

III-9. Optical Properties and Energy Band Structure of ZnS-CdS Single Crystals

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Absorption and reflection spectra of ZnS-CdS single crystals of different composition are investigated in the polarized light at 300, 77 and 20.4°K. From the absorption and exciton position, and dependences of the forbidden gap, spin-orbit splitting and splitting by the crystal field upon the sample composition are obtained. The concentration dependences of the electron and hole effective masses for the ZnS-CdS system are calculated.

§ 1. Introduction

Two semiconductors of similar crystal structure and slightly different lattice parameters intermix, as a rule, partly or completely. The hexagonal-type ZnS crystals form a continuous set of solid solutions with CdS.¹⁾

The ZnS-CdS crystals are good phosphors whose luminescent properties were investigated in a series of papers for both pure²⁾ and doped³⁾ crystals. Their photoelectric properties were also studied.^{1,4)} The optical properties of ZnS-CdS crystals, however, have not yet thoroughly investigated. Only a few works dealt with the low-temperature reflection spectra of the ZnS-CdS system^{5,6)} and their absorption spectra.^{7,8)} In a recent work⁹⁾ dealing with the ZnS-CdS thin film it was shown that the forbidden gap varies linearly with the sample composition. However, in order to have full understanding of the change in parameters of ZnS-CdS band structure due to substitution of Cd atoms by Zn atoms, more complete measurements of optical properties are required.

For this purpose measurements are made of the fundamental absorption edge and the reflection spectra of ZnS-CdS single crystals with polarized light. The results will be mentioned in the present paper.

§ 2. Experiment

For the investigation single crystals, grown by the sublimation,¹⁾ were used in the form of thin plates. All crystals were carefully tested for single monophasing and single crystallization

by x-rays. These measurements and data on the crystal percentage were given elsewhere.¹⁾

The optical investigations are made by a usual method. The absorption curves were measured photoelectrically. The multiple transmittance in the plane-parallel plate¹⁰⁾ is taken into account. The monochromator SPM-2¹¹⁾ was used as a dispersive system. In calculation of absorption coefficient the reflection was considered as identical both for pure and mixed single crystals. This approximation gives a small error. The reflection spectra were measured at a normal incidence on the crystal by a photographic method under intermediate and low dispersion. The maximum error in the measurements of the absorption coefficient is 10%.

§ 3. Results and Discussion

Figure 1 shows the results of measurements on absorption edge in the polarized light at 20.4°K. With the increase of Zn concentration in CdS, the absorption edge is smoothly shifted towards short waves. For mixed as well as for pure CdS crystals, the absorption edge is described by an exponential function (the Urbach rule¹²⁾) of the emission energy, *i.e.* the absorption is in the longwave side of the exciton absorption band. The absorption edge in mixed crystals is rather flat in contrast with that in the pure CdS and ZnS crystals. The change in slope of the absorption curves of mixed crystals is basically associated with the exciton broadening resulting in a decrease of the exciton absorption intensity (see Fig. 1, curve 2).

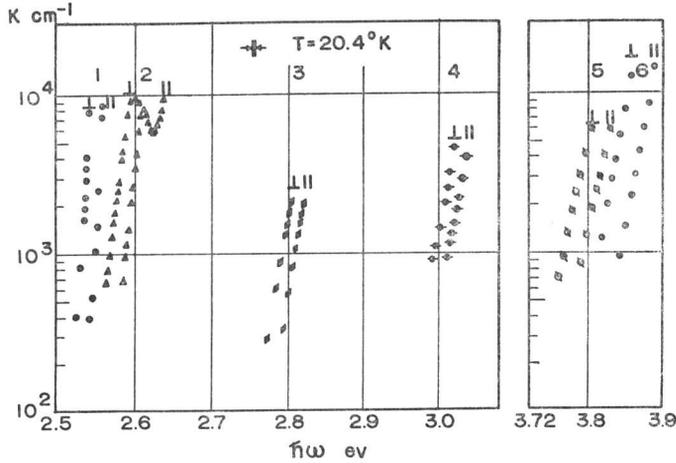


Fig. 1. Spectral dependence of the absorption coefficient for two light polarizations of ZnS-CdS crystals at 20.4°K. The curves 1-6 are for $x=0; 0.06; 0.28; 0.49; 0.96; 1.0$, respectively.

From measurements of the absorption edge the magnitude of the forbidden gap E_0 and its dependence upon the sample composition are obtained. The forbidden gap was determined by taking into account the exciton ionization energy. The latter was assumed to change linearly from CdS to ZnS. The forbidden gap was found to vary nonlinearly with the composition (Fig. 2).

The exciton bands were studied from the reflection spectra, since there were no sufficiently thin crystals available to investigate absorption spectra. As shown earlier,⁵⁾ the reflection spectra of mixed crystals are similar to those of pure substances, *i.e.* three typical exciton bands A, B and C (transitions $\Gamma_9 \rightarrow \Gamma_7$, $\Gamma_7 \rightarrow \Gamma_7$ and $\Gamma_7 \rightarrow \Gamma_7$) are observed.

The exciton bands of mixed crystals are broader than those of pure ZnS and CdS.

At comparable Zn and Cd concentrations this broadening is so large that the exciton bands are practically no longer observable in the low-temperature reflection spectra. Consequently, for such composition of mixed crystals a strong lattice distortion occurs which results in a deformation of energy bands and broadens the exciton bands. Such substantial local deformation is apparently caused by nonlinear change in distance between valence and conduction bands with the sample composition (Fig. 2).

From the position of three exciton bands A, B and C and from Hopfield theory¹³⁾ one may determine such essential energy spectrum parameters as spin-orbit splitting of valence bands Δ_{so} and splitting by the crystal field Δ_c and also establish their dependence upon the sample composition. These calculations are accurate enough so far as the position of the exciton band can be precisely determined as is the case at low concentration of one component. At comparatively high Zn concentrations in CdS Δ_{so} and Δ_c are calculated only approximately. In the region, where Δ_{so} and Δ_c are determinable they are nearly linear to the sample composition. Earlier it was shown for CdS-CdSe¹⁴⁾ and CdS-CdTe¹⁵⁾ systems that their spin-orbit splitting is mainly determined by the number of inner electrons and increases from 0.063 eV for CdS till 0.95 eV for CdTe. In the present case Δ_{so} shows comparatively little change: from 0.063 eV for CdS to 0.085 eV for ZnS. This is due to the fact that Te has much more electrons than S, while Zn has less electrons comparing to Cd.

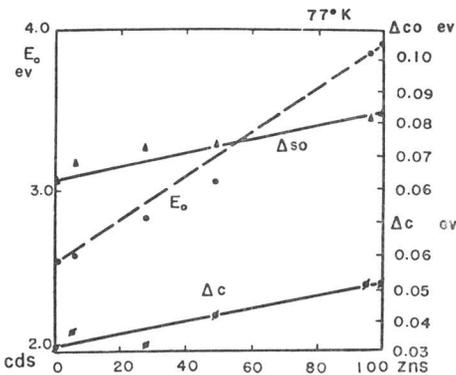


Fig. 2. The forbidden gap E_0 the spin-orbit splitting Δ_{so} and splitting by the crystal field Δ_c vs. the ZnS-CdS crystals composition.

A small change in the splitting by crystal field (from 0.031 eV to 0.053 eV) seems to indicate a slight change in the crystal field, *i.e.* ZnS and CdS compounds are similar in chemical binding.

Using the *KP* method, Cardona showed¹⁶⁾ that the electron effective mass in the conduction band can be presented as

$$\frac{m}{m^*(\Gamma_{1c})} = 1 + \frac{P^2}{2[E_p(\Gamma_{15c}) - E_p(\Gamma_{15v})]} \times \left\{ \left[\frac{E_p(\Gamma_{15c}) - E_p(\Gamma_{15v}) + E(\Gamma_{15}) - E(\Gamma_{25'})}{3} \right] \times \left(\frac{2}{E_0} + \frac{1}{E_0 + \Delta_{80}} \right) - \frac{E_p(\Gamma_{15c}) - E_p(\Gamma_{15v}) - E(\Gamma_{15}) + E(\Gamma_{25'})}{E_p(\Gamma_{15c}) - E_p(\Gamma_{15v}) - E_0} \right\}$$

where Γ is the representation of corresponding bands for Ge structure ($\Gamma_{15}, \Gamma_{25'}$) and the zinc blende structure ($\Gamma_{15c}, \Gamma_{15v}$), E_0 is optical gap of the given semiconductor and $P^2 = (2/3 m) \langle \Gamma_{1c} | p_x | \Gamma_{4v}^z \rangle^2$ for semiconductors of CdS type.

Hence, to determine the effective mass of the electrons one must know P^2, E_0, Δ_{80} and corresponding energy differences $E(\Gamma_{15}) - E(\Gamma_{25'})$ for Ge and $E_p(\Gamma_{15c}) - E_p(\Gamma_{15v})$ for the semiconductor under investigation. In our case P^2 was taken to be 21 eV.¹⁶⁾ $E(\Gamma_{15}) - E(\Gamma_{25'}) = 3.05$ eV, $E_p(\Gamma_{15c}) - E_p(\Gamma_{15v})$ changes from 5.7 eV for ZnS to 6.1 eV for CdS.¹⁶⁾ Using E_0 and Δ_{80} obtained above, m/m^* was calculated as a function of the concentration. The results are presented in Fig. 3.

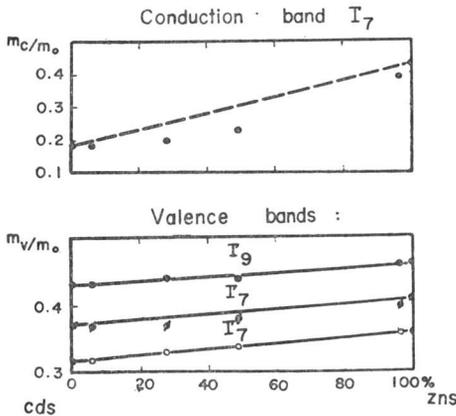


Fig. 3. The electron and hole effective masses vs. the ZnS-CdS crystal composition.

The electron effective mass varies nonlinearly with the sample composition.

In the similar way the effective masses of the hole density states ($m_v^* = (m_{\perp}^2 m_{\parallel})^{1/3}$) in the three valence bands Γ_9, Γ_7 and Γ_7^p were estimated using expressions derived in ref. 16). The results are also given in Fig. 3. As is seen, the effective masses in all three subbands linearly vary with the sample composition.

Thus, on the basis of absorption and reflection spectra measurements the concentration dependences of the energy structure parameters are obtained for ZnS-CdS crystals.

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