Defect Structure of Cl and Cu Doped CdS Heat Treated in Cd and S$_2$ Vapor

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The concentration of chlorine and copper, the Hall effect, and the photoluminescence of CdS : Cl : Cu annealed in cadmium and sulphur vapors were measured. The results were analyzed using quasichemical approximations. The structure of predominating copper and chlorine defects is proposed and their role in the formation of electrical and luminescent characteristics of cadmium sulfide is studied.

1. Introduction

The characteristics of semiconductor materials necessary for optoelectronics, particularly those of the $A^{II}B^{VI}$ type, are obtained by doping with impurities and deviating from stoichiometry. For $A^{II}B^{VI}$ compounds the most common impurities used are chlorine as a donor and copper as an acceptor (1, 2). Deviations from stoichiometry are achieved by annealing the compound in vapors of the host component (3–5). The presence of oxygen (6–8) and the cooling conditions of the material after high temperature treatment (4, 9) also play an essential role in the formation of semiconductor characteristics. The effect of halogen donors and metal acceptors on the characteristics of $A^{II}B^{VI}$ compounds was studied with regard to establishing photosensitivity and luminescence (1, 10–13) as well as the formation of high-temperature (HT) point defects (3, 4, 14, 15).

This paper reports on studies of the characteristics of $A^{II}B^{VI}$ compounds and their

dependence on the chemical composition and thermal treatment conditions (16–19) with the aim to establish the structure of chlorine and copper defects in cadmium sulfide.

2. Experiment and Results

The cadmium sulfide powder was doped (in the liquid phase of CdCl$_2$) with chlorine during the recrystallization process in a two-zone quartz ampoule (20). The optimum concentration for obtaining finely dispersed monocrystalline powder was about 10 mole% CdCl$_2$ (21). For the Hall measurements, undoped CdS monocrystals were added to the powder suspension. Copper was added to cadmium sulfide from an aqueous solution of CuCl$_2$ by diffusion annealing (19). The high-temperature thermodynamic equilibrium was achieved by firing the material in a two-zone ampoule at 973 K for 4 hr under an excess pressure of Cd or of S$_2$. This was followed by rapid cooling, to freeze in the high-temperature atomic defects, by dropping the ampoule into ice water. The chlorine and copper content was

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determined by potentiometric titration and by atomic-absorption analysis, respectively. The concentration of free electrons was calculated from Hall measurements. Photoluminescence was excited with a LG-70 (440 nm) laser. The photoluminescence (PL) spectra were measured at 77 and 293 K using standard apparatus (*17, 18*). The PL bands were differentiated by a Gaussian analysis (*4*) using a computer. The solubility of chlorine in CdS as a function of temperature and pressure of cadmium vapors is shown in Figs. 1 and 2, respectively, from which we conclude that

$$[Cl] \sim p_{Cd}^{\gamma_{Cl}}, \tag{1}$$

where

$$\gamma_{Cl} = 0, \tag{2}$$

and

$$[Cl] = 4 \times 10^{20} \exp(-0.32 \ eV/kT), \ cm^{-3}. \tag{3}$$

Thus, the solubility of chlorine in cadmium sulfide does not depend on the component vapor pressure. The value of solubility enthalpy is 0.32 eV. The copper content added into CdS:Cl (below the solubility limit, see (*16*)), does not depend on p_{Cd}, as is seen from Fig. 2. When the Cu concentration exceeds the solubility of chlorine, the solubility of Cl rises (Fig. 3a). The Cu concentration does not depend on p_{Cd} in the region of simultaneous solubility of Cl and Cu (see Fig. 2). Hence
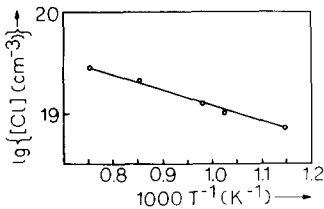
$$[Cu] \sim p_{Cd}^{\gamma_{Cl}}, \tag{4}$$

FIG. 1. Temperature dependence of chlorine solubility in cadmium sulfide.
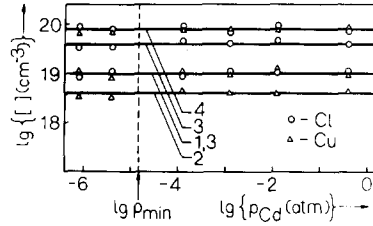

FIG. 2. Cadmium vapor pressure dependence of chlorine and copper concentration in cadmium sulfide. Numbers correspond to the samples (materials) listed in Table I.

where

$$\gamma_{Cu} = 0 \tag{5}$$

With the rise of [Cu] the low-temperature (LT) concentration of free electrons n_{LT} measured at 293 K remains at a high level as long as [Cu] < [Cl]; it falls steeply when [Cu] ≥ [Cl]. With oxygen present, the decrease in concentration of free electrons shifts toward smaller copper concentrations (Fig. 3b). Similarly, when the material is cooled slowly the decrease in n_{LT} shifts toward smaller Cu concentrations (Fig. 3b). In the region [Cu] = [Cl] photoconductivity was detected; (this is not shown in Fig. 3b). The low-temperature free electron concentration (see Fig. 4) does not depend on p_{Cd} at $p_{Cd} < p_{min}$ where p_{min} is the minimum CdS vapor pressure at the annealing temperature. This was established by annealing in sulfur vapor. However, n_{LT} rises as the $\frac{1}{4}$ power of p_{Cd} when $p_{Cd} > p_{min}$, and steeply increases in region $p_{Cd} \approx p_{min}$, i.e.,

$$n_{LT} \sim p_{Cd}^{\gamma_n^*} \tag{6}$$

where

$$\gamma_n^* = 0 \qquad p_{Cd} < p_{min} \qquad \text{(region I)} \tag{7}$$

$$= \tfrac{1}{4} \qquad p_{Cd} > p_{min} \qquad \text{(region II).} \tag{8}$$

The intensity of PL emission band ϕ_i (*i* is the band index) varies with the ratio of [Cl]
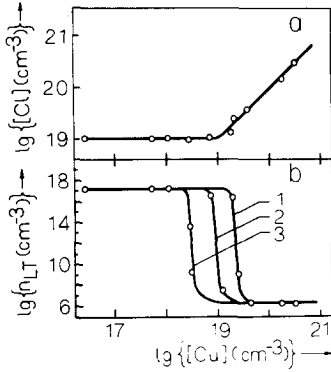
FIG. 3. Chlorine solubility in cadmium sulfide (a) and LT concentration of free electrons (b) as a function of copper content in cadmium sulfide: (1) rapid cooling in vacuum, (2) rapid cooling in oxygen atmosphere, (3) slow cooling in vacuum.

and [Cu], and when [Cu] = [Cl]

$$\phi_i \sim p_{Cd}^{\gamma_i} \qquad (9)$$

where

$$\gamma_i = 0, \qquad (10)$$

over the whole range of p_{Cd} values. If [Cu] < [Cl], a steep decrease in ϕ_i is detected near $p_{Cd} = p_{min}$ (Fig. 5).

Thus, one can obtain numerical values of γ_{Cl}, γ_{Cu}, γ_n^*, and γ_i, see Table I, as well as the variation of the Cl solubility in CdS with
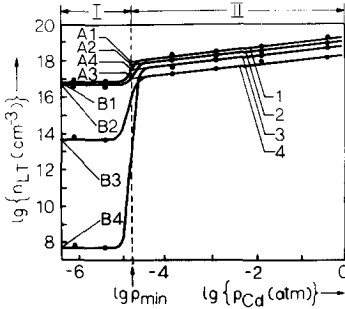

FIG. 4. The LT free electron concentration dependence of cadmium vapor pressure; the numbers correspond to the samples (materials) listed in Table I. (A1–A4) intersection points of the straight line n_{LT} (p_{Cd}) continuation with p_{min} line in region II; (B1–B4) n_{LT} concentrations in region I (p_{Cd} approximately equal to 10^{-6} atm)
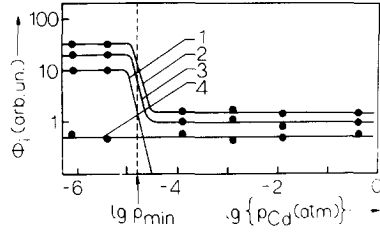

FIG. 5. PL emission band intensity dependence of the cadmium vapor pressure: (1) $\lambda_{max} = 730$ nm; (2–4) $\lambda_{max} = 1030$ nm. The numbers represent the samples listed in Table I.

Cu, see Fig. 3a and Eqs. (11), (12). These serve as initial data for the defect analysis of CdS:Cl and CdS:Cu:Cl.

$$[Cl] \sim [Cu]^0 \qquad at \quad [Cu] < [Cl] \qquad (11)$$

$$[Cl] \sim [Cu]^1 \qquad at \quad [Cu] = [Cl] \qquad (12)$$

3. Discussion

3.1. Defect Concentration Slopes

Quasichemical reactions and corresponding mass action relations for the system under study are given in Table II (the activity of $CdCl_2$ is taken as I). Reaction 1 is analogous to the reaction of CdI_2 solubility in CdS (14). Solving the system of equations in Table II with respect to p_{Cd} and n (n represents the equilibrium concentrations of free electrons at high temperature, $T = 973$ K), we obtain for [X] (X is the defect symbol) the following power functions (16):

$$[X] \sim p_{Cd}^{\delta} n^{\eta} \qquad (13)$$

Using (3, 4, 16)

$$n \sim p_{Cd}^{\gamma_n}, \qquad (14)$$

and substituting Eq. (14) into Eq. (13), we get an explicit dependence of [X] upon p_{Cd}, namely

$$[X] \sim p_{Cd}^{\gamma}, \qquad (15)$$

where

$$\gamma = \delta + \gamma_n \eta. \qquad (16)$$

TABLE I

THE STARTING PARAMETERS FOR CdS:Cu:Cl

Mater. series no.	Concentrations (cm⁻³)				Slopes									
	$[Cl]$	$[Cu]$	n_{LT} point A (Fig. 4)	n_{LT} point B (Fig. 4)	γ_{Cl} I, II	γ_{Cu} I, II	γ_n^* I	γ_n^* II	γ_n I	γ_n II	γ_{730} I	γ_{730} II	γ_{1030} I	γ_{1030} II
1	10^{19}	2×10^{15}	10^{18}	5×10^{16}	0	0	0	$\frac{1}{4}$	$-\frac{1}{2}$	$\frac{1}{4}$	0	—	—	—
2	4×10^{19}	4×10^{18}	5×10^{17}	5×10^{16}	0	0	0	$\frac{1}{4}$	$-\frac{1}{2}$	$\frac{1}{4}$	—	—	0	0
3	4×10^{19}	10^{19}	10^{17}	4×10^{13}	0	0	0	$\frac{1}{4}$	$-\frac{1}{2}$	$\frac{1}{4}$	—	—	0	0
4	7.5×10^{19}	7.5×10^{19}	3×10^{17}	4×10^{7}	0	0	0	$\frac{1}{4}$	$-\frac{1}{2}$	$\frac{1}{4}$	—	—	0	0

The high-temperature concentrations of electrons were not measured in our experiment; instead, we used the values of γ_n^* (Table I) for finding γ_n.

Due to the ionization of uncompensated chlorine donors the high conductivity and, consequently, the high concentration of free electrons in region II approaches the [Cl] value at $p_{Cd} > 1$ atm; see Fig. 4. Thus, the electroneutrality equation (ENE) may be written as

$$n = [Cl_S^-] \qquad (17)$$

A similar situation is encountered in CdS:I, where the negative charge of the free electrons is compensated for by the positive charge of I_S^- (*14*). After rapid cooling, proceeding on the assumption that the high-temperature atomic defects were frozen in (*3, 4*), the low-temperature concentration of free electrons n_{LT} differs from Eq. (17) only by constant multiplier; see Section 3.5. Therefore,

$$\gamma_n = \gamma_n^* = \tfrac{1}{4} \qquad \text{(region II)}. \qquad (18)$$

With a reduction of p_{Cd}, the steep decline in n_{LT} sets in at the point of exact compensation of the chlorine donors by the native acceptors. When [Cu] < [Cl_S^-] the effect is due to self-compensation; when [Cu] > [Cl_S^-] the effect arises from "copper" acceptors. This leads to the substitution of the ENE in region II, Eq. (17), by a new one for region I, namely

$$[\text{acceptor}] = [Cl_S^-] \qquad \text{(region I)}. \qquad (19)$$

The defect concentration in the sulfur sublattice cannot decrease with an increase of p_{Cd} (in the wide range of p_{Cd}), and cannot increase in the cadmium sublattice (*4*). Thus, to prevent hole conductivity (CdS is a typical electron semiconductor (*10*)), we have to assume that the acceptor and Cl_S^- concentrations do not depend on p_{Cd} in region II; i.e., for these defects $\gamma = 0$. Substituting in Eq. (16) the values of $\delta = \frac{1}{2}$ and η

TABLE II

QUASICHEMICAL REACTIONS FOR Cd : SCu : Cl AND RELATED EQUILIBRIUM CONSTANTS

No.	Reaction	Mass action relation
1	$CdCl_2(l) + Cd(g) = 2Cd_{Cd} + 2Cl^{\cdot}_S + 2e' + H_1$	$[Cl^{\cdot}_S]^2 n^2/p_{Cd} = K_1$
2	$CdS(s) = Cd(g) + 1/2S_2(g); H_2$	$p_{Cd}p_{S_2}^{1/2} = K_2$
3	$O = V^{\cdot\cdot}_S + 2e' + 1/2S_2(g) + H_3$	$[V^{\cdot\cdot}_S]n^2 p_{S_2}^{1/2} = K_3$
4	$O = V''_{Cd} + V^{\cdot\cdot}_S + H_4$	$[V''_{Cd}][V^{\cdot\cdot}_S] = K_4$
5	$V^x_{Cd} = V'_{Cd} + h^{\cdot} + E_5$	$[V'_{Cd}]p/[V^x_{Cd}] = K_5$
6	$V'_{Cd} = V''_{Cd} + h^{\cdot} + E_6$	$[V''_{Cd}]p/[V'_{Cd}] = K_6$
7	$V^x_S = V^{\cdot}_S + e' + E_7$	$[V^{\cdot}_S]n/[V^x_S] = K_7$
8	$V^{\cdot}_S = V^{\cdot\cdot}_S + e' + E_8$	$[V^{\cdot\cdot}_S]n/[V^{\cdot}_S] = K_8$
9	$Cl^x_S = Cl^{\cdot}_S + e' + E_9$	$[Cl^{\cdot}_S]n/[Cl^x_S] = K_9$
10	$Cl^{\cdot}_S = Cl'_i + V^{\cdot\cdot}_S + H_{10}$	$[Cl'_i][V^{\cdot\cdot}_S]/[Cl^{\cdot}_S] = K_{10}$
11	$Cl^x_i = Cl^{\cdot}_i + h^{\cdot} + E_{11}$	$[Cl^{\cdot}_i]p/[Cl^x_i] = K_{11}$
12	$O = e' + h^{\cdot} + E_{12}$	$np = K_{12}$
13	$Cu^x_{Cd} = Cu'_{Cd} + h^{\cdot} + E_{13}$	$[Cu'_{Cd}]p/[Cu^x_{Cd}] = K_{13}$
14	$Cu'_{Cd} = V''_{Cd} + Cu^{\cdot}_i + H_{14}$	$[V''_{Cd}][Cu^{\cdot}_i]/[Cu'_{Cd}] = K_{14}$
15	$Cu^x_i = Cu^{\cdot}_i + e' + E_{15}$	$[Cu^{\cdot}_i]n/[Cu^x_i] = K_{15}$
16	$Cu'_{Cd} + Cu^{\cdot}_i = Cu'_{Cd}Cu^{\cdot}_i + H_{16}$	$[Cu'_{Cd}Cu^{\cdot}_i]/[Cu'_{Cd}][Cu^{\cdot}_i] = K_{16}$
17	$Cu'_{Cd} + Cl^{\cdot}_S = Cu'_{Cd}Cl^{\cdot}_S + H_{17}$	$[Cu'_{Cd}Cl^{\cdot}_S]/[Cu'_{Cd}][Cl^{\cdot}_S] = K_{17}$
18	$V''_{Cd}Cl^x_S = V''_{Cd}Cl^{\cdot}_S + e' + E_{18}$	$[V''_{Cd}Cl^{\cdot}_S]n/[V''_{Cd}Cl^x_S] = K_{18}$

$= -1$ for $Cl^{\cdot}_S$, see Table III, we obtain the condition $0 = \frac{1}{2} - \gamma_n$, where

$$\gamma_n = \frac{1}{2} \quad \text{(region I).} \quad (20)$$

Substituting Eqs. (18) and (20) into Eq. (16), we calculate γ for point defects. γ for the complex defects is obtained by summing up γ of monodefects that form the complex defect (16). The values of δ, η, and γ and for monodefects, as well as those of some complex defects of CdS : Cl : Cu, are specified in Table III.

To establish the structure of the main defects CdS : Cl and CdS : Cl : Cu, responsible for (i) the solubility of chlorine and copper, (ii) electroneutrality, and (iii) photoluminescence, one must establish defects having γ values that coincide with γ_{Cl}, γ_{Cu}, γ_n, and γ_i, respectively.

3.2. Predominant Chlorine and Copper Defects

In the equation of material balance (EMB) for chlorine the total concentration

of chlorine in the Brouwer approximation (3, 4) is equated with the concentration of the predominant chlorine defect. Therefore, γ of this defect is identified with γ_{Cl}, see Eq. (2);

$$\gamma = \gamma_{Cl} = 0 \quad (21)$$

over the whole range of p_{Cd}, see Fig. 2. Monodefects (Table III) do not satisfy this condition. Among the bidefects, $Cl^{\cdot}_S Cl'_i$ and $Cl^x_S Cl^x_i$ do satisfy the condition. Nevertheless, since the chlorine ion cannot easily be accommodated in the relatively tight interstitial space of the wurtzite type lattice of $A^{II}B^{VI}$ compounds (4), due to its large ionic radius, then the above-mentioned defect associations cannot occur in significant concentrations in CdS. Among the triple defects the neutral complex $V''_{Cd}(Cl^{\cdot}_S)_2$ satisfies Eq. (21). From the physical viewpoint this defect can exist: $(Cl^{\cdot}_S)_2$ can be covalent in analogy to those complexes which form two-atomic molecules in gases (3). The binding between $(Cl^{\cdot}_S)_2$ and V''_{Cd} (+ and −

TABLE III

Values of σ, η, and γ for Defects in CdS : Cu : Cl

No.	Defect	σ	η	γ I $\gamma_n = \frac{1}{2}$	γ II $\gamma_n = \frac{1}{4}$
1	$V_S^{··}$	1	−2	0	$\frac{1}{2}$
2	$V_S^·$	1	−1	$\frac{1}{2}$	$\frac{3}{4}$
3	V_S^x	1	0	1	1
4	V_{Cd}''	−1	2	0	$-\frac{1}{2}$
5	V_{Cd}'	−1	1	$-\frac{1}{2}$	$-\frac{3}{4}$
6	V_{Cd}^x	−1	0	−1	−1
7	$Cl_S^·$	$\frac{1}{2}$	−1	0	$\frac{1}{4}$
8	Cl_S^x	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$
9	Cl_i'	$-\frac{1}{2}$	1	0	$-\frac{1}{4}$
10	Cl_i^x	$-\frac{1}{2}$	0	$-\frac{1}{2}$	$-\frac{1}{2}$
11	e'	0	1	$\frac{1}{2}$	$\frac{1}{4}$
12	$h^·$	0	−1	$-\frac{1}{2}$	$-\frac{1}{4}$
13	$V_{Cd}''Cl_S^·$	$-\frac{1}{2}$	1	0	$-\frac{1}{4}$
14	$V_{Cd}''Cl_S^x$	$-\frac{1}{2}$	2	$\frac{1}{2}$	0
15	$V_{Cd}'Cl_S^x$	$-\frac{1}{2}$	1	0	$-\frac{1}{4}$
16	$V_{Cd}'Cl_S^·$	$-\frac{1}{2}$	0	$-\frac{1}{2}$	$-\frac{1}{2}$
17	$V_{Cd}''(Cl_S)_2$	0	0	0	0
18	$V_{Cd}'(Cl_S)_2$	0	−1	$-\frac{1}{2}$	$-\frac{1}{4}$
19	Cu_{Cd}'	$-\frac{1}{2}$	1	0	$-\frac{1}{4}$
20	Cu_{Cd}^x	$-\frac{1}{2}$	0	$-\frac{1}{2}$	$-\frac{1}{2}$
21	$Cu_i^·$	$\frac{1}{2}$	−1	0	$\frac{1}{4}$
22	Cu_i^x	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$
23	$Cu_{Cd}'Cu_i^·$	0	0	0	0
24	$Cu_{Cd}'Cu_i^x$	0	1	$\frac{1}{2}$	$\frac{1}{4}$
25	$Cu_{Cd}^xCu_i^·$	0	−1	$-\frac{1}{2}$	$-\frac{1}{4}$
26	$Cu_{Cd}^xCu_i^x$	0	0	0	0
27	$Cu_{Cd}'Cl_S^·$	0	0	0	0
28	$Cu_{Cd}'Cl_S^x$	0	1	$\frac{1}{2}$	$\frac{1}{4}$
29	$Cu_{Cd}^xCl_S^·$	0	−1	$-\frac{1}{2}$	$-\frac{1}{4}$
30	$Cu_{Cd}^xCl_S^x$	0	0	0	0
31	$(Cu_{Cd})_2''$	−1	2	0	$-\frac{1}{2}$
32	$(Cu_{Cd})_2'$	−1	1	$-\frac{1}{2}$	$-\frac{3}{4}$
33	$(Cu_{Cd})_2^x$	−1	0	−1	−1

charged particles) is Couloumbic; therefore, the EMB for chlorine is written as

$$Cl = 2[V_{Cd}''(Cl_S)_2]. \qquad (22)$$

The high concentration of $V_{Cd}''(Cl_{Te})_2$ was detected in CdTe : Cl at $[Cl] > 10^{17}$ cm^{-3}; this also testifies to the validity of Eq. (22). It was shown that the processes of forming multiparticle impurity and native defect ag-

gregates with a structure similar to the chemical compound ($CdCl_2$) predominates at high impurity concentrations and high annealing temperatures (3, 22). A similar complex $V_{Cd}''(Cl_{Se}')_2$ for CdSe : Cl was proposed in (23). At high temperatures in $A^{II}B^{VI}$ compounds with no coactivators (donors), copper occupies the sites of the metal sublattice (Cu_{Cd}', the acceptor), as well as interstitials (Cu_i, the donor) in approximately equal concentrations (16, 22, 25). In the presence of a high concentration of chlorine the charge on Cu_{Cd}' is obviously compensated for by the charge on $Cl_S^·$ (4). Since in our case the defect concentrations in cadmium sulfide are high, we should anticipate the formation of associates $Cu_{Cd}'Cl_S^·$ (3, 4, 19) at high temperatures. The EMB of copper is given by

$$[Cu] = [Cu_{Cd}'Cl_S^·]. \qquad (23)$$

From Eqs. (23) and (5) it follows that

$$\gamma_{Cu_{Cd}'Cl_S^·} = \gamma_{Cu} = 0. \qquad (24)$$

Equation (24) is used in calculating δ, η, and γ of copper defects in Table III.

Let us note that the formation of huge chlorine and copper clusters near extended defects of the crystal lattice (dislocations, intercrystal faces, etc.) also leads to Eqs. (21) and (24). Such formations were defected in the crystals of $Pb_{1-x}Sn_xTe$, for example, doped with Ga, Cd, and Zn (26). Nevertheless, in our case, the predominant formation of chlorine and copper precipitates as a separate phase inside the CdS crystals is excluded. It is seen in Fig. 3a that a simultaneous impurity (Cu and Cl) solubility is encountered which is closely connected with point defects (3, 4, 27).

3.3. Predominant Charge Defects

In the Brouwer approximation to the ENE the concentrations of predominant negatively and positively charged defects are equated. In our study the problem is

reduced to finding $-$ and $+$ defect pairs with the same value of γ:

$$\gamma_- = \gamma_+. \qquad (25)$$

In region II, e' ($\gamma = \frac{1}{4}$) and $Cl_S^{\cdot}$ ($\gamma = \frac{1}{4}$) satisfy Eq. (25), see Table III; thereby, the validity of the ENE Eq. (17) is confirmed. In region I the $+$ charge of $Cl_S^{\cdot}$ ($\gamma = 0$) must be compensated by $-$ charge of the acceptor, so that again one has a value of $\gamma = 0$; see Section 3.1. This condition is satisfied by Cl_i', $V_{Cd}'Cl_S^{\cdot}$, V_{Cd}'', $V_{Cd}''Cl_S^{\cdot}$, and Cu_{Cd}'; see Table III. The Cl_i' concentration diminishes because of its small probability; see Section 3.2. $V_{Cd}'Cl_S^{x}$ represents an example of an inverse population—the upper level (Cl_S^{x}) is occupied, the lower (V_{Cd}') is vacant—and cannot be realized under equilibrium conditions. Due to the high degree of association of V_{Cd}'' with $Cl_S^{\cdot}$ one finds that $[V_{Cd}''Cl_S^{\cdot}] >$ $[V_{Cd}'']$. If $[Cu] < [Cl_S^{\cdot}]$, then $V_{Cd}''Cl_S^{\cdot}$ plays the role of acceptor. If $[Cu] > [Cl_S^{\cdot}]$ then Cu_{Cd}' acts as an acceptor. Consequently, the ENE in region I is expressed as

$$[V_{Cd}''Cl_S^{\cdot}] = [Cl_S^{\cdot}] \quad \text{at} \quad [Cu] < [Cl_S^{\cdot}] \quad (26)$$

$$[Cu_{Cd}'] = [Cl_S^{\cdot}] \quad \text{at} \quad [Cu] > [Cl_S^{\cdot}] \quad (27)$$

We conclude that the predominant charged defects in CdS : Cl and CdS : Cl : Cu appear to be $V_{Cd}''Cl_S^{\cdot}$ (region I), e' (region II), and $Cl_S^{\cdot}$ (region I, II); and Cu_{Cd}' (region I), e' (region II), and $Cl_S^{\cdot}$ (region I, II), respectively.

3.4. Photoluminescence Centers

To establish the defect structures that are responsible for the PL emission bands displayed in Fig. 5 it is necessary to correlate the integral intensity of i–PL emission bands with the concentration of the centers corresponding to the band. In (17, 28) it was shown that in the case of stationary excitation ϕ_i is proportional to the product of free electrons concentration and to the concentration of unoccupied emission centers responsible for the i-emission band.

According to (29) the electron capture on a luminescent center is a radiative process. It is easy to show that for $n \gg p$, as is the case here, $\phi_i \sim [X_i]$. Therefore, γ of the defect responsible for the i–Pl-emission band is equal to γ_i (see Eq. (10)).

$$\gamma = \gamma_i = 0. \qquad (28)$$

From Table III it appears that in region I and II the condition expressed in Eq. (28) is satisfied by $Cu_{Cd}'Cl_S^{\cdot}$ and $V_{Cd}''(Cl_S^{\cdot})_2$. Therefore, the PL emission band of CdS : Cu : Cl, ([Cu] = [Cl]) at $\lambda_{max} = 1030$ nm (Fig. 5) may be associated with the marked defects. Similarly, according to (17, 29) the PL center at $\gamma_{max} = 1030$ nm is identified with $Cu_{Cd}'Cl_S^{\cdot}$. The PL-emission bands at $\lambda_{max} = 730$ nm of CdS : Cu : Cl, [Cl] $\gg$ [Cu] (see Fig. 5) can be connected with $V_{Cd}''Cl_S^{\cdot}$ which is the center of self-activated (SA) emission (1, 30, 31). The concentration of this center decreases with increasing p_{Cd} in region II (see Table III), which roughly coincides with the variation of the band intensity at $\lambda_{max} = 730$ nm as a function of p_{Cd} (Fig. 5).

3.5. Defect Concentrations at $p_{Cd} = p_{min}$ and Brouwer Diagrams

For plotting the Brouwer diagrams it is necessary to know the slopes of the separate types of defects and the concentration values of those defects for at least one point on the scale p_{Cd}. The slopes were determined in Section 3.1. It is convenient to calculate the defect concentration in the Brouwer approximation at the boundary of regions I and II, i.e., at $p_{Cd} = p_{min}$. First n, $[Cl_S^{\cdot}]$, and $[Cu_{Cd}'Cl_S^{\cdot}]$ should be determined. In the Brouwer approximation at the point $p_{Cd} = p_{min}$, the electron concentration is given by $n = [Cl_S^{\cdot}] = [Cu_{Cd}'Cl_S^{\cdot}]$. In region II free electrons are produced by reaction 9; see Table II. Taking into consideration Eq. (17) and the EMB for Cl_S

$$[Cl_S] = [Cl_S^{\cdot}] + [Cl_S^{x}] \qquad (29)$$

we get from the mass action law for reaction 9 (Table II):

$$[Cl_S] = \tfrac{1}{2}K_9\left(\sqrt{1 + \frac{4[Cl_S]}{K_9}} - 1\right), \quad (30)$$

$$K_9 = K_{09}\exp\left(-\frac{E_9}{kT}\right) \quad (31)$$

$$K_{09} = N_c = 2\left(\frac{2m_e^* kT}{h^2}\right)^{3/2} \quad (32)$$

where Cl_S represents the total concentration of chlorine substitutional defects; K_{09}, the preexponential factor; $E_9 \equiv E_d$, the ionization energy of the Cl_S donor, $E_9 \approx 0.03$ eV (32); N_c, the statistical factor for the conduction band; m_e^* the effective mass of the free electrons $m_e^* \approx 0.2\ m_e$ (33, 34). For the chosen values of E_9 and m_e^*:

$$K_{9LT} \equiv K_9(293\ \text{K}) = 6 \times 10^{17}\ \text{cm}^{-3} \quad (33)$$

$$K_{9HT} \equiv K_9(973\ \text{K}) = 8.4 \times 10^{18}\ \text{cm}^{-3}. \quad (34)$$

Using the low-temperature value of n_{LT} at the point $p_{Cd} = p_{min}$ where n_{LT} (p_{min}) is equal to $[Cl_S]_{LT}$ (see Table IV) we find $[Cl_S^x]_{LT}$ from the mass action law for reaction 9 as

$$[Cl_S^x]_{LT} = [Cl_S]_{LT}^2\, K_{9LT}^{-1} \quad (35)$$

Substituting the values of $[Cl_S]_{LT}$ and $[Cl_S^x]_{LT}$ into Eq. (29), one obtains $[Cl_S]_{LT}$. To find the corresponding concentrations at high temperatures we proceed on the assumption that under rapid cooling the HT atomic defects are frozen in (3, 4):

$$[Cl_S]_{LT} = [Cl_S]_{HT} = [Cl_S]. \quad (36)$$

on substituting Eqs. (35) and (33) into Eq. (29) we can determine $[Cl_S]_{HT}$ (p_{min}), and, consequently, $n_{HT}(p_{min})$ as well as $[Cu'_{Cd}Cl_S]_{HT}$ (p_{min}). By substituting the value of K_{9HT} for K_{9LT} in Eq. (35) we obtain $[Cl_S^x]_{HT}$. The results of these calculations are presented in Table IV.

The concentration of free holes is established from the mass action law for reaction 12 (Table II):

TABLE IV

PREDOMINANT IMPURITY DEFECT CONCENTRATIONS (cm⁻³) IN CdS:Cu:Cl AT $p_{Cd} = p_{min}$ (APPROXIMATED FROM THE II REGION) FOR $T = 973$ K

Mater. series no.	Cl_S	Cl_S^x	e'	$h^\cdot$	Cu'_{Cd}	Cu_{Cd}^x	$V''_{Cd}Cl_S$	$V''_{Cd}Cl_S^x$	$Cu'_{Cd}Cl_S$	$V''_{Cd}(Cl_S)_2$
1	2.15×10^{18}	5.5×10^{17}	2.15×10^{18}	1.88×10^8			2.15×10^{18}	5.5×10^{17}	2×10^{15}	2.85×10^{18}
2	8.34×10^{17}	8.28×10^{17}	8.34×10^{17}	4.8×10^8	8.34×10^{17}	2×10^9			3.16×10^{18}	1.8×10^{19}
3	1.15×10^{17}	1.6×10^{15}	1.15×10^{17}	3.5×10^9	1.15×10^{17}	2×10^9			9.9×10^{18}	1.5×10^{19}
4	4.28×10^{17}	2.18×10^{16}	4.28×10^{17}	9.5×10^8	4.28×10^{17}	2×10^9			7.46×10^{19}	2×10^{17}

$$p = K_{12}^{-1}n, \qquad (37)$$

$$K_{12} \equiv K_i = N_c N_v \exp\left(-\frac{E_i}{kT}\right), \quad (38)$$

where N_v is the statistical factor of the valence band and E_i, the width of the forbidden band. The values of p are calculated with E_i (973 K) ≈ 2.2 eV (*1*), $m_h^* = 0.7\ m_e$ (*33*). N_v (973 K) = 8×10^{19} cm^{-3} and N_c (973 K) = 1.2×10^{19} cm^{-3}, given in Table IV. Cu'_{Cd} is established from the mass action law for reaction 13 (Table II)

$$[Cu_{Cd}^x] = K_{13}^{-1}[Cu'_{Cd}]p, \qquad (39)$$

$$K_{13} = N_v \exp\left(-\frac{E_{13}}{kT}\right) \qquad (40)$$

where $E_{13} \equiv E_a$ is the acceptor ionization energy; $E_a \approx 0.5$ eV (*10*). The total concentration of substitutional copper is

$$[Cu_{Cd}] = [Cu'_{Cd}] + [Cu_{Cd}^x]. \qquad (41)$$

Using an analogous procedure, $[V''_{Cd}Cl_S^{\bullet}]$ is found, taking the ionization energies for donor and acceptor levels as equal to $E_d = 0.03$ eV and $E_a = 0.5$ eV, respectively; see Table IV.

The concentrations of the predominant copper defect $Cu_{Cd}Cl_S$ ([Cu] < [Cl]) is established from the EMB for copper:

$$[Cu] = [Cu_{Cd}Cl_S] + [Cu_{Cd}]. \qquad (42)$$

To find $[Cu'_{Cd}Cl_S^{\bullet}]$ and $[Cu'_{Cd}Cl_S^x]$, a relation analogous to Eq. (35) was used, with $E_d = 0.03$ eV, and the EMB for $Cu_{Cd}Cl_S$

$$[Cu_{Cd}Cl_S] = [Cu'_{Cd}Cl_S^{\bullet}] + [Cu'_{Cd}Cl_S^x]. \quad (43)$$

$[Cu_{Cd}^x Cl_S^{\bullet}]$ and $[Cu_{Cd}^x Cl_S^x]$ are neglected because of their low values. The concentration of the predominant chlorine defect $V_{Cd}(Cl_S)_2$ ([Cu] < [Cl]) is established from the EMB for chlorine:

$$[Cl] = 2[V_{Cd}(Cl_S)_2]$$
$$+ [Cu_{Cd}Cl_S] + [Cl_S]. \quad (44)$$

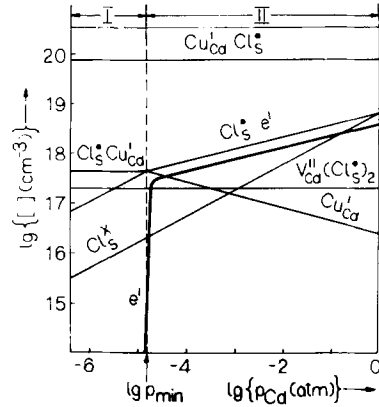The predominant charge defects are taken as $Cl_S^{\bullet}$ and Cu'_{Cd} or e', the charged complex

FIG. 6. The Brouwer diagram for CdS : Cu : Cl (sample 4).

defects such as $V_{Cd}(Cl_S)_2$ should be present in considerably smaller concentration than $[Cl_S]$, $[Cu'_{Cd}]$ or n; hence they are also considerably smaller than the concentration of the neutral complex $V''_{Cd}(Cl_S)_2$. Therefore,

$$[V_{Cd}(Cl_S)_2] \approx [V''_{Cd}(Cl_S)_2]. \qquad (45)$$

The calculated concentration values of the predominant copper and chlorine defects are given in Table IV.

On the basis of the data in Table IV the Brouwer diagram for CdS : Cl : Cu is plotted in Fig. 6.

4. Summary

We conclude that chlorine in cadmium sulfide occupies the sites on the sulfur sublattice by forming donor $Cl_S^{\bullet}$. To neutralize these sites, corresponding acceptors V''_{Cd} are produced (through the self-compensation effect), if [Cl] $\gg$ [Cu]. The interaction of $Cl_S^{\bullet}$ and V''_{Cd} determines the high level of association of these defects, with the predominant formation of $V''_{Cd}(Cl_S)_2$ which is the principal chlorine defect in CdS : Cl : Cu at [Cl] $\gg$ [Cu]. If chlorine is present in cadmium sulfide, copper mainly occupies the sites of the cadmium sublattice as Cu'_{Cd}, thereby compensating for the charge of

chlorine donors Cl_S. With increasing copper concentration the degree of association of Cu'_{Cd} with Cl_S also increases. At [Cu] $\approx$ [Cl] the association of these defects becomes the predominating copper and chlorine defect in cadmium sulfide, which leads to the simultaneous solubility of donors and acceptors.

References

1. M. AVEN AND J. S. PRENER (Eds.), "Physics and Chemistry of II–VI Compounds," North-Holland, Amsterdam (1967).

2. M. ALTOSAAR, P. KUKK, E. MELLIKOV, AND V. VALDNA, Proceedings of the 9th International Symposium on Photon-Detectors. Budapest, 1980, p. 175.

3. F. A. KRÖGER, "The Chemistry of Imperfect Crystals," North–Holland, Amsterdam (1964).

4. A. M. GURVICH, "Vvedenie v fizicheskuyu khimiyu kristallofosforov" ("Introduction to Physical Chemistry of Crystallophosphors"), Vòshaya Schola, Moscow (1971).

5. K. MOCHIZUKI AND K. IGAKI, Japan. J. Appl. Phys. 18, 1447 (1979).

6. S. KITAMURA, J. Phys. Soc. Japan 16, 2430 (1961).

7. R. H. BUBE, J. Electrochem. Soc. 113, 793 (1966).

8. H. A. AARNA, P. L. KUKK, AND M. T. NÔGES, Proc. Tallinn Technical Univ. No. 279, 67 (1969).

9. P. L. KUKK, Izv. Akad. Nauk SSSR, Neorg. Mater. 16, 1509 (1980).

10. R. H. BUBE, "Photoconductivity of Solids," Wiley, New York (1960).

11. I. B. ERMOLOVICH, G. I. MATVIEVSKAYA, G. S. PEKAR, AND M. K. SHEINKMAN, Ukr. Fiz. Zh. 18, 733 (1973).

12. H. KAWAI, S. KUBONIWA, AND T. HOSHINA, Japan. J. Appl. Phys. 13, 1593 (1974).

13. S. SHIONOYA, J. Lumin. 1, 17 (1970).

14. H. R. VYDYANATH, S. S. CHERN, AND F. A. KRÖGER, J. Phys. Chem. Sol. 34, 1317 (1973).

15. C. CANALI, G. OTTAVIANI, R. O. BELL, AND F. V. WALD, J. Phys. Chem. Sol. 35, 1405 (1974).

16. P. L. KUKK, H. A. AARNA, AND M. P. VOOGNE, Phys. Status Solidi A 63, 389 (1981).

17. P. L. KUKK AND A. J. ERM, Phys. Status Solidi A 67, 395 (1981).

18. P. L. KUKK, Ö. V. PALMRE, AND E. J. MELLIKOV, Phys. Status Solidi A 70, 35 (1982).

19. M. E. ALTOSAAR AND P. L. KUKK, Izv. Akad. Nauk SSSR, Neorg. Mater. 18, 1475 (1982).

20. J. BOOMGAARD, F. A. KRÖGER, AND H. J. VINK, J. Electron. 1, 212 (1955).

21. M. E. ALTOSAAR AND J. V. HIIE, Proc. Tallinn Technical Univ. No. 404, 71 (1976).

22. N. V. AGRINSKAYA AND O. A. MATVEYEV, Fiz. Techn. Poluprov. 10, 162 (1976).

23. V. M. ARORA AND W. D. COMPTON, J. Appl. Phys. 43, 4499 (1972).

24. A. M. GURVICH, Uspekhi Khim. 35, 1495 (1966).

25. L. DVOŘAK AND Z. KUPKA, Acta Univ. Palacki. Olomuc. Fac. Rerum Nat. 41, 15 (1973).

26. A. M. GASKOV, N. G. LISINA, V. P. ZLOMANOV, AND A. V. NOVOSELOVA, Dokl. Akad. Nauk SSSR 261, 95 (1981).

27. V. M. GLAZOV, A. J. KISELEV, AND A. Y. POTEMKIN, Zh. Fiz. Khim. 51, 2788 (1977).

28. K. COLBOW, Phys. Rev. 141, 742 (1966).

29. M. K. SHEINKMAN, N. E. KORSUNSKAYA, I. V. MARKEVICH, AND T. V. TORCHINSKAYA. Izv. Akad. Nauk SSSR, Ser. Fiz. 40, 2290 (1976).

30. Y. SHIRAKI, T. SHIMADA, AND K. F. KOMATSUBARA, J. Appl. Phys. 45, 3554 (1974).

31. N. SUSA, H. WATANABE, AND M. WADA, Japan J. Appl. Phys. 15, 2463 (1976).

32. H. H. WOODBURY AND M. AVEN, Phys. Rev. B 9, 5195 (1974).

33. C. S. FULLER, W. KAISER, AND C. D. THURMOND, J. Phys. Chem. Sol. 17, 301 (1961).

34. J. J. HOPFIELD AND D. G. THOMAS, Phys. Rev. 122, 35 (1961).