THE CONTRIBUTION OF EXCITON-PHONON INTERACTION AND CATION DISORDER TO NEAR-BAND-EDGE EXTRINSIC ABSORPTION IN II-III$_2$-VI$_4$ COMPOUNDS

A.N. Georgobiani and V.V. Ursaki

P.N.Lebedev Physical Institute, Academy of Sciences of the USSR,
117924 Moscow

S.I. Radautsan and I.M. Tiginyanu

Institute of Applied Physics, Academy of Sciences of the Moldavian SSR,
277028 Kishinev

Results of a study of near-band-edge absorption in both initial and annealed CdGa$_2$S$_4$ and CdIn$_2$S$_4$ single crystals at different temperatures are presented. Exciton-phonon interaction and cation disorder are shown to determine the absorption edge in CdGa$_2$S$_4$ and CdIn$_2$S$_4$ compounds correspondingly.

1. INTRODUCTION

The nonmagnetic II-III$_2$-VI$_4$ compounds are of a great interest because of their high photosensitivity, intensive luminescence and unique nonlinear characteristics[1]. Strong tails in the absorption edge have been observed in many of those semiconductors, the nature of which being not unambiquosly established up to now. For the purpose of identifying some mechanisms of extrinsic absorption in the vicinity of band gap energy E_g of II-III$_2$-VI$_4$ semiconductors we have investigated in detail the absorption edge in CdGa$_2$S$_4$ and CdIn$_2$S$_4$ crystals.

CdGa$_2$S$_4$ is a tetrahedrally coordinated semiconductor which crystallize in the defect chalcopyrite structure with space-group S_4^2. It is known, that 1/4 of cation sites in that material are unoccupied and form the so-called stoichiometric vacancies. Cadmium thiogallate is a direct semiconductor with E_g^d = 3.77 eV at 10 K (dE_g^d/dT = -1.9 x x 10^{-4} eV/K)[2]. As to the CdIn$_2$S$_4$ compound, it crystalized in a cubic spinel structure with O_h^7 spacegroup. This material does not contain stoichiometric vacancies. It is of interest to note that Cd and In atoms are capable of occupying both tetrahedral and octahedral sites in the lattice of CdIn$_2$S$_4$ crystals with an order-disorder transition at 130° C.[3] Cadmium thioindate is an indirect semiconductor with E_g = 2.28 eV at 300 K. The interband

gap for the direct transition has a value of 2.62 eV at room temperature (dE_g^d/dT = -4.3 x 10^{-4} eV/K)[4].

2. EXPERIMENTAL ASPECTS

Absorption spectra of initial as well as of annealed CdGa$_2$S$_4$ and CdIn$_2$S$_4$ single crystals were investigated. For experiments platelets with dimensions 3 x 3 x 0.1 mm^3 were prepared from bulk single crystals grown by iodine transport technique. The absorption coefficient α at different temperatures was evaluated by using the data of transmission corrected for reflection losses. The annealing was performed in an argon atmosphere at 400° C. After that a part of single crystals was water quenched, while another part was furnace-cooled. The set-up employed allows the spectral features to be determined with an accuracy not worse than 0.02 eV.

3. RESULTS AND DISCUSSION

Fig. 1 shows the absorption curves of initial CdGa$_2$S$_4$ at different temperatures. It is seen, that the absorption coefficient varies exponentially with the energy of light.The slope of the straight lines lg α = f(hw) is dependent on the temperature.The analysis shows, that the absorption of CdGa$_2$S$_4$ in the investigated spectral range follows the Urbach rule:

$$\alpha = \alpha_0 \exp\left[-\frac{\sigma(E_0 - \hbar\omega)}{\kappa T}\right]$$

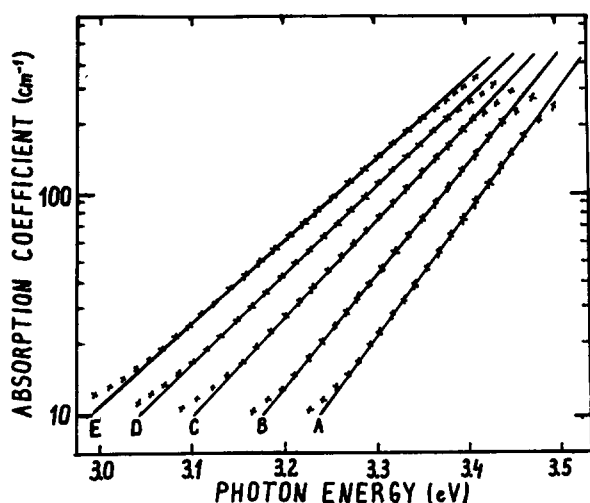where α_0 and E_0 are constants characterizing the material envolved (in the

Fig. 1. The spectral dependence of absorption coefficient of $CdGa_2S_4$ at different temperatures (A=80 K, B =150 K, C=250 K, D=300K, E=330 K).

Fig. 2. Absorption spectra of both initial (a) and annealed $CdIn_2S_4$ crystals (b) at different temperatures (A= =80 K, B=170 K, C=250 K, D=330 K): (1) samples annealed at 400°C with following furnace-cooling, (2) samples annealed at 400°C with following water quenching.

case of $CdGa_2S_4$ they equal $5 \times 10^3 cm^{-1}$ and 3.7 eV respectively). Parameter σ determines the slope of the absorption curve at each given temperature. It equals 0.218 and 0.085 at 80 and 300 K correspondingly.

The behaviour of the absorption edge of $CdGa_2S_4$ single crystals with temperature gives evidence for participation of phonons in the absorption process. Taking into account the existence of excitons in $CdGa_2S_4$, one may expect that there is exciton-phonon interaction which determines the absorption edge. The energy of phonons interacting with excitons has been estimated by using the formula [5]

$$\sigma(T) = \sigma_0 \frac{2\kappa T}{\hbar \omega_{ph}} th \frac{\hbar \omega_{ph}}{2\kappa T}$$

where σ_0 is a constant parameter. The value $\hbar \omega_{ph} \simeq 43$ meV was obtained. It is to be emphasized, that phonons with such energy have been indeed observed in the infrared absorption spectra of $CdGa_2S_4$ compound [6].

Let us pass to the consideration of the absorption spectra of $CdIn_2S_4$ single crystals. In this case an exponential dependence of the absorption edge on photon energy is also observed, although the slope of the straight lines lg α = $= f(\hbar\omega)$ practically is not dependent on temperature. The absorption edge paralelly shifts with temperature at a rate -8×10^{-4} eV/K, which is consistent with the value of dE_g^*/dT of that compound. So, the absorption edge in $CdIn_2S_4$

does not obey the Urbach rule. Quasi-continuously distributed electron traps ihnerent to $CdIn_2S_4$ seem to contribute to near-band-edge absorption, the traps being caused in our opinion by intrinsic disorder. Taking into account the
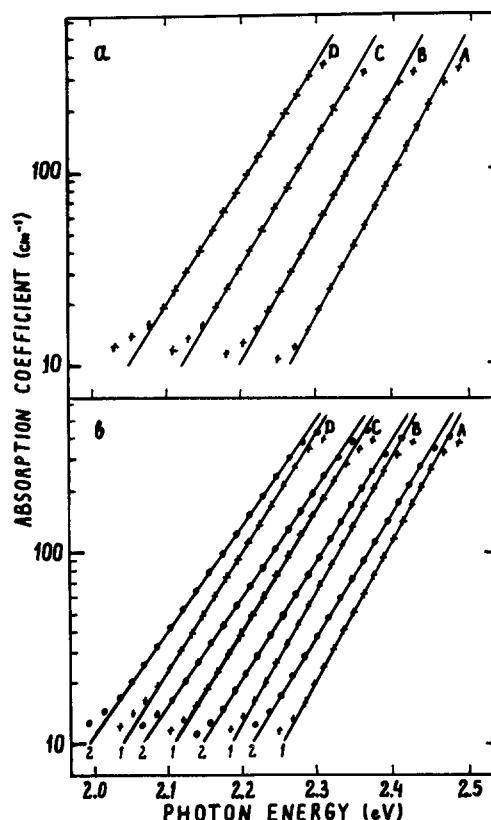
same value of electronegativities of Cd and In atoms (1.7 eV) and practically the same ionic radii ($R_{Cd}2+ = 0.99 \times$ $\times 10^{-8}$ cm; $R_{In}3+ = 0.92 \times 10^{-8}$ cm), one may expect the disorder to be bound with Cd-In exchange. Indeed, as was earlier shown[1], antistructural defects of $(Cd_{In}In_{Cd})$ - type give rise to localised levels below the bottom of the conduction band of the material. An intensive Cd-In exchange takes place in $CdIn_2S_4$ at 130°C, resulting in the occurence of a second order phase transition.[3]

Interesting data have been obtained by us when studying the absorption spectra of annealed $CdIn_2S_4$ single crystals. The annealing of samples at 400°C with following furnace-cooling almost does not deform the absorption edge, while the analogous annealing with following water quenching of samples shifts the curves of the absorption edge to lower energies. In the light of the ob-

tained data one may assume the water quenching to freeze a high amount of antistructural defects in the lattice of $CdIn_2S_4$ ($N > 10^{20}$ cm^{-3}).

So, in spite of the absence of stoichiometric vacancies, $CdIn_2S_4$ contains a high amount of localized states giving rise to the absorption edge tail. These states are generated mainly by antistructural cation defects. Cation disorder allows $CdIn_2S_4$ to be considered as an intermediate phase between crystalline and amorphous materials. As to $CdGa_2S_4$ single crystals, its absorption edge does not change in the process of annealing. This fact agree with the low probability for the formation of antistructural defects in $CdGa_2S_4$.

Thus, the absorption edge tails in $II-III_2-VI_4$ compounds may be caused by both exciton-phonon interaction and cation disorder. The first mechanism predominantes provided that the parameters of cations (electronegativities, ionic radii, masses) strongly differ. It was established that exciton-phonon interaction determines the absorption edge in $CdGa_2S_4$. In the case of $CdIn_2S_4$ (Se, Te)$_4$ compounds one may expect the cation disorder to give the main contribution to extrinsic absorption in the vicinity of the band gap energy.

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