Cd} V'_S$  in the III region at  $N_{Cl} > N_{Ag}$  while  $(Ag'_{Cd} Ag'_i)_2$  is replaced by  $Ag'_i$  at  $N_{Ag} > N_{Cl}$  (compare Tables 4 and 5). Hence it follows that increasing cadmium vapour pressure causes the increase of the concentration of sulphur vacancies at small incorporated Ag concentration and also the replacement of Ag in lattice sites ( $Ag'_{Cd}$ ) by Cd ( $Cd^{\bar{x}}_{Cd}$ )

 Table 4. Values of  $\gamma$  for defects in CdS:Ag:Cl in region III (Figs 4 and 5)

EMB for Ag: EMB for Cl: ENC:		$N_{Cl} > N_{Ag}$ $N_{Ag} = [Ag'_{Cd} V'_S]$ $N_{Cl} = 2[V'_{Cd} (Cl'_S)_2]$ $n = [Cl'_S]$		$N_{Ag} > N_{Cl}$ $N_{Ag} = [Ag'_i]$ $N_{Cl} = 2[Ag'_{Cd} (Cl'_S)_2]$ $n = 2[V'_S]$	
No.	Defect	$\gamma$	Centre	$\gamma$	Centre
1	$V''_S$	1/2		1/3	
2	$V''_{Cd}, S''_i$	-1/2	<i>G</i>	-1/3	<i>G</i>
3	$V'_S$	3/4		2/3	
4	$V'_{Cd}, S'_i$	-3/4		-2/3	
5	<i>n</i>	1/4		1/3	
6	$S'_{Cd}$	-9/4		-7/3	
7	$Cl'_S$	1/4		1/3	
8	$V''_{Cd} Cl'_S$	-1/4		0	
9	$V''_{Cd} (Cl'_S)_2$	0		0	
10	$Ag'_{Cd}$	-3/4		-1/3	
11	$Ag'_i$	-1/4		0	
12	$Ag'_{Cd} Ag'_i$	-1	<i>O</i>	-1/3	<i>O</i>
13	$Ag'_{Cd} Cl'_S$	-1/2	<i>R</i>	0	<i>R</i>
14	$(Ag'_{Cd} Cl'_S)_2$	-1	<i>s</i>	0	
15	$(Ag'_{Cd})_2$	-3/2		-2/3	
16	$(Ag'_{Cd} S'_{Cd})'$	-11/4		-7/3	
17	$Ag'_{Cd} V'_S$	0		1/3	
18	$(Ag'_{Cd} Ag'_i)_2$	-2		-2/3	<i>s</i>

leading to the transition of Ag to interstitials ( $\text{Ag}_i$ ). The predominance of  $\text{Ag}_i$  in CdS:Ag at high cadmium vapour pressure was also detected in [15–17]. The increase of cadmium vapour pressure causes the increase of the free electron concentration  $n$  which became the predominant negatively-charged defect in the III region. From Table 4 it follows:  $\gamma_n = 1/4(N_{\text{Cl}} > N_{\text{Ag}})$  and  $\gamma_n = 1/3(N_{\text{Ag}} > N_{\text{Cl}})$ . The value  $\gamma_n = 1/4$  was also found by measuring the high-temperature conductivity in CdS:Cl single crystals at  $p_{\text{Cd}} > p_{\text{min}}$  [12]. This corresponds to our results measured at small silver concentration ( $N_{\text{Cl}} > N_{\text{Ag}}$ ). The value  $\gamma_n = 1/3$  is characteristic of intrinsic II–VI compounds at high temperature and high metallic component vapour pressure [16, 17]. At the same time  $\gamma_n = 1/3$  was also found under analogous conditions in CdS:Ag with a small added silver concentration [17]. Therefore it is seen that lightly-doped CdS prepared at high cadmium vapour pressure becomes self-compensated:  $n = [\text{V}_s^-]$ .

Our quasicheical analysis showed that the green edge emission  $G$ -band in CdS:Ag:Cl is not caused by the doping impurities Ag and Cl. It is well-known that the green edge emission in CdS at 77 K is related to an electron transition from the bottom of the conduction band to a shallow acceptor level [18–20], but the nature of this acceptor is somewhat vague. It is possible that such acceptors are the substitutional defects Li and  $\text{Na-Li}_{\text{Cd}}$  and  $\text{Na}_{\text{Cd}}$  having shallow acceptor levels  $E_A = 0.16\text{--}0.17$  eV [21]. Electron bombardment studies of CdS crystal led to the conclusion that the  $G$ -emission band may be caused by interstitial sulphur ions  $\text{S}_i^-$  [22]. The same conclusion was made in [23, 24]. As is seen in Tables 3 and 5,  $\text{S}_i^-$  and  $\text{V}_{\text{Cd}}$  have the same values of  $\alpha$ ,  $\beta$  and  $\gamma$ , which is why our quasicheical method does not separate these defects. At the same time the quasicheical behaviour of  $\text{Li}_{\text{Cd}}$  or  $\text{Na}_{\text{Cd}}$  may be identical to  $\text{V}_{\text{Cd}}$  or  $\text{S}_i^-$ . The models of the  $G$ -centres proposed in Tables 3 and 4 can be treated as possible versions of the nature of those centres.

#### 4. CONCLUSION

An interpretation of the results obtained by the quasicheical luminescence method in CdS:Ag:Cl leads to the classification of the nature of the centres responsible for impurity emission bands:

$O$ -centre— $\text{Ag}_{\text{Cd}}^+ \text{Ag}_i^-$ ,  $R$ -centre— $\text{Ag}_{\text{Cd}}^+ \text{Cl}_s^-$ . Predominant impurity defects are also found to represent the neutral complexes, for example  $\text{V}_{\text{Cd}}^0 (\text{Cl}_s)_2$ . At the same time they act as non-radiative recombination centres— $s$ -centres.

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