

High-Temperature Conductivity Relaxation in Undoped CdS and CdSe Single Crystals

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The high-temperature conductivity (HTC) relaxation in CdS and CdSe single crystals, caused by a steep change of cadmium vapor pressure P_{Cd} , was measured. For obtaining a steep change of P_{Cd} improved van Doorn equipment was used. Conductivity measurements were carried out using the Van der Pauw method. It was shown that the Cd diffusion from gaseous phase into CdS and CdSe platelets leads to a conductivity time-dependence function $\sigma(t)$ in the form of a sum of decreasing exponents, indicating that the rate of HTC relaxation is limited by the chemical diffusion of cadmium. A correlation between chemical and tracer-diffusion coefficients was found. Values of activation energies and preexponential factors for both types of diffusion were determined. The results are discussed using a model for transformation of Cd_i into $V_{s,se}^{..}$ previously proposed by Chern and Kröger for chemical self-diffusion in CdTe.

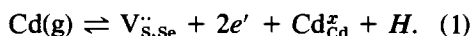
Introduction

The recent interest in kinetical characteristics of quasi-chemical defect formation reactions in semiconductors can be explained by the need to choose optimum cooling rates from crystallization or doping temperature to room temperature for obtaining "frozen-in" defect concentrations, resulting in needed photoelectrical and luminescent qualities. For that purpose the luminescent methods of investigation are given (1) and a series of measurements on zinc selenide were carried out (2).

In this paper the data of high-temperature conductivity (HTC) relaxation measurements are used for determination of the kinetical scheme and the activating energy of quasi-chemical defect formation reactions in cadmium sulfide and selenide.

The HTC relaxation studies in CdS (3-5) and CdSe (6-8) single crystals in the tem-

perature range where native defects become dominant ($T \geq 600^\circ C$) have shown that the HTC relaxation process can be described by an exponential function law with time constant τ . Such a dependence is characteristic of first-order reactions (9). Since diffusion can be considered to be a first-order reaction (9), it is concluded that the rate of reaction responsible for the HTC relaxation is limited by diffusion (3-8). In the temperature range where native defects are dominant the conductivity of CdS and CdSe shows a Cd vapor pressure dependence p_{Cd}^γ ($\gamma = \frac{1}{2}$) (10-12). This dependence corresponds to the formation of excess cadmium in CdS and CdSe crystals by the reaction (10-12)



Approximation of the electroneutrality condition (10-12)

$$n = 2[V_{s,se}^{\bullet}] \quad (2)$$

gives, for the free electron concentration n ,

$$n = (2Kp_{Cd})^{1/3} \\ = (2K_0)^{1/3} p_{Cd}^{1/3} \exp(-H/3kT), \quad (3)$$

where K is the equilibrium constant of reaction (1), H the enthalpy of (1), and K_0 the preexponential factor. Since the electron mobility depends only slightly on p_{Cd} (7) the conductivity σ is proportional to n : $\sigma \sim n \sim p_{Cd}^{1/3}$. It has been suggested that cadmium diffusion in cadmium chalcogenides takes place via interstitials (3, 4, 6, 7, 13) or vacancies (14).

Experimental

Samples with dimensions of $0.8 \times 5 \times 15$ mm were cut from undoped CdS and CdSe single crystals grown by the sublimation and Bridgeman technique, respectively. The samples were polished, etched in HNO_3 and KOH , and washed in triply distilled water. An extraction technique was used to purify the samples. The samples were placed in a quartz ampoule and the van Doorn method was used to control the cadmium vapor pressure (15). The van Doorn equipment was substantially improved by establishment of a multizone temperature profile in the condensation region of Cd. This removed the main drawback of the method—formation of liquid cadmium drops and their falling into the hot zone. Repeated evaporation of Cd in the multitemperature zone makes possible very sharp changes in the Cd vapor pressure. The improvements made it possible to maintain the cadmium vapor pressure constant for a long time or to change it abruptly (within a fraction of a second) as needed for rapid relaxation measurements of HTC in undoped CdS and CdSe. The electrical measurements were carried out using the Van der Pauw method.

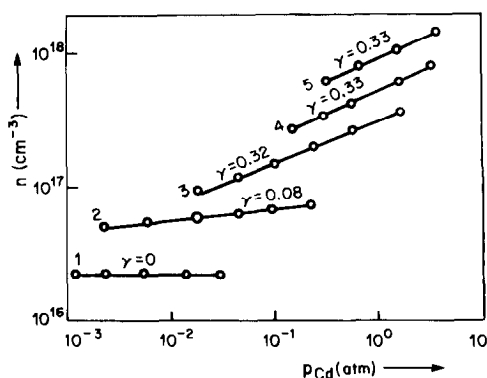


FIG. 1. Electron concentration as a function of Cd vapor pressure at various temperatures for undoped CdS. (1) 480°C; (2) 630°C; (3) 680°C; (4) 830°C; (5) 950°C.

Results and Discussion

Relaxation of HTC in the Range where Native Defects Control Conductivity

As seen in Figs. 1 and 2, for our undoped CdS and CdSe crystals the dependence of HTC on cadmium vapor pressure ($\sigma \sim p_{Cd}^{\gamma}$) occurs with $\gamma = \frac{1}{3}$ above 650°C. HTC relaxation curves were obtained in that temperature range. Isothermal HTC relaxation was induced by a stepwise change in p_{Cd} . The result is shown in Figs. 3 and 4. An analysis

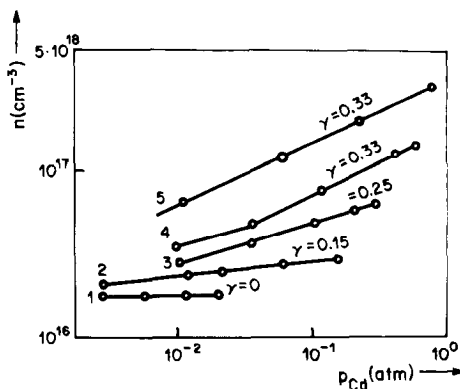


FIG. 2. Cd vapor pressure dependence of electron concentration at various temperatures for undoped CdSe. (1) 460°C; (2) 517°C; (3) 636°C; (4) 700°C; (5) 790°C.

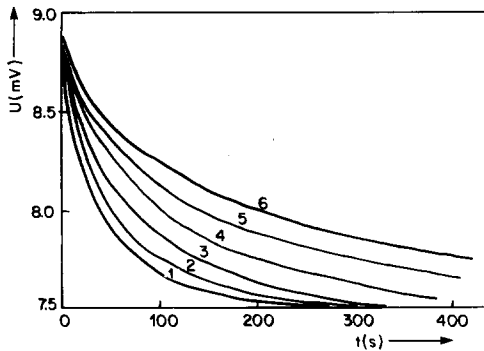


FIG. 3. Resistivity relaxation for CdS; Cd vapor pressure is increased. (1) 833°C; (2) 800°C; (3) 751°C; (4) 725°C; (5) 687°C; (6) 644°C.

of these curves shows deviations from a simple exponential behavior, particularly in the initial stage.

Chemical Diffusion of Cadmium

In the case of the approximated electroneutrality condition Eq. (2) the conductivity is proportional to the excess Cd concentration in the sample (16). The excess cadmium content changes during the cadmium diffusion into the CdS and CdSe crystal. The conditions correspond to diffusion from a source with constant Cd activity into a sample with definite dimensions, and the time dependence of the relative amount of the diffusant is described by the infinite sum

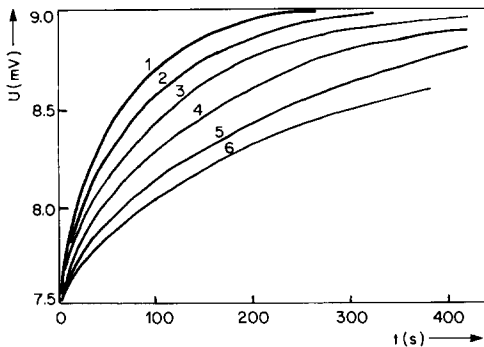


FIG. 4. Resistivity relaxation for CdSe; Cd vapor pressure is decreased. (1) 833°C; (2) 800°C; (3) 751°C; (4) 725°C; (5) 687°C; (6) 644°C.

of decreasing exponents (17),

$$\frac{Q(t)}{Q_\infty} = 1 - \frac{8}{\pi^2} \sum_{k=0}^{\infty} (2k+1)^{-2} \exp\left[-(2k+1)^2 \frac{t}{\tau}\right], \quad (4)$$

where $Q(t)$ is the total amount of diffusant (here excess Cd) in the sample at time t ; Q_∞ is the equilibrium value of $Q(t)$, when $t \rightarrow \infty$; $\tau = d^2/\pi^2 D$, where d is the thickness of the thin sample; and D is the diffusion coefficient. In case of diffusion from a vapor into an isotropic binary crystal D is the coefficient of chemical diffusion \bar{D} (18, 19). The reverse process—diffusion from a solid to a gaseous phase—is described by a formula similar to Eq. (4) (17),

$$\frac{Q(t)}{Q_0} = \frac{8}{\pi^2} \sum_{k=0}^{\infty} (2k+1)^{-2} \exp\left[-(2k+1)^2 \frac{t}{\tau}\right], \quad (5)$$

where Q_0 is the initial ($t = 0$) value of $Q(t)$. For suggested proportionality between σ and Q normalized conductivities $y(t)$

$$= \frac{\sigma(t) - \sigma_0}{\sigma_\infty - \sigma_0} = \frac{Q(t)}{Q_\infty} \quad (p_{\text{Cd}} \text{ is increased}) \text{ and}$$

$$y(t) = \frac{\sigma(t) - \sigma_\infty}{\sigma_0 - \sigma_\infty} = \frac{Q(t)}{Q_0} \quad (p_{\text{Cd}} \text{ is decreased})$$

are represented by Eqs. (4) and (5), respectively; $\sigma(t)$ is the conductivity at the time moment t ; σ_0 = conductivity at $t = 0$; and σ_∞ = conductivity at $t = \infty$. A good agreement between calculated and experimental curves is obtained when suitable values of τ are chosen (see Fig. 5). This agreement can be taken as a verification of the statement that the HTC relaxation in CdS and CdSe is really determined by diffusion—the chemical diffusion of cadmium. Values of the coefficients of the chemical diffusion of cadmium in CdS and CdSe, \bar{D} , determined from values of τ at various temperatures are given in Table I. Parameters of

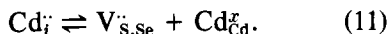
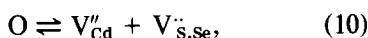
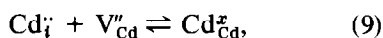
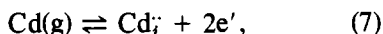
$$\bar{D} = \bar{D}_0 \exp(-\bar{E}/kT) \quad (6)$$

determined from plots of τ versus $10^3/T$ shown in Fig. 6 are given in Table II.

Kinetical Scheme of the Excess Cadmium Formation Reaction

In thermodynamical equilibrium the Schottky disorder is considered to be dominant in $A^{II}B^{VI}$ compounds (10-12, 20). This leads to incorporation of Cd as expressed by Eq. (1) with the electroneutrality condition Eq. (2). Recent experimental ESR studies indicate that sulfur vacancies predominate over Cd interstitials in CdS (21).

Therefore, the situation is similar to that in CdTe found by Chern and Kröger (22), and the kinetical scheme of Eq. (1) may be written



Equation (7) describes the adsorption of cadmium atom at the sample's surface and its incorporation (with simultaneous double ionization) in the interstitial sites of the crystal close to the surface. Equation (8) represents diffusion of interstitial cadmium

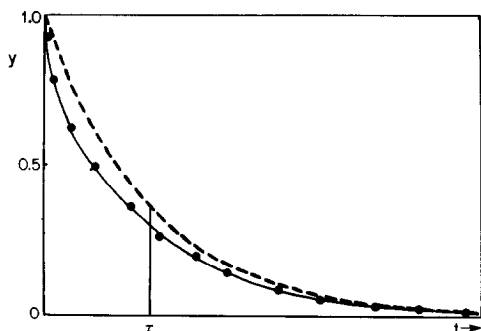


FIG. 5. Exponential function ($y \sim \exp(-t/\tau)$)—dashed line. Comparison of calculated according to Eq. (5) (solid line) and experimental (solid circles) relaxation curves.

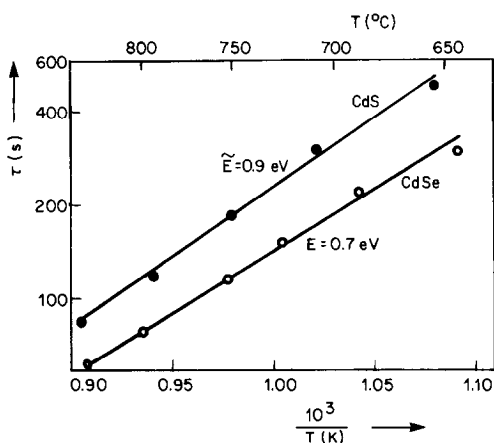


FIG. 6. Temperature dependence of time constant τ of the high-temperature conductivity relaxation for CdS and CdSe.

ions into the crystal from interstitial site z into the neighboring interstitial site $z+1$, etc. The migrating Cd_i is gradually transformed into $V_{\text{S,Se}}^{\cdot\cdot}$ by: (a) capturing of Cd_i by V_{Cd}'' (Eq. (9)) leading to an increased concentration of $V_{\text{S,Se}}^{\cdot\cdot}$ according to a shift in Eq. (10), or (b) building up the regular cadmium sublattice by reaction (11) when Cd_i reaches inner surfaces (at dislocations, small-angle grain boundaries, etc.). A diffusion of electrons into the bulk of the crystal takes place simultaneously with Eq. (8) with the particle current of e' equal to twice that of Cd_i (ambipolar diffusion).

The conductivity of the sample is determined by free electrons, produced by Eq. (7); processes Eqs. (8) to (11) do not contribute to the free electron concentration. Equation (7) leads to a quasi-equilibrium in a thin surface layer. The addition rate of new cadmium atoms from the gaseous phase is equal to the leaving rate of Cd_i and e' from the surface layer. As this process is caused by the concentration gradients and ultimately leads to a homogeneous distribution of excess cadmium atoms, it constitutes a chemical diffusion.

Cd_i is the major mass carrier in diffusion, but the Cd excess Q in the crystal is

TABLE I
TEMPERATURE-DEPENDENCE DATA OF TIME CONSTANT OF HIGH-TEMPERATURE CONDUCTIVITY
RELAXATION FOR CdS AND CdSe, AND CORRESPONDING CHEMICAL DIFFUSION COEFFICIENTS \bar{D}

CdSe	$T(^{\circ}\text{C})$	644	687	725	751	800	833
	$\tau(\text{sec})$	290	216	144	109	77	60
	$\bar{D}(\text{cm}^2/\text{sec})$	2.2×10^{-6}	3.0×10^{-6}	4.5×10^{-6}	5.9×10^{-6}	8.4×10^{-6}	1.08×10^{-5}
CdS	$T(^{\circ}\text{C})$	653	706	748	791	831	
	$\tau(\text{sec})$	478	302	182	118	84	
	$\bar{D}(\text{cm}^2/\text{sec})$	1.4×10^{-6}	2.1×10^{-6}	3.6×10^{-6}	5.5×10^{-6}	7.7×10^{-6}	

Note. $\bar{D} = d^2/\pi^2\tau$, $d = 0.08$ cm.

$$Q = [\text{Cd}_i^{\cdot}] + [\text{V}_{\text{s,se}}^{\cdot\cdot}]. \quad (12)$$

From Eq. (2) it follows that

$$[\text{V}_{\text{s,se}}^{\cdot\cdot}] \gg [\text{Cd}_i^{\cdot}]. \quad (13)$$

Correlation between the Coefficients of Chemical and Tracer Diffusion

Now we shall establish the correlation between the coefficients of chemical and self-diffusion of Cd. Currents of the most mobile particles—electrons j_e and interstitial ions of cadmium j_{Cd} —are expressed as (4)

$$\frac{1}{2}j_e = j_{\text{Cd}} = -\alpha D_{\text{Cd}} \frac{d}{dx} [\text{Cd}_i^{\cdot}], \quad (14)$$

where D_{Cd} is the coefficient of self-diffusion of Cd_i^{\cdot} , and α is the coefficient which takes into consideration the ambipolar character of diffusion. For ambipolar diffusion of e' and Cd_i^{\cdot} , $\alpha = 3$ (22). On the other hand, j_e and j_{Cd} are expressed with the help of the coefficient of chemical diffusion of Cd— \bar{D} :

$$\frac{1}{2}j_e = j_{\text{Cd}} = -\bar{D} \frac{dQ}{dx}. \quad (15)$$

From Eqs. (12), (14), and (15) we get the relation between \bar{D} and D_{Cd} ,

$$\bar{D} = 3D_{\text{Cd}} \left\{ 1 + \frac{d[\text{V}_{\text{s,se}}^{\cdot\cdot}]}{d[\text{Cd}_i^{\cdot}]} \right\}^{-1}. \quad (16)$$

The determination of the second term in brackets reduces to the determination of the relation between $\text{V}_{\text{s,se}}^{\cdot\cdot}$ and Cd_i^{\cdot} . For that reason we propose that, analogously to Eq. (7), the Eqs. (9)–(11) are also locally in an equilibrium, and therefore we may write

$$\frac{[\text{Cd}_i^{\cdot}]_0 n^2}{p_{\text{Cd}}} = K_1, \quad (17)$$

$$\frac{1}{[\text{Cd}_i^{\cdot}][\text{V}_{\text{Cd}}^{\cdot\cdot}]} = K_2, \quad (18)$$

$$[\text{V}_{\text{Cd}}^{\cdot\cdot}][\text{V}_{\text{s,se}}^{\cdot\cdot}] = K_3, \quad (19)$$

where $[\text{Cd}_i^{\cdot}]_0$ is the average concentration of Cd_i^{\cdot} when Eq. (7) operates in the thin surface layer of sample.

From Eqs. (18) and (19) we get, for the diffusion zone,

$$d[\text{V}_{\text{s}}^{\cdot\cdot}]/d[\text{Cd}_i^{\cdot}] = K_2 K_3. \quad (20)$$

TABLE II
PARAMETERS OF CHEMICAL DIFFUSION OF CADMIUM (\bar{D}, \bar{E}) AND TRACER DIFFUSION OF CADMIUM (D_0^*, E^*)
IN CdS AND CdSe

Material	\bar{D}_0 (cm^2/sec)	\bar{E} (eV)	K_0 (atm^{-1})	H (eV)	D_0^* (cm^2/sec)	E^* (eV)
CdS	0.1	0.9	3×10^{-6}	2.0	6.6×10^{-5}	1.6
CdSe	1.6×10^{-2}	0.7	4.4×10^{-5}	1.8	2.6×10^{-5}	1.4

Substituting Eq. (20) into Eq. (16), we get the relation between \tilde{D} and D_{Cd} in the diffusion zone

$$\tilde{D} = 3D_{\text{Cd}}(1 + K_2K_3)^{-1}. \quad (21)$$

Using the well-known relation between the self-diffusion coefficient D_{Cd} and the tracer-diffusion coefficient D^* (23),

$$D^* = D_{\text{Cd}}[\text{Cd}_i^-], \quad (22)$$

we get

$$\tilde{D} = \frac{3D^*}{(1 + K_2K_3)[\text{Cd}_i^-]}. \quad (23)$$

During the diffusion from the near-surface layer, $[\text{Cd}_i^-]$ is a function of the distance from the surface x and of the time t . The reaction zone Eq. (7) can be treated as an unlimited source of Cd_i^- . Hence Cd_i^- corresponds to the solution of Fick's equation in case of diffusion from an unchangeable source into a sample with definite dimensions (17),

$$[\text{Cd}_i^-](x, t) = [\text{Cd}_i^-]_0 \beta(x, t), \quad (24)$$

where

$$\beta(x, t) = 1 - \frac{4}{\pi} \sum_{k=0}^{\infty} (2k + 1)^{-1} \exp\left[-(2k + 1)^2 \frac{t}{\tau}\right] \sin \frac{(2k + 1)\pi}{d} x. \quad (25)$$

$[\text{Cd}_i^-]_0$ is calculated from Eqs. (17) and (3):

$$[\text{Cd}_i^-]_0 = (2K)^{-2/3} K_1 p_{\text{Cd}}^{1/3}. \quad (26)$$

Substituting Eqs. (24) and (26) into Eq. (23), we get

$$\tilde{D} = \frac{3D^*}{(1 + K_2K_3)(2K)^{-2/3} K_1 p_{\text{Cd}}^{1/3} \beta(x, t)}. \quad (27)$$

The expression Eq. (27) relates the coefficients of chemical diffusion (\tilde{D}) and tracer diffusion (D^*) of cadmium in the nonequilibrium case for arbitrary moments of time t and distance x from surface in a thin plane-parallel sample with the thickness d , in which the exchange of material with the gaseous phase takes place through the two

side surfaces. Equation (27) is symmetrical with regard to the opposite side surfaces.

Reaching the equilibrium ($t \rightarrow \infty$, $\beta \rightarrow 1$) $V_{\text{S,Se}}$ will yield a dominant positively charged defect homogeneously distributed in the whole crystal, which leads to $K_2K_3 \gg 1$, and we may, in Eq. (27), abandon the unit in brackets. Taking into consideration Eqs. (17), (18), and (19), and also Eqs. (2) and (3), our formula Eq. (27) will take a form of the well-known relation between \tilde{D} and D^* in the case of homogeneous distribution of defects in the crystal (cf. for example, (4)):

$$\tilde{D} = \frac{3D^*}{(\frac{1}{4} K p_{\text{Cd}})^{1/3}}. \quad (28)$$

Representing \tilde{D} and D^* in the form of Eq. (6)-type expressions and taking into consideration Eqs. (3) and (28), we get the relation between the kinetical parameters of chemical and tracer diffusion of cadmium:

$$\tilde{D}_0 = 3(4/K_0 p_{\text{Cd}})^{1/3} D_0^*, \quad (29)$$

$$\tilde{E} = E^* - \frac{1}{3}H. \quad (30)$$

Substituting the values of \tilde{D}_0 and \tilde{E} into Eqs. (29) and (30), and also K_0 and H (the latter ones coincide well with the values determined in (10, 11) for CdS and in (12) for CdSe), we get the values of D_0^* and E^* for CdS and CdSe (see Table II). The values of enthalpy H of Eq. (1) and activation energy of chemical diffusion of cadmium \tilde{E} as a limiting phase of Eq. (1) allow us to construct the cross section of the surface of potential energy of reacting systems depending on reaction coordinate in the case of Eq. (1) in CdS and CdSe (see Fig. 7).

The obtained kinetical parameters of diffusion in CdS and CdSe coincide rather well with the data given in (3-5, 24), but differ from the data given in (7, 25). Different values of diffusion characteristics given by different authors are evidently explained by the different degree of purity and crystal perfection of the CdS and CdSe single crystals.

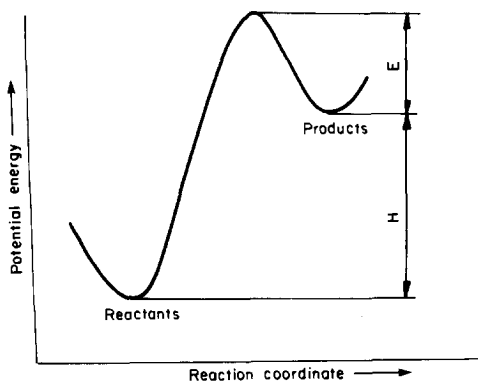


FIG. 7. Cross section of potential energy surface of reacting system on reaction coordinate for the reaction $\text{Cd}(\text{g}) \rightleftharpoons \text{V}_{\text{S,Se}} + 2e' + \text{Cd}_{\text{Cd}} + H$; $H = 2.0 \text{ eV}$, $\bar{E} = 0.9 \text{ eV}$ (CdS) and $H = 1.8 \text{ eV}$, $\bar{E} = 0.7 \text{ eV}$ (CdSe).

tals used in experiments. The same situation appears in Ge and Si crystals, where kinetical parameters of self-diffusion depend on the concentration and type of impurities and also on the presence of defects such as dislocations acting as traps for diffused particles (26). Evidently the average lifetime of Cd_i with regard to trapping will depend on the concentration of the traps, (see, for example, (9)). Accordingly one expects a dependence of τ and \bar{D} on the degree of crystal perfection of the crystals used. Therefore diffusion, particularly the cooling rate from the preparation temperature to room temperature, is important.

Summary

High-temperature conductivity relaxation in CdS and CdSe single crystals is measured using improved van Doorn equipment. It is shown that relaxation rate is limited by chemical diffusion of cadmium. The diffusion parameters are determined. Predominant mass carriers are Cd_i . Excess cadmium in CdS and CdSe occur in the form of $\text{V}_{\text{S,Se}}$.

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