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S. I. Radautsan. Investigation of Compound Semiconductive Materials in the Moldavian SSR. Experimental study of semiconductors was begun in Moldavia in 1953 at Kishinev State University under the supervision of Prof. M. V. Kot. It is now being developed successfully in the institutes of the Moldavian Academy of Sciences and in a number of the republic's higher educational institutions.

The laboratories of the Institute of Applied Physics of the Moldavian Academy and the departments of the Kishinev Polytechnic Institute are engaged in work on the preparation of compound semiconductors, coordinated study of their properties, and the development of semiconductor devices from them. The objects of study have been defect-type diamond-like semiconductors such as $A_2^3B_3^6$ and solid solutions in them[1,2], excess semiconductors of the $A_2^3B_2^5$ type[3], gallium and indium phosphides[4,5], zinc telluride[6] and solid solutions in them, phases in the cadmium-indium-selenium-tellurium[7], zinc (cadmium)-indium-sulfur[8], and indium-antimony-tellurium[9] systems, and other materials.

Thermal, x-ray-phase, and microstructural analytical methods have been used to study interactions in the ternary indium-antimony-tellurium, indium-arsenic-tellurium, cadmium-indium-selenium, cadmium-zinc-tellurium, and indium-phosphorus-selenium systems, and in certain binary sections of the types $A^3B^5 - A_2^3B_3^6$, $A^2B^6 - A_2^3B_3^6$, and $A^2B^6 - A_2^5B_3^6$. Phase diagrams were constructed as a result of the studies, and new semiconductive phases were discovered, e.g., In_3SbTe_2, In_4SbTe_3[10], InP_2Se_4[11], and $CdIn_6Se_{10}$[12]. One of the methods of mathematical planning—the simplex array method[13]—was used for the first time in constructing the phase diagrams of the ternary systems.

Data on phase equilibria in the systems studied were used as a basis for development of a technology for production of the semiconductive materials in the crystalline and vitreous states. Methods were also developed for preparation of anisotropic media based on the indium antimonide-nickel antimonide system and dislocation-free gallium phosphide whiskers[14]. Work has also been done on the production of thin films and microconductors based on compound semiconductors.

Samples of these systems are used to study the mechanical-property anisotropy and dislocation structure that appear around indentations and scratches. In particular, a qualitative explanation has been offered for the hardness anisotropy observed in the zinc telluride-cadmium telluride system, and it has been shown that slip systems constitute the basic factor leading to the hardness anisotropy of these crystals[15].

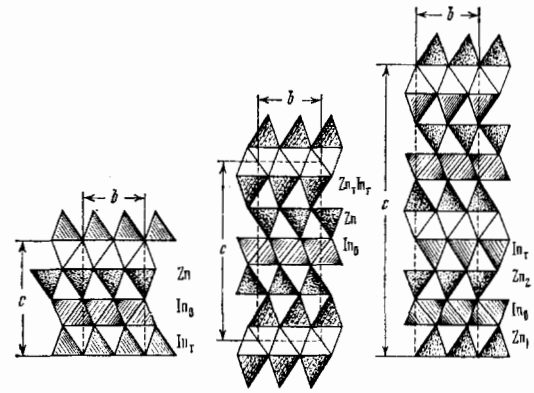

FIG. 1. Projections of structures onto the plane $(2\bar{1}\bar{1}0)$ of the single-packet polytype $ZnIn_2S_4$ (x = 0.25) (a), the two-packet polytype $Zn_3In_2S_5$ (x = 0.40) (b), and the single-packet polytype $Zn_3In_2S_6$ (x = 0.50) (c).

The structures of $Zn_3In_2S_6$[16] and $Zn_2In_2S_5$[17] were deciphered for the first time by x-ray methods. Polytypism of the ternary phases in the $ZnS - In_2S_3$ system was observed and investigated[18]. Figure 1 presents models of the polytype structures of three compounds in this system, which crystallize with hexagonal symmetry and differ, according to composition, in respect to the lattice parameter along the c axis and the layered disposition of the cations in the tetrahedral and octahedral spaces. The ternary phases of this system can be assigned the general formula $Zn_mIn_2S_{3+m}$, where m = 1, 2, 3, ... The composition of the phase is determined by the number m. The number of sulfur atoms in the unit cell of the polytypic modification family of a given phase is determined as N = Z(3 + m) (Z is the number of packets in the elementary cell). The formation of various polytypic modifications has made it possible to explain the physical-property scatter reported in the literature for the ternary phase $ZnIn_2S_4$.

The energy-band structure and spectral features of the local states of certain A^3B^5, A^2B^5, and A^2B^6, $A^2B_2^3C_4^6$ crystals, their solid solutions, and vitreous $A_2^5B_3^6$ semiconductors have been investigated. Band structures were constructed for the first time in the region of the interband-gap minima of certain crystals of the types $A^2B_2^3C_4^6$, $A_2^3B_3^6$, and A^2B^5. Values of the energy intervals at the vital points of the Brillouin zone and the splitting due to the crystal field, the spin-orbital interaction, and other effects have been determined. An effect of surface state on the nature of interband transitions in cadmium telluride and mercury telluride crystals and their solid solutions has been observed.

The kinetic coefficients of cadmium arsenide and phosphide single crystals in strong magnetic fields have been studied as functions of field intensity, and the energy-spectrum parameters of the carriers have been determined[3].

The luminescence properties of compound semiconductors have been investigated. It has been shown that the luminescence centers in crystals of the cadmium-indium-sulfur and zinc-indium-sulfur systems are nonstoichiometric structural defects of the cation-vacancy type with tetrahedral or octahedral coordination of the anions. A relation between the forms of polytypism and features of the luminescence bands has been observed in the zinc-indium-sulfur system[18]. Thus, Fig. 2 shows luminescence spectra of a single crystal of

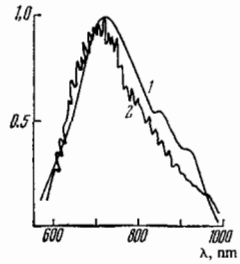

FIG. 2

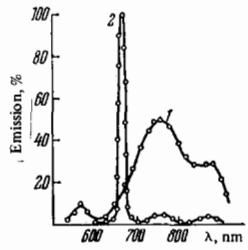

FIG. 3

FIG. 2. Luminescence spectra of single crystal of the three-packet polytype of $ZnIn_2S_4$ (curve 1) and various intergrown polytypes of the same compound (2).

FIG. 3. Luminescence of $CdIn_2S_4$ single crystals at the two-photon excitation levels $I_e \approx 10^{25}$ kV/cm^2·sec (1) and $I_e \approx 10^{26}$ kV/cm^2·sec (2).

the pure three-packet polytype $ZnIn_2S_4$ (curve 1) and a specimen in which several other polytypes grew along with it (curve 2). A fine structure is observed on the latter curve, with an oscillation period on the order of 0.2 – 0.4 eV.

Processes of isoelectronic-center association in gallium phosphide and their participation in radiative recombination have been studied. An interference effect of the wave function of an exciton, associated with pairs consisting of an isoelectronic acceptor-like nitrogen atom and an isoelectronic donor-like antimony atom, has been observed. Stimulated emission of gallium phosphide, indium phosphide, and $CdIn_2S_4$ crystals on two-photon excitation was detected. Studies of the luminescence spectra of $CdIn_2S_4$ at various levels of excitation by light flashes from a ruby laser (Fig. 3) showed that a strong narrow band with a maximum at 660 nm appears at exciting-light intensities around 10^{26} kV/cm^2 sec[19].

A characteristic property of the vitreous semiconductors is a high density of local states distributed quasicontinuously in the forbidden band, states that determine the electronic properties of these substances in many respects. The structural features of the local-state energy spectrum in vitreous arsenic sulfide and alloys based on it have been studied on the basis of coordinated investigation of optical, photoelectric, and thermal-stimulation effects in the Laboratory of Semiconductor Photoelectric Properties. It has been shown that a quasicontinuous distribution of local states obtains in the forbidden bands of these materials, and the parameters of this distribution have been determined. Groups of centers with high concentration have been observed against the background of the quasicontinuous distribution[20]. These results have made it possible to recommend the investigated materials as elements in photosensitive systems.

Impurity energy spectra and compensation have been studied in indium phosphide doped with chromium, iron, and silicon. Diodes that exhibit volt-ampere characteristics of the S and N types have been made from semi-insulator indium phosphide, and the low-frequency current oscilaltions observed in such diodes have been investigated[21].

A design and technology have been elaborated for matrix photodetectors and light sources based on heterotransitions in the aluminum arsenide-gallium arsenide system[22]. The detectors have a response speed of 10^{-8} sec and a sensitivity on the order of 300 mA/W. The light sources have an external quantum efficiency of 0.5% at a radiating energy of 1.7 eV. The devices were grown from the liquid phase by the selective epitaxial method.

$CdIn_2S_4$, CdP_2, and InP Schottky diodes have been made, and the switching effect has been obtained in $CdIn_2S_4$ and In_2S_3. The high sensitivity of the Schottky photodiodes has made it possible to determine the energies of the phonons accompanying optical transitions at the edge and center of the Brillouin zone in $CdIn_2S_4$ and CdP_2 crystals.

Sulfide crystals in the $A^2B^6 - A_2^3B_3^6$ sections are promising as efficient phosphors and coherent radiators, photodetectors for a broad region of the spectrum, storage devices, and fast current switches.

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V. A. Moskalenko. The Theory of Superconductors with Overlapping Energy Bands. Energy bands overlap near the Fermi level in various metals and alloys. This overlap must be taken into account in superconductivity theory for more accurate determination of the parameters of real superconductors.

A model that takes account of the possible formation of bound electron pairs with opposite momenta and spins within each band was proposed in[1] for the simplest case in which two energy bands overlap. The model assumes the existence of two spherical cavities of the Fermi surface in the neighborhood of which—in energy intervals of width $2\omega_n$ (n = 1, 2)—conduction electrons participate in the formation of the superconductive state. Since the momenta of these cavities are assumed to be different, the formation of bound electron pairs from electrons belonging to different bands is not considered.

Interband interaction of electrons results in an additional indirect interaction of electrons within each band. As a result of this interaction superconductivity intervenes simultaneously in both bands and has a single critical temperature. A review of the basic results obtained in the theory of pure two-band superconductors will be found in[2]. Below we present the basic results obtained on the basis of the model in[1] for superconductors with nonmagnetic and paramagnetic impurities.

The impurity-atom concentration is assumed to be small, so that the relaxation time of the band electrons on the impurity is substantially larger than the reciprocal Fermi energy and, consequently, the individuality of the Bloch electrons of the individual bands is preserved.

As a result of interband scattering of electrons by a nonmagnetic impurity with relaxatinn times τ_{12} and τ_{21}, where 1 and 2 are the band numbers, this impurity has the effects of weakening the correlation between the bound-pair electrons, with a resulting decrease in the critical temperature T_c[3] of the two-band semiconductor, reducing its ordering parameters Γ_n[4], giving rise to a single energy gap in the elementary excitation spectrum, and strongly smearing the electron-state densities of both bands near the corresponding ordering parameters[4].

With the condition that the frequencies ω_n are approximately the same and equal to the Debye frequency, the critical temperature of a two-band superconductor with a nonmagnetic impurity is determined from the equation

$$a\xi_c^2 - b\xi_c + c = 0, \tag{1}$$

where

$$\xi_c = \ln\frac{2\gamma\beta_c\hbar\omega_D}{\pi} \quad \left(\beta_c = \frac{1}{k_B T_c}\right), \quad a = N_1N_2(V_{11}V_{22} - V_{12}^2),$$
$$b = b_0 + aI, \quad c = 1 + \varepsilon I;$$

here

$$b_0 = N_1V_{11} + N_2V_{22}, \quad I = \psi\left(\frac{1+(\beta_c\rho/\pi)}{2}\right) - \psi\left(\frac{1}{2}\right)$$
$$\left(\rho = \frac{\hbar}{2}\left(\frac{1}{\tau_{12}} + \frac{1}{\tau_{21}}\right)\right), \quad \varepsilon = b_0 - \tau \quad \left(\tau = \frac{N_1^2V_{11} + N_2^2V_{22} + 2N_1N_2V_{12}}{N_1 + N_2}\right).$$

At a low impurity concentration ($\beta_c\rho \ll 1$), the value of T_c decreases linearly as the concentration rises[3]. At the higher impurity concentration ($\beta_c\rho \gg 1$), ξ_c is determined from the equation

$$\xi_c \approx \frac{1+\varepsilon\eta}{\tau + a\eta}, \quad \eta = \ln\frac{\rho}{\hbar\omega_0} + \frac{\pi^2}{6(\beta_c\rho)^2}. \tag{2}$$

In the weak-coupling limit, T_c tends to a nonzero limit with rising impurity concentration:

$$T_c \to \frac{2\gamma}{\pi}\hbar\omega_D e^{-1/\tau}. \tag{3}$$

Vanishing of T_c under the influence of a nonmagnetic impurity is impossible, even with the special relation $a = \epsilon\tau$ between the constants N_n and V_{nm} of the model under consideration. In a two-band superconductor with a paramagnetic impurity, interband exchange scattering of electrons by the impurity with relaxation times τ_{nn}^s produces an additional mechanism lowering T_c and the ordering parameters, over and above the effect of the nonmagnetic impurity[5,6]. At the paramagnetic-impurity concentration determined by the condition

$$(1 - \beta_{11} - \beta_{12} + \alpha_1)(1 - \beta_{22} - \beta_{21} + \alpha_2) = \alpha_1\alpha_2, \tag{4}$$

where

$$\beta_{nm} = \frac{\hbar}{\Gamma_n\tau_{nm}^s}, \quad \alpha_1 = \frac{\hbar}{2\tau_{12}\Gamma_1}, \quad \alpha_2 = \frac{\hbar}{2\tau_{21}\Gamma_2},$$

the gap ω_g in the elementary-excitation spectrum vanishes, and then the superconductivity disappears when the critical impurity concentration is reached[5]. Unlike the single-band system with paramagnetic impurity[7], the two-band case has a critical concentration determined not only by T_{c0}, but also by the parameters N_n and V_{nm} of the system.

The ratios $n_n(\omega)$ of the electron-state densities in the superconductive $N_n(\omega)$ and normal N_n states,

$$n_n(\omega) = \frac{N_n(\omega)}{N_n} = \pm\,\mathrm{Im}\left(\frac{u_n(z)}{\sqrt{1-u_n^2(z)}}\right)_{z=\omega\pm i0+}, \tag{5}$$

and the related functions are determined on the basis of solution of the equations

$$\frac{z}{\Gamma_1} = u_1(z) - \frac{\beta_{11}u_1(z)}{\sqrt{1-u_1^2(z)}} + \frac{\alpha_1(u_1(z)-u_2(z))}{\sqrt{1-u_2^2(z)}} - \frac{\beta_{12}u_1(z)}{\sqrt{1-u_2^2(z)}},$$
$$\frac{z}{\Gamma_2} = u_2(z) - \frac{\beta_{22}u_2(z)}{\sqrt{1-u_2^2(z)}} + \frac{\alpha_2(u_2(z)-u_1(z))}{\sqrt{1-u_1^2(z)}} - \frac{\beta_{21}u_2(z)}{\sqrt{1-u_1^2(z)}}; \tag{6}$$

the ordering parameters Γ_n of the system are found from the equation system