Deep and resonance states in A^{IV} B^{VI} semiconductors

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This review presents the results of experimental and theoretical studies to detect and investigate deep levels associated with impurities and intrinsic defects in A^{IV} B^{VI} semiconductors. Group-III impurities are discussed in greatest detail. The experiments (electrophysical, optical, thermophysical) indicate the existence of localized and resonance states in materials doped with indium and thallium, and also (less unambiguously) with gallium and aluminum. Stabilization of the chemical potential is especially clearly manifested in indium doping, and it leads to an extremely high electrical homogeneity of the specimens, as revealed by the long-term relaxation of the concentration of nonequilibrium electrons. The Fermi level substantially varies with the composition of the material, the temperature, and the pressure. Upon doping with thallium, one observes a strong resonance scattering of holes, an electronic heat capacity arising from the impurity, and superconductivity caused by the presence of resonance states. The theoretical and experimental data on localized and resonance states associated with vacancies and complexes of intrinsic defects, and also with impurities of transition metals, bismuth, cadmium, tin, and germanium are reviewed. The genesis of the levels, the energy of interaction of electrons at an impurity center, relaxation mechanisms, and superconductivity are discussed.

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1. INTRODUCTION

The problem of impurity states in $A^{IV} B^{VI}$ semiconductors, the history of its development, and its current state are quite unique. The solid solutions PbTe-SnTe and PbSe-SnSe have had a level of study of band spectra, of mechanisms of scattering of charge carriers, and of phonon spectra of the lead chalcogenides (PbTe, PbSe, PbS) that approaches the classical semiconductors such as Ge, Si, and the $A^{III} B^V$ compounds. At the same time, an insignificant number of publications had been devoted to impurity states up to the beginning of the 1970s. It was known that one can alter the type of conduction and control the concentrations of electrons and holes within broad limits with intrinsic defects (deviations from stoichiometry), and by doping with elements of groups I, III, V, and VII of the periodic table and with transition metals. However, the literature contained very few papers on observation of levels in the forbidden band. Also these papers were not corroborated with detailed and varied studies and did not inspire faith in their reliability.

In the 1970s the problem of impurity states lay at the center of attention of researchers of the $A^{IV} B^{VI}$ compounds. This arose both from the demands of practice and from the discovery of the behavior, unusual in many respects, of certain dopants and defects, and the character of their influence on the properties of these compounds. In 1971–1973 Leningrad physicists published studies that interpreted the features of the properties of PbTe, PbSe, and SnTe doped with indium on the basis of the concept of localized states on the background of the allowed spectrum (quasilocal, resonance states). The results of these studies are presented in Sec. 3 of this review.

Following the first publications, extensive studies have been performed on the electrophysical, optical, photoelectric, and magnetic properties, etc., of $A^{IV} B^{VI}$ compounds doped with group-III impurities. The great variety of experimental data could mostly be explained from a unified standpoint in the model of localized states, which must be classified in their genesis among the group of "deep" states. The energy of these states varies over a broad range, depending on the type of impurity (Al, Ga, In, Tl) and the composition of the matrix, and also on the pressure, temperature, and impurity concentration. Thus the impurity levels can lie both in the forbidden band and on the background of the allowed spectrum.

The systematic development of this model allowed prediction, and then realization, of new methods of controlling the properties of A^{IV} B^{VI} compounds. In particular, upon doping with indium it was possible to obtain crystals with an extreme spatial homogeneity of carrier concentration and to make possible high stability of properties with a weak sensitivity to the effect of uncontrolled impurities and defects (Sec. 3a). In the systems Pb_{1-x} Ge_x Te(In) and Pb_{1-x} Sn_x Te(In), one can obtain extremely low concentrations lower by several orders of magnitude than those previously attained (Sec. 3b). In the narrow-gap semiconductors Pb_{1-x} Sn_x Te(In), unique potentialities were obtained for observation, study, and application of the metal-dielectric transition by varying the composition of the matrix, the pressure, and the temperature (Sec. 3b). The effects of long-period relaxation of nonequilibrium carriers in Pb_{1-x} Sn_x Te(In) (Sec. 3e), superconductivity in PbTe $\langle Tl \rangle$ with critical temperatures unusually high for semiconductors (Sec. 4d), and resonance scattering of holes in PbTe, PbSe, and PbS doped with thallium (Sec. 4b) are of undoubted scientific and practical interest.

Other dopants and defects run behind the group-III dopants in intensity of study and number of publications. Nevertheless, experimental evidence has been obtained in the past decade of the existence of deep and quasilocal levels in $A^{IV} B^{VI}$ compounds involving vacancies (Sec. 5b), or arising upon doping with cadmium, transition metals, and even isovalent impurities, e.g., tin in PbS and PbSe (Sec. 5a). Deep levels have been found in the forbidden band of lead chalcogenides upon autocompensation of donor and acceptor dopants that are attributable to complexes of intrinsic defects (Sec. 5c).

The experimental studies have stimulated theoretical studies. In particular, the use of the strong-coupling approximation in determining the electronic spectrum of vacancies has enabled explanation of the charge states and doping action of vacancies, and also has permitted a symmetry classification of the vacancy terms (Sec. 5b). The hypothesis has been advanced that the energy of interaction of electrons lying at a single center is negative, and attempts at theoretical substantiation of this hypothesis have been made (Sec. 3d). Concepts have been adduced of Jahn-Teller instability of the crystal environment of a defect when its charge state is altered (Sec. 3e).

This review presents the results of studies performed

since 1971 on deep and resonance states in $A^{IV} B^{VI}$ compounds involving various impurities, mainly group-III. In addition to presenting and systematizing the facts and conclusions, the authors have striven to reveal the logic of the studies, the experimental methods, and the schemes of the arguments on the basis of which the conclusions have been drawn on the existence of these states, their characteristics and genesis, to note the contradictions and unclear problems, and to single out the topical problems, and to discuss them as much as possible.

2. FEATURES OF THE PROPERTIES OF $A^{\rm IV}$ $B^{\rm VI}$ SEMICONDUCTORS. THE SPECIFICS OF THE PROBLEM OF IMPURITY STATES

The compounds discussed in this review (PbTe, PbSe, SnTe, GeTe, and their mutual solid solutions) have similar physical properties.¹⁾

1. The lead chalcogenides crystallize with an NaCl-type cubic lattice. The high-temperature phases of GeTe and SnTe have the same structure; a structural phase transition occurs with decreasing temperature to a rhombohedral or orthorhombic modification that differs little from the cubic form (e.g., in GeTe the angle of rhombohedral distortion is $\sim 2^{\circ}$). In their type of chemical bonding all these materials belong to the polar semiconductors, and the bonding is mixed: ionic-covalent-metallic.

An essential and common feature of the properties of these compounds is the high lattice polarizability ($\varepsilon_0 \sim 10^{2} - 10^{3}$ and higher) and a substantial difference (by an order of magnitude or more) between the static dielectric permittivity ε_0 and the high-frequency value ε_{∞} . According to the Lyddane-Sachs-Teller relationship, this property involves the difference between the frequencies of the longitudinal (ω_{LO}) and transverse (ω_{TO}) long-wavelength optical phonons and the existence of a soft transverse mode.

The frequency of the soft mode decreases (and ε_0 increases) with decreasing temperature. In GeTe, SnTe, and the solid solutions $Pb_{1-x} Sn_x$ Te this leads to a transition to a ferroelectric phase. The phase-transition temperature is sensitive to the concentration of charge carriers. In the purest specimens of SnTe it is of the order of 100 K, and in GeTe is ~670 K.

2. The $A^{IV} B^{VI}$ compounds crystallize with considerable deviations from stoichiometry. The intrinsic defects (predominantly vacancies, although Frenkel' defects and antistructural defects are not ruled out) are electrically active. The equilibrium concentrations of vacancies in the lead sublattice (acceptors) and the chalcogen sublattice (donors) are usually $\sim 10^{18}$ - 10^{19} cm⁻³. Only by special technological methods can one reduce the carrier concentration to levels of 10^{16} - 10^{17} cm⁻³. Tin and germanium tellurides always have p-type conduction owing to the presence of a large number of vacancies of the group-IV element ($\sim 10^{20}$ cm⁻³). Here the Fermi level lies deep in the valence band, and the Fermi surface is large. This impedes study of the band spectra of

¹⁾One can find the most detailed description of the properties of the lead chalcogenides in the monograph of Ref. 1, to which we shall refer, when presenting the studies published up to 1968.

SnTe and GeTe near the maxima.

3. The band spectra of these semiconductors in the cubic phase are very similar. In particular, the widths of the forbidden band have similar values ($\sim 0.2-0.3 \text{ eV}$).

The absolute extrema of the electron and hole bands in the lead chalcogenides lie at the very same point of the Brillouin zone—as its edge in the $\langle 111 \rangle$ direction (the *L*-point). Direct optical transitions near the intrinsic absorption edge are allowed.

The wave functions of the electrons at the extrema of the conduction band transform according to the odd representation L_6^- , and at the extrema of the valence band by the even representation L_6^+ , if one takes the lead site as the center of symmetry. The isoenergy surfaces near the extrema amount to families of four ellipses extended in the directions of the $\langle 111 \rangle$ rotation axes (as in n-Ge).

The effective masses m^* are small at the edges of the bands and increase upon moving away from them. This involves the existence of a small "direct" forbidden band. The nonparabolicity is described approximately by a Kane-type model. With increasing temperature, the width of the forbidden band and the effective masses increase, and the degree of nonparabolicity decreases. Upon isotropic compression these changes have the opposite sense.

Table I presents the values of the band parameters and certain other parameters of the lead chalgogenides from the review monograph of Ref. 1.

4. A number of studies, both of the lead chalcogenides and of germanium and tin tellurides have adduced the concept of a band of heavy holes whose edge at low temperatures lies below the L-extrema of a spacing of ~ 0.2 eV and more. The theoretical calculations indicate the existence of a maximum of the valence band or a saddle point at the Σ -point of the Brillouin zone ((110) direction). The isoenergy surfaces near the Σ -point are extended along the (100) direction, and the number of equivalent extrema is 12. We should note that the information on the characteristics of the second valence band given by different authors is rather contradictory.

5. In SnTe, in contrast to the lead chalcogenides, the L_6^+ -states lie above L_6^- . That is, an inversion occurs of the principal extrema of the electron and hole bands. The optical width of the forbidden band E_g is ≈ 0.2 eV. The extremal points lie on the same face of the Brillouin zone as in the lead chalcogenides, but are somewhat displaced from the L-point.² With the relatively high value of the Fermi energy caused by the high concentration of holes, the Fermi surface consists of ellipsoids of rotation extended along $\langle 111 \rangle$ and distorted by protuberances extended along $\langle 100 \rangle$ (from the ends of the ellipsoids to the Σ points).³

The band structure of GeTe is complicated by the rhombohedral distortion, which is substantial up to relatively high temperatures, and which leads, as in Bi, to splitting of the L-extrema into L- and T-extrema. The split-off extrema can play the role of the experimentally observed second valence band.⁴ In the cubic phase the isoenergy surfaces have protuberances and bridges between the ends of the ellipses.⁴ SnTe and GeTe show Type II superconductivity.⁵ The critical temperature T_c depends strongly on the hole concentration. The highest attained value is $T_c \sim 0.3$ K.

6. The lead chalcogenides form continuous series of solid solutions with one another, with E_g , m^* , and many other parameters varying smoothly with the composition.

An inverted band scheme is realized in the solid solutions $Pb_{1-x} Sn_x$ Te (which are also a continuous series): E_g initially decreases with increasing x, and then the terms L_6^+ and L_6^- change places and E_g increases with increasing x.¹ At low temperatures the inversion point corresponds to x = 0.35, but at 300 K to $x \approx 0.65$. The values of m^* near the

TABLE I. Fundamental parameters of the lead chalcogenides.¹

Parameters	PbTe	PbSe	PbS	Method of determination	
ϵ_0 (300 K)	400	250	175	Lyddane-Sachs-Teller	
ε _∞	33	24	17	Infrared reflection	
ħω _{LO} , eV	0.0136	0,0165	0.0263	Tunnel effect in a	
ħω _{TO} , eV (300 K)	0,00 39	0,0054	0.0082	p-n junction Infrared reflection	
$E_{\rm g}$, eV ($T=0$ K)	0,19	0,165	0,286	Magnetooptic absorption	
$\partial E_g/\partial T$, eV/K (77-300 K) m^* in units of $m_e(T=0 \text{ K})$	4.10-4	4.10-4	4.10-4	Optical absorption	
$m_{\parallel p}^*$	0,31	0,068	0,105	1	
$m_{\parallel \mathbf{n}}^{\bullet}$	0,24	0,070	0,105	Shubnikov-de Haas effect	
$m_{\perp p}^{*}$	0,022	0,034	0,075		
$m_{\perp n}^{*}$	0.024	0,040	0,080	\ }	
$u, cm^2/V \cdot s (4.2 K)$	ĺ				
u _n	8.105	1,4.1 0⁵	7·104	1)	
up	2,5.105	5,8.105	8.104	Hall mahility	
$u, cm^2/V \cdot s (300 \text{ K})$					
u _n	1730	1000	610]]	
up	840	1000	620])	
		Į	1	1	

band edges follow E_g . The solid solutions $Pb_{1-x} Sn_x Se$ have analogous properties.

In the system Pb_{1-x} Ge_x Te the region of solid solutions on the PbTe side is restricted to compositions with $x \leq 0.3$. Upon adding GeTe to PbTe, the value of E_g increases rather rapidly, with $\partial E_g / \partial x \approx 1.4$ eV.⁶

7. The fundamental mechanisms of scattering in the lead chalcogenides at not too low temperatures are scattering by acoustic phonons and polar scattering by optical phonons. Coulomb scattering by impurities is weakened by the high dielectric permittivity. Therefore even ionized impurities scatter carriers primarily by their core regions, whose dimensions are of the order of atomic dimensions. This gives rise to high mobilities at low temperatures (see Table I), even in specimens having concentrations of defects or impurities of ~ 10^{18} cm⁻³.

8. Halogen atoms, which have seven electrons in the outer shell, replace chalcogens, which have six electrons. The halogens (I, Br, Cl) have a deep donor action, and doping of the lead chalcogenides with them makes it possible to obtain specimens with concentrations of electrons of the order of 10²⁰ cm⁻³. Admixtures of alkali metals (Na, Li) replacing the A^{IV} elements (cations) are acceptors capable of generating hole concentrations above 10²⁰ cm⁻³. Admixtures of group-V elements (Bi, Sb) also replace the cations but, having one electron more in the outer shell than the replaced atoms, they have a donor action. Similar simple arguments lead to the conclusion that group-III impurities (In, Tl, Ga), which also replace the group-IV atoms, must be acceptors. However, actually their doping action proves to be more complicated: thallium in the lead chalcogenides is really an acceptor, gallium is a donor, while indium exerts a limited donor effect on the lead chalcogenides and an acceptor effect on tin telluride. The study of the local and quasilocal levels, which constitutes the theme of this review, enables one to a considerable extent to understand the nature of the intermediate valency of indium and other dopants.

Now let us examine the properties described above of the $A^{IV} B^{VI}$ compounds from the standpoint of the problem of impurity levels, and in particular, let us discuss the difficulties of detecting and studying localized states.

1. Owing to the high dielectric permittivity and the low effective mass of the carriers, wave functions of shallow Coulomb centers must overlap and merge into an allowed band, even at relatively low impurity concentrations (in PbTe, for example, at $10^{13}-10^{14}$ cm⁻³). Owing to the large concentration of impurities and intrinsic defects, it proves to be impossible to observe hydrogen-like levels in $A^{IV} B^{VI}$ compounds. In order to diminish the overlap of the wave functions, strong magnetic fields (up to 15 T) have been employed. However, even in this case freezing-out of the carriers was not found in the purest specimens (with carrier concentrations below 10^{16} cm⁻³), even at very low temperatures (~1 K) (see the review by Heinrich⁷).

2. High concentrations of unfrozen carriers give rise to considerable difficulties in studying deep levels. As a rule, reports of observing them pertain to compensated specimens in which the carrier concentrations and the densities of found levels were far lower than the content of impurities. The properties of such specimens are poorly reproducible, and it is practically impossible to ascribe the levels reliably to a concrete impurity.

3. Owing to the ineffectiveness of Coulomb scattering of current carriers, one cannot estimate the charge of an impurity center from mobility data.

4. High polarizability can weaken the repulsion of electrons at a given center and bring the levels corresponding to different charge states of the center so close together that it is difficult to resolve them.

5. The presence of a Stokes shift (owing to a difference in the values of ε_0 and ε_∞) must complicate the identification and classification of levels from data on the temperature-dependence of the carrier concentration and from optical and photoelectric spectra.

6. The existence of a soft phonon mode and an associated lattice instability can lead to deformation of the crystal environment of an impurity and to different positions of the impurity in the lattice, which complicate and increase the variety of manifestations of the properties of the impurities.

3. IMPURITY STATES OF INDIUM IN A^{IV} B^{VI} SEMICONDUCTORS

a) Indium doping in PbTe

An admixture of indium in lead telluride has a definitely donor character. However, despite the high solubility of InTe in PbTe (more than 20 mole percent with conservation of the NaCl structure⁸), the Hall concentration of electrons does not exceed several times 10^{18} cm⁻³.^{8,9} Studies of transport phenomena performed by the authors of Refs. 10 and 11 have confirmed the data of Refs. 8 and 9 and have filled out the details substantially.

A strong and nonmonotonic temperature-dependence of the Hall coefficient (Fig. 1), unusual for n-PbTe, has been found in Ref. 10. Studies of the electric-conductivity, Hall, and thermo-emf coefficients, the transverse Nernst-Ettingshausen effect, and also the magnetothermo-emf were used to determine the effective mass of the density of states. The



FIG. 1. The Hall constant in PbTe-InTe.^{10,11} InTe content (mole percent): 1-1.0; 2-3.0; 3-6.0.

latter proved to be the same as in pure PbTe. Hence it was concluded that carriers of a single type participate in the transport phenomena, and that introduction of indium in considerable amounts (up to 6%) does not alter the dispersion law of electrons in the conduction band.

The level of the chemical potential calculated under these assumptions from the Hall concentration lies 0.06– 0.08 eV above the bottom of the conduction band at $T \leq 77$ K. It rapidly decreases with increasing temperature and crosses the bottom of the band in the range T = 250-400 K.

In contrast to PbTe doped with halogens or superstoichiometric lead, PbTe $\langle In \rangle$ is characterized by a strong pressure-dependence of the Hall coefficient.¹⁰ Isotropic compression up to 14 kbar at T = 300 K increases the Hall concentration by a factor of 3 to 5 (depending on the indium content and on the deviation from stoichiometry). The level of the chemical potential is elevated here by several hundredths of an electron volt.

The dependence of the Hall coefficient on the indium concentration, the temperature, and the pressure has been explained by the existence of a level that arises upon introducing indium into PbTe.²⁾ At low temperatures it lies above the bottom of the conduction band, and drops with increasing temperature into the forbidden band. Isotropic compression shifts it upward in the energy scale (Fig. 2). At low temperatures the Fermi energy increases with increasing content of indium and reaches the quasilocal level, whereupon further increase in the concentration of free electrons ceases, and the Fermi energy is stabilized near the impurity level. Upon shifting up (with pressure) or down (with temperature), the level draws the Fermi level along with it. This leads to corresponding changes in the Hall concentration. Besides depressing the impurity level, increasing temperature increases the degree of its thermal ionization. Quantitative calculations show that, starting at a certain temperature that depends on N_{In} , the latter factor becomes predominant and causes a change of sign of d R /d T.

Analysis of the experimental data on the Hall effect has yielded a position of the level $\varepsilon_i = 0.07 \pm 0.01$ eV at T = 0 K, a temperature-dependence of $\partial \varepsilon_i / \partial T = -(3 \pm 1) \times 10^{-4}$ eV/K, and a pressure-dependence of $\partial \varepsilon_i / \partial P \approx 5 \times 10^{-6}$ eV/bar.

In order to estimate the number of states in the impurity band, experiments^{10,11} have been undertaken on the supplementary doping of PbTe(In) with the ordinary donor and acceptor impurities (I, Na, excess Te, Pb). When $N_{\rm I}$, $N_{\rm Na}$ $\geq N_{\rm In}$, appreciable changes in the Hall concentration occur. With doping with I, Fig. 3 shows the n ($N_{\rm I}$) relationship for $N_{\rm In} = 0.9 \times 10^{30}$ cm⁻³. For the same indium concentration, a transition to hole conduction occurs upon introducing $\sim 10^{20}$ cm⁻³ of an Na admixture. Excesses of Pb and Te with respect to stoichiometric also do not cause appreciable changes in the Hall concentration.

The presented results offer grounds for two conclusions. First, all or almost all of the In atoms yield impurity



FIG. 2. Influence of quasilocal states on the concentration of free electrons.

states in a narrow energy interval while occupying identical positions in the PbTe lattice. Second, the impurity band possesses amphoteric donor-acceptor properties, with the capacity of the impurity band amounting to two electrons per indium atom, whereas in the absence of other donors and acceptors electrons occur at the impurities in the amount of one electron per atom (or somewhat less if we take into account the fact that a relatively small fraction of the electrons enters the conduction band).

A very simple explanation of these properties is based on the assumption that the energy of interaction of two electrons at a single impurity center is small in comparison with the other characteristic quantities essential to the experiment under study.

In fact, when the energy of interaction of electrons at a single impurity center is positive (U > 0), one must observe two levels of stabilization of the Fermi energy:



FIG. 3. Influence of supplementary iodine doping on the concentration of free electrons in PbTe $\langle In \rangle$.¹¹ T = 77 K, $N_{In} = 0.6$ atom percent.

²⁾For brevity, we shall call it the indium level, regardless of whether the levels are created directly by indium atoms or by defects that arise (or are manifested) upon indium doping (See Sec. 5b).

$$\mu_1 = \varepsilon_1, \quad \mu_2 = \frac{\varepsilon_2}{2} = \frac{2\varepsilon_1 + U}{2} = \varepsilon_1 + \frac{U}{2}.$$

Here ε_1 and ε_2 are respectively the energies of one- and twoelectron states. No change in the concentration of charge carriers was observed within the limits of error of the measurements of the Hall constant (~5%) as long as the content of the additional acceptor (Na) or additional donor (I) did not reach the In content, i.e., ~10²⁰ cm⁻³. This is an order of magnitude larger than the number of states below the impurity level (~7×10¹⁸ cm⁻³). With allowance for the errors of measurement and calculation, the two possible stabilization levels μ differ by no more than 0.005 eV. That is, we have $U \ll \mu$ and $U < k_0 T$ when T>77 K. The statistics of the electrons in impurity states for this model coincides with the statistics of electrons in a narrow impurity band, although the states are not delocalized. The mean number of electrons per impurity atom is

$$f_1 = 2 \left(1 + e^{(e_1 - \mu)/hT} \right)^{-1}. \tag{1}$$

We shall examine below the other assumption—that the energy of interaction of two electrons lying at a single impurity center is negative—in discussing magnetic properties (Sec. 3d).

The relative changes in the Hall concentration and the chemical potential upon supplementary doping are small if the temperature is low and $N_{\rm I}$, $N_{\rm Na} < N_{\rm In}$. However, they increase with increasing temperature. We can see this from a formula that stems from (1):

$$\mu - \varepsilon_1 = kT \ln \frac{f_1}{2 - f_1}, \qquad (2)$$

With decreasing temperature, ε_1 and μ approach one another and the error of determining ε_1 decreases. At liquidhelium temperature we have $|\mu - \varepsilon_1| < 0.002$ eV for a filling of the impurity states f_1 from 0.01 to 1.99. Therefore studies have been performed at 4.2 K to find more precisely the energy of the impurity states, as well as the energy range Γ (width of the impurity band) that they occupy.

Repeated measurements in specimens prepared by various methods (zone melting, the Bridgman method, metalceramics) with an In content from 0.3 to 2.5 atom percent have yielded a value of the Hall concentration of $(7.0 \pm 0.1) \times 10^{18}$ cm⁻³, i.e., with a scatter not exceeding the experimental errors. These values of the concentration at 4.2 K correspond to a value $\varepsilon_1 \approx \mu = 0.073 \pm 0.001$ eV. Thus one cannot detect an ε_1 ($N_{\rm In}$) variation up to 2.5 atom percent In.

The absence of an appreciable influence of the dopant concentration on the position of the level implies that the wave functions of the impurity states overlap but weakly, even at an indium content of the order of 2 atom percent, and the radius of localization cannot appreciably exceed a value of the order of 10–15 Å. That is, the impurity state is localized in a region of the order of one to two unit cells.

Upon supplementary doping with iodine (within the range $N_{\rm I} < N_{\rm In} = 1$ atom percent), the Hall concentration and the Fermi energy are altered by excesses of tellurium or lead by no more than 3%. Hence we can conclude that the

width of the band is $\Gamma \leq 0.005$ eV for $N_{\text{In}} = 1$ atom percent.

The existence of a very narrow peak in the density of states on the background of the allowed spectrum, with an energy that does not depend on the indium concentration, stabilizes the Fermi level with respect to the edge of the conduction band. This must lead to a high spatial homogeneity of the concentration of free carriers.

Usually in PbTe doped with iodine or containing vacancies, just as in other semiconductors, the magnetoresistance in the region of classically strong magnetic fields increases linearly with the magnetic field. This is explained by microinhomogeneities in the distribution of impurities. However, in specimens of PbTe doped with indium, the resistance approaches saturation¹¹ upon reaching strong-magneticfield conditions, in accord with the theory for homogeneous semiconductors.

An even more striking proof of the unique concentration homogeneity of PbTe specimens containing indium has been obtained in the study of Lykov and Chernik¹² of the Shubnikov-de Haas effect. In a specimen containing 1 atom percent indium, they detected at 2 K oscillations associated with from 7 to 28 Landau levels (Fig. 4).

Analysis of the Dingle temperature showed that the spread of the Landau levels involving fluctuations of $\mu - \varepsilon_c$ does not exceed 2×10^{-4} eV.

In passing we note that the carrier concentration determined from the Shubnikov-de Haas effect coincides with the Hall concentration, and that the shape and orientation of the Fermi surface and the magnitude of the effective mass are the same up to 2 atom percent In as in pure PbTe.

Among the other studies of PbTe $\langle In \rangle$,¹³⁻²⁰ we shall briefly discuss the results of studying electron scattering in this material. The existence of quasilocal states in the conduction band gives grounds for expecting strong resonance scattering by the In atoms. Measurements performed at low (liquid-helium) temperatures, where the mobility is mainly determined by scattering by impurities, have shown^{11,15,19} that the scattering cross-sections of carriers by the In atoms prove to be the usual values ($\sim 10^{-16}$ cm⁻³), which are characteristic of scattering by the core of the impurity potential. At high temperatures the scattering cross-section increases (by more than an order of magnitude at 300 K). We shall



FIG. 4. Oscillations of the transverse magnetoresistance in PbTe $\langle In \rangle$.¹² $N_{In} = 1.1$ atom percent, T (K): 4.2 (1) and 2.1 (2).

continue further the discussion of scattering by an In impurity in Sec. 4b, together with discussing the resonance scattering by a Tl impurity.

Now let us take up the results of the study of Chernikov et al.^{19,20} of impurity states in PbTe at high concentrations of indium. These studies examined the electric properties of the solid solution Pb_{1-x} In_x Te over a broad range of variation of x from 0.01 to ~0.2. It is interesting and remarkable that it was possible to employ concepts of an impurity level for qualitative description of the properties of such concentrated solid solutions.

The Hall content at 4.2 K is extremely stable for $x \leq 0.025$, and monotonically increases beyond this limit. The increase is as much as two orders of magnitude for $x \sim 0.2$. This law has been explained by the shift in the impurity level and concomitantly in the chemical potential toward the edge of the conduction band. The calculations of the chemical potential from the Hall concentration yielded the low-temperature position of the impurity level as a function of x shown in Fig. 5.

The decrease in the electric conductivity $\sigma_{4,2}$ with increasing x arises both from the decrease in electron concentration owing to the shift of the level and from the increase in their scattering by the impurities. This smooth decrease in σ is replaced at $x \approx 0.12$ by a rapid decline that reaches several orders of magnitude at $x \approx 0.2$. The authors of Ref. 19 explain this by the existence of relief features in the potential at the edge of the conduction band.

One should expect a sharp decline in σ when the chemical potential, which decreases with increasing x, enters the relief region. This implies an estimate of its magnitude, $V_{\rm p} \sim 0.02-0.03$ eV.

One can naturally associate the appearance of relief features with spatial fluctuations in the impurity concentration, since in this composition region $\mu \approx \varepsilon_i$ depends on x and fluctuates along with it. These views are confirmed by experiment: the unusually clear pattern of quantum oscillations and saturation of the classical background of the magnetoresistance in large fields is observed only in specimens with $x \leq 0.02$ and rapidly disappears with increasing x,¹⁹ although the mobility up to x = 0.12 varies smoothly: $u \sim x^{-1}$.

Another source of the relief features in the potential can also be the decomposition of the solid solution into phases having different values of x. The possibility of such a decomposition caused by an $\varepsilon_i(x)$ dependence is pointed out in Ref. 21.

Reference 20 has studied the temperature-dependence



FIG. 5. Dependence of the position of the impurity level in PbTe $\langle In \rangle$ on the indium concentration at low temperatures.¹⁹

of the kinetic coefficients in specimens with a high content of In. The authors treat the rapid growth in σ , the decline in the thermo-emf and the Hall coefficient, and the small positive value of the Nernst-Ettingshausen coefficient at T = 100-300 K and $x \sim 0.2$ as manifestations of hopping conduction via the impurities. They estimate its activation energy ($\varepsilon_3 \approx 0.003$ eV), and hence conclude that there is a large energy scatter in the position of the level at high values of x.

b) Indium doping in other A^{IV} B^{VI} materials

The model of the impurity level of In in PbTe and the conclusions about its features have served as a starting point for studying other materials of the A^{IV} B^{VI} group doped with the same impurity.

If the potential that gives shape to the impurity wave function is localized in a region not too greatly exceeding the dimensions of the unit cell, then the energy and other characteristics of the impurity state must depend substantially on the individual features of the replacing and replaced atoms and their nearest environment. Moreover, we should expect an appreciable effect of the differences in the band structure of the solvent material, in particular, a change in the relative arrangement of the bands. In this connection, it is of considerable interest to study the behavior of an indium impurity in isostructural, isovalent solid solutions in which the band structure varies smoothly with the composition.

The objects of study have been indium-doped PbSe, PbS, SnTe, and the solid solutions PbSe-PbTe, PbTe-SnTe, PbTe-GeTe, and PbTe-PbSe-SnTe.

Just as in PbTe $\langle In \rangle$, all these materials at high indium content exhibit a stabilization of the concentration of charge carriers at a level that depends very weakly on N_{In} , but varies substantially with the composition of the matrix. Upon supplementary doping, the change in the Hall concentration is considerably less (by several orders of magnitude at low temperatures) than the concentration of the introduced impurity.

In PbSe²² the Hall concentration of electrons practically coincides with the In content up to $N_{\rm In} \approx 0.8$ atom percent, and then the $n(N_{\rm In})$ relationship at 77 K saturates at the level 1.2×10^{20} cm⁻³. We note that the solubility limit of In in PbSe amounts to 3.3%.⁸ If we adopt the concept of a quasilocal level (Fig. 2), then we should consider that as many as 1.2×10^{20} electrons can be distributed below it in the conduction band at 77 K. This corresponds to an energy $\varepsilon_i \approx 0.3$ eV. That is, the In level lies considerably higher than in PbTe. The rate of displacement of the level was estimated from the temperature-dependence of $n: \partial \varepsilon_i / \partial T \approx -2.5 \times 10^{-4} \text{ eV/K}$.

In PbTe_{1-x} Se_x solid solutions,²³ the limiting concentration of electrons, which corresponds to saturation of the $n(N_{\rm In})$ relationship, smoothly varies with the composition. In the saturation region, $\mu \simeq \varepsilon_i$ proves to be an almost linear function of x (Fig. 6a).

Analogous studies of PbS $\langle In \rangle$ imply that, if a quasilocal level is also formed in this compound, it lies higher than in PbSe: $\varepsilon_i \gtrsim 0.32$ eV.

While a replacement of the chalcogen (Te \rightarrow Se, S) shifts



FIG. 6. Dependence of the position of the impurity level of In on the composition of the solid solution.²³ a) $PbTe_{1-x}Se_x$; b) $Pb_{1-x}Sn_xTe$; c) $(PbTe)_{0.7}$ $(PbSe)_{0.3-x}$ $(SnTe)_x \cdot L_6^-$ is denoted as L_6' , and L_6^+ as L_6 .

the indium level upward from the edge of the conduction band, a partial replacement of lead by its analogs (Sn, Ge) has the opposite effect. In the Pb_{1-x} Sn_x Te system²³ in the region of compositions adjoining PbTe (x < 0.3), indium doping gives rise to n-type conduction. The Hall concentration in this region decreases with increasing content of tin (Fig. 7). An analysis of μ (x, T) leads to the conclusion that there is a linear decrease in the spacing between the impurity level and the edge of the conduction band, i.e., there is an extremum of L_6^- (Fig. 6b). When x > 0.25, the level lies in the forbidden band, and if its rate of displacement is maintained also at higher Sn contents, then in the region of 40 mole percent it must enter the valence band, whose ceiling here is formed by the L_6^- states. If we adopt the assumption that the impurity states are only half filled with electrons (Sec. 3a), then, when they enter the valence band, they should give rise to hole conduction, as is confirmed by experiment. The rate



FIG. 7. The Hall constant in $Pb_{1-x} Sn_x Te$; (In).²³ $N_{In} = 0.6$ atom percent; T (K) = 300 (1) and 77 (2).

of variation of $\varepsilon_i - \varepsilon_{L_6^-}$ with increasing x as calculated from $\mu(x)$ is the same here as in the n-region (Fig. 6b). Extrapolation of this relationship to x = 1 yields $\varepsilon_i - \varepsilon_{L_6^-} = -(0.3 - 0.4)$ eV. This does not contradict the limiting concentration of holes in SnTe $\langle In \rangle$.²⁴

In the region of compositions where the impurity level lies in the forbidden band, it effectively compensates the action of other impurities and uncontrolled defects and gives rise to a carrier concentration close to the intrinsic. In the low-temperature region one can obtain here a carrier concentration unusually low for $A^{IV} B^{VI}$ semiconductors.

In the Pb_{1-x} Ge_x Te \langle In \rangle solid solutions studied up to x = 0.3,²⁵ the $\varepsilon_i(x)$ relationship is even stronger. The impurity level intersects the bottom of the conduction band at $x \approx 0.1$, while at x = 0.3 we have $\varepsilon_i - \varepsilon_c = -0.1$ eV. With the latter composition the Hall concentration of electrons at 77 K is of the order of 10^{11} - 10^{12} cm⁻³.

In the multicomponent system $(PbTe)_{0.7} (PbSe)_{0.3-x} \times (SnTe)_x$; which was studied by Erasova *et al.*,²³ the energy of the level varies linearly with x between the values corresponding to Pb_{0.7} Sn_{0.3} Te and PbTe_{0.7} Se_{0.3} (Fig. 6c).

Experiments on uniaxial deformation of indium-doped thin layers of $Pb_{0.8}$ $Sn_{0.2}$ Te, $Pb_{0.7}$ $Ge_{0.3}$ Te,²⁶ and PbSe lead to the conclusion that the level is shifted with respect to the edge of the conduction band in the same sense and approximately with the same pressure coefficient as in PbTe.

While using the fact that one can simultaneously and independently vary the width of the forbidden band and the Fermi energy over a broad range by varying the composition of the solid solution, the temperature, and the pressure, Akimov, Brandt, *et al.*²⁷⁻²⁹ have studied galvanomagnetic and oscillatory effects in solid solutions $Pb_{1-x} Sn_x Te(In)$. In particular, they realized a gap-free state and transitions of the dielectric-metal type, with electron and hole conduction.

As an example of a dielectric-metal transition that they obtained, let us examine the change in the properties of Pb_{0.75} Sn_{0.25} Te(In) under pressure at low (liquid-helium) temperatures.²⁸ Figure 8 shows the pressure-dependences of the positions of the impurity level of indium and the edges of the electron and hole bands (up to 18 kbar). In the absence of pressure the level lies in the forbidden band ($\varepsilon_i \approx$



FIG. 8. Diagram of the shift of the impurity level of In in $Pb_{0.75} Sn_{0.25} Te$ (0.5 atom percent In) under pressure at liquid-helium temperatures.

-0.021 eV), the conduction is of semiconductor type, the electron concentration at 4.2 K is extremely low ($\sim 3 \times 10^2 \times cm^{-3}$), and Shubnikov-de Haas oscillations are not observed. Upon increasing the pressure, the level approaches the edge of the conduction band, and coincides with it at $P \approx 4.5$ kbar. In the interval 4.5 < P < 12.5 kbar, the conductions are observed, and the pressure-dependence of the extremal cross-section of the Fermi surface has the shape of a symmetric curve with a maximum (a parabola). At P > 12.5 kbar the Shubnikov-de Haas effect disappears. Thus one observes in the very same specimen under pressure a transition of the type dielectric-metal-dielectric, with the resistance varying by seven orders of magnitude.

Probably $Pb_{1-x} Sn_x Se\langle In \rangle$ and $(PbSe)_{1-x} (SnTe)_x \langle In \rangle$ can become objects of study of just as great interest. For the latter system Drabkin *et al.*³⁰ have shown that the chemical potential stabilized by indium doping intersects the forbidden band in the range x = 0.3-0.5.

Gruzinov et al.³¹ have studied the position of the Fermi level in $Pb_{1-x} Sn_x$ Te and $PbTe_{1-y} Se_y$ doped with indium at high temperatures (up to 900 K).

Drabkin, Parfen'ev, et al.³² studied the galvanomagnetic and oscillatory effects in thin monocrystalline layers of $Pb_{1-x} Sn_x Te(In)$ and found a characteristic variation in the stabilization level of the Fermi energy and the mobility in the temperature region of the phase transition.

The results of the experimental studies of transport phenomena presented in this section have confirmed the view of the influence of the matrix composition on the energy of the impurity states and have revealed new potentialities of controlling the properties of $A^{IV} B^{VI}$ materials by doping them with indium.

c) Optical absorption

All the studied $A^{IV} B^{VI}$ semiconductors doped with indium have shown a supplementary optical absorption whose intensity depends on the impurity concentration. When one singles out the supplementary absorption α_{sup} from the background of the fundamental band and the absorption by free carriers, characteristic features are found in its spectral and concentration dependences that enable one to associate it with electronic transitions between impurity and band states.

In PbTe and the solid solutions PbTe-SnTe and PbTe-GeTe, where the indium level lies near the edge of the conduction band or in the forbidden band, it has been possible to

A large supplementary absorption, which reaches values of 10^4 cm⁻¹, has been found by Drabkin et al.^{16,33} in PbTe(In). The intensity of the supplementary absorption increases with the indium content. As was implied by the Hall-effect data (Sec. 3a), the indium level lies in the conduction band at room temperature and below. Therefore one does not find a red boundary of the spectrum at 300 K, and the estimates of the position of the level from optical data have been made from the dependence of the absorption coefficient on the concentration of impurity electrons for a fixed frequency ω . The concentration of impurity electrons is determined by the number N_{In} of impurity centers and their degree of occupation f_i . Having a set of specimens with different values of the chemical potential (in addition to In, excess tellurium or iodine had been introduced into them), the authors of Ref. 16 chose a value of ε_i that caused the following relationship to be fulfilled for all the specimens:

$$\frac{\alpha_{sup}}{N_{In}f_1(e_1-\mu)} = \text{const},$$
(3)

Here the function $f_i(\varepsilon_i - \mu)$ is given by Eq. (2). At 300 K this could be done with $\varepsilon_i \approx 0.02$ eV.

At high temperatures the impurity level shifts into the forbidden band, and according to the results of Veis *et al.*,¹⁷ the high-temperature (575–725 K) spectra of α_{sup} ($\hbar\omega$) have a distinct red boundary (Fig. 9). The "optical" energy of the



FIG. 9. Optical absorption in PbTe $\langle In \rangle$.¹⁷ T = 625 K; N_{In} (atom percent) = 2 (1) and 1 (2); 3— α_{sup} for PbTe < 1 atom percent In.

level determined from the boundary frequency amounts to -0.08 eV at 600 K and varies with the temperature with the coefficient $\partial \varepsilon_i / \partial T \approx -2 \times 10^{-4} \text{ eV/K}$. Extrapolation to T = 300 K yields $\varepsilon_i = -0.02 \text{ eV}$, which differs by 0.04 eV from the "thermal" energy determined from the Hall effect and from the dependence of the optical absorption on the electron concentration. The form of the spectrum α_{sup} ($\hbar\omega$) agrees with the assumption of a narrow impurity band ($\Gamma < kT$).

The fact that the thermal and optical energies of ionization of the levels are close together implies a small value of the Stokes shift (no more than 0.04 eV). Hence, if we know the dielectric permittivity, we can make a lower estimate of the radius of localization of the impurity states: $R \leq 10$ Å, by using the formula:

$$\Delta \varepsilon_1 = \frac{e^2}{2R} \left(\frac{1}{\varepsilon_{\infty}} - \frac{1}{\varepsilon_0} \right). \tag{4}$$

An upper estimate of R close to the lower estimate has been made above (Sec. 3a) from the weakness of the dependence of the position of the level on the indium concentration. Thus we can assume that $R \sim 10-15$ Å, i.e., of the order of two lattice constants.

The studies of the optical absorption in other $A^{IV} B^{VI}$ compounds doped with indium also confirm the existence of localized states. Figure 10 shows the $\alpha(\hbar\omega)$ relationships and the supplementary-absorption bands that have been distinguished for $Pb_{1-x} Sn_x Te\langle In \rangle^{17}$ and $Pb_{1-x} Ge_x Te\langle In \rangle^{.25}$ The compositions of the solid solutions and the tempera-



FIG. 10. Optical absorption in solid solutions doped with indium.^{17,25} $N_{\rm in} = 0.6$ atom percent; 1—Pb_{0.8} Sn_{0.2} Te, T = 475 K; 1'— $\alpha_{\rm sup}$; 2—Pb_{0.7} Ge_{0.3} Te, T = 300 K; 2'— $\alpha_{\rm sup}$.

tures of experiment were chosen so as to make the impurity level lie deep enough in the forbidden band. A red boundary of the supplementary-absorption spectrum was observed. The form of the bands indicates that they arise from transitions from a level to a band, while their position in the spectrum agrees well with the energy of the impurity state estimated from data on transport phenomena.

In the absorption spectrum of PbSe $\langle In \rangle$, Globus *et al.*³⁴ have also found supplementary bands with a distinct red boundary. In a specimen with 0.6 atom percent In and a concentration of electrons of 1.7×10^{19} cm⁻³, which corresponds to $\mu \approx 0.1$ eV, the red margin is $\hbar \omega_{mar} = 0.15$ eV. The sum $\hbar \omega_{mar} + \mu \simeq 0.25$ eV is close to the position of the impurity level at 300 K as determined²² from transport effects. Therefore we can assume that the supplementary absorption is associated with transitions of electrons from the conduction band to the impurity level, which lies considerably higher than the chemical potential, and therefore is practically empty.

Thus the study of optical absorption confirms, and in a number of cases substantially supplements, the information obtained by studying transport phenomena on the impurity states of indium in $A^{IV} B^{VI}$ compounds.

d) Magnetic properties. Interaction between impurity electrons

The results of the experiments described above (Sec. 3a) imply that two states per indium atom are contained in the peak of the density of states stabilizing the Fermi level. This assumption is equivalent to the assumption of smallness of the interaction energy of two electrons of opposite spins localized near the same impurity atom. In a more general model the energy of two electrons at an impurity is $\varepsilon_2 = 2\varepsilon_1 + U$, where U is the interaction energy.

If the energy U > 0 (the electrons repel one another) and is large, in practice no more than one electron can be found at an impurity atom. This case as applied to PbTe(In) has been discussed in Refs. 10 and 11. To explain the stabilization of the chemical potential in this approach, one must assume that the impurity states of indium, even without supplementary introduction of an acceptor (Na), are to a considerable extent emptied and compensated by the uncontrolled lead vacancies (see also Sec. 5c). If this is true, then the stabilized value of μ corresponds to a single-electron state, while the two-electron state lies higher by at least 0.2 eV. This model enables one to understand the saturation of the Hall coefficient with increasing In concentration. However, it is difficult to explain in this way the results of supplementary doping with iodine and sodium (see Sec. 3a).

Andreev *et al.*³⁵ have treated the opposite case of U < 0, in which there is a rather strong attraction between electrons lying at the same impurity center. According to Ref. 35, an effective attraction between electrons can arise from the polarization of the crystal by the localized electrons. Here it has been shown³⁶ that the correlation of the motion of electrons of opposite spins plays a substantial role. The model of impurity electrons attracting one another is analogous to the model of Anderson³⁷ proposed at about the same time for amorphous semiconductors. The substantiation of these concepts and the conclusions drawn from them are described in detail in the two reviews of Moĭzhes and Drabkin.^{38,39} Hence we shall restrict the treatment here to brief remarks.

In Ref. 35, as in Refs. 10 and 11, we were concerned with strongly localized impurity states to which one can ascribe a slightly diffuse energy level. In contrast to Refs. 10 and 11, the states treated in Ref. 35 are two-electron states as a result of the effective attraction between the electrons. The energy of two one-electron states (neutral In atoms) proves to be higher than a two-electron state (an In⁻ ion). Hence all the neutral centers are converted into charged centers according to the reaction $2In \rightarrow In^- + In^+$. (We indicate the charges of the In atoms and ions here with respect to the charge of the Pb atoms that they replace. If we assume that in the ionic lattice Pb exists in the form of the ion Pb²⁺, then instead of In⁻ and In⁺ we should write respectively In⁺ and In³⁺.)

Just as in the case of a negligibly small interelectronic interaction, stabilization of the Fermi level upon varying the concentration of indium and of other impurities occurs in the case of attractive electrons. Upon introducing donor or acceptor impurities, the two-electron impurity states of indium are filled or emptied. As long as there are both filled and empty impurity states, the Fermi energy is stabilized at the level $\tilde{\varepsilon}_i = \varepsilon_2/2 = (\varepsilon_i - |U|)/2$. All the above-described rules hold also in this case, with the quantity $\tilde{\varepsilon}_i$ playing the role of the thermal energy of the impurity state.

The qualitative difference between the two concepts, which differ in sign and magnitude of the interelectronic interaction, is manifested upon examining the magnetic properties. In the model of a two-electron level, all the impurities exist in states with zero spin moment, and impurity paramagnetism must be absent. Actually, attempts to observe various paramagnetic effects in PbTe and Pb_{1-x} Sn_x Te have yielded negative results: EPR,³⁵ impurity paramagnetic susceptibility,⁴⁰⁻⁴² and Schottky heat capacity arising from transitions of electrons between two impurity states having opposite spins in a magnetic field.⁴² The absence of paramagnetism is a serious argument favoring the model of a two-electron level.

Another proof of pairing of electrons has been obtained by Drabkin *et al.*⁴³ in studying x-ray photoelectron spectra. The spectral lines associated with excitation of deep levels undergo a chemical shift depending on the charge state of the atoms. The experimental spectra showed two peaks corresponding to two charge states of the indium atoms (In^{3+} and In^+).

On the other hand, there are experimental data that oppose the concept of a two-electron level. Analysis of the lattice thermal conductivity can yield evidence whether the impurity atoms exist in a neutral or a charged state, since the scattering of phonons by the lattice distortions surrounding charged atoms are considerably stronger than at neutral impurities. It turned out⁴⁴ that in PbTe the mean effective scattering cross-section of phonons by In atoms is smaller by a factor of 2.5 than by I atoms. Hence they concluded that a considerable fraction of the In atoms exists in a state neutral with respect to Pb. Supplementary doping with iodine of the indium-containing specimens leads to a larger supplementary thermal resistance than doping with iodine alone, since the charged iodine atoms not only scatter phonons effectively themselves, but also, by donating electrons, they charge the indium atoms.

Within the framework of the model of paired electrons, it is difficult to explain the closeness of the thermal and optical energies of the impurity state.

As regards the paramagnetism of impurities, the explanation of its smallness by other types of pairing is not ruled out. If we assume a disordered distribution of the impurity, we can discuss the pairing of spins at nearest neighbors as in the formation of covalent bonds in a molecule. Antiferromagnetism of the system of impurity electrons can occur in the presence of correlation in the distribution of impurity atoms.

Thus the problem of the magnitude and sign of the interaction between impurity electrons requires further study.

e) Long-term relaxation. Interaction of impurity electrons with the lattice

The polarization of the lattice by localized electrons has already been adduced in discussing the possible reasons for the effective attraction between impurity electrons.³⁵ The interaction of impurity electrons with the crystal lattice has been at the center of attention of investigators since the discovery of long-term relaxation of the non-equilibrium concentration of electrons in PbTe and $Pb_{1-x} Sn_x$ Te doped with group-III impurities. At low (liquid-helium) temperatures, the processes of overflow of electrons between impurity and band states has proved to be long-term with characteristic times up to several hours. Long-term relaxation has been observed in many experiments in which equilibrium was disturbed by various methods: radiation, giving rise to photoconductivity (Vul et al.^{45,46} Akimov, Brandt et al.,⁴⁷ and Lykov and Chernik⁴⁸), a quantizing magnetic field (Akimov, Brandt, et al., 49 Lykov and Chernik¹²), a strong electric field (Akimov, Brandt et al.⁵⁰), and fast temperature change (Drabkin et al.³²).

Akimov, Brandt *et al.*⁴⁹ employed a quantizing magnetic field for creating a nonequilibrium metallic state. In passing through the ultraquantum limit, the number of states in the conduction band below the In level increases, and the electrons overflow from the impurities into the band. When one removes the magnetic field, the concentration of electrons in the band and the Fermi level are above the equilibrium values. In the presence of long-term relaxation this nonequilibrium state persists for a prolonged time.

Figure 11 shows the patterns observed at T = 2 K of the Shubnikov-de Haas oscillations in $Pb_{1-x} Sn_x Te\langle In \rangle$ under pressure, where the impurity level lies in the conduction band ($\varepsilon_i = 0.01$ eV, $n_0 = 4 \times 10^{15}$ cm⁻³). Long-term relaxation in this material is observed at temperatures below 20 K. At 2 K the overflow process lasts for several hours, but it can be accelerated by short-term (3 min) heating to 20 K with subsequent "freezing" of the equilibrium state in a 60-kOe magnetic field. After rapid (3 min) removal of this field, the state is nonequilibrium and the pattern of Shubnikov-de



FIG. 11. Form of the recording of the oscillations of $\partial \rho / \partial H$ (ρ is the electric resistivity) in Pb_{0.75} Sn_{0.25} Te $\langle In \rangle$ under a pressure of 5.4 kbar.⁴⁹ Curves 1 and 7 correspond to the equilibrium state, and 2—6 to nonequilibrium states.

Haas oscillations corresponds to a concentration of electrons above the equilibrium concentration. Curve 1 in Fig. 11 was recorded before introducing the 60-kOe magnetic field that destroyed the initial equilibrium. Curve 2 was recorded immediately after turning this field off, when the concentration of electrons in the band was twice as large as the initial concentration. Curves 3-6 were recorded respectively after 5, 10, 30, and 60 min, as the Fermi surface gradually contracts. Finally, curve 7, which coincides with 1, was obtained after short-term heating of the specimen $2K \rightarrow 20K \rightarrow 2K$ at H = 0, after which the specimen returns to the initial equilibrium state.

The long-term relaxation is explained by the magnitude of the oscillations of the Hall coefficient, which is depressed in comparison with calculation, in pulsed magnetic fields up to 250 kOe in PbTe(In).¹² The oscillations of the Hall coefficient directly reflect the concentration of electrons in the band that varies because of the overflow of carriers between the band and the levels as the magnetic field is varied.

In the presence of long-term relaxation one observes an anomalously high photoconductivity, which exceeds the dark conductivity by several orders of magnitude.^{45,47} The photosensitivity is so large that one even observes in the experiments an effect caused by the radiation from the parts of the cryostat, which has a higher temperature than the specimen,^{45,48} as well as by the radiation from the source, which has a temperature of only 12 K.⁴⁷

Under the conditions of long-term relaxation with induction of nonequilibrium states by an electric field up to 200 V/cm, one observes complex N- and S-shaped volt-ampere characteristics.⁵⁰

The existing explanations of long-term relaxation reduce to the idea that the surrounding crystal lattice must become rearranged upon changing the charge state of the impurity. Concrete types of lattice rearrangement that have been discussed include: dielectric polarization (Moĭzhes and Drabkin,^{38,39} Kaĭdanov and Nemov⁵²), the Jahn-Teller effect and a structural phase transition (Volkov *et al.*^{53,54}), and deformation of the nearest environment of the impurity (Kagan and Kikoin⁵⁵).

Let us explain the mechanism of long-term relaxation with a very simple example in which the electronic energy depends linearly on the deformation. (Volkov and Pankratov⁵⁴ proposed such a dependence for a Jahn-Teller center. The arguments presented below mainly follow Ref. 54). In this case the total energy of a center occupied by an electron is

$$E_1 = \frac{\Delta^2}{2\Delta_0} + (e_0 - \Delta). \tag{5}$$

Here $\Delta^2/2\Delta_0$ is the elastic energy of the local deformation; ε_0 is the electronic energy in the absence of deformation; and $(-\Delta)$ is its variation caused by deformation. At the equilibrium position we have $\Delta = \Delta_0$, and

$$E_i = \varepsilon_0 - \frac{\Delta_0}{2} \equiv \varepsilon_i. \tag{6}$$

This quantity determines the thermal energy of activation of the center. The energy of optical activation involves the electronic component of the energy of the center $\varepsilon_0 - \Delta_0$.

Thus the difference between the optical and the thermal energy (the Stokes shift) is $\Delta_0/2$.

Figure 12 shows the energy of an occupied center (E_1) and the sum of the energies of an electron at the Fermi level in the band and an empty center (E_0) in the special case in which the impurity center lies in the allowed band and the chemical potential is stabilized at the level $\mu = \varepsilon_i$. According to the Franck-Condon principle an electronic transition occurs with an unchanged configuration of the lattice $(\Delta = \text{const})$. This implies that a radiationless electronic transition from a band state to an impurity state occurs at values $\Delta = \Delta_A$ corresponding to the point of intersection of the curves E_0 and E_1 . A fortuitous appearance of the lattice configuration Δ_A with an empty center requires the deformation energy $\varepsilon_A = \Delta_A^2/2\Delta_0$. Thus the latter plays the role of the energy of activation of the lifetime of electrons in the band. In the special case, $\mu = \varepsilon_i$ being treated, it coincides with the energy of activation of the lifetime of bound electrons and is equal to $\Delta_0/8$ (i.e., a fourth of the Stokes shift). Upon taking into account the estimates of the Stokes shift made in Sec. 3c. we conclude that the energy of activation is of the order of



FIG. 12. Energy of an electron at an impurity center and in the conduction band at the Fermi level with allowance for lattice deformation. E_0 —electron in the band with center empty; E_1 —electron at the center; ε_A —activation energy for band-level transitions.

0.01 eV. At temperatures of the order of 2 K this energy of activation suffices to increase the relaxation time by many orders of magnitude.

In a more exact theory one must allow for the fact that the state of the crystal lattice is not characterized by a definite value of the deformation, but undergoes local oscillations about the equilibrium position with the frequency Ω . The classical theory holds at high temperatures, at which the quantity kT is large in comparison with the energy $\hbar\Omega/2$ of the zero-point vibrations. The case of low temperatures $kT \leq \hbar\Omega/2$ was also treated in Ref. 54. In this case another exponential $\exp(-\Delta_0/2\hbar\Omega)$, which characterizes the probability of tunneling through the barrier, appears in the expression for the transition probability instead of $\exp(-\epsilon_A/kT)$. In order to explain long-term relaxation, the quantum energy of the local vibrations must be substantially smaller than the Stokes shift, which does not exceed 0.04 eV. This implies that the lattice polarization, which is characterized by the energy of a longitudinal optical phonon (0.0136 eV in PbTe) is ill-suited for giving rise to long-term relaxation. It is preferable to consider the shift of the impurity atom from its central position, which is apparently characterized by the energy of the soft mode ($\sim 0.002-0.004 \text{ eV}$). One of the reasons for such a breakdown of cubic symmetry of the lattice can be the Jahn-Teller effect,⁵⁴ and another can be the smallness of the ionic radius of indium.³⁸

4. DOPING WITH OTHER GROUP-III ELEMENTS IN A" B"

a) Thailium doping in lead chaicogenides

We have formulated above some ideas (Sec. 3b) that lead one to expect substantial differences in the characteristics of impurity states, including the energy, for different group-III dopants. Actually, while indium is a donor in the lead chalcogenides, doping with thallium manifests acceptor properties.

The transport phenomena in lead chalcogenides doped with thallium have been studied by Nemov *et al.*^{52,56-65} The dependence of the Hall concentration on N_{T1} tends to saturate, and here the limiting hole concentration (~10²⁰ cm⁻³ in PbTe and PbSe and ~5×10¹⁹ cm⁻³ in PbS^{52,56,57}) is severalfold smaller than the solubility of thallium.

A comparison of the lead chalcogenides doped with Tl with the same materials doped with Na shows no appreciable differences in the magnitude of the thermo-emf, the Nernst-Ettingshausen effect, or the Hall mobility in the region of relatively small concentrations. Considerable differences are manifested near the saturation concentration: in specimens containing Tl the thermo-emf is substantially decreased at low temperatures, the mobility declines by an order of magnitude or more, and $\partial R / \partial T$ increases severalfold.

Measurements of the Hall effect in the low-temperature region with simultaneous doping of PbTe with thallium and a supplementary acceptor (sodium) reveal the stabilizing role of the thallium admixture: over a broad range of variation of $N_{\rm Na}$, the Hall concentration of holes, and hence the chemical potential, remain constant. Stabilization of the chemical potential also occurs upon introducing excess lead (a donor) into specimens doped with thallium.

One can explain all these features by assuming that thallium doping gives rise to a quasilocal level inside the valence band. Let us assume, as in the case of In, that the impurity states in the absence of ionization are only half-filled with electrons. Then we can understand how they manifest themselves as acceptors when they appear in the valence band. Supplementary doping by donors or acceptors that do not yield a level hardly alters the concentration of holes in the valence band as long as the impurity band is part filled. However, supplementary doping makes it possible to displace the Fermi level with respect to the middle of the impurity band. Here one can alter the density of impurity states at the Fermi level over a broad range. This substantially affects the lowtemperature heat capacity discussed above, the resonance scattering, and the temperature and the critical magnetic field of the transition to the superconductive state.

The change in the degree of filling of the impurity band substantially affects such properties of the material as the temperature-dependence of the Hall coefficient. With increasing Na content, the increase in R with temperature in the temperature region 100–200 K is replaced by a decline with an unchanged magnitude of R (T = 77 K). This happens because, when the band is largely filled with holes, the thermal supply of holes occurs mainly from the impurity band inside the valence band. However, with low filling it occurs from the valence band into the impurity band. Consequently the concentration of holes in the valence band, and hence the value of R with high and low filling vary in opposite directions with the temperature.

Study of the quasilocal states of Tl in the lead chalcogenides is impeded by the presence of a band of heavy holes lying approximately in the same region as the impurity band of Tl (0.15–0.25 eV from the edge of the valence band). One can qualitatively explain many features in the concentration- and temperature-dependences of the kinetic coefficients by the redistribution of the holes between the bands, and also by interband scattering. Thus, Ref. 66 has ascribed the differences in properties of specimens doped with Tl and Na to the influence of thallium on the scattering of holes without adducing quasilocal states. However, one cannot even explain the experiments on supplementary doping of $PbTe\langle Tl \rangle$ with sodium and excess lead with a two-band model without a Tl impurity band. Additional arguments favoring the picture of quasilocal Tl states arise from study of resonance scattering, the tunneling effect, the heat capacity and superconductivity, as well as optical experiments. We shall now proceed to present the results of these experiments.

The optical absorption in lead chalcogenides doped with thallium has been studied by Veĭs *et al.*^{59,61–64,67,68} In the absorption spectra of PbSe⁶¹ and PbSe_{1-x} S_x⁶⁴ having hole concentrations small in comparison with the concentration corresponding to stabilization of the Fermi level, one distinctly observes supplementary absorption bands that arise upon thallium doping owing to optical transitions of electrons from the impurity band to the top of the valence band (Fig. 13). The position of these bands in the spectrum, which varies from 0.20 \pm 0.02 eV for PbS to 0.26 \pm 0.01 eV for PbSe at 300 K, agrees with the estimates made in study-



FIG. 13. Optical absorption in PbSe_{1-x}S_x $\langle T1 \rangle$.⁶⁴ $N_{T1} = 0.5$ atom percent; 1—PbSe, T = 358 K; 1'— a_{sup} ; 2—PbSe_{0.7}S_{0.3}, T = 300 K; 2'— a_{sup} ; 3— a_{sup} for PbS, T = 300 K.

ing the kinetic coefficients. In contrast to the data obtained from specimens containing indium, the character of the $\partial l_{up}(\hbar\omega)$ relationship indicates an appreciable broadening of the band. At 300 K this amounts to (0.01 ± 0.02) eV in PbSe, and PbS, and increases to 0.06 eV in the solid solution PbSe_{0.5}S_{0.5}.

Impurity bands have also been distinguished in the absorption spectra of PbTe $\langle T1 \rangle$,^{63,68} although here they are manifested less clearly than in PbSe and PbS. While in PbSe and PbS the Tl level at low temperatures lies above the second valence band, in PbTe it lies in the immediate vicinity of its edge. The shape of the spectrum shows that the impurity band is rather highly diffuse: the width of the impurity band varies from 2 kT to 6 kT upon increasing the thallium content from 0.1 to 1.5 atom percent.

The peaks in the density of states caused by the Tl and In bands in PbTe are manifested in the volt-ampere characteristics of PbTe $\langle Tl \rangle$ -PbTe $\langle In \rangle$ tunnel diodes.¹⁸ Near zero bias one sees a relatively broad spike (~0.01 V) of conductivity, and a narrow peak (~0.001 V) on its background. On the basis of the concepts of In and Tl impurity bands with allowance for their differing width, one can associate the first of these features with tunneling transitions of electrons between Tl impurity states in the p-region and band states in the n-region. The latter can be associated with transitions in which the In impurity band participates.

b) Resonance scattering

Scattering of holes in thallium-doped lead chalcogenides has been studied in Refs. 52, 60, and 67. At thallium concentrations that are not too large (up to 2×10^{19} cm⁻³), the cross-section for scattering of carriers by thallium atoms proved to be of the order of 10^{-16} cm⁻³, as in doping with indium (Sec. 3a) as well as with sodium and halogens. The cross-section depends weakly on the degree of filling of the valence band, as should happen in the case of scattering by the short-range part of the potential of the impurities.

However, at thallium concentrations $\gtrsim 5 \times 10^{19}$ cm⁻³, the scattering cross-section for holes increases sharply by more than an order of magnitude.⁵² (Fig. 14). The sharp (resonance) growth occurs in a narrow interval of μ in the region of the proposed energy of the Tl impurity band. The scattering cross-sections of both light and heavy holes prove large



FIG. 14. Scattering cross-section of light holes at a thallium impurity in PbTe.⁵² The calculation is performed for different ratios of the mobilities of heavy and light holes; 0.3; 1.0; 3.0; 10.0.

in comparison with those of sodium. The observed effect has been explained by resonance scattering by a quasilocal level.⁵²

The resonance scattering proves to be closely associated with the width of the impurity band.⁶⁹ There are several possible reasons for the broadening of the level; a) nonstationarity of the impurity states, or in other words, hybridization of the band and impurity states whenever the level is a resonance level, i.e., falls in the allowed band; b) overlap of wave functions, which converts the local levels into an impurity band; c) inhomogeneity of the specimen and interaction of randomly distributed impurities giving rise to scatter of the impurity levels. Analysis of the resonance scattering by impurities yields information on the causes of band broadening.

The strong localization of impurity states enables one to use the formulas for s-scattering, both in the case of ordinary and of resonance scattering. Upon using the Breit-Wigner formula⁶⁹ for the cross-section of resonance s-scattering, we obtain the following expression for the relaxation time

$$\boldsymbol{\tau}_{res} \left(\boldsymbol{\varepsilon} \right) = \frac{\hbar \rho_0}{\rho_1 \left(\boldsymbol{\varepsilon} \right) \gamma} \,. \tag{7}$$

Here ρ_0 is the density of states in the allowed band; γ is the width of the resonance level involving hybridization of impurity and band states; and ρ_1 is the density of impurity states. When the $\rho_1(\varepsilon)$ curve is bell-shaped, we can approximate the latter with the formula

$$\rho_{i}(e) = \frac{N_{1}}{\pi!} \frac{\Gamma}{(e - e_{i})^{2} + (\Gamma/2)^{2}} \cdot$$
(8)

Here Γ is the total width of the impurity band arising from all the acting broadening mechanisms; and N_1 is the impurity concentration at which resonance scattering takes place.

At low temperatures $kT < \Gamma$, the electric conductivity is proportional to the relaxation time for $\varepsilon = \mu$. If the doping is done with thallium or simultaneously with thallium and sodium, one can express the quantity $\mu - \varepsilon_1$, and hence also $\rho_i(\mu)$ and $\tau_{res}(\mu)$, in terms of the quantity

$$k^{(k)} = \frac{1}{2} + \frac{N_{\rm Na} - p}{2N_{\rm Tl}} , \qquad (9)$$

The latter characterizes the degree of filling of the impurity band with holes. Consequently the electric conductivity is described by the expression

$$\sigma = \frac{(3\pi^2)^{1/3} e^2 p^{4/3}}{4\pi\hbar N_{\rm Tl}} \frac{m_{\rm d}^*}{m_{\rm c}^*} \frac{\Gamma}{\gamma} \left\{ 1 + \tan^2 \left[\pi \left(k^{(k)} - \frac{1}{2} \right) \right] \right\}.$$
(10)

Here m_d^{\bullet} and m_c^{\bullet} are the effective masses of the density of states and the conductivity. Equation (10) enables one to obtain information from the experimental values of σ on the value of γ/Γ , and thus on the nature of the broadening of the impurity band.

The processing of the data on resonance scattering in PbTe(Tl) is impeded by the presence of the second valence band. In calculating σ one must introduce two adjustable parameters γ_1/Γ and γ_h/Γ , where γ_1 and γ_h are the partial widths arising from hybridization of the impurity states with states in the bands of light and heavy holes. Nevertheless, the condition $\gamma/\Gamma \leq 1$ ($\gamma = \gamma_1 + \gamma_h$) allows one to perform the calculation unambiguously. Here it turns out in PbTe(Tl),

first, that the mobilities of the light and heavy holes in the presence of resonance scattering are close together, and second, that $\gamma/\Gamma \sim 1$. That is, hybridization is the main cause of broadening of the impurity band.

However, since the value of Γ depends on the Tl concentration, and also on the composition of the solution in solid solutions (Sec. 4a), other mechanisms of broadening are also not ruled out. For example, the increase in Γ in the solid solution PbSe_{1-x} S_x as compared with PbS and PbSe that was mentioned in Sec. 4a has been explained⁶⁴ by local fluctuations in the composition of the solid solution.

Supplementary doping of PbTe $\langle Tl \rangle$ with sodium substantially affects the resonance scattering by altering the filling coefficient $k^{(h)}$.⁶⁵ A minimum of σ is observed when $k^{(h)} \approx 1/2$. That is, the Fermi level is close to the middle of the band ε_i , and the shape of the $\sigma(N_{Na})$ curve is described satisfactorily by Eqs. (9) and (10).

Thus, in contrast to indium, thallium in the lead chalcogenides scatters carriers strongly and in resonance fashion. We can assume that the absence of resonance scattering in PbTe(In) at low temperatures arises from the same processes as does the long-term relaxation (Sec. 3d). Since the long-term relaxation disappears at T > 20 K, we can expect the appearance of resonance scattering also in PbTe(In) with increasing temperature.

Actually, at T > 77 K, the scattering cross-section of indium increases with the temperature.^{11,15} If we approximate the temperature-dependence of the impurity scattering with an exponential, then the energy of activation proves to be of the order of 10^{-2} eV.

The mobility increases upon supplementary doping of specimens containing indium with iodine.⁷⁰ One can easily understand this from the standpoint of resonance scattering: upon supplementary doping the Fermi level shifts from the middle of the impurity band, and the resonance scattering decreases.

The strong dependence of the density of impurity states ρ_i on the energy gives rise, in line with Eq. (7), to a strong and nonmonotonic energy-dependence of the relaxation time of free carriers. Correspondingly this affects the thermo-emf. This effect has been observed in the lead chalcogenides doped with thallium: PbS,⁵⁷ PbSe,⁶⁰ and PbTe.⁶⁷ By using the information on the width of the impurity band obtained from optical data (Sec. 4a), one can calculate the thermo-emf and gain satisfactory agreement with experiment.⁶⁷

Let us discuss the information on the magnitude of γ obtained by studying resonance scattering.

The lack of an appreciable resonance scattering of electrons by an indium impurity at low temperatures means that the broadening of the level caused by hybridization of impurity states with band states is negligibly small: $\gamma \ll \Gamma$. If we allow for the fact that also the value of Γ is rather small (Sec. 3a), then we obtain a very small upper estimate for γ ($\gamma \ll 10^{-6} \text{ eV}$).

On the contrary, for the thallium level we find $\gamma/\Gamma \sim 1$, while the value of Γ is as much as several hundredths of an electron-volt, and γ is several orders of magnitude larger than for In. Apparently the small density of states in the electron band, near the edge of which the resonance level of indium in PbTe lies, is one of the reasons for the smallness of γ in this material. On the contrary, the thallium level, which lies near the edge of the heavy valence band, proves substantially more diffuse.

Another factor that affects the magnitude of the hybridization is the symmetry properties. If the impurity lies at a lattice node, the wave function of the impurity electron transforms according to the irreducible representations of the cubic group. In particular, it has a definite parity, just like the Bloch wave functions at the point L. If the parity of the predominant component of the wave function of an electron in the band near which the level lies is opposite to the parity of the impurity wave function, the level is spread only weakly, owing to the smallness of the overlap integral. The Bloch wave functions near the edges of the electron and hole bands where the levels of In and Tl respectively have opposite parity. This can be the reason for the substantial difference in the magnitude of γ for the levels of In and Tl. The situation here can resemble the results presented below in Sec. 5b of the analysis by Volkov and Pankratov⁵⁴ of the symmetry of the wave functions of states involving vacancies.

Interaction with the lattice, which increases the lifetime of an electron in an impurity state (Sec. 3e) should also substantially diminish the magnitude of γ .

c) Heat capacity of PbTe(TI)

When we allow for the spike in the density of electronic states in the energy region where the impurity band lies, we can expect a considerable contribution of the impurity states to the electronic component of the heat capacity, especially in the situation in which the Fermi level lies near the density maximum. One of the most direct methods of observing an impurity band is based on measuring the low-temperature heat capacity. The high concentration of impurities and lack of strong spreading of the impurity band, which are characteristic of $A^{IV} B^{VI}$ semiconductors doped with group-III elements, render the method especially suitable for application to these materials.

Konstantinov, Chernik, et al.71 have studied the impurity states of thallium in lead telluride by measuring the lowtemperature heat capacity. The measurements of the heat capacity in the temperature range $\sim (1-4)$ K at thallium concentrations of 0.5 and 1.25 atom percent showed that introduction of thallium gives rise to a peak in the density of electronic states that can be distinctly observed with the aid of supplementary doping with sodium (Fig. 15). At a Tl concentration of 0.5 atom percent, if sodium has not been introduced (the impurity band is almost completely filled with electrons), or if the sodium concentration is ~ 1 atom percent (the band is almost empty), the density of states ρ as determined from the heat capacity is approximately the same as in the absence of thallium. Yet if the Fermi level is close to the middle of the band (~ 0.5 atom percent Na), the density of states ρ is 4–5 times larger than without thallium. The $\rho_i(\varepsilon)$ curve is bell-shaped, with a form satisfactorily de-



FIG. 15. Dependence of the electronic heat-capacity coefficient $\gamma = c_e/T$ in PbTe on the Na concentration for different T1 constants: 1––0.5 atom percent; 2––1.25 atom percent.⁷¹

scribed by Eq. (8). An estimate of the width Γ of the impurity band from the maximum of ρ_i yields 0.02–0.03 eV for N_{TI} = 0.5 atom percent. With increasing N_{TI} the width of the level increases, so that the value of $\rho_i^{(max)}$ hardly changes. Both the magnitude of Γ and its increase with increasing TI content agree satisfactorily with the results of the optical measurements (Sec. 4a).

The estimates of Ref. 71 have shown that one should expect the greatest effect of impurity electronic heat capacity in PbTe doped with In. However, attempts to observe this effect in PbTe(In) have not been successful. Evidently the reason for failure is the long-term relaxation (Sec. 3e), which makes the impurity electronic heat capacity practically unobservable. The existence of impurity heat capacity upon doping PbTe with thallium means that there is no long-term relaxation in this case.

d) Superconductivity in PbBe(Ti)

While measuring the heat capacity in PbTe in order to study the impurity states of thallium, Chernik and Lykov^{72,73} found a jump in heat capacity in the temperature range between 1 and 2 K, which they ascribed to a transition to the superconductive state (Fig. 16). This explanation was confirmed by measurements of the electric conductivity, by suppression of the singularities in the temperature-dependence of the heat capacity and the electric conductivity by a magnetic field, and also by the observation of a negative magnetocaloric effect. The relationship between the jump in the heat capacity and the magnitude of its electronic component in the normal state gave convincing proof of the bulk character of the superconductivity. The large magnitude of the magnetocaloric effect, which was studied in fields considerably smaller than the critical field (which suppresses the superconductivity) indicate the penetration of the magnetic field into the volume of the specimen. This implies that PbTe \langle Tl \rangle is a type-II superconductor.⁷³ The study of the superconductivity of PbTe $\langle Tl \rangle$ has been continued in Refs. 74-76.

The discovery of superconductivity in PbTe $\langle TI \rangle$ is one of the most interesting and unexpected results obtained in studying group-III dopants. Searches for superconductivity in p-PbTe $\langle Na \rangle$ have yielded a negative result⁷⁷ down to a temperature of 0.009 K, although the concentrations of impurities and holes were as much as 5×10^{20} cm⁻³. At the



FIG. 16. Temperature-dependences of the molar heat capacity (a), the resistivity (b), and second critical magnetic field (c) in a PbTe specimen with a T1 concentration of 1.5 atom percent.⁷³ 1—heat capacity at H = 0; 2—for H > 2.5 kOe; 3—in an undoped specimen of PbTe with a concentration of holes $\sim 4 \times 10^{18}$ cm⁻³.

same time, upon Tl doping the threshold concentration of holes above which superconductivity is observed amounts to $(4-5) \times 10^{19} \text{ cm}^{-3}$, ⁷⁶ i.e., an order of magnitude smaller than in SnTe $(4 \times 10^{20} \text{ cm}^{-3})$ and GeTe $(8 \times 10^{20} \text{ cm}^{-3})$.⁵ With increase in Tl content up to 1–2 atom percent $(p \le 10^{20} \text{ cm}^{-3})$, T_c increases to 1.4 K.^{72,76} This considerably exceeds the maximum values for SnTe (0.25 K), GeTe (~0.3 K) and other known superconductive semiconductors (TlBiTe₂, SrTiO₃, Ba_x Sr_{1-x} TiO₃, Ca_x Cr_{1-x} TiO₃). PbTe \langle Tl \rangle also differs from the stated superconductors in values of the upper critical field ($H_{c2}(0) \approx 0.5 T$) and of the Ginzburg-Landau parameter ($\varkappa \sim 80$) greater by about an order of magnitude.⁷³

Varied hypotheses have been advanced on the mechanism of superconductivity in PbTe(Tl). Reference 74 has discussed the possibility that the superconductivity is caused, as in SnTe and GeTe, by the presence of a multivalley Σ -subband with a large density of states. Here sodium doping increases its energy spacing from the top of the valence band, so that the Fermi level does not fall into it, while doping with thallium, a neighbor of lead in the periodic table, weakly perturbs the band spectrum and practically does not affect the position of the band of heavy holes. On the contrary, the authors of Ref. 79 consider that thallium doping can cause a substantial rearrangement of the band spectrum, mainly in the region of the unstable Σ -extremum.

An attempt has been made⁸⁰ to reveal experimentally the role of phonons in the mechanism of superconductivity of PbTe \langle Tl \rangle . Upon supplementary doping with germanium (up to 0.75 atom percent), a noticeable softening of *TO*-phonons was established from heat-capacity measurements, whereas T_c declines sharply even with small additions of Ge. This does not agree with the concepts of the BCS theory on the favorable influence of soft phonon modes on T_c .

Substantial information on the nature of the superconductivity in thallium-doped PbTe has come from experiments on specimens in which the degree of filling of the impurity band was varied by supplementary doping with sodium.^{65,81} These experiments leave little doubt that the appearance of superconductivity closely involves the specific properties of the impurity states of thallium. It has turned out⁶⁵ that superconductivity is found only when the Fermi level enters the impurity band, from below or above. The relationship of T_c and H_{c2} to the degree of filling of the band is bell-shaped (Fig. 17), with the maximum values of $T_c \approx 2.2$ K and $H_{c2}(0) \approx 1.3$ T approximately corresponding to half-filling. These relationships are analogous to those obtained for the intensity of resonance scattering (resistivity) and the density of states ρ at the Fermi level in the normal state. The latter was determined in Ref. 65 from the relationship between $H_{c2}(0)$ and T_c .⁸² That is, it corresponded to the den-



FIG. 17. Dependence of the temperature T_c , the second critical magnetic field H_{c2} (0), the resistivity in the normal state ρ , and the density of states $N(E_F)$ on the filling coefficient of the impurity band with holes in PbTe $\langle T1, Na \rangle$ in relative units (referred to the values for $N_{Na} = 0$).⁶⁵

sity of states of pairing electrons. The value of ρ determined in this way exceeds by an order of magnitude the density of band states ρ_0 in PbTe without Tl, and it is close to the ρ found from heat-capacity measurements (Sec. 4c). Hence one can conclude that the electrons that exist in hybridized states (i.e., mainly impurity states) become paired.

Since thallium doping sharply decreases the mobility, and the value of T_c correlates with the intensity of resonance scattering, we can assume that the scattering enhances the electron-electron interaction that leads to superconductivity, in agreement with Ref. 83.

It is also assumed possible in PbTe \langle Tl \rangle for electrons to pair at centers having a negative correlation energy, in line with the theoretical concepts developed in Refs. 84–86.

The elucidation of the concrete mechanism of superconductivity in PbTe $\langle TI \rangle$ is a first-rank problem for further studies. A non-phonon mechanism of pairing is not ruled out. In one way or another, the discovery and study of superconductivity yields new proofs of the existence of resonance states of thallium and new methods for studying them.

e. Gallium and aluminum doping

An admixture of Ga in PbTe, while acting as a donor, allows one to obtain a concentration of electrons an order of magnitude larger than with an admixture of In. In the system PbTe-GaTe at contents of Ga less than 0.5 atom percent, as a rule the concentration of electrons is considerably less than the concentration of Ga atoms, while in a number of cases the specimens have p-type conductivity. Introduction of superstoichiometric lead leads to $n \approx N_{Ga}$. However, even this method did not allow an electron concentration at 77 K exceeding 6×10^{19} cm⁻³ in specimens prepared by the metal-ceramic method.⁸⁷ The $n(N_{Ga})$ relationship tends to saturate at this level, although $N_{\rm Ga}$ reaches 5×10^{20} cm⁻³, which incidentally does not exceed the solubility limit. If we attribute the stabilization of the chemical potential to the action of a quasilocal level, then its energy amounts to $\varepsilon_{\rm i} = 0.21 \pm 0.01$ eV at 77 K, and $\varepsilon_{\rm i} = 0.19 \pm 0.02$ eV at 300 K.

The optical-absorption data obtained in the same study⁸⁷ at 300 K correlate with this result. The measurements were performed on specimens of PbTe(Ga) containing varying admixtures of excess Te, whereby the concentration of electrons was varied over the range $(0.6-4) \times 10^{19}$ cm⁻³. Additional bands were detected in the absorption spectra whose intensity increased with the Ga content, while the red boundary shifted monotonically toward longer wavelengths with increasing Hall concentration. The value of $\hbar\omega_{boundary} + \mu \sim 0.19$ eV coincides with the energy ε_i found from the Hall effect. This allowed the authors of Ref. 87 to consider that the long-wavelength band involves transitions of electrons from the conduction band into an empty quasilocal level.

However, studies conducted later by other authors^{47,88-90} of gallium-doped PbTe ($N_{\text{Ga}} \leq 0.5$ atom percent) and solid solutions based on it have led to conclusions that the behavior of this dopant is far more complex than that of indium. In particular, Akimov *et al.*⁹⁰ studied galvanomagnetic and oscillatory effects in $Pb_{1-x} Sn_x Te\langle Ga \rangle$ (x = 0.19-0.20), and found a jumpwise transition from n- to ptype conduction upon increasing the pressure. The jump occurs near 2.8 kbar, while no dielectric state is observed at any pressure. The same happens at atmospheric pressure for x > 0.2.

On the contrary, upon gallium-doping of PbTe and $Pb_{1-x} Sn_x Te$ (x = 0.18; 0.30) and $Pb_{1-x} Ge_x Te$ (x = 0.03; 0.05), Drabkin *et al.*^{88,89} observed a dielectric state, with the Fermi level stabilized in the forbidden band near its middle. Thus the results of Refs. 87–90 do not agree with one another and have no unambiguous interpretation. Perhaps the contradiction of the results that have been obtained stems from the dependence of the properties of Ga-doped specimens on the technique of preparation (see Sec. 5c) and on the amount of introduced dopant. In further studies of materials doped with gallium, the concept of a quasilocal level in the conduction band can play the role of one of the working hypotheses.

Upon doping PbTe with aluminum in n-type specimens not too strongly compensated, a level in the conduction band with the energy $\varepsilon_i \approx 0.3$ eV has been discovered⁹¹ in the conduction band by an optical method. If we assume that $\varepsilon_i \approx 0.2$ eV for gallium, in line with Ref. 87, it turns out that the position of the impurity band in the series Al-Ga-In-T1 varies monotonically with the atomic number: the levels of Al and Ga in PbTe lie high in the conduction band, the level of In near the edge of the conduction band, and the level of T1 in the valence band.

f) Source of the levels associated with group-III doping in $A^{IV} B^{VI}$ compounds

The experimental data presented in the previous sections convincingly indicate the existence of impurity states in $A^{IV} B^{VI}$ semiconductors doped with group-III elements. Such localized states can be created by the short-range potential of an impurity or defect. In the various compounds and solid solutions that we have treated, the impurity level can lie either in the forbidden band or in both of the allowed bands.

The strong localization of the impurity state, the strong dependences of the position of the level on the temperature, the pressure, the composition of the solid solution, and the type of impurity rule out a genetic connection of the level with the L-extrema near which it lies, and they allow one to classify it among the "deep" levels that split off from farlying bands and cannot be described by the effective-mass approximation.

We shall try to clarify the genetic connection of the level with the energy bands by using the strong-coupling approximation (for the sake of definiteness, we shall speak of PbTe doped with In). In the strong-coupling approximation the lower conduction bands are formed from the 6p-states of lead (three doubly degenerate bands). Directly below the forbidden band lie three doubly degenerate bands formed from the 5p-states of tellurium. The doubly degenerate 6s-band of Pb lies 3-4 eV deeper than the 5p-band of Te, and the 5s-



FIG. 18. Localized levels split off from the valence bands of PbTe by Pb vacancies (a) and Te vacancies (b) according to the calculation of Ref. 108.

band of Te even deeper by 2-3 eV (see below in Sec. 5b, Fig. 18). When replacing lead in the lattice, indium can considerably perturb the bands formed from the atomic states of lead. An essential point here is that the outer shells of the indium atom are characterized by greater energy than the outer shells of the lead atom having the same orbital moments. In particular, the 5s level of indium lies 2 eV above the 6s level of lead.⁹² It is not ruled out that the indium level, when splitting upward from the 6s band of lead, will fall in an energy region lying near the forbidden band.

The presented hypothesis makes it possible to explain why indium, which has one electron fewer than lead in the outer shell, has a donor action in PbTe. Just like lead, indium gives up two electrons to the bond in the valence p-band of Te. Upon splitting the doubly degenerate level, which falls in the conduction band near its edge, from the s band of Pb, indium has one electron for filling this level, which either remains in the level or enters the conduction band, depending on the position of the Fermi level. Upon supplementary doping with iodine, the level can accept another electron if the energy of repulsion of the electrons is small.

If the level falls in the valence band (In in SnTe, Tl in lead chalcogenides), its ability to accept an electron causes the dopant to have an acceptor $action.^{3)}$

The model that we have presented is the simplest, but not the only model to describe the mechanism of the donoracceptor action of group-III dopants. The fundamental features of the model are retained if the level splits off from the upper valence bands (p-bands of Te). Section 5b will discuss another mechanism of indium doping involving vacancy levels of Te.

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5. DEEP AND RESONANCE STATES ASSOCIATED WITH OTHER IMPURITIES AND DEFECTS

a) Doping with groups II and V and transition metals. Isovalent impurities

The states involving impurities of groups other than group III have been studied in less detail. The greatest attention has been paid to cadmium, and impurity states of Cd in the forbidden band and in the conduction band of PbTe and Pb_{1-x} Sn_x Te have been reported (Rosenberg *et al.*⁸ Akimov et al.,⁴⁷ Chashchin et al.,⁹⁴⁻⁹⁶ Veïs and Nemov,⁹⁷ Shotov et al.⁹⁸). However, there are considerable discrepancies in the results obtained by different authors to characterize the positions of the impurity levels and the properties of the impurity states. We should bear in mind the fact that the obtained information on impurity states can be distorted by the self-compensation of impurities by vacancies that occurs in many cases. The creation of a large number of vacancies upon doping can substantially decrease the carrier concentration, and even give rise to impurity states involving vacancies, bivacancies, complexes, etc. (see Sec. 5c).

In PbTe doped with bismuth, a relatively broad impurity band has been observed⁹⁹ approximately 0.2 eV above the edge of the conduction band.

Upon doping PbTe and Pb_{1-x} Sn_x Te with the transition metals Ti (Prokof'eva *et al.*^{100,101}), Cr (Sizov *et al.*¹⁰²), and Mn (Lashkarev *et al.*¹⁰²⁻¹⁰⁴), resonance states were found in the conduction band at a spacing of the order of 0.1– 0.2 eV from the edge of the band.

The discovery of Prokof'eva *et al.*¹⁰⁵⁻¹⁰⁷ of a compensating donor action of Sn and Ge in the lead chalcogenides was unexpected. It had been assumed prior to these studies that these isoelectric substitution dopants do not alter the carrier concentration. The studies of the electrophysical properties of PbS and PbSe containing small admixtures of Sn and Ge have shown that replacement of Pb by an element of the same group gives rise to localized and quasilocal states. In PbS the states of Sn lie in the forbidden band, in PbSe they lie in the valence band, and in PbTe they sink so deep that they cannot affect temperature phenomena. An effect of donor states of Ge was noted in all three lead chalcogenides.

In order to verify these views, the charge state of Sn has been studied¹⁰⁶ by Mössbauer spectroscopy. It turned out that doping of the studied materials with sodium gives rise to a Mössbauer spectrum of Sn^{+4} lines alongside the Sn^{+2} lines. That is, Sn proves to be a doubly-charged donor, and the impurity states are two-electron states.

b) Vacancy levels

The theoretical calculations of "deep" levels involving vacancies in $A^{IV} B^{VI}$ compounds performed by various methods have made it possible to understand the experimentally well known donor and acceptor action of anion and cation vacancies. It has been established that vacancies of both types cause the splitting of several energy levels from the five upper valence bands. Here many of them lie in the energy region corresponding to the conduction band. Figure 18 shows the results of a calculation of the vacancy levels in

³The study of Weiser⁹³ has attempted to explain the donor or acceptor action of group-III impurities in PbTe by starting with the ionization potentials of the isolated atoms and by allowing for the interaction of the impurities with the crystal environment.

PbTe performed by Parada and Pratt¹⁰⁸⁻¹¹⁰ by the method of Koster and Slater based on an augmented-plane-wave calculation of the band structure. The calculations of Hemstreet¹¹¹ by the cluster method yielded close-lying results. Similar results have also been obtained for other lead chalcogenides and for tin telluride.^{110,111}

As we see from the diagram, a Te vacancy strongly perturbs the atomic states of Te; four doubly-degenerate levels enter the conduction band, and the number of states in the valence band is diminished by eight. In formation of a vacancy, six electrons are removed along with the Te atom, and the remaining extra two electrons enter the conduction band.

A Pb vacancy strongly perturbs only the s-band of Pb, while giving one doubly degenerate level to the conduction band and decreasing the number of states in the valence band by two. The removed Pb atom bears with it four electrons, and two holes appear in the valence band.

Thus a Te vacancy is a donor, a Pb vacancy is an acceptor, and in both cases two carriers arise per vacancy. In contrast to an acceptor Pb vacancy, a Te donor vacancy gives rise to several leads near the forbidden band, one of which lies only ~ 0.03 eV above the edge of the conduction band. In calculations performed by the cluster method,¹¹¹ one of the levels involving a chalcogen vacancy lies within the forbidden band. Of course, we should not consider this to be a substantial discrepancy between the theories if we allow for the limited accuracy of the theoretical calculations of the energy spectra of electrons in solids.

Volkov and Pankratov^{54,112} have examined the states involving vacancies in A^{IV} B^{VI} semiconductors using the strong-coupling method that they developed, in which the Bloch and localized wave functions are constructed from atomic p-orbitals. They concluded that the strong repulsive potential of a chalcogen vacancy splits a state from the valence band with an odd function (with the center at the chalcogen node). Without taking into account the spin-orbital interaction, the wave functions of the vacancy states transform according to the representation Γ_{15} . The spin-orbital interaction splits the triplet Γ_{15}^{-} into the singlet Γ_{6}^{-} and the doublet Γ_{8} . Here the doublet lies below the singlet in energy, owing to the repulsive potential of the vacancy. Thus the classification of the impurity states by symmetry led to the conclusion that one doubly degenerate level exists (fourfold degenerate upon allowing for spin) in the presence of cubic symmetry, instead of the two close-lying levels (0.546 and 0.548 Rydbergs) obtained by Parada and Pratt.¹⁰⁸ Capture of an electron by this level must lead to a Jahn-Teller deformation of the crystal environment of the defect and removal of the degeneracy.

According to the results of this symmetry analysis, the parity of states involving a chalcogen vacancy in lead chalcogenides coincides with the parity of the states of electrons in the valence band near the L-extremum, and is opposite to the parity of the states near the edge of the conduction band. Therefore the resonance level of a chalcogen vacancy in the conduction band must spread substantially more weakly than in the valence band, as happens in the case of the resonance levels observed upon doping with indium and thallium, respectively (Sec. 4b).

A number of reports exist on observation of vacancy levels in PbTe,^{7,113-115} Pb_{1-x} Sn_x Te $(x \sim 0.2)^{116-119}$ and Pb_{1-x} Sn_x Se.¹²⁰

An analysis of the temperature-dependence of the Hall coefficient in Pb_{0.82} Sn_{0.18} Te with an electron concentration of the order of $10^{15}-10^{17}$ cm⁻³ led Sizov *et al.*¹¹⁶ to conclude that half of the electrons given by the Te vacancies are frozen at low temperatures. The authors¹¹⁶ propose that one of the impurity states predicted by the theory in the conduction band of PbTe drops below the edge of the band upon adding Sn. Owing to localization of one electron at the vacancy, the charge of the latter is diminished, and paramagnetic states appear at low temperatures with unpaired spins. This results in a number of consequences that were found by Bratashevskii *et al.*^{117,118}: a decrease in scattering by ionized impurities, an increase in the mobility, EPR, ferromagnetic ordering, and also a Kondo effect as observed by Lashkarev *et al.*¹¹⁹

Important information on the levels associated with intrinsic defects in PbTe has been obtained by Heinrich et al.^{7,114,115} by using ion implantation. Upon bombarding PbTe with Pb, Te, and Xe ions, a large number of defects was created in the layer of the specimen near the surface that increased with the radiation dose. Here the electron concentration in the layer proved to be of a magnitude somewhat above 10^{18} cm⁻³, independently of the radiation dose, the type and energy of the implanted ions, and the carrier concentration in the specimen before irradiation. The authors of the study consider that the stabilization of the concentration arises from quasilocal levels in the conduction band caused by tellurium vacancies. The energy of the quasilocal state determined from the electron concentration proved to be 0.055 eV at 0 K and 0.005 eV at 300 K, in satisfactory agreement with the results of the theoretical calculations described above. In the solid solution $Pb_{1-x} Sn_x$ Te, the level shifted into the forbidden band with increasing x.

Attention is called to the remarkable closeness of the energy of the vacancy quasilocal state, and its dependence on the temperature and the Sn content with the corresponding parameters of the level observed in specimens of PbTe and Pb_{1-x} Sn_x Te doped with indium. This coincidence offered grounds to Volkov and Pankratov⁵⁴ for proposing that, in specimens doped with indium, the level is created by Te vacancies, rather than In atoms. However, to confirm this hypothesis, since vacancies are formed in a concentration of $\sim 10^{20}$ cm⁻³ upon In doping, one must elucidate why they do not affect the density of the material⁸ and why paramagnetic effects are not observed at them, whereas they occur in pure specimens without In.¹¹⁶⁻¹¹⁹ Also one must explain the experiments on supplementary doping with iodine and sodium described in Sec. 3a.

c) Autocompensation and levels of complexes of intrinsic defects

One of the manifestations of quasilocal states is the smallness of the concentration of free carriers in comparison

with that of the introduced dopants. However, qualitatively the same result can arise from a completely different phenomenon-the autocompensation of donors or acceptors by intrinsic defects, e.g., vacancies. The essence of autocompensation consists in the fact that it becomes energetically favorable to form intrinsic lattice defects that yield charge carriers of the opposite sign when electrically active dopants have been introduced into the specimen. Owing to the autocompensation, the change in carrier concentration is substantially less than the concentration of the introduced impurities.

Upon introducing large concentrations of donors (I. Cl. In, Ga) into the lead chalcogenides and their analogs, one observes a considerable increase (by an order of magnitude or more) in the solubility of superstoichiometric tellurium. In doping with acceptors (Tl, Na), the solubility of excess lead increases.^{56,58,78,87,121} This phenomenon has been employed to vary the degree of filling of the impurity states of In, Ga, and Tl, and the concentration of free carriers. It is difficult to control this process, especially when growing crystals from the melt.

Very low concentrations of carriers in PbSe and PbS doped with Tl and Na have been obtained by autocompensation.^{58,78} The autocompensation effect must also be taken into account in discussing the effect of other impurities, e.g., Ga and Cd, for which the pattern of levels is not yet fully clear. Perhaps the low carrier concentrations in gallium doping of solid solutions based on PbTe^{88,90} at $N_{Ga} \leq 0.5$ atom percent arise precisely from autocompensation, rather than due to local states in the forbidden land.

The latter also are not ruled out, although they are not necessarily associated with Ga atoms. Acceptor states deep in the forbidden band have been found in PbSe and PbS doped with Tl and Na at a high degree of compensation (over 0.95) with superstoichiometric lead.¹²² Their concentration is lower by two orders of magnitude than the content of impurities, while the energy does not depend on the type of the latter (Tl or Na). The authors have proposed that these states involve complexes of intrinsic defects (e.g., bivacancies), whose formation in the stated amounts is very likely, since the concentration of monodefects in the studied specimens is as great as 10^{20} cm⁻³.

6. CONCLUSION

The studies performed in the past decade and presented in this review have substantially expanded the information and concepts concerning the behavior of impurities and defects in A^{IV} B^{VI} semiconductors. The experiments have shown with a great degree of reliability the existence of deep localized and resonance states. New, often unexpected and unusual potentialities for controlling the properties of materials used in infrared technology, thermoelectricity, tensometry, and other fields of semiconductor technology have been discovered. Interesting hypotheses have been advanced in the field of theory, and a new approach has been developed for describing and calculating both the band structure and the localized and resonance levels.

The data presented in this review indicate the nontriviality of the problems involving impurity states in A^{IV} B^{VI} se-

miconductors. In our opinion, they convincingly substantiate the need of expanding the frontier of studies in this field. Among the first-rank problems we must include characterizing more precisely the states that arise upon doping with group-III elements, the levels involving intrinsic defects and complexes of them, and elucidating the structure of the defects responsible for any given levels. Doping with cadmium, zinc, bismuth, and other hetero- and isovalent impurities requires further experimental study. Among the pressing theoretical problems we can cite the elucidation of the genetic connection of the impurity levels with the energy bands, the mechanism of long-term relaxation, the interaction between electrons at a single impurity center, and the mechanism of superconductivity.

All the stated problems are of considerable practical, as well as scientific interest.

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