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OPTICAL SPECTRA OF THE $A^2B^4C_2^5$ TYPE SEMICONDUCTORS

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Résumé. — Les spectres d'absorption et les spectres dérivés obtenus par la méthode de modulation de longueur d'onde ont été étudiés au voisinage du bord d'absorption fondamentale de composés ternaires $A^2B^4C_2^5$ à gap pseudo-direct. Les spectres de réflexion de quelques composés $A^2B^4C_2^5$ à gap direct ont été mesurés dans la région de 1 à 12 eV et exploités par analyse de Kramers-Kronig.

Abstract. — The wavelength modulated and conventional absorption spectra of pseudodirect bandgap $A^2B^4C_2^5$ compounds have been investigated in the region of the absorption edge. The reflectance spectra of some direct bandgap $A^2B^4C_2^5$ semiconductors have been measured in the range 1 to 12 eV and the Kramers-Kronig analysis has been performed.

1. Introduction. — The $A^2B^4C_2^5$ -type semiconductors compose the separate group among the ternary compounds [1] and are the electronic analogues of the A^3B^5 semiconductors. The possibilities of technical applications have stimulated the studies of their physical properties and the calculations of the energy band structure. The investigations of the modulated reflectance of $A^2B^4C_2^5$ compounds [2] allowed one to enhance the main structures in the optical spectra and determine their energies with high accuracy. From the comparison of the energies of the peak with the characteristic gaps in the calculated band structure [3] and on the basis of the transformation of the Brillouin zone passing from sphalerite structure to chalcopyrite one, the model has been proposed [4] for interpretation of the optical spectra of ternary compounds. In the modulated absorption spectra of pseudodirect bandgap $A^2B^4C_2^5$ compounds a fine structure has been observed [5] in the vicinity of the fundamental absorption edge.

In the present work the optical transitions at the edge of the pseudodirect bandgap $A^2B^4C_2^5$ compounds have been further investigated by means of the studies of thermo-, wavelength-modulated and conventional absorption spectra. The reflectance spectra of the direct band gap semiconductors $ZnSnP_2$, $CdSnP_2$, $ZnSnAs_2$ and $CdSnAs_2$ have been investigated in the region of the fundamental absorption band and Kramers-Kronig analysis has been performed.

2. Experimental. — The investigations were carried out on single crystals of chalcopyrite structure. X-ray diffraction studies were performed, and oriented samples of thickness 50 to 200 μm were prepared with

c-axis lying in a plane of the reflecting surface. The reflecting surface of $CdSiP_2$ single crystals was a (011) face. The absorption spectra of $ZnSiAs_2$, $ZnGeP_2$, $ZnSiP_2$ and $CdSiP_2$ were measured in polarized light at 77 K in the region of the absorption edge. The absorption coefficient has been calculated taking into account the multiple reflections of the light beam in the sample.

The wavelength modulated absorption (WMA) spectra of $ZnSiAs_2$, $ZnGeP_2$, $ZnSiP_2$ and $CdSiP_2$ were obtained in polarized light at 4.2 K using the single-beam technique and an experimental arrangement described elsewhere [5]. The amplitude of wavelength modulation was varied from 1 to 5 meV, and was chosen to be considerably smaller than the halfwidth of the characteristic peculiarities in the WMA spectra.

The thermoabsorption (TA) and thermoreflectance (TR) spectra of the $A^2B^4C_2^5$ compounds were measured in polarized light using the method of indirect heating. Unidirectional square-wave voltage of frequency 3.2 Hz was applied to the silicon plate or SnO_2 layer. A conventional phase-sensitive detection with lock-in amplifiers [6] was used. The dc temperature of the various samples placed in a cryostat at liquid nitrogen temperature was 80 to 120 K depending on the experimental conditions. In TA measurements of $ZnSiP_2$ the power dissipated in the heater at 320 K was 5 times larger than that at 80 K.

The reflectance spectra of $ZnSnP_2$, $CdSnP_2$, $ZnSnAs_2$ and $CdSnAs_2$ were studied in unpolarized light at 300 K in the range 1 to 12 eV using the experimental arrangement described elsewhere [7]. The reflecting surface of the samples was finally polished with diamond paste down to 0.5 μm particle size. The surface of $CdSnP_2$ samples was natural (112) faces.

3. Experimental results and discussion. — **3.1 ABSORPTION EDGE OF PSEUDODIRECT BANDGAP $A^2B^4C_2^5$ COMPOUNDS.** — The energy band structure [3] of $ZnSiAs_2$, $ZnGeP_2$, $ZnSiP_2$ and $CdSiP_2$ calculated by pseudopotential method shows the lowest conduction band minima to be $\Gamma_3(0, 0, 0)$ and $(T_1 + T_2)(0, 0, \pi/a)$ derived respectively from $X_1(0, 0, 2\pi/a)$ and $X_1(0, 2\pi/a, 0)$, $X_1(2\pi/a, 0, 0)$ of the binary analogues. Regarding the $A^2B^4C_2^5$ compound of chalcopyrite structure as a binary analogue of sphalerite structure strained along $\langle 001 \rangle$ axis, one can get that the minimum Γ_3 is located at energy lower than $T_1 + T_2$. The conduction band minima $\Gamma_2(X_3)$, $N_1(L_1)$ and $\Gamma_1(\Gamma_1)$ are located at higher energies. These semiconductors are called as pseudodirect bandgap $A^2B^4C_2^5$ compounds [8] since their forbidden energy gap is derived from indirect one of their binary analogues.

The WMA spectra of pseudodirect bandgap compounds at 4.2 K are shown on the left side of figure 1. The structures A', B', C' (notation as in [2]) marked by arrows are interpreted as pseudodirect optical transitions. These transitions occur from the top

of threefold degenerate valence band splitted by crystal-field and spin-orbit interaction into the subbands Γ_6 , Γ_7 , Γ_6 , to the lowest conduction band Γ_6 (Γ_3 without inclusion of the spin-orbit coupling). The third structure C' for $ZnSiAs_2$ is not observed because of the large spin-orbit splitting of the valence band [2]. This interpretation is mainly based on the following experimental results. 1) The polarization dependences of the structures A', B', C' correspond to the selection rules for the pseudodirect optical transitions [3]. 2) The energies of these structures agree with theoretical ones [3] and those obtained from the energy band structure of their binary analogues. 3) The energetic separations between the structures A', B', C' are approximately equal to those between the peaks A, B, C, caused by direct transitions $\Gamma_6, \Gamma_7, \Gamma_6 \rightarrow \Gamma_7$, in the thermoreflectance spectra (Fig. 1). In the TR spectrum of $ZnSiP_2$ the structures B, C are not resolved but the separation of two peaks corresponds to that between the structure A' and the mean energy of the structures B' and C'. The energetic distance between the peaks A and A' shows immediately the gap $\Gamma_1-\Gamma_3$ [5] in the conduction band of the investigated compounds.

The crystal-field and spin-orbit splittings of the valence band of pseudodirect bandgap $A^2B^4C_2^5$ compounds were calculated from experimental data using the quasicubic model applicable for the ternary compounds of chalcopyrite structure [9]. The obtained splittings at 4.2 K agree well with those [5] at 77 K.

When the temperature is lowered from 77 to 4.2 K ([5] and Fig. 1), the structures A', B', C' shift to higher energies by 5 to 9 meV. The energetic separation between A' and B' seems to be slightly reduced. At 4.2 K the structures are better resolved and somewhat enhanced. The relative intensity between the peaks A', B', C' in the WMA spectra remains approximately unchanged at various temperatures and thus allow one to rule out the phonon origin of these structures.

The shapes of the structures in the WMA spectra of $ZnSiAs_2$ and $ZnGeP_2$ can be described by the derivative of the absorption coefficient [10, 11] in the region of the parabolic critical point of the M_0 type. The structures A', B', C' for $ZnSiP_2$ seem to be caused by the optical transitions to the local level near Γ_3 . The shape of the WMA spectrum of $ZnSiP_2$ can be represented by the derivative of the Lorentzian line [10] taking the scaling factor and the broadening parameter Γ as adjustable ones. The temperature coefficients of the energy and broadening parameter of the absorption lines, dE/dT and $d\Gamma/dT$, are $\sim -2.3 \times 10^{-4}$ and 0.1×10^{-4} eV/K for A', -2.8×10^{-4} and 0.3×10^{-4} eV/K for structures B', C'.

This interpretation of the WMA spectra is confirmed by the investigations of the TA spectra of $ZnSiP_2$ (Fig. 2). It is known, that the shape of the TA spectrum in the vicinity of the absorption line may be caused by the temperature shift and broadening of this line. As is seen from figures 1 and 2, the wavelength and temperature modulated absorption spectra are almost equivalent.

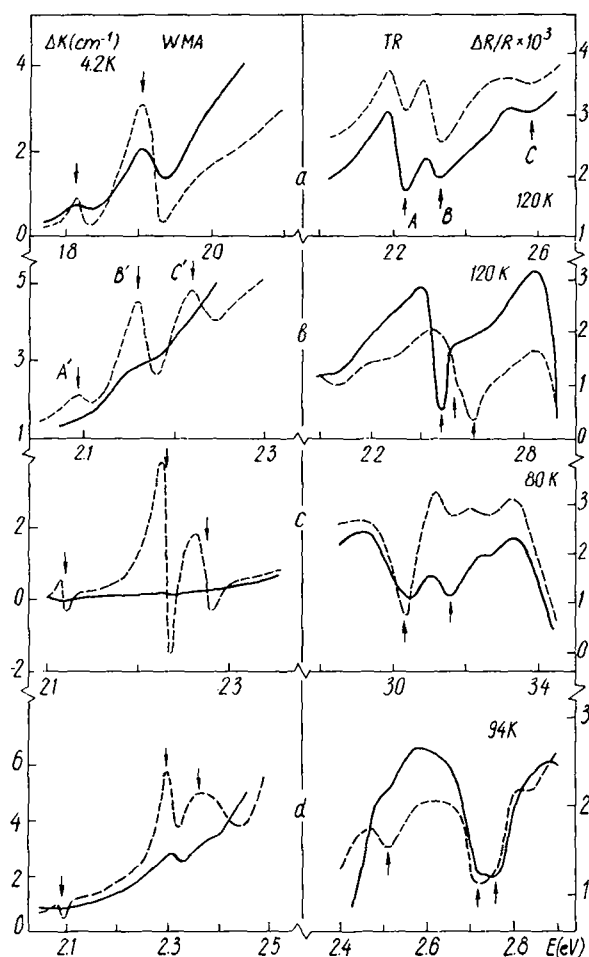


FIG. 1. — The WMA (at 4.2 K) and TR spectra of $ZnSiAs_2$ (a), $ZnGeP_2$ (b), $ZnSiP_2$ (c), $CdSiP_2$ (d) in polarized light for $e \parallel c$ (solid lines) and $e \perp c$ (dotted lines).

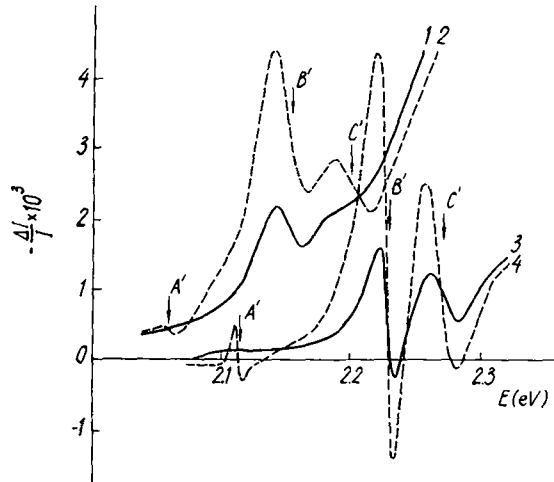


FIG. 2. — The TA spectra of ZnSiP₂ sample of thickness 104 μ m in polarized light for $e \parallel \langle 11\bar{1} \rangle$ (solid line) and $e \perp c$ (dotted line) at 320 K (curves 1,2) and 80 K (curves 3,4).

lent. Therefore, the TA spectra of ZnSiP₂ are concluded to be mainly caused by the shift of the absorption line. The contribution of the temperature broadening to the TA spectrum is considerably weaker, that is in a good agreement with the evaluation of dI/dT from WMA spectra. It is to be noted, that the magnitude of the modulated absorption spectra slightly increases with photon energy. This can be due to the contribution of the interband optical transitions.

The structures A', B', C' interpreted by the pseudodirect transitions are considerably weaker, than the peaks A, B, C due to the direct transitions. As a rule, the first ones are not observed in the modulated reflectance spectra [2]. For only ZnGeP₂ the structures B' and C' have been noticed [12] in the electroreflectance spectra at 300 K, the peak B'', C'' caused by pseudodirect optical transition $\Gamma_5 \rightarrow \Gamma_2$ has been found [6] in the TR spectra at 120 K, and the structures B' and B'', C' have been observed [13] in the wavelength modulated reflectance spectra at 5 K.

The impurities are known to have a strong influence on the magnitude of the residual absorption in ZnGeP₂ [14], ZnSiAs₂ [15], ZnSiP₂ [16] and CdSiP₂ [17]. Therefore, the observation of the structures due to the intrinsic absorption of the material becomes difficult in the low absorption region. The absorption spectra at the edge of the investigated compounds are presented in figure 3. For only ZnSiP₂ some structures corresponding with the peaks B', C' in WMA spectra are clearly seen. For the other compounds the structures due to the pseudodirect transitions are masked by the structureless background. However, the pronounced polarization of the pseudodirect transitions enhances the absorption for $e \perp c$ in the lower absorption region. The comparison of figures 1 and 3 shows the correlation between the polarization dependence of the absorption coefficient at the edge and that of the peak A which is due to the

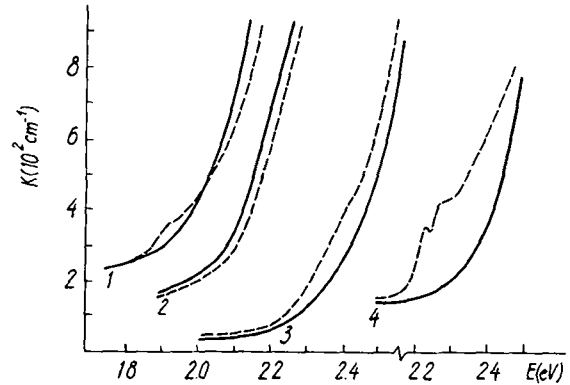


FIG. 3. — The absorption spectra of pseudodirect bandgap $A^2B^4C_2^5$ compounds in polarized light for $e \parallel c$ (solid lines) and $e \perp c$ (dotted lines) at 77 K: 1) ZnSiAs₂, 2) ZnGeP₂, 3) CdSiP₂, 4) ZnSiP₂. The absorption coefficient of ZnSiP₂ is multiplied by factor 2.

lowest direct optical transitions. Therefore, the absorption edge of the investigated compounds is concluded to be caused both by the pseudodirect transitions and the transitions to the tails of the density of states of higher lying conduction band Γ_1 . The influence of the direct transitions on the absorption edge of pseudodirect bandgap $A^2B^4C_2^5$ semiconductors comes also from the difference between the pressure coefficients determined from the shift of the absorption edge [8] and those of the structures in the WMA spectra [18]. It should be noted that the temperature dependence of the absorption background indicates the possible contribution of the indirect optical transitions to the absorption edge of the investigated pseudodirect bandgap ternary compounds.

3.2 OPTICAL PROPERTIES OF THE DIRECT BANDGAP $A^2B^4C_2^5$ COMPOUNDS IN THE FUNDAMENTAL ABSORPTION BAND. — The early investigations of the reflectance [19-24] and electroreflectance [4, 25-28] spectra of ZnSnP₂, CdSnP₂, ZnSnAs₂ and CdSnAs₂ have been performed in order to study a fine structure of the optical spectra. The energy band structure of $A^2B^4C_2^5$ compounds has been found to be more complicated than that of their binary analogues. Although, the changes of the relative intensities of the optical transitions passing from A^3B^5 to $A^2B^4C_2^5$ semiconductors have not been studied. In most cases [20-24] the reflection coefficients have been measured in arbitrary units or in the narrow spectral region and the Kramers-Kronig analysis has not been performed. Therefore, the investigations of the reflectance in a wide spectral range are of interest.

3.2.1 Reflectance Spectra. — The reflectance spectra of ZnSnP₂, CdSnP₂, ZnSnAs₂ and CdSnAs₂ single crystals in unpolarized light at 300 K are presented in figure 4. As it is seen, two regions can be defined in the spectral range 1 to 12 eV. The first one extended up to ~ 8 eV is characterized by the sharp structures (peaks $E_{1,2}$, $E_{3,4}$, E_6 , E_{11} , E_{15} , E_{16}) due to the inter-

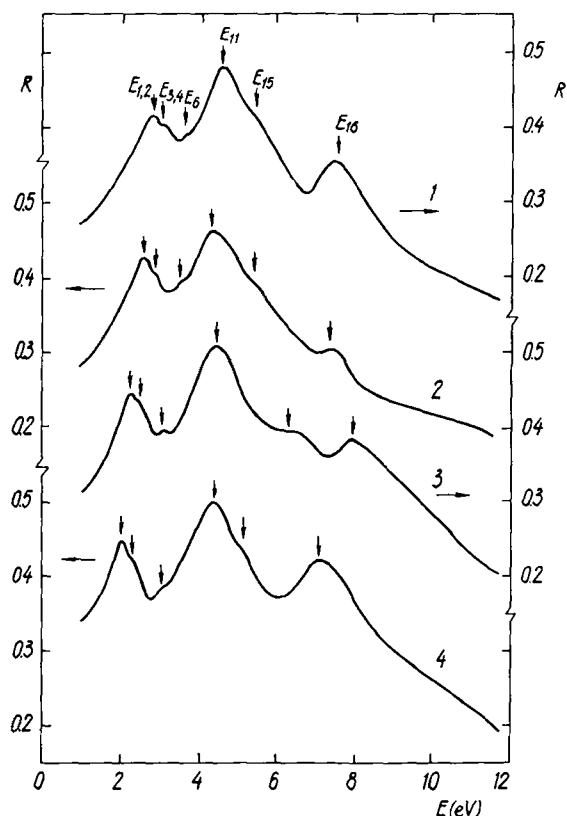


FIG. 4. — The reflectance spectra of ZnSnP_2 (1), CdSnP_2 (2), ZnSnAs_2 (3) and CdSnAs_2 (4) at 300 K. The notation of the reflectance peaks is the same as in modulated reflectance spectra of $\text{A}^2\text{B}^4\text{C}_2^5$ compounds [2, 4, 7].

band optical transitions from the valence band to the conduction band. The second reflectivity region is characterized by a rapid decrease of the reflection coefficient indicating that the sum of the oscillator strengths of the valence band is exhausted.

The energies of the reflectance peaks (Fig. 4) are listed in table I along with the previous reflectance [19-24] and electroreflectance [4, 25-27] data.

The comparison of the reflectance spectra of $\text{A}^2\text{B}^4\text{C}_2^5$ compounds (Fig. 4) with those of their binary analogues A^3B^5 [29] shows the following correlation: 1) the number of the main bands and their relative intensities are approximately equal, 2) the main reflectance peaks of the ternary compounds are shifted to lower energies, 3) the strongest peak E_{11} (Fig. 4) in $\text{A}^2\text{B}^4\text{C}_2^5$ crystals is broader and less intensive than the strongest peak E_2 in the reflectance spectra of the A^3B^5 compounds [29].

The similarity of the reflectance spectra of ZnSnP_2 , CdSnP_2 , ZnSnAs_2 , CdSnAs_2 (Fig. 4) and those of their binary analogues [29] shows the close relation between their energy band structures. Thus, the principal peaks in the reflectance spectra of ternary $\text{A}^2\text{B}^4\text{C}_2^5$ compounds are concluded to be mainly caused by those optical transitions in chalcopyrite Brillouin zone which have been derived from the direct transitions in sphalerite and have been responsible for the basic structures in the optical spectra of the A^3B^5 semiconductors.

Therefore, the structures $E_{1,2}$, $E_{3,4}$ (Fig. 4, Table I) correspond to the peaks E_1 , $E_1 + \Delta_1$ in the optical spectra of A^3B^5 semiconductors [29]. The latter peaks have been caused by the optical transitions $A_3 \rightarrow A_1$ including the close-lying transitions $L_3 \rightarrow L_1$ at the boundary of the Brillouin zone. The non-cubic chalcopyrite crystal field and spin-orbit coupling split the A_3 and L_3 into four subbands. In addition, the strong interaction of the close-lying levels L_3 and Σ_1 in chalcopyrite leads to the separation of the bands A_3 and L_3 [24]. Therefore, the doublet $E_{1,2}$, $E_{3,4}$ in the reflectance spectra and the quadruple structure in the electroreflectance spectra [2] are caused by the optical transitions from these valence bands to the lowest conduc-

TABLE I

Energies (in eV) of the peaks in the reflectance (R) and electroreflectance (ER) spectra of ZnSnP_2 , CdSnP_2 , ZnSnAs_2 and CdSnAs_2

	$E_{1,2}$	$E_{3,4}$	E_6	E_{11}	E_{15}	E_{16}	Ref.
ZnSnP_2	2.86	3.1	3.6	4.65	5.7	7.7	R (*)
	2.7	—	4.14 ?	4.6	—	—	R [19]
	2.80 2.96	3.11	3.6	—	—	—	ER [25]
CdSnP_2	2.62	2.95	3.54	4.35	5.5	7.3	R (*)
	2.62	2.81	3.6	4.3	5.1	—	R [23]
	2.57 2.67	2.90 2.99	3.53	4.32	—	—	ER [4]
ZnSnAs_2	2.31	2.56	3.06	4.54	6.5	7.9	R (*)
	2.30	2.53	3.06	4.6	6.6	7.7	R [20]
	2.24 2.35	2.56	3.06	4.32 4.75	—	—	ER [26]
CdSnAs_2	2.06	2.40	3.0	4.5	5.3	7.2	R (*)
	2.08	2.39	3.04	4.6	5.6	7.2	R [20]
	2.12	2.42	3.10	4.5	—	7.7	R [21]
	2.02 2.12	2.42	2.95	4.3	—	—	ER [27]

(*) Present data.

tion band. The relatively high intensity of the doublet $E_{1,2}$, $E_{3,4}$ in the reflectance spectra of $A^2B^4C_2^5$ shows these optical transitions to occur in a wide region of the Brillouin zone. Following the accepted model, the peak E_6 in the reflectance spectra of $A^2B^4C_2^5$ compounds (Fig. 4) is to be compared with the weak structure E'_0 on the low energy side of the strongest reflectance peak E_2 of A^3B^5 semiconductors [29]. The structure E'_0 is caused by the transitions $\Gamma_{15} \rightarrow \Gamma_{15}$ and $\Delta_5 \rightarrow \Delta_1$. The lower symmetry chalcopyrite lattice results in the splitting of Γ_{15} into Γ_4 and Γ_5 and finally — into Γ_6 , Γ_7 , Γ_6 when the spin-orbit coupling is taken into account. In addition, the degeneracy of the star of wave vector Δ is partly lifted in chalcopyrite. The line Δ along the direction $\langle 001 \rangle$ at $k < \pi/a$ transforms into the line $A(k_x = 0, k_y = 0)$. Therefore, the number of transitions, which causes the structure E'_0 in A^3B^5 , strongly increases in chalcopyrite ternary compounds. The existence of one peak E_6 in reflectance spectra and some peaks in electroreflectance [2] shows the splittings of the corresponding levels to be small.

The strongest peak E_{11} in the reflectance spectra of the investigated compounds (Fig. 4) corresponds to the peak E_2 in A^3B^5 . The peak E_2 is assigned to the optical transitions $X_5 \rightarrow X_1$, $X_5 \rightarrow X_3$ and $\Sigma_2 \rightarrow \Sigma_1$ [30]. The asymmetric potential of chalcopyrite lattice divides the critical points X into two groups, T and Γ . The branches of the Σ -wave vector star become nonequivalent, four of those in the xy plane are perpendicular to the c axis and the angle between the c axis and other eight branches is $\sim 45^\circ$. These transformations of the energy bands cause probably the larger width and lower intensity of the reflectance peak E_{11} compared with the peak E_2 in A^3B^5 [29]. The oscillator strength of the corresponding optical transitions is distributed in a wide energy region but the peak E_{11} remains to be the strongest one in agreement with the calculated reflectance spectra of $ZnGeP_2$ [31].

The weak structure E_{15} and the strong peak E_{16} are comparable with the structures E'_1 and d' in A^3B^5 and can be attributed to the optical transitions derived from $L_3 \rightarrow L_3$ and $L_3 \rightarrow L_1^u$ in sphalerite. The corresponding transitions in chalcopyrite Brillouin zone occur from the $N_1(L_3)$ valence band into the $N_1(L_3)$ and $N_1(L_1^u)$ conduction bands, respectively.

3.2.2 Kramers-Kronig analysis. — The optical constants of $ZnSnP_2$, $CdSnP_2$, $ZnSnAs_2$ and $CdSnAs_2$ were calculated from the reflectance spectra (Fig. 4) using the Kramers-Kronig relations. The extrapolation of the reflectance coefficient $R(E)$ to the energies $E > 12$ eV was made by method described in [29], and the refraction coefficient values were used in the lower energy region.

The shape and the relative intensities of the peaks in the $\epsilon_1(E)$, $\epsilon_2(E)$ spectra of ternary compounds are very similar to those of their binary analogues. This is clearly seen in figure 5 where the spectral dependences of the dielectric constant of $CdSnAs_2$ and $InAs$ [29]

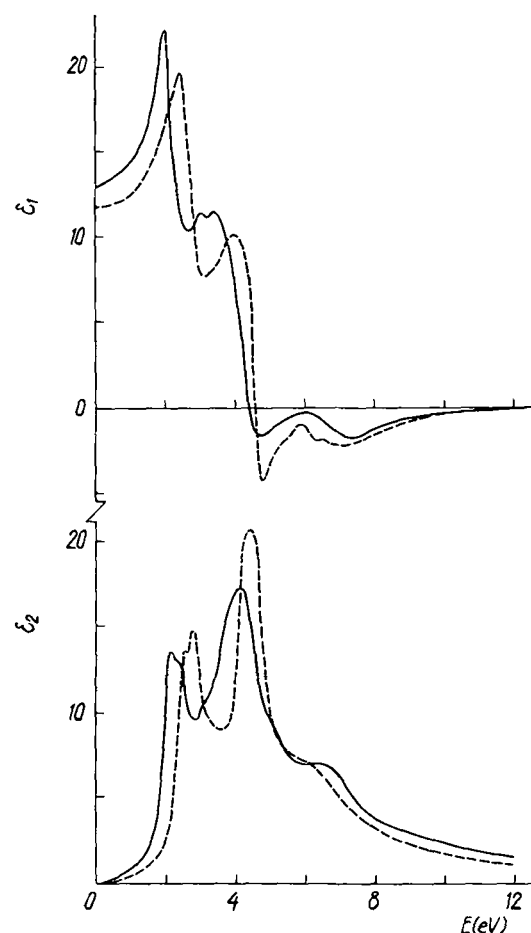


FIG. 5. — The spectra of $\epsilon_1(E)$ and $\epsilon_2(E)$ for $CdSnAs_2$ (solid line) and $InAs$ [29] (dotted line).

are presented. The main bands in the $\epsilon_1(E)$ and $\epsilon_2(E)$ spectra of ternary compounds are slightly shifted to lower energies, the width of the main bands in $\epsilon_2(E)$ are

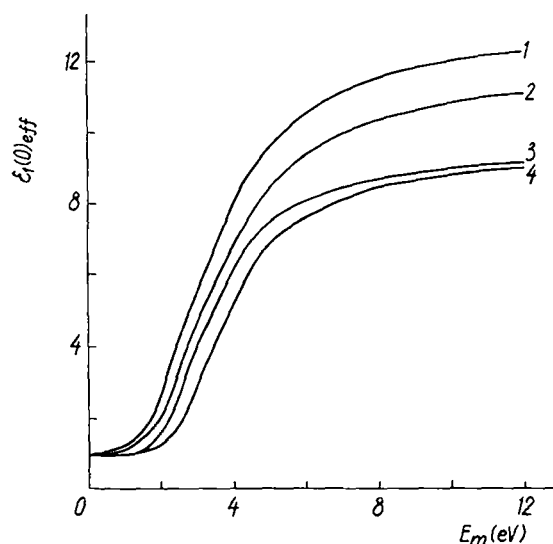


FIG. 6. — The dependences of $\epsilon_1(0)_{eff}$ on the upper limit of integration E_m for $CdSnAs_2$ (1), $ZnSnAs_2$ (2), $CdSnP_2$ (3) and $ZnSnP_2$ (4).

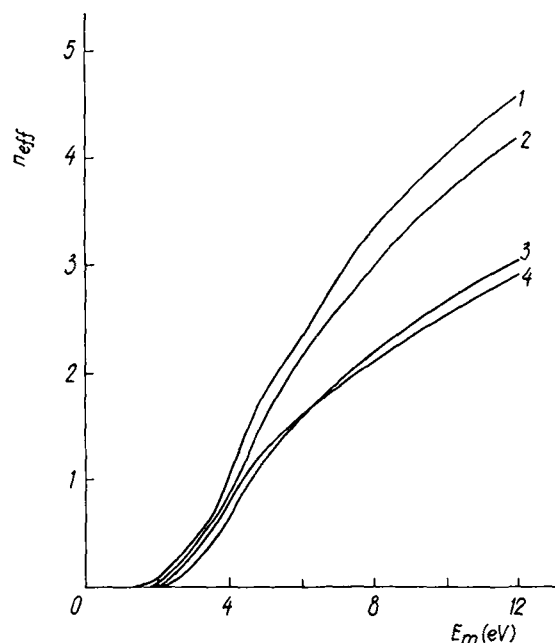


FIG. 7. — The dependences of n_{eff} on the upper limit of integration E_m for CdSnAs_2 (1), ZnSnAs_2 (2), CdSnP_2 (3) and ZnSnP_2 (4).

larger, the maximum values of ε_2 are lower and $\varepsilon_1(0)$ is higher as compared with the corresponding values of their binary analogues. The increase of the electronic part of the static dielectric constant $\varepsilon_1(0)$ in ternary semiconductors is related with the shift of the $\varepsilon_2(E)$ spectrum into the lower energy region. The sum rule [29] of the oscillator strengths allows one to calculate the effective dielectric constant $\varepsilon_1(0)_{\text{eff}}$ caused by the optical transitions in the investigated spectral region and to determine the effective number of elec-

trons per atom, n_{eff} taking part in the interband transitions.

The calculated dependences of the effective dielectric constant $\varepsilon_1(0)_{\text{eff}}$ on the upper limit E_m of integration for ZnSnP_2 , CdSnP_2 , ZnSnAs_2 and CdSnAs_2 are shown in figure 6. These dependences tend to saturate at energies higher than ~ 6 eV. Therefore, the main contribution to the electronic dielectric constant is shown to come from the strong optical transitions up to ~ 6 eV. The values of $\varepsilon_1(0)_{\text{eff}}$ at $E_m = 12$ eV are 9.0, 9.1, 11.0 and 12.2 for ZnSnP_2 , CdSnP_2 , ZnSnAs_2 and CdSnAs_2 , respectively and are close to the experimental data of $\varepsilon_1(0)$. The small difference between $\varepsilon_1(0)$ and $\varepsilon_1(0)_{\text{eff}}$ is probably caused by the contribution of d-electrons to the dielectric constant.

The calculated dependences of n_{eff} on E_m for ZnSnP_2 , CdSnP_2 , ZnSnAs_2 and CdSnAs_2 are shown in figure 7. The values of n_{eff} at $E_m = 12$ eV for ternary compounds are close to those of their binary analogues [29]. Therefore, the sum of the oscillator strengths for the transitions between the valence band and conduction band only slightly changes passing from A^3B^5 to $A^2B^4C_2^5$ semiconductors.

4. Conclusions. — The absorption edge of the pseudodirect bandgap $A^2B^4C_2^5$ compounds is formed by both pseudodirect and direct optical transitions. The strong direct optical transitions into the tails of the density of states of higher lying conduction band are responsible for the polarization dependences of the absorption coefficient at the edge.

The relative intensity of the main peaks in the reflectance and dielectric constant spectra of $A^2B^4C_2^5$ compounds is similar to that of their binary analogues, A^3B^5 . The broadening and lower intensity of the peaks in ternary compounds are caused by the splitting of the corresponding energy bands.

References

- [1] BORSHCHEVSKII, A. S., GORYUNOVA, N. A., KESAMANLY, F. P., NASLEDON, D. N., *Phys. Stat. Sol.* **21** (1967) 9; BORSHCHEVSKII, A. S., VAIPOLIN, A. A., VALOV, YU. A., GORYUNOVA, N. A., KESAMANLY, F. P., NAZAROV, A., PROCHUKHAN, V. D., CHALDYSHEV, V. A., *Poluprovodniki A²B⁴C₂⁵* (Sovetskoe Radio, Moskva) 1974; SHAY, J. L., WERNICK, J. H., *Ternary Chalcopyrite Semiconductors* (Pergamon Press, London) 1975.
- [2] SHILEIKA, A., *Surf. Sci.* **37** (1973) 730.
- [3] POPLAVNOI, A. S., POLYGALOV, YU. I., CHALDYSHEV, V. A., *Izv. Vyssh. Uchebn. Zaved Fiz.* **11** (1969) 58; **6** (1970) 95.
- [4] KAVALIUSKAS, J., KARAVAEV, G. F., LEONOV, E. I., ORLOV, V. M., CHALDYSHEV, V. A., SHILEIKA, A., *Phys. Stat. Sol.* (b) **45** (1971) 443.
- [5] BABONAS, G., AMBRAZEVIČIUS, G., GRIGOREVA, V. S., NEVIERA, V., ŠILEIKA, A., *Phys. Stat. Sol.* (b) **62** (1974) 327.
- [6] RAUDONIS, A., GRIGOREVA, V. S., PROCHUKHAN, V. D., ŠILEIKA, A., *Phys. Stat. Sol.* (b) **57** (1973) 415.
- [7] KAVALIUSKAS, J. F., RAUDONIS, A. V., SHILEIKA, A. Yu., BORSHCHEVSKII, A. S., UNDALOV, YU. K., *Fiz. Tekh. Poluprov.* **8** (1974) 1549.
- [8] BENDORIUS, R., PROCHUKHAN, V. D., ŠILEIKA, A., *Phys. Stat. Sol.* (b) **53** (1972) 745.
- [9] ROWE, J. E., SHAY, J. L., *Phys. Rev.* **B 3** (1971) 451.
- [10] BATZ, B., in *Semiconductors and Semimetals*, Eds. A. C. Beer, R. K. Willardson (Academic Press, New York and London) **9** (1972) p. 315.
- [11] RABII, S., FISCHER, J. E., *Surf. Sci.* **37** (1973) 576.
- [12] SHAY, J. L., TELL, B., BUEHLER, E., WERNICK, J. H., *Phys. Rev. Lett.* **30** (1973) 983.
- [13] DE ALVAREZ, C. V., COHEN, M. L., KOHN, S. E., PETROFF, Y., SHEN, Y. R., *Phys. Rev.* **B 10** (1974) 5175.
- [14] RAY, B., PAYNE, A. J., BURRELL, G. J., *Phys. Stat. Sol.* **35** (1969) 197.
- [15] SNELL, J. E., BURRELL, G. J., MOSS, T. S., MABBERLEY, J. C., *Proc. IX Internat. Conf. Phys. Semicond.* (Moscow) **2** (1968) 1227.

- [16] BELLE, M. L., VALOV, Yu. A., GORYUNOVA, N. A., ZLATKIN, L. B., IMENKOV, A. N., KOZLOV, M. M., TSARENKOV, B. V., *Dokl. Akad. Nauk SSSR* **163** (1965) 606.
- [17] LUGOVSKII, V. V., RADZIVIL, V. P., TKACHUK, I. Yu., SHARENKO, V. E., *Fiz. Tekh. Poluprov.* **6** (1972) 1911.
- [18] BABONAS, G., BENDORIUS, R., ŠILEIKA, A., *Phys. Stat. Sol.* (b) **62** (1974) K 13.
- [19] SOBOLEV, V. V., *Izv. Akad. Nauk SSSR, Ser. Neorg. Mater.* **9** (1973) 1060.
- [20] DONETSKIKH, V. I., SOBOLEV, V. V., *Izv. Akad. Nauk Moldavskoi SSR, Ser. fiz.-tekh. i mat. nauk* **1** (1973) 40.
- [21] ZLATKIN, L. B., IVANOV, E. K., *Fiz. Tekh. Poluprov.* **3** (1969) 926.
- [22] ZLATKIN, L. B., IVANOV, E. K., STARTSEV, G. P., *Phys. Stat. Sol.* (a) **1** (1970) 661.
- [23] PIKHTIN, A. N., RAZBEGAIEV, V. N., GORYUNOVA, N. A., LEONOV, E. I., ORLOV, V. M., KARAVAEV, G. F., POPLAVNOI, A. S., CHALDYSHEV, V. A., *Phys. Stat. Sol.* (a) **4** (1971) 311.
- [24] STOKOWSKI, S. E., *Phys. Rev.* **B 6** (1972) 1294.
- [25] KRIVAITĖ, G. Z., KRADINOVA, L. V., SHILEIKA, A. Yu., *Fiz. Tekh. Poluprov.* **6** (1972) 2306.
- [26] KRIVAITĖ, G. Z., KORNEEV, E. F., SHILEIKA, A. Yu., *Fiz. Tekh. Poluprov.* **5** (1971) 2242.
- [27] KAVALIAUSKAS, J. F., VUL, S. P., SHILEIKA, A. Yu., *Fiz. Tekh. Poluprov.* **5** (1971) 2209.
- [28] SHAY, J. L., BUEHLER, E., WERNICK, J. H., *Phys. Rev.* **B 2** (1970) 4104.
- [29] PHILIPP, H. R., EHRENREICH, H. in *Semiconductors and Semimetals*. Eds. Willardson, R. K., Beer, A. C. (Academic Press, New York) **3** (1967) p. 93.
- [30] ASPNES, D. E., STUDNA, A. A., *Phys. Rev.* **B 7** (1973) 4605.
- [31] ALVAREZ, C. V., COHEN, M. L., *Phys. Rev. Lett.* **30** (1973) 979.