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Mercury telluride—a zero-gap semiconductor

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A review is made of the principal properties of mercury telluride which is a member of a new class of substances—zero-gap semiconductors. The factors responsible for the zero-gap state of mercury chalcogenides are discussed. It is shown that an inverted band structure is formed mainly because of relativistic corrections. Specific properties of mercury telluride are related to its zero gap, p -type electron states in the conduction band, nonparabolicity of this band, resonance impurity states, and permittivity anomalies. An analysis is made of the conditions for the appearance of a forbidden gap in mercury telluride under the influence of external factors.

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1. INTRODUCTION. ZERO-GAP STATE OF MATTER

The energy spectrum of electrons in an ideal lattice of a solid, derived in the one-electron approximation allowing for the symmetry properties of the periodic electric potential acting on electrons, represents a system of quasicontinuous bands separated by forbidden energy gaps.^[1] The dynamic properties of electrons are described by the dispersion law $E(\mathbf{k})$, where E is the energy of an electron and \mathbf{k} is its wave vector. All the electron states in the periodic potential field of a crystal are characterized by wave vectors lying inside or on the surface of a Brillouin zone which represents a region in \mathbf{k} space inside which the energy is a quasicontinuous function of \mathbf{k} . The principal physical properties of solids can usually be described on the basis of the knowledge of $E(\mathbf{k})$ in the direct vicinity of the valence band maximum and the conduction band minimum, and of the relative positions of these band extrema. If the valence band is separated by a forbidden band, which is usually called the energy gap, from an empty conduction band, the solid is an insulator. If the conduction band is partly filled or if the valence and conduction bands overlap on the energy scale, we are dealing with a metal. A semimetal is the term usually employed for a metal whose band overlap is slight and a semiconductor is an insulator whose gap is so small (less than 2 eV) that significant amounts of electrons can be transferred thermally from the valence to the conduction band.

A basically new situation appears when the band overlap in a semimetal becomes zero or when the gap in a semiconductor disappears so that the valence and con-

duction bands are just in contact. A substance with such a band structure represents a boundary between semiconductors and semimetals and is known as a zero-gap (gapless) semiconductor or a metal with a point Fermi surface. Since a zero-gap semiconductor can be converted (for example, by pressure or a magnetic field) into a material which is ordinarily a semiconductor or metal, it is sometimes more convenient to speak of the zero-gap state of matter.^[2]

The main theoretical ideas on the zero-gap state and its specific properties were developed by Abrikosov and Beneslavskii.^[3–5] They demonstrated that, in some cases, the symmetry conditions permit contact between the valence and conduction bands at one point in the \mathbf{k} space.

In the case of cubic crystals, there may be contact between several branches of the energy spectrum at a singularity and the dependence $E(\mathbf{k})$ in the vicinity of this point may be purely linear, or two bands may be in contact, one with a linear dependence and the other with a quadratic, or two bands with the quadratic dependence may be in contact. This conclusion follows from the one-electron approximation and, therefore, an additional analysis has been made of the influence of the electron-electron interaction on such an energy spectrum. It is justifiable to assume that the permittivity ϵ_0 of such a semiconductor is high and the interaction is weak, so that it can be considered by perturbation theory using the Green function of noninteracting particles as the zeroth approximation. It is then found that, in the case of semiconductors exhibiting a linear dependence $E(\mathbf{k})$, the spectrum has a slowly varying factor and the

corrections due to many-electron effects are small. In quantum electrodynamics, this situation is known as the "zero-charge" case. The situation is quite different for the quadratic dispersion law when the interaction becomes strong in the vicinity of the band contact point (this singular region is bounded by $E_s \leq m^* e^4 / 2\hbar^2 \epsilon_0^2$ on the energy scale and by $k_s \geq m^* e^2 / \hbar^2 \epsilon_0$ in the case of momentum). By analogy with quantum electrodynamics, this can be called the "tight-binding" case. The one-electron energy spectrum remains unchanged in the range of large momenta $k > k_s$ but, in the singular region, the Green function of electrons may have poles and these poles are complex with an imaginary part of the same order as the real part, i.e., in this region, the concept of quasiparticles breaks down. However, the methods employed in the theory of phase transitions^[6] can be used^[3] to find some parameters of such a zero-gap semiconductor directly from Green functions and not via the quasiparticle spectrum. Green functions and other quantities should then be sought in the form of self-similar (scaling-invariant) functions of their own arguments with power-law asymptotes. The relationship between the various power exponents is found from self-consistency requirements. In this way, only two power exponents remain unknown but it is possible to form such combinations of physical quantities which depend on these exponents that they disappear from the expressions and only the universal constants remain.

Abrikosov^[5] later used new methods of the theory of phase transitions^[7,8] in a detailed investigation of the region in the vicinity of the band contact point. He found that the effective electron and hole masses became equal in this region and that the valence and conduction bands should become "isotropic." Moreover, the singular region ($E < E_s$ and $k < k_s$) could be divided into a region with $E_1 < E < E_s$, $k_1 < k < k_s$ ($E_1 \approx 2.5 \times 10^{-4} E_s$, $k_1 \approx 1.6 \times 10^{-2} k_s$), where the electron-electron interaction was important but the spectrum was still of the single-particle type, and the region of true tight binding $E < E_1$ and $k < k_1$, where the one-electron spectrum was strongly damped. Abrikosov calculated, for both regions, the exponents in the power laws describing physical quantities.

Abrikosov and Beneslavskii^[3] obtained frequency, temperature, and other dependences of such zero-gap semiconductor properties as the permittivity, magnetic susceptibility, electronic specific heat, conductivity, and Hall coefficient. A comparison of these dependences with the behavior of the corresponding physical properties of semiconductors, metals, and superconductors shows that zero-gap semiconductors represent a basically new state of matter, which differs in its properties from those known already.

There are several substances in which the zero-gap state is stable and related to the symmetry of the crystal (these are known as the symmetry-induced zero-gap semiconductors).¹⁾ These materials crystallize in the diamond or zinc-blende structure and include gray tin (α -Sn) and mercury chalcogenides: HgTe, HgSe, and β -HgS. In these materials, the bands come into contact at the point in the Brillouin zone with the highest

symmetry and the contact is not affected by any factor that does not change the crystal symmetry. However, we must point out immediately that it has not yet been possible to observe the zero-gap state described in^[2-5] in its pure form. This is due to the fact that the properties of a substance can be governed largely by the many-electron effects near the band contact point only if the temperature of the substance is low and the substance itself is extremely pure and free of imperfections. The first condition is easy to satisfy by modern cryogenic methods. However, in the case of the second condition, we find that, for example, in the case of HgTe, the impurity concentrations have been reduced below 10^{15} cm^{-3} and the energy range $E_s \approx 10^{-3} \text{ eV} \approx E_F$ has been approached for $n_d \approx 1 \times 10^{15} \text{ cm}^{-3}$. However, the energy range $E < E_1 \approx 10^{-4} E_s$ cannot yet be attained experimentally for any of the substances in question. Nevertheless, studies of HgTe have revealed several phenomena associated with the zero-gap state and such properties of HgTe as the anomalously high electron mobility, valence band structure, behavior of impurity levels, and frequency dependence of the permittivity cannot be explained correctly at all if the electron-electron interaction is ignored.

We shall consider the specific properties of mercury telluride which is the most thoroughly investigated member of the class of zero-gap semiconductors.

2. GENERAL DESCRIPTION OF MERCURY TELLURIDE²⁾

Mercury telluride is a binary compound which is formed as a result of the interaction between equiatomic proportions of an element belonging to group II in the Mendeleev Table (mercury) and a group VI element (tellurium). Like other II-VI and III-V compounds, mercury telluride has the zinc-blende (sphalerite) structure. The zinc-blende lattice consists of two interpenetrating fcc lattices displaced relative to one another along the cube diagonal by one quarter of the length of this diagonal. This structure differs from that of diamond because the atoms in the sublattices are different and, in particular, one sublattice of HgTe contains mercury atoms and the other tellurium atoms. Mercury has two valence electrons (subshell 6s) and tellurium—six valence electrons (subshell 5s and partly filled subshell 5p); the sum of the valence electrons of two nearest-neighbor atoms is always eight. Thus, as in diamond, each atom has four valence electrons to form four valence bonds directed along the axes of a regular tetrahedron. The formation of four valence bonds requires four unpaired electrons. It follows from the Pauli principle that one of the s electrons should be transferred to a p orbital. Thus, a quadrivalent sp^3 state is formed: one valence electron is in the s state and three of them in the p state. Moreover, the differ-

¹⁾ Moreover, the transition to the zero-gap state under the action of external factors (change in composition, hydrostatic pressure, etc.) was observed experimentally in $\text{Bi}_{1-x}\text{Sb}_x$ alloys of semimetals^[2,9] and in semiconductor alloy systems $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ and $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$.^[10,11]

²⁾ A summary of the principal properties of HgTe is given in^[12].

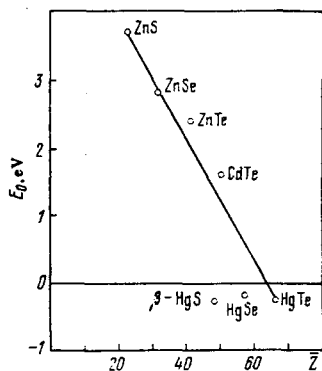


FIG. 1. Dependence of the energy gap E_0 on the average atomic number \bar{Z} of II-VI compounds with the zinc-blende structure.

ence between the charges of the atomic cores of Hg^{2+} and Te^{6+} is responsible for the mixed ionic-covalent binding in HgTe . Another important property of the zinc-blende structure, associated with the presence of two different atoms, is the absence of a center of inversion.

One of the features of mercury telluride is that considerable deviations from stoichiometry arise easily in this compound. Therefore, the properties of HgTe are largely governed by the presence of point defects which are equivalent—from the point of view of electrical properties—to atoms of foreign impurities. Mercury telluride can be obtained in *n*- and *p*-conduction forms. The donor and acceptor concentrations in HgTe are usually controlled by deviations from stoichiometry produced by heat treatments carried out at certain temperatures and mercury vapor pressures.

The understanding of the energy band structure and principal properties of mercury telluride has depended largely on the progress in the technology of preparation of this material. Single crystals are now available in which the 4.2°K electron density is $n \approx 1 \times 10^{15} \text{ cm}^{-3}$ and the mobility is $\mu_n \approx 1 \times 10^6 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{sec}^{-1}$.^[13,14]

The first measurements of the electrical properties of HgTe , carried out by Soviet scientists back in the fifties,^[15] demonstrated that the thermal width of the energy gap (forbidden band) of this compound is unusually small. In the next decade, considerable experimental material on mercury telluride and alloys based on it was accumulated in many laboratories in the world but the proposed band models failed to explain or match some of the most important properties of this compound. For example, galvanomagnetic measurements have established that the thermal gap of HgTe does not exceed several millielectron-volts. Since the effective electron mass is approximately proportional to the energy gap, this very narrow gap should correspond to a very small effective mass. However, in the case of HgTe , the mass is found to be equal to the mass of electrons in indium antimonide whose gap is $\sim 0.23 \text{ eV}$. Another unexplained observation is the mobility of electrons which is higher in alloys of mercury and cadmium tellurides (with low cadmium concentrations) than in HgTe , although disordered solid solutions have

more defects and this should reduce the mobility compared with the pure binary compound. These contradictions are removed completely by the inverted band structure model proposed by Groves and Paul^[16] to explain the properties of gray tin.

3. INVERTED BAND MODEL AND ITS APPLICATION TO MERCURY TELLURIDE

The application of the Groves-Paul model to the band structure of mercury chalcogenides was an important step forward in studies of the properties of HgTe and its alloys. The model is based on a comparison of the energy gaps exhibited at the center of the Brillouin zone Γ by isoelectronic series of III-V and III-VI semiconductors. In these semiconductors, the edges of the conduction band Γ_6 and of the valence band Γ_8 are located at the center of the Brillouin zone. The gap between them is the forbidden band width. It has been established empirically that an increase in the average atomic number of a compound \bar{Z} should result in a more or less monotonic reduction in the gap (Fig. 1). Groves and Paul^[16] postulated that, in the case of semiconductors formed from elements in the lower rows in the Mendeleev Table, the states Γ_6 and Γ_8 might not only approach each other but might be even inverted, i.e., $E_0 = E(\Gamma_6) - E(\Gamma_8)$ might become negative. However, the simple empirical law $E_0 = f(\bar{Z})$ fails to explain why $\beta\text{-HgS}$ and HgSe with $\bar{Z} = 48$ and 57 have $E_0 \approx -0.2 \text{ eV}$, whereas CdTe with $\bar{Z} = 50$ has $E_0 = +1.6 \text{ eV}$. In view of this, we have to consider in greater detail the relativistic effects in the formation of an inverted band structure and of its features in HgTe .

A. Influence of relativistic corrections on band distribution in zinc-blende semiconductors

The relativistic effects^[17,18] must be allowed for in the calculations of the energy band structure of semiconductors formed from heavy-element atoms whose nuclear charge Ze is large. These effects can be described on the basis of the relativistic Dirac equation approximated by the nonrelativistic Pauli equation. In this case, the relativistic correction to the total Hamiltonian can be expressed in the form

$$\mathcal{H}_{\text{rel}} = \mathcal{H}_D + \mathcal{H}_{m,i} + \mathcal{H}_{s-o};$$

here, \mathcal{H}_D is the Darwin correction, which is sometimes called the contact interaction operator (it governs the additional energy of the interaction of *s* electrons with the nucleus); $\mathcal{H}_{m,i}$ is the correction to the kinetic energy operator due to an increase in the mass of a particle with its velocity; \mathcal{H}_{s-o} is the spin-orbit interaction operator. The spin-orbit interaction adds a new term to the Hamiltonian, shifts the energy levels, and (a point of particular importance) splits these levels in the case of degeneracy because the states are now classified not in accordance with the orbital momentum *l* but in accordance with the total momentum *j*; the *s* states (orbital quantum number *l* = 0) remain unchanged, whereas the *p* states (*l* = 1) are split into states in which the spin is parallel (*j* = 3/2) and antiparallel (*j* = 1/2) to the or-

TABLE I. Relativistic corrections (eV) for s -type conduction band and p -type valence band at Γ in Brillouin zone of II-VI compounds with zinc-blende structure^[17] (Δ and $E_{m,i}^p$ represent spin-orbit splitting and shift due to mass increase in p state; $E^s = E_{m,i}^s + E_D$, where $E_{m,i}^s$ and E_D are displacements due to mass increase and the Darwin term for s states).

Compound	Z	Δ	E^s	$E_{m,i}^p$	Δ_{exp}
ZnS	23	0.11	-0.42	-0.07	0.072 ¹⁹
ZnSe	32	0.50	-0.63	-0.36	0.43 ¹⁹
ZnTe	41	1.06	-0.94	-0.82	0.9 ¹⁹
CdTe	50	1.09	-1.54	-0.86	0.92 ²⁰
HgS	48	0.24	-3.91	-0.26	
HgSe	57	0.63	-4.12	-0.48	0.45 ²¹
HgTe	66	1.19	-4.43	-0.86	1.08 ²²

bital momentum. The Darwin correction and that due to the dependence of the mass on the velocity have the same symmetry as the potential. Therefore, these corrections cannot split degenerate levels but simply shift them, and the shift is much greater for the valence s electrons closer to the nucleus than for the p valence electrons. The Darwin correction for the p electrons is generally zero.

The relativistic effects in crystals are allowed for in the same way as for free atoms but the central field of an atom is replaced with the periodic field of the crystal. It should be noted that in the case of II-VI compounds the conduction band state of Γ_6 -type symmetry is formed from atomic functions of the s electrons of the metal and the valence band state Γ_8 is formed from the atomic functions of the p electrons of the chalcogen. This is illustrated clearly in Table I, which shows that, for example, in the case of tellurides, the corrections Δ and $E_{m,i}^p$ to the state Γ_8 are almost unaffected, whereas the corrections to $\Gamma_8(E^s)$ increase strongly on transition from Cd to Hg because of the increase in Ze of the metal atom.

The formation of bands at the point Γ is demonstrated schematically in Fig. 2 for cadmium telluride (a) and mercury telluride (b). A comparison of the energy band structures of these two substances is justified because their lattice constants differ by less than 0.5% and the change in the energy gap due to the reduction in the interatomic distance on transition from CdTe to HgTe should not exceed 0.09 eV,^[23] so that the role of the relativistic corrections can be studied in its purest form.

If the relativistic effects are ignored, the states of the Γ_6 and Γ_8 symmetry in CdTe and HgTe are separated by approximately the same initial energy gap E_{in} . Without allowance for the spin, the state Γ_6 is nondegenerate and the state Γ_8 , formed by the p functions, is triply degenerate. In the case of CdTe, the corrections E_D and $E_{m,i}$ result in the displacement of Γ_6 and Γ_8 but their relative positions are not greatly affected. The spin-orbit interaction lifts partly the degeneracy by splitting Γ_8 into two levels: one is a doubly degenerate state Γ_8 , forming the valence bands of the heavy and light holes E_{V1} and E_{V2} , and the other is a state Γ_7 , responsible for the split-off valence band E_{V3} . The state

Γ_6 forms the conduction band E_C . The gap between Γ_6 and Γ_8 , denoted by $E_0 = E(\Gamma_6) - E(\Gamma_8)$, is the forbidden band (Fig. 2a).

The forms of the conduction band E_C and of the light-hole band E_{V2} are governed largely by the interaction between them. The intensity of this interaction is proportional to $P^2/|E_0|$ (P is the matrix element of the momentum operator representing the "interaction" between the states Γ_6 and Γ_8) and it governs the curvature of these bands and, consequently, the effective masses of the carriers in them.^[24] The valence band E_{V1} does not interact with the conduction band and only allowance for the influence of the more distant bands makes the effective masses of the heavy holes differ from the free-electron mass.

The energies E_D and $E_{m,i}$ for HgTe are considerably larger than for CdTe, so that the state Γ_6 is located much lower on the energy scale (Fig. 2b). The spin-orbit interaction, which splits the valence bands, shifts the state Γ_6 below Γ_8 . Thus, we can expect the bottom of the conduction band Γ_6 to be located below the top of the valence band Γ_8 and the conduction band to intersect two valence bands at $k \neq 0$. However, such a band distribution is impossible: states with the same momentum but with different symmetry cannot intersect. This gives rise to an inverted band structure: the band curvature changes its sign when the sign of the energy difference $E_0 = E(\Gamma_6) - E(\Gamma_8)$ between them changes; then, the state Γ_6 forms the light-hole band E_{V2} and the state Γ_8 , which interacts with the latter band, gives rise to the conduction band E_C . Since the heavy-hole band E_{V1} does not interact with Γ_8 , its curvature does not change as a result of inversion of E_{V2} and E_C . The state Γ_8 remains degenerate but it is now in contact with the heavy-hole and conduction bands, i.e., a zero-gap semiconductor is formed. The quantity E_0 , sometimes called a negative forbidden band of semiconductors with an inverted band structure, is not the forbidden band width in the generally accepted sense in solid state physics: it simply governs the interaction between the conduction and light-hole bands.

The first experimental proof of the inverted band structure of mercury telluride was obtained^[25] in hydrostatic pressure experiments based on the fact that in all the diamond or zinc-blende semiconductors the

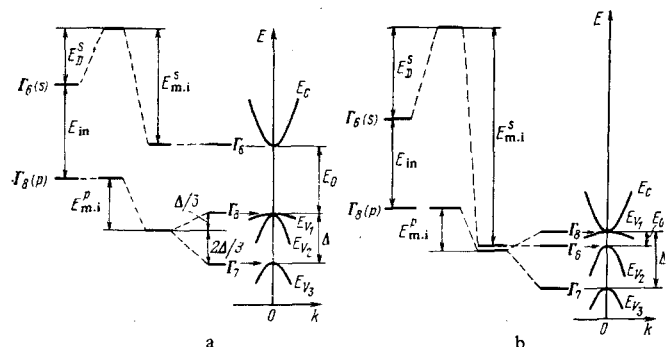


FIG. 2. Formation of energy bands at the point Γ in the case of CdTe (a) and HgTe (b).

state Γ_6 moves upward with pressure faster than Γ_8 . In ordinary semiconductors, such as CdTe and InSb, this increases the energy gap (forbidden band width). Measurements of the thermoelectric power carried out on heavily doped n -type HgTe demonstrated that this power decreased with rising pressure but the Hall coefficient and, consequently, the electron density were independent of pressure. In the case of a strongly degenerate electron gas, we have $\alpha \propto 1/E_F$ if $n = \text{const}$ and the rise of the Fermi energy can only be due to a reduction in the effective electron mass m^* . Since the matrix element of the interaction between Γ_6 and Γ_8 is approximately the same for all the zinc-blende materials, i.e., it depends weakly on the lattice constant, in the first approximation we may assume that the value of P is independent of pressure. Since $m^* \propto E_0/P^2$, the reduction in the effective mass can occur only if E_0 decreases and the fall of E_0 under the action of pressure is possible only if Γ_6 lies above Γ_8 .

Later measurements of several electrical properties and, particularly, magneto-optic experiments yielded reliable proof of the inverted band structure of HgTe.^[26,27]

Several theoretical calculations have been made of the energy band structure of HgTe and other conductors of the same class on the basis of the one-electron model. The correct energy band spectrum is obtained by modifying the calculations so as to allow for the relativistic effects. The need for this allowance is self-evident if we consider methods similar to those based on first principles, particularly the orthogonalized plane wave (OPW) method. Thus, self-consistent OPW calculations of Herman *et al.*,^[28] in which the crystal potential was formed by a spatial superposition of nonrelativistic potentials of atoms and molecules,^[29] could not even give the correct sign of the energy gap E_0 of α -Sn and mercury chalcogenides. The relativistic effects in the OPW method can be allowed for as first-order corrections to perturbation theory,^[30] but it is more correct to use the method of Soven,^[31] who calculated the energy band structure of thallium ($Z = 81$) directly from the Dirac equation. Relativistic OPW calculations of the spectra of α -Sn^[32] and mercury chalcogenides^[33] based on a similar approach gave results in good agreement with the experimental data. For example, without any empirical corrections, Pollak *et al.*^[32] used the relativistic self-consistent Liberman potentials^[34] and the exchange potential in the Kohn-Sham approximation^[35] to obtain $E_0 = -0.416$ eV for α -Sn (the experimental value was $E_0 = -0.413$ eV.^[36]).

In empirical and semiempirical methods, the reference points in the calculations are the most reliable parameters determined experimentally and, therefore, an inverted position of the Γ_6 and Γ_8 levels is regarded as an *a priori* known quantity. The freedom of choice of the adjustable parameters is frequently such that good agreement is obtained between calculations and experiment even without allowance for the relativistic effects but the mathematical procedure used to achieve this may have no physical meaning. Thus, in the method of empirically corrected OPW's proposed by Her-

man^[33,37] the nonrelativistic band structure of HgTe and HgSe, calculated from the first principles, is corrected in accordance with the experimental data on interband optical transitions. The adjustable parameters are the correction to the symmetric component of the Fourier coefficient of the crystal potential ΔV_{111} and the corrections to the energies of the core states of cations $\Delta E_{\text{c}ot}^{\text{cat}}$ and anions $\Delta E_{\text{c}ot}^{\text{an}}$. The first correction displaces the potential in the intervals between the lattice sites, whereas the second and third displace the core potentials of the indicated ions. The energy spectra of α -Sn, HgTe, and HgSe, calculated in this way, are in good agreement with the experimental results since the shift of the energy levels produced by these corrections "simulates" allowance for the relativistic effects and, at the same time, compensates simplifications of the OPW method such as the approximate nature of the exchange potential and lack of allowance for many-electron effects.

In the Green function method, whose relativistic variant was used by Overhof^[38] to calculate the band structure of HgSe and HgTe, the adjustable parameter is frequently the potential between atomic spheres V_0 , which is varied to achieve agreement between E_0^{theor} and E_0^{exp} . However, Overhof^[38] obtained the necessary value of the gap and avoided a positive V_0 by displacing the atomic s levels of HgTe, i.e., by selecting the potential V_0 to be different for the s bands and for the p and d bands.

The empirical pseudopotential (EPP) method depends even more strongly on the experimental results. In its relativistic modification, applied by Bloom and Bergstresser^[39] and by Chadi *et al.*^[40] to mercury telluride, the form factors of the pseudopotential $V^{s,A}$ are selected so as to obtain the best agreement with the experimental values of the energy gap at several points in the Brillouin zone from which the spin-orbit splittings are excluded. Then, the spin-orbit form factors are adjusted to obtain agreement with the spin-orbit splitting at the points Γ and L . The form factors obtained in this way are in good agreement with those of the model pseudopotential,^[41] where they are selected on the basis of the results of ionic spectroscopy. The model pseudopotential method, including allowance for the screening of the ionic potential in the form suggested by Penn, was also used in the calculation of the spectrum of HgTe.^[42]

All these calculation methods give a general energy band structure of HgTe along the principal symmetry axes with the same precision as for other II-VI and III-V semiconductors. Generally, the energy band structure of a zero-gap semiconductor is basically similar to the band spectrum of an ordinary semiconductor, with the exception of the vicinity of the point Γ (Fig. 3). However, as pointed out above and as will be shown specifically for HgTe in Sec. 5C, the vicinity of the contact point cannot be described by the one-electron approximation.

It is interesting to note that the inversion of the states Γ_6 and Γ_8 in mercury chalcogenides can also be demonstrated without calculation of the band structure but simply on the basis of spectroscopic parameters de-

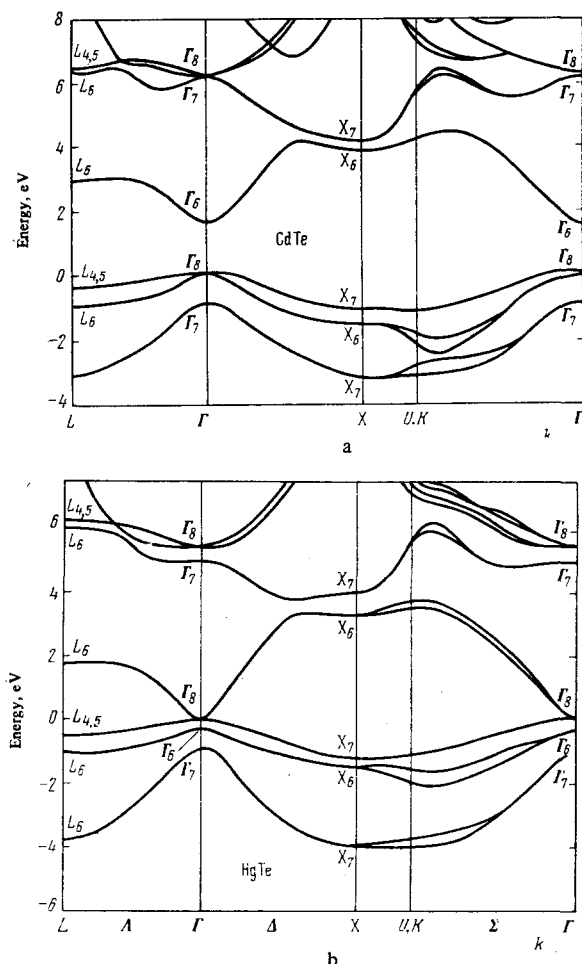


FIG. 3. Energy band structures of CdTe (a) and HgTe (b) calculated by the empirical pseudopotential method.^[40]

scribing covalent and ionic contributions to the tetrahedral bonds of these compounds.^[43] This was done in detail for $Pb_{1-x}Sn_xTe$ by Wemple,^[44] who showed that the replacement of lead with tin in this compound interchanged the role of anions and cations and that the ionicity vanished at the transition point corresponding to inversion of the states L_6^+ and L_6^- .

B. Overlap of valence and conduction bands in mercury telluride

The absence of a center of inversion from the zinc-blende structure gives rise to linear terms in $E(k)$. It follows from the perturbation theory that the corrections for terms linear in k are negligible for the states Γ_8 and their presence results in the splitting of the band maxima and their shift away from the point $k=0$. The large effective mass results in the greatest shift of the heavy-hole band E_{V_1} . In the case of InSb, the magneto-reflection measurements indicate that the maxima of the heavy-hole band are displaced and the energy shift along the $[111]$ direction, measured from the energy at the point $k=0$, amounts to about 0.1 meV, i.e., the forbidden band seems to decrease by this amount. A basically different situation appears in the case of an inverted band structure in which the heavy-hole and conduction bands are degenerate at the point $k=0$. In HgTe, the

displacement of the heavy-hole band maxima results in an overlap ΔE between E_{V_1} and E_C (Fig. 4). The maximum overlap is found along $[111]$ axes and vanishes along $\langle 100 \rangle$. The value of ΔE of mercury chalcogenides has not yet been determined by direct methods. Theoretical estimates^[38,42] give $\Delta E \approx 0.3-0.1$ meV for HgTe. An analysis of the temperature dependence of the Hall coefficient of a sample of HgTe, retaining its intrinsic conduction to the lowest temperatures (at $T=0.1^\circ K$, we have $n=p=5.7 \times 10^{14} \text{ cm}^{-3}$), is given in^[46]. The maximum possible overlap found in this way is 1.0 meV. This value of ΔE follows for the same sample also from the Shubnikov-de Haas effect.^[14] However, in the case of a sample with $n=2.1 \times 10^{15} \text{ cm}^{-3}$, the same method gives the overlap $\Delta E \approx 1.5$ meV,^[47] i.e., there is a tendency for the overlap to depend on the electron density. The hypothesis of the influence of the impurity (extrinsic) electron density on the energy spectrum of HgTe, also put forward in a different form in^[48,49], is particularly interesting because it explains the anomalously large band overlap in other mercury chalcogenides HgSe and β -HgS. These substances can be obtained only in the n -type form with electron densities of at least 10^{17} cm^{-3} in the case of HgSe and at least 10^{18} cm^{-3} in the case of β -HgS. The overlap calculated for these densities amounts to several tens of millielectronvolts,^[50,51] which cannot be attributed simply to the absence of an inversion center. Some authors^[52] put forward the hypothesis of the presence of a side valence band in HgSe and β -HgS (for example, in the vicinity of the point L in the Brillouin zone), which would give rise to an additional overlap with the conduction band. However, this band structure is in sharp contrast to the structures of all other compounds with the zinc-blende lattice and is not supported by theoretical calculations. It is more reasonable to assume that the large overlap is due to the distortion of the band structure by electrically active lattice defects, which are always present in these compounds. In fact, β -HgS is generally unstable under normal conditions (at room temperature, it can be stabilized only by introducing a large number of impurities), whereas the effective Szegedi charge of HgSe is $e_s^* = 0.76$,^[53] which is close to the ionicity maximum (0.785) above which the zinc-blende lattice loses its stability, as predicted by the theory of Phillips and Van Vechten. This assumption is also confirmed by the fact that, for the minimum donor concentration $n_d = 1.1 \times 10^{17} \text{ cm}^{-3}$, Krevs *et al.*^[54] obtained the band overlap $\Delta E = 18$ meV for HgSe, whereas Lehoczky *et*

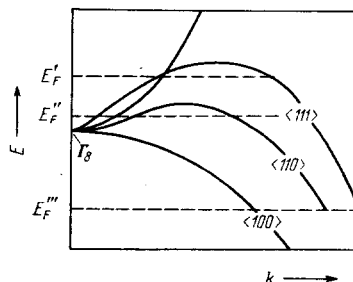


FIG. 4. Dependence $E(k)$ for the valence band of HgTe along various directions.^[45]

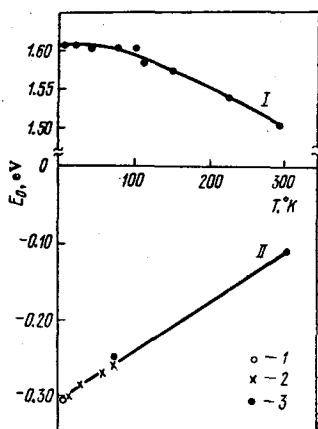


FIG. 5. Temperature dependences of E_0 of cadmium telluride (I) and mercury telluride (II). The values of E_0 for CdTe are taken from^[59]; 1) data from^[60]; 2) from^[61]; 3) from^[62].

al.^[53] found by an analogous calculation method that $\Delta E = 5.0$ meV for purer samples ($n_d \approx 3.6 \times 10^{16} \text{ cm}^{-3}$), which was close to the overlap of HgTe.

Formally, the presence of the overlap makes mercury chalcogenides semimetals. However, the negligible size of the overlap is responsible for the observation that mercury telluride has all the properties of zero-gap semiconductors. This justifies fully the classification of HgTe as a zero-gap semiconductor.^[55]

What are the most obvious consequences of the zero gap in HgTe? First of all, the temperature dependence of the intrinsic carrier density is not an activation-type law, $n_i \propto \exp(-E_0/kT)$, but is a power law, $n_i \propto T^{3/2}$. Moreover, in the case of a perfectly pure crystal at $T=0$, any electric field (no matter how weak) can transfer electrons from the valence to the conduction band, i.e., the current-voltage characteristic should not have an ohmic region.^[57] Ivanov-Omskii and his colleagues^[58] observed experimentally a steep rise of the electron density with the electric field. In particular, they established that the electric-field heating of pure HgTe crystals was, to some extent, equivalent to thermal heating. For example, in a field of 12 V/cm, the electron density in a sample at 4.2°K was the same as that in a near-zero field at 20°K.

C. Anomalous temperature dependence of energy gap E_0

The unusual temperature dependence of the energy gap E_0 in lead chalcogenides is one more consequence of the inverted band structure.

In ordinary semiconductors, where E_0 is the forbidden band, its temperature dependence is due to two factors^[11]: the thermal expansion of a crystal, i.e., the change in the lattice constant $(\partial E_0/\partial T)_\epsilon$, and the interaction of carriers with phonons $(\partial E_0/\partial T)_{ph}$. These two coefficients are negative for all zinc-blende semiconductors and the net result is $\partial E_0/\partial T < 0$ with the change in E_0 due to the electron-phonon interaction increasing with temperature. Therefore, in the range of temperatures much lower than the Debye value, the contribution $(\partial E_0/\partial T)_{ph}$ is negligibly small and E_0 varies rapidly at high temperatures. A good illustration of this depen-

dence is $E_0(T)$, reported for cadmium telluride (curve I in Fig. 5).

Mercury chalcogenides and, particularly, HgTe behave quite differently (curve II in Fig. 5). It is clear from Fig. 5 that, for these compounds, we have, first, $\partial E_0/\partial T > 0$ and, secondly, E_0 varies linearly with temperature right down to the lowest values of the latter. If we bear in mind that the lattice constant of HgTe decreases with temperature^[53] in the same way as the lattice constants of other III-V and II-VI compounds, we have to assume either the existence of a third positive term associated, like the sign of E_0 , with the relativistic effects^[23,59] or that $(\partial E_0/\partial T)$ changes sign in the case of an inverted band structure.^[26] However, since the electron-phonon interaction has almost no effect on the band curvature^[64] and, consequently, on m^* , the second hypothesis is in conflict with the temperature dependence $m^*(T)$: it follows from the experimental results^[65] that the effective mass of electrons in HgTe decreases with rising temperature.

Attempts to explain $E_0(T)$ on the basis of the Brooks-Yu theory proved fruitless^[66,59] although this theory has been applied successfully to lead telluride^[67] characterized, like HgTe, by $E_0/\partial T > 0$.

4. CONDITIONS FOR APPEARANCE OF ENERGY GAP IN MERCURY TELLURIDE. TRANSITION FROM ZERO-GAP TO ORDINARY SEMICONDUCTOR

There are several types of external factor which can alter the energy band structure of mercury telluride so as to produce an energy gap. This can be achieved without altering the crystal symmetry by reducing the relativistic effects as a result of, for example, replacement of some of the mercury atoms with a lighter element. This is observed in $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ alloys (x represents the molar percent of cadmium), which are disordered isoelectronic substitutional solid solutions at all compositions. The effects due to disorder in such alloys and, particularly, the spreading of the band edges and density-of-states tails in the forbidden band are negligible in such alloys^[68] and their properties can be described by the usual band structure models. Overhof^[38] demonstrated that the main result of the addition of CdTe is the displacement of the Γ_6 level formed by the s electrons of the metal toward higher energies. A continuous change takes place from the energy spectrum of HgTe (Fig. 2b) to that of CdTe (Fig. 2a). Measurements of the photosensitivity maximum,^[69] optical absorption edge,^[70] and Hall effect under hydrostatic pressures^[71] demonstrated that the value of E_0 varies almost linearly with the composition, passing through zero at certain temperature-dependent compositions (Fig. 6). The empirical formulas for $E_0 = f(x)$ obtained by different methods^[69-71] differ slightly from one another. A good agreement with the experimental dependences is obtained by calculating the energy band structure of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ employing the model^[42] and empirical^[73] pseudopotential methods, and the $k \cdot p$ method.^[74] Slight deviations from the linearity of $E_0(x)$, amounting to 0.1 eV for $x=0.5$,^[70] were explained^[22] by the two-band dielectric method of Van Vechten.^[68]

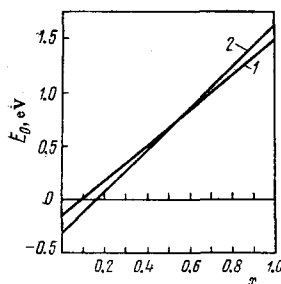


FIG. 6. Dependences E_0 on composition of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ alloys at 295°K (1) and 4.2°K (2).

Figure 7 shows schematically the changes in the band structure of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ alloys. At certain values of x , the three bands E_C , E_V , and E_{V_2} come into contact and the zero-gap (ZG) material transforms into an ordinary semiconductor (OS) (the point of contact is then described as the ZG-OS transition). For example, at 4.2°K, the variation of cadmium in the alloys from 0 to 0.155 produces a series of zero-gap semiconductors with different values of E_0 and the variation of x from 0.165 to 1.0 produces semiconductors with a forbidden band ranging from 0 to 1.6 eV. Since E_0 governs, irrespective of its sign, the form of the conduction and light-hole bands, the effective mass of electrons m_0^* tends to zero at the point of transition to two separate bands (Fig. 8).

In addition to the HgTe - CdTe alloys, there is a large number of solid solutions based on mercury chalcogenides in which a similar transition is observed (Table II). It is clear from Table II that mercury chalcogenides form solid solutions not only with group II chalcogenides but also with MnTe and $\text{III}_2\text{-VI}_3$ defect compounds. Moreover, solid solutions are also formed between mercury chalcogenides themselves^[77] (HgTe - HgSe , HgSe - β - HgS , HgTe - β - HgS). These are zero-gap semiconductors with properties intermediate between the binary compounds.

The transition from an inverted to an ordinary band structure can also be produced by hydrostatic pressure. In HgTe , as in other zinc-blende and diamond compounds, the level Γ_6 moves more rapidly under hydro-

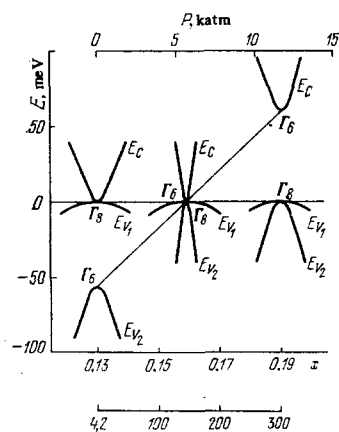


FIG. 7. Transition from zero-gap to ordinary semiconductor in $\text{Cd}_{0.13}\text{Hg}_{0.87}\text{Te}$ under the influence of hydrostatic pressure, temperature, or change in composition. All the band parameters used in the calculations were taken from^[71].

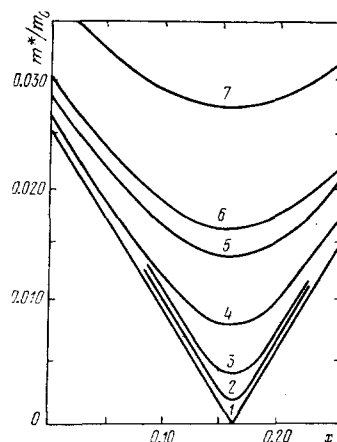


FIG. 8. Dependences of the effective mass of electrons in $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ plotted for different electron densities at 4.2°K^[76]: 1) effective mass at the bottom of the conduction band; 2) $1 \times 10^{14} \text{ cm}^{-3}$; 3) $1 \times 10^{15} \text{ cm}^{-3}$; 4) $1 \times 10^{16} \text{ cm}^{-3}$; 5) $6 \times 10^{17} \text{ cm}^{-3}$; 6) $1 \times 10^{17} \text{ cm}^{-3}$; 7) $5 \times 10^{17} \text{ cm}^{-3}$.

static pressure along the energy scale than does Γ_8 and this reduces E_0 . At sufficiently high pressures, there is an inversion of Γ_6 and Γ_8 and a forbidden band appears, i.e., hydrostatic pressure is equivalent to the formation of a $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ solid solution with increasing cadmium content (Fig. 7). In pure HgTe at 293°K, the ZG-OS transition occurs at 10 katm.^[85] In the case of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$, an increase in x causes Γ_6 and Γ_8 to approach each other and a lower pressure is needed for the same transition.^[86] However, we must bear in mind that $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ exhibits, at pressures slightly higher than those corresponding to the ZG-OS transition, a phase transition involving the transformation of the zinc-blende structure to the hexagonal cinnabar structure (for $x \leq 0.12$) or to the rocksalt structure (for $x \geq 0.12$),^[85] which may lead to an incorrect interpretation of the results.^[87]

The appearance of a forbidden band under hydrostatic pressure was also observed at 14 katm applied to a p - n junction made of $\text{Cd}_{0.11}\text{Hg}_{0.89}\text{Te}$ ($E_0 = -50 \text{ meV}$ at 77°K). The current-voltage characteristic of the junction remained ohmic in the range $P < 6 \text{ katm}$, but, at higher pressures, it became rectifying. The contact potential, equal to E_0 in p - n junctions with a degenerate electron and hole gas, increased linearly with pressure from zero at 6 katm to +70 meV at 14 katm.^[88]

The ZG-OS transition can also be observed quite

TABLE II. Alloys based on mercury chalcogenides exhibiting transition from zero-gap to ordinary semiconductor.

Material	Temperature T , °K	Composition, x	Reference
$\text{Cd}_x\text{Hg}_{1-x}\text{Te}$	292	0.08 ± 0.01	62
$\text{Zn}_x\text{Hg}_{1-x}\text{Te}$	77	0.142 ± 0.002	62
$\text{Cd}_x\text{Hg}_{1-x}\text{Se}$	300	0.07	78, 79
$\text{Cd}_x\text{Hg}_{1-x}\text{S}$	295	0.1	80
$\text{Zn}_x\text{Hg}_{1-x}\text{S}$	295	0.05	81
$\text{Mn}_x\text{Hg}_{1-x}\text{Te}$	295	0.04	81
$\text{Mn}_x\text{Hg}_{1-x}\text{Te}$	77	0.13	82
$(\text{In}_2\text{Te}_3)_x - (\text{Hg}_3\text{Te}_3)_{1-x}$	77	0.06 ± 0.02	83
$(\text{Ga}_2\text{Te}_3)_x - (\text{Hg}_3\text{Te}_3)_{1-x}$	300	0.045 ± 0.01	84

clearly in the pressure dependence of the electron mobility. At the transition point, we have $m^* \rightarrow 0$ and this should give rise to a mobility maximum. This maximum was observed experimentally by many authors.^[23,88,89,90] Brandt *et al.*^[90] found that the electron mobility at 2 °K in $\text{Cd}_{0.13}\text{Hg}_{0.87}\text{Te}$ was about $10^7 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{sec}^{-1}$ in the region of the transition.

The high positive value of the temperature coefficient of the energy gap of some compositions may increase the temperature of the ZG-OS transition (Fig. 7). This was observed experimentally by Groves *et al.*^[91] in an investigation of the interband magnetoabsorption of $\text{Cd}_{0.16}\text{Hg}_{0.84}\text{Te}$. At 25 °K, this alloy had $E_0 \approx -0.01 \text{ eV}$ and $\Gamma_8 - \Gamma_8$ transitions were observed between the valence and conduction bands across the zero-width forbidden band. At 90 °K, this alloy was characterized by $E_0 \approx +0.01 \text{ eV}$ and $\Gamma_8 - \Gamma_8$ transitions occurred across this gap.

The forbidden band of HgTe behaves in a basically different manner when this material is subjected to uniaxial compression. This is due to the fact that anisotropic deformation disturbs the symmetry of the cubic crystal and this lifts the band degeneracy at the point Γ_8 .^[92] In ordinary semiconductors such as InSb, this results in the splitting of the light-hole from the heavy-hole band whereas, in semiconductors with an inverted band structure, the conduction band is split off, i.e., an energy gap forms. This effect was observed by Roman and Ewald,^[93] who investigated transport phenomena in $\alpha\text{-Sn}$ under uniaxial compression. When the load was increased, the temperature dependence of the Hall coefficient changed from $R_H \propto T^{-3/2}$ to a steeper characteristic $R_H \propto T^{-3/2} \exp(\Delta E_0/k_B T)$, where E_0 is the gap produced by deformation (in the case of $\alpha\text{-Sn}$ and HgTe, the electron mobility is much higher than the mobility of holes, so that, in the intrinsic conduction region, we have $R_H = -1/en_i$). A similar dependence may be expected for HgTe, with the exception of very low pressures when the influence of the valence and conduction bands may be manifested.

The forbidden band of HgTe may also appear in a quantizing magnetic field. Quantization of the orbital motion of electrons splits the energy bands with quasi-continuous level distributions into magnetic Landau subbands or levels. The separation between them is equal to the cyclotron energy $\hbar\omega_c$, where $\omega_c = eH/m^*c$. The zeroth Landau level in the conduction band is then located above the bottom of the band (measured in the absence of the magnetic field) and the separation is $\hbar\omega_c/2$ (similarly, the zeroth level in the valence band drops below the top of this band). Moreover, a magnetic field lifts the spin degeneracy and each Landau level splits into two sublevels separated by $g\mu_B H$ on the energy scale; here, g is the spectroscopic splitting factor and μ_B is the Bohr magneton. In comparison with the orbital splitting, it is better to express the spin splitting energy as $\hbar eH/m^*c$, where m^* is the spin effective mass of carriers. The bottom of the band may rise or fall in a magnetic field, relative to its position in $H = 0$, depending on the ratio of the spin and orbital effective masses.

In the case of HgTe, we have $m^s > m^*$ but we must bear in mind that the conduction and valence bands are degenerate at the Γ_8 level and, in the case of Landau levels with small quantum numbers, the Luttinger effects (called, not quite correctly, the quantum effects)^[94] become decisive. In the case of degenerate valence bands in Ge and InSb, they produce nonequidistant magnetic subbands of the heavy and light holes which are then difficult to distinguish, whereas, in the case of HgTe, it is not even clear which levels belong to the conduction band and which to the valence band, and whether a gap forms. The exact position of the Landau levels in HgTe were calculated by Zawadzki and Kowalski^[95] on the basis of the Luttinger method^[94] allowing for all the features of the inverted band structure. Zawadzki and Kowalski established that the application of a quantizing magnetic field to HgTe lifted the bottom of the conduction band and depressed the top of the valence band, producing an energy gap (Fig. 9) but its value was found to be considerably less than one would have expected on the basis of the simple quantum theory of nondegenerate isotropic bands. The experimental manifestation of a gap in a magnetic field was reported for HgTe by Girit *et al.*,^[96] who observed a low-temperature exponential rise of the longitudinal magnetoresistance when the magnetic field was increased sufficiently. This effect was attributed to a reduction in the intrinsic carrier density on the appearance of a gap.

An energy gap produced by a magnetic field is reduced by an electric field. Since an electric field applied normally to a magnetic field shifts the band edges in the opposite direction, it follows that the gap may disappear for certain values of the magnetic and electric fields.^[96b,97]

All the external agencies described above transform a zero-gap semiconductor into an ordinary one. Recently, Liu and Leung^[98] predicted a transition of a zero-gap semiconductor to a semimetallic state under the action of uniaxial tension. In this case, the conduction band moves faster along the energy scale than does

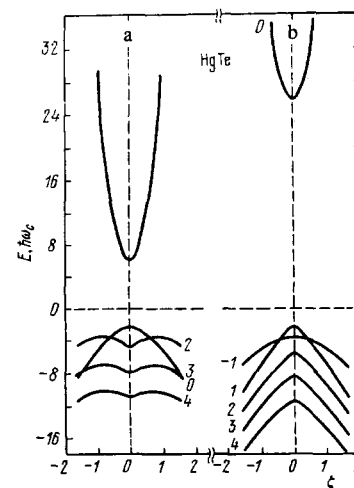


FIG. 9. Landau levels and formation of an energy gap in HgTe.^[95] Series: a) $m, j = 3/2, -1/2$; b) $m, j = 1/2, -3/2$.

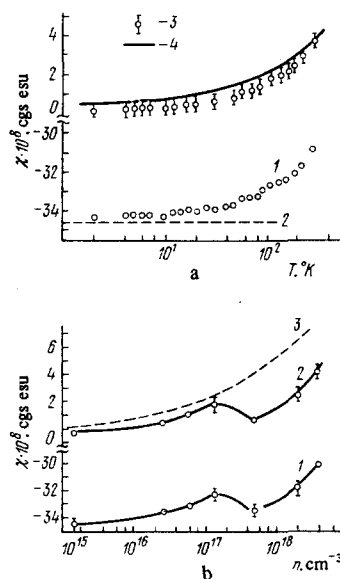


FIG. 10. a) Temperature dependences of the specific magnetic susceptibility^[101]: 1) experimental susceptibility χ_{exp} ; 2) lattice susceptibility χ_{latt} ; 3) electron susceptibility $\chi_{\text{exp}} - \chi_{\text{latt}}$; 4) theoretical electron susceptibility. b) Dependences of the specific magnetic susceptibility on the electron density^[101]: 1) experimental susceptibility; 2) electron susceptibility; 3) theoretical electron susceptibility.

the valence band and this should result in the overlap and distortion of the energy bands.

5. CHARACTERISTICS OF CONDUCTION AND VALENCE BANDS OF MERCURY TELLURIDE

A. *p*-Type nature of electron states in conduction band

Some of the specific properties of HgTe are observed because the conduction band of this compound is not formed from the *s* functions, as in ordinary zinc-blende semiconductors, but from the *p* functions and has the Γ_8 symmetry. The magnetic susceptibility of carriers is particularly sensitive to the band origin. It has been established^[99] that in a band formed from the *s* functions the carriers are always diamagnetic, whereas in a band formed from the *p* functions the carriers may be diamagnetic or paramagnetic, depending on the interaction with other bands.

Detailed investigations of the magnetic susceptibility of mercury telluride were reported in^[100-102]. Measurements of the temperature and composition dependences of the magnetic susceptibility of HgTe and suitable extrapolations were used to find the lattice susceptibility. This susceptibility was diamagnetic, as in the case of other II-VI compounds, and it obeyed the empirical dependence $\chi_{\text{latt}} \propto Z$. Since the lattice susceptibility was almost independent of temperature and electron density, and the contribution of holes could be ignored because of their large mass, subtraction of the lattice component from the measured susceptibility should give the susceptibility of the electron gas (Fig. 10). It was established that, throughout the investigated range of temperatures and densities, the electron gas was paramagnetic, which was possible only in the case

of an inverted band structure. A comparison of the magnetic properties of HgTe and *p*-type InSb demonstrated^[102] that the behavior of the magnetic susceptibilities of electrons in HgTe and light holes in InSb was similar, which confirmed the identity of the symmetry of the E_C band of HgTe and of the E_{v2} band of InSb.

Another consequence of the *p*-type nature of the conduction band is its anisotropy. The conduction band of ordinary semiconductors is isotropic at the point Γ in the limit $k \rightarrow 0$. The anisotropy only appears for large values of *k* when the *p* functions become mixed with the *s* functions.^[103]

The anisotropy of the Γ_8 conduction band was observed experimentally for α -Sn^[104] and HgSe.^[105] This anisotropy is slight and it is not possible to reveal it by such a classical method as the dependence of the magnetoresistance on the angle between electric and magnetic fields.^[19] A much more sensitive method is the angular dependence of the Shubnikov-de Haas oscillations. This method was used by Galazka *et al.*^[105] in determining the anisotropy parameter of HgSe and the influence of the conduction band occupancy on this parameter. They established that the anisotropy and its dependence on the electron density indicated that the conduction band had the symmetry Γ_8 .

Attempts to detect a similar anisotropy in the case of HgTe were unsuccessful; conversely, several authors^[90, 106, 107] stressed that the Shubnikov-de Haas oscillations in HgTe and $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ were independent of the direction between the magnetic and electric fields. The cause of this was difficult to identify because the theoretical calculations^[72] predicted this anisotropy.

The symmetry of the conduction band affected also the electron mobility. It was thus found^[108] that the experimental value of the low-temperature Hall mobility in pure HgTe crystals was almost an order of magnitude higher than the theoretical value calculated on the assumption that the electrons were scattered by the Coulomb potential (ionized impurities or holes) allowing for the Brooks-Herring screening of the scattering centers. The agreement with the theory was improved^[109, 110] when allowance was made for the angular dependence of the probability of the scattering of electrons belonging to the band formed by the *p* functions. In this band, the scattering through large angles is less and, therefore, when the band occupancy is low, the mobility of electrons is almost twice as high as in the band formed from the *s* functions.

The role of the scattering of electrons by phonons increases with rising temperature. A theoretical calculation shows^[111] that, in the case of an inverted band structure, the mobility, limited by the scattering on polar optical phonons, also increases by a factor of 2 if we allow for the nature of the conduction-band wave functions. In the case of the band with the Γ_8 symmetry, the interaction of electrons with acoustic phonons also changes,^[112] but the influence of this change on the net mobility is slight because the acoustic scattering mechanism is not very effective in HgTe.^[108]

B. Conduction band nonparabolicity and spin properties of electrons

We have mentioned that the gap E_0 governs the interaction between the bands E_C and E_{V_2} . Since the absolute intensity of this interaction is independent of the sign of E_0 , the Kane theory^[24] developed for the bands of indium antimonide is fully suitable for HgTe and its alloys. When the Kane theory is used in the two-band approximation, i.e., when the energy of the spin-orbit interaction is $\Delta \gg E_0$, kP , and the interaction with the distant zones is ignored it gives the following analytic expression for the conduction band:

$$E_C = \frac{\hbar^2 k^2}{2m_0} + \frac{1}{2} \left(|E_0| + \sqrt{|E_0|^2 + \frac{4}{3} 8P^2 k^2} \right).$$

It is clear from the above expression that the conduction band is parabolic, i.e., that $E \propto k^2$, only near the bottom of the band for small values of the wave vector $kP \ll E_0$. As k rises, the conduction band becomes nonparabolic: its curvature decreases and the effective mass of electrons rises. Applying the standard expression for the effective mass

$$\frac{m^*}{m_0} = \frac{\hbar^2}{m_0} \left(\frac{1}{k} \frac{\partial E}{\partial k} \right)^{-1}$$

and replacing P with its energy equivalent $(2m_0/\hbar^2)P^2 = E_p$, we obtain the following formula for the effective mass in a nonparabolic band:

$$\frac{m^*}{m_0} = \left[1 + \frac{2}{3} \left(\left| \frac{E_0}{E_p} \right|^2 + \frac{4\hbar^2 k^2}{3m_0 E_p} \right)^{-1/2} \right]^{-1}.$$

If the electron gas is degenerate (n -type zero-gap semiconductors are practically always degenerate), the measured quantity is the effective mass corresponding to the Fermi energy.

If $k=0$, we obtain the following formula for the effective mass of electrons at the bottom of the conduction band:

$$\frac{m_0^*}{m_0} = \left(1 + \frac{2}{3} \left| \frac{E_p}{E_0} \right| \right)^{-1}.$$

In the case of a degenerate gas and spherical constant-energy surfaces, the value of k corresponding to the Fermi level is $k_F = (3\pi^2 n)^{1/3}$, where n is the electron density. We can use this expression to find the relationship between the effective mass and electron density. Numerous investigations of the reflection,^[113] magnetoreflexion,^[114] thermoelectric power in classically strong magnetic fields,^[115] and Shubnikov-de Haas oscillations,^[116] carried out on n -type HgTe crystals in a wide range of carrier densities and temperatures, have shown that the dependence of the effective mass m^* on the electron density is in good agreement with the two-band Kane model in the range of energies extending to at least 0.25 eV above the bottom of the conduction band. By way of example, Fig. 11 shows the theoretical dependence and the values of the effective mass deduced from the reflection measurements.^[113]

Investigations of the nonparabolicity of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$

alloys are of special interest. Here, in the region of the ZG-OS transition, we have the limiting case of the Kane model: the conduction band energy is an almost linear function of the wave vector, the effective mass at the bottom of the conduction band tends to zero, and the effective mass at the Fermi level depends particularly strongly on the electron density (Fig. 8). Experimental determinations of the dependence $m^*(n)$ ^[115-117] confirmed that the Kane model was also applicable to this case. The details of the behavior of the electrons in the $E_0 \rightarrow 0$ limit were discussed by Tal'yanskii.^[118]

An important parameter representing the effects associated with the shift and splitting of the energy levels in the presence of a magnetic field is the g spectroscopic splitting factor of electrons. The spin-orbit interaction can result in a large deviation of the g factor of electrons in a solid from the g factor of free electrons, which is 2. Like the effective mass, the g factor is governed mainly by the intensity of the interaction between the bands E_C and E_{V_2} and, in the case of nonparabolic bands, it is a function of k . The following expression for the g factor was obtained for semiconductors with an inverted band structure by Kacman and Zawadzki^[119,120]:

$$g(k) = 2 \left[1 - \left(\frac{m_0}{m^*} - 1 \right) \frac{\Delta}{3E(k) + 2\Delta} \right].$$

This expression differs from $g(k)$ for an ordinary InSb-type semiconductor because it does not contain the energy gap so that the spin-orbit interaction has less influence on the g factor and, if the band occupancy is low, $E(k)=0$, this factor is independent of Δ . In the case of a nonparabolic conduction band, the separation between the Landau levels and their spin splitting decreases with increasing number of the levels. In the region of the ZG-OS transition in sufficiently pure samples, the g factor reaches anomalously high values (Fig. 12), which—in combination with the small effective mass of electrons—make $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ an extremely convenient material for investigating quantum transport phenomena^[126,127] and of spin, cyclotron, and mixed resonances.^[125]

The above expression for $g(k)$ is based on the Yafet theory,^[128] which makes exact allowance for the interaction between the three bands (Γ_8 , Γ_6 , and Γ_7) and ignores the interaction with all the other bands. Therefore, this theory is most appropriate for the description

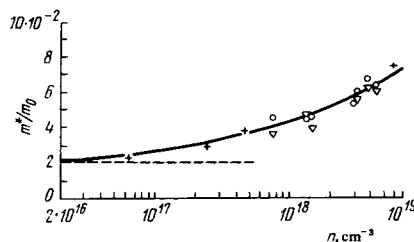


FIG. 11. Dependence of the effective mass of electrons in HgTe on their density at 300°K.^[112] The continuous curve represents calculations based on the two-band Kane theory and the symbols are the experimental values.

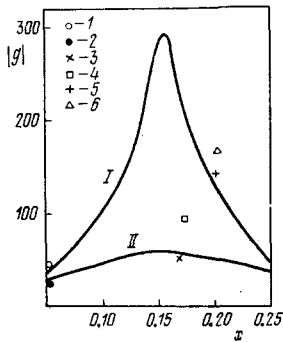


FIG. 12. Dependences of the $|g|$ factor of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ on the composition for different electron densities: I, II) theoretical dependences for densities of 1×10^{15} and $1 \times 10^{17} \text{ cm}^{-3}$, respectively; experimental results for samples with different densities (cm^{-3}): 1) 2×10^{15} from [121]; 2) 3.5×10^{17} from [122]; 3) 1.2×10^{17} from [123]; 4) 1.5×10^{15} from [124]; 5) 2.3×10^{15} from [106]; 6) 9×10^{14} from [125].

of the Landau levels with high quantum numbers and of samples with high carrier densities, i.e., in those cases when the nonparabolicity is considerable. As pointed out earlier, the Luttinger effects associated with the degeneracy of Γ_8 are decisive in the case of the Landau levels with low quantum numbers in pure samples and the nonparabolicity can then be ignored. Guldner *et al.* [60] investigated the interband absorption in HgTe with $n = 4 \times 10^{15} \text{ cm}^{-3}$ and found that the transitions between the zeroth and first Landau levels were described best by the Luttinger theory, [54] whereas the energies of the transitions between the levels with $N \geq 2$ were described better by the three-band model. [119, 120, 128]

A more correct approach is simultaneous allowance for the nonparabolicity and Luttinger effects, proposed by Pidgeon and Brown [129] for the description of magnetic levels in p -type InSb and applied subsequently to HgTe [14, 26] and $\alpha\text{-Sn}$. [36] However, analytic expressions are not then used and calculations are made by numerical methods on a computer.

C. Valence band structure

The principal properties of HgTe , associated with the conduction band features, are relatively well understood and explained whereas final conclusions cannot yet be drawn for the valence band.

We may assume that the heavy-hole band of HgTe is of the same form as in InSb (Fig. 4). In this case, the constant-energy surfaces (Fermi energy E_F') of samples with low hole densities are ellipsoids oriented along the [111] axes. An increase in the density of these holes gradually enlarges these ellipsoids so that a concave surface with unfilled states is formed at low values of k (Fermi energy E_F'). Finally, at high densities (Fermi energy E_F''), the constant-energy surfaces are deformed spheres, as in p -type Ge . Basically similar results were also obtained in an investigation of the lattice thermal conductivity of p -type HgTe . [45] However, the results reported in [45] could not be interpreted unambiguously. In particular, they could be explained not only by a complex

valence band but also by the formation of an impurity band merging with the valence band at sufficiently high acceptor concentrations. Clearly, the analogies with the valence bands of III-V semiconductors are valid only in the range $E \geq E_F''$. At these high concentrations ($p_a = 10^{18} - 10^{19} \text{ cm}^{-3}$), Ivanov-Omskii *et al.* [131, 132] determined the optical effective mass of holes $m_p^{op} \approx 0.6m_0$ and the effective density-of-states mass $m_p \approx (0.4 - 0.6)m_0$. These values were close to the corresponding values of m_p in III-V compounds. [133]

In an analysis of the structure of the valence band at lower energies, one has to allow for the fact that, in the case of HgTe , we have, at the point Γ_8 , not two degenerate fully occupied valence bands, separated by E_0 from the conduction band, but the valence and conduction bands which can be regarded as a half-filled band. In this case, terms linear in k appear in the electron and hole spectra even in the one-electron approximation when allowance is made for the exchange interaction. [134, 135] However, the electron spectrum is then modified in the range $E < E_s$ and $k < k_s$, whereas, in the case of holes, allowance for the actual relationship between the effective masses in the bands $m_p > m^*$ makes the many-electron effects important even for $E \approx E_p \approx (m_p/m^*)E_s$ and $k \approx k_p \approx (m_p/m^*)k_s$. [136] In the range $E \ll E_p$ and $k \ll k_p$, the electron-electron interaction becomes decisive and the heavy-hole band is a linear function of k . In contrast to terms linear in k , associated with the absence of a center of inversion in HgTe (Fig. 4), the linearity due to many-electron effects is isotropic; moreover, if the overlap is

$$\Delta E < \left(\frac{3\pi}{32} \right)^2 \frac{m_p e^4}{\epsilon_s^2 \hbar^2}.$$

the electron-electron interaction destroys the overlap. [135]

It has been established that many-electron effects are retained in the temperature range $k_B T \ll E_p = (m_p/m^*)E_s$. Consequently, instead of $n_i \propto T^{3/2}$, we find that, in this range, the temperature dependence of the intrinsic carrier density is $n_i \propto [T \ln(T/E_s)]^{3/2}$.

Since $m_p/m^* \geq 20$ for HgTe , approximate estimates indicate that, in the case of holes, the singular region of mercury telluride is limited to the density range $p_a < 10^{17} - 10^{18} \text{ cm}^{-3}$. Unfortunately, the effective mass of holes in the range $p_a < 10^{18} \text{ cm}^{-3}$ is not known although an investigation of this mass would provide the most direct confirmation of the conclusions reached in [135, 136].

6. IMPURITY STATES IN MERCURY TELLURIDE

The possible energies of impurity states in a zero-gap semiconductor should lie in the continuous spectrum of the allowed states of the conduction or valence band. This was first pointed out by Liu and Brust. [137] This situation is not basically new in the physics of semiconductors. States degenerate with the conduction band, also called resonance states, [138] appear in the case of transition metal impurities in II-VI compounds [139] and in the case of impurities associated with the side minima in the Brillouin zone. [140]

Initially, the experimental results were interpreted on the basis of the *a priori* assumption that donors and acceptors in HgTe and $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ were ionized at any temperature or concentration. This has been justified for a long time but as the technology of crystal preparation has improved, it has become possible to investigate purer samples. This has led to the discovery of anomalies which may have been due, *inter alia*, to complex behavior of impurities. Several empirical models of the impurity states have been developed but the first theoretical investigation of this subject was that of Gel'mont and D'yakonov.^[141] They established that, in a real spectrum of a zero-gap semiconductor such as HgTe, in which the effective electron mass m^* was much greater than the hole mass m_p , the spreading of the donor levels exceeded their ionization energy so that there was no localization of impurity electrons at the donor centers. Thus, donors are always ionized and even at $T=0$ the density of free electrons is equal to the donor concentration. Donors may become deionized only on the application of uniaxial compression, i.e., when a forbidden gap appears.^[93] Acceptors behave differently. If $m^* < m_p$, the presence of an acceptor gives rise to fairly sharp peaks in the density of states at energies which correspond to discrete acceptor levels in an ordinary *p*-type semiconductor and these peaks (acceptor levels) lie within the range of allowed states in the conduction band and become quasilocal. The relative width of such levels is proportional to $(m^*/m_p)^{3/2}$ and the ground-state energy is of the order of the Bohr energy of a hole. Thus, in the case of HgTe, the ground-state energy of an acceptor is much greater than E_g and the characteristic length of a change in the acceptor wave function (Bohr radius of a hole) is short compared with the Bohr radius of an electron. Therefore, the one-electron approximation used in^[141] is quite suitable for the calculation of acceptor levels. Allowance for many-electron effects^[135] does not alter basically the general pattern but simply reduces the ionization energy of acceptors from 6 to 2 meV. The electron-electron interaction has a considerable influence on the position and width of higher excited acceptor levels whose Bohr radius is comparable with the Bohr radius of an electron.

The presence in the conduction band of acceptor levels with a finite ionization energy should give rise to some singularities of the transport effects in HgTe. For example, if there are no donors, intrinsic conduction in HgTe appears at lower temperatures than does extrinsic conduction since the forbidden band width is zero and intrinsic carriers appear earlier than holes associated with acceptors, whose ionization requires a thermal energy of the order of the energy of the ground state of the level. If acceptors are present, the low-temperature conduction in HgTe is of *n*-type irrespective of the donor and acceptor concentrations. When the temperature is increased, ionization of an acceptor level begins and compensation takes place; in a certain range of temperatures, the free electron density decreases with rising temperature because of the capture of electrons by acceptors. This was observed experimentally by Neifel'd *et al.*,^[142] who used the position

of a minimum of the dependence $n(T)$ in estimating the ground state energy of an acceptor $E_a = 2.4 \pm 0.3$ meV and found this value in good agreement with the theory.^[141]

The existence of resonance states in the conduction band of mercury telluride was demonstrated most convincingly in magneto-optic experiments.^[143,144] Investigations of the magnetoabsorption in *p*-type HgTe at 4.2°K ^[143] revealed not only the oscillations associated with $\Gamma_6 - \Gamma_8$ interband transitions but also peaks identified as transitions from the zeroth Landau level in the light-hole band to discrete acceptor levels lying 0.7 and 2.2 meV above the top of the valence band. A level with an ionization energy of 0.7 meV was also discovered in an investigation of the $\Gamma_6 - \Gamma_8$ interband magnetoabsorption.^[144]

The results of investigations of transport phenomena in *p*-type HgTe are not so unambiguous. Many authors^[15,62,145-147] discovered nonmonotonic variations in the temperature dependences of the Hall coefficient, electrical conductivity, and Hall mobility of electrons in pure samples of HgTe, in conflict with the classical theory predicting a uniform variation of these quantities. We may assume that at low temperatures, when the intrinsic carrier density is low, the Fermi level E_F lies below the acceptor levels. When the temperature is increased, the carrier density rises and the Fermi level shifts deeper into the conduction band. When this level coincides with an acceptor level ($E_A = E_F$), resonant scattering of electrons takes place and this reduces their mobility. If we know the energy band parameters of HgTe, we can calculate the position of the Fermi level at temperatures at which these anomalies are observed and thus find the depth of the acceptor level. Finck *et al.*^[147] obtained in this way the values $E_{a1} = 2.25$ meV and $E_{a2} = 9.5$ meV. Ivanov-Omskii *et al.*^[148] investigated the dependences of the conductivity of HgTe on the electric field and found regions where the rise in conductivity with the field slowed down. They estimated the average energy of electron overheating at which this effect was observed (~ 4 meV) and attributed it to the fact that, in this case, the electron energy was equal to the ionization energy of acceptor levels, which resulted in resonant scattering of electrons. One should add that Walukiewicz^[149] suggested that nonmonotonic variations of the transport coefficients were due to resonant scattering of electrons by optical phonons.

Interesting results were obtained in investigations of zero-gap *p*-type $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ alloys in a wide range of hydrostatic pressures.^[90,150] It was established^[90] that an acceptor level spread into an impurity band at acceptor concentrations of the order of 10^{17} cm^{-3} . An increase in pressure altered the band spectrum (Fig. 7) but the acceptor band linked to the heavy-hole band was not displaced, whereas the conduction band shifted upward. The overlap of the conduction and impurity bands then disappeared and, at sufficiently high pressures, the samples behaved as ordinary semiconductors with an impurity hole band.

One should point out, however, that the results obtained by various authors differ considerably. For example, according to the results reported in^[147], the

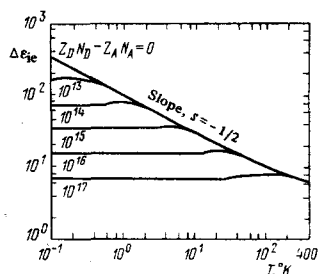


FIG. 13. Temperature dependences of $\Delta\epsilon_0$ of α -Sn plotted for various donor concentrations.^[164]

ionization energy of the acceptor levels increases strongly with the cadmium concentration in the above system of alloys, reaching its maximum for compositions corresponding to the ZG-OS transition, whereas, according to^[90], the depth of the acceptor level was independent of x in the investigated range of compositions ($0.10 \leq x \leq 0.13$). Finally, many features exhibited by p -type zero-gap semiconductors were discovered^[151,152] in investigations of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ samples with $x = 0.20$ – 0.23 , in which the forbidden band reached 120 meV. Clearly, progress in the understanding of impurity states in HgTe and $\text{Cd}_x\text{Hg}_{1-x}$ will largely depend on the completeness and correctness of allowance for certain factors in the interpretation of the experimental results; these factors include the actual origin of impurity states,³⁾ macro- and microinhomogeneities specific to $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$, the possibility of the appearance of surface inversion layers,^[153] and the presence of additional types of carrier, such as heavy electrons in an impurity acceptor band.^[154,155]

7. PERMITTIVITY OF MERCURY TELLURIDE

One of the aspects of the energy band structure of HgTe is its stability at low temperatures in samples with low impurity concentrations because the Coulomb attraction of electrons and holes between bands that are not separated by an energy gap may destabilize the ground state of the system, giving rise to bound electron-hole pairs. If the exciton binding energy is $E_B > k_B T$, a new state of matter, known as the exciton insulator, may be observed.^[134,156,157]

The formation of the exciton insulator phase was first observed experimentally in $\text{Bi}_x\text{Sb}_{1-x}$ alloys by Brandt *et al.* (see^[2,61]). The question of the existence of such a phase in HgTe has not yet been answered, in spite of a large number of theoretical investigations of this problem.^[156–161] However, it is clear that the Coulomb interaction between electrons and holes in HgTe is weakened considerably by the static permittivity anomaly^[162] associated with the many-electron effects.

The static permittivity of zero-gap semiconductors is a function of the wave vector k and it can be represented as the sum of three terms:

$$\epsilon_0(q) = \epsilon_{ia}(q) + \epsilon_{ie}(q) + \Delta\epsilon_{ie}(q).$$

The first term $\epsilon_{ia}(q)$ is due to intraband transitions. It vanishes in the absence of free carriers. The term $\epsilon_{ie}(q)$ is related to all the interband transitions, with the exception of $\Gamma_8 \rightarrow \Gamma_8$. In the limit $q \rightarrow 0$, it tends to a constant value. Ordinary semiconductors are characterized by permittivities with just the first two terms. The correction $\Delta\epsilon_{ie}(q)$ is due to transitions from the valence to the conduction band, both of which belong to the same Γ_8 state in HgTe. Liu and Brust^[162] demonstrated that, in the case of a perfectly pure zero-gap semiconductor, this term diverges: $\Delta\epsilon_{ie}(q) \propto q^{-1}$ at $T = 0^\circ\text{K}$ in the limit $q \rightarrow 0$. Extrinsic carriers^[163] and rising temperature^[164] remove this divergence. Nevertheless, it is clear from Fig. 13 that this term can make a considerable contribution to the total permittivity of sufficiently pure samples at low temperatures. Since the exciton binding energy is given by $E_B \propto 1/\epsilon_0^2$, allowance for the permittivity anomaly shifts the formation of the exciton phase to temperatures not attainable in practice (Fig. 14). However, we must bear in mind that all the calculations of the permittivity of zero-gap semiconductors were made in the random phase approximation^[166] and Abrikosov^[136] showed that this approximation was inapplicable in the tight-binding range ($k \ll k_*$, $E \ll E_*$). Therefore, the calculated results plotted in Fig. 14 should be regarded as tentative because it is not yet known how $\epsilon_0(k)$ behaves at very low temperatures. Experimental investigations^[46] of the transport properties of HgTe with $n = p = 5.7 \times 10^{14} \text{ cm}^{-3}$ showed that, at least down to $T \approx 0.1^\circ\text{K}$, there was no transition to the exciton phase in the form predicted by Sherrington and Kohn.^[156] The anomalous magnetism^[101] observed in pure samples at 10–30°K is attributed in^[161,162] to the appearance of a mixed triplet and singlet phase of an exciton insulator. However, a more convincing explanation is provided by Ivanov-Omskiĭ *et al.*, who attributed the anomalous magnetism to the paramagnetism of electrons at acceptor levels which become ionized in the same temperature range.

The permittivity anomaly predicted by Liu and Brust^[162] affects the low-temperature electron mobility. The predominant scattering mechanism at low temperatures is that due to the screened Coulomb potential for which the electron mobility is $\mu_n \propto \epsilon_0^2$. The use in calculations of the value of ϵ_0 , depending on the carrier density,^[163] and allowance for other special features

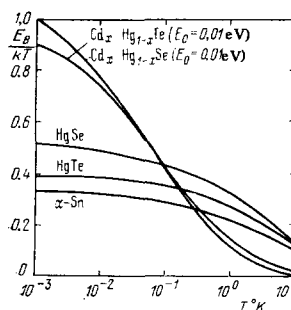


FIG. 14. Temperature dependences of the exciton binding energy in zero-gap semiconductors.^[165]

³⁾It is known that p -type conduction in HgTe may be due to group II elements (copper, silver, and gold) or to mercury vacancies.

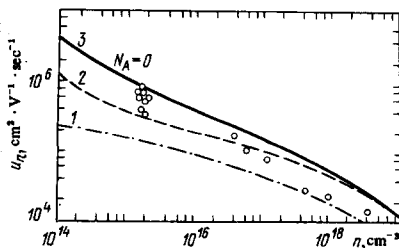


FIG. 15. Dependences of the mobility of electrons in HgTe at 4.2°K on their density: 1) without allowance for the anomaly of ϵ_0 and symmetry of the Γ_8 band; 2) with allowance for the symmetry of Γ_8 but without allowance for the anomaly of ϵ_0 ; 3) with allowance for the symmetry of Γ_8 and the anomaly of ϵ_0 [110]; the circles are the experimental data from [108].

of the conduction band explains the anomalously high mobility in pure HgTe at low temperatures and the nature of the density dependence $u_n(u)$ [109, 110] (Fig. 15). If allowance is made for the angular dependence of the probability of electron scattering and for the permittivity anomaly, the theoretically calculated mobility in HgTe with $n = 1.6 \times 10^{15} \text{ cm}^{-3}$ is found to be an order of magnitude higher than the value obtained by the classical Brooks-Herring method and it fits well the experimental data from curve 3 at high densities is clearly due to the compensation of the samples. Curve 3 is calculated on the assumption that there is no compensation ($N_A = 0$). Moreover, an increase in the permittivity should result in damping of helicon waves in zero-gap semiconductors by an amount two orders of magnitude less than in ordinary semiconductors. [109]

It is interesting to note that, since the anomaly $\epsilon_0(q)$ is associated with the band degeneracy at the point Γ_8 , it disappears under the action of external agencies, such as uniaxial compression [109] or magnetic field, [170] which lift this degeneracy. In the latter case, the field dependences of the magnetoresistance should have a region with $\omega\rho \propto H^{1.0}$, which is due to a change in the type of screening potential under the action of a magnetic field. [170]

The absence of a forbidden band also gives rise to anomalies of the high-frequency permittivity. [165, 171, 172] In the far infrared, the complex permittivity can be expressed in the adiabatic approximation⁴⁾ as follows

$$\epsilon(\omega) = \epsilon_{ph}(\omega) + \epsilon_{ia}(\omega) + \epsilon_{ie}(\omega) + \Delta\epsilon_{ie}(\omega);$$

here, $\epsilon_{ph}(\omega)$ is the phonon contribution to the permittivity and the second term $\epsilon_{ia}(\omega)$ is associated with intraband transitions of free carriers. The permittivity of ordinary semiconductors has only one term associated with interband transitions $\epsilon_{ia}(\omega)$, which tends to a constant value ϵ_∞ for $\omega < E_0/\hbar$. In the case of a zero-gap semi-

⁴⁾The adiabatic approximation is well justified for ordinary semiconductors when the forbidden band is considerably greater than the phonon energy, but, in the case of zero-gap semiconductors, we have to allow for the nonadiabaticity in considering, for example, the phonon spectrum. [130] Possible consequences of the failure of the adiabatic approximation in the calculation of $\epsilon(\omega)$ are considered in [172].

conductor, this condition cannot be satisfied and $\epsilon_{ia}(\omega)$ is understood to be the contribution of all interband transitions with the exception of $\Gamma_8 - \Gamma_8$ and which becomes constant for $\omega < E'_0/\hbar$, where E'_0 is the minimum separation between the valence and conduction bands at other points in the Brillouin zone,

$$\Delta\epsilon_{ie}(\omega) = \Delta\epsilon'(\omega) + i\Delta\epsilon''(\omega),$$

where $\Delta\epsilon'(\omega)$ and $\Delta\epsilon''(\omega)$ are the real and imaginary components of the term associated with interband transitions associated with just one state Γ_8 in a zero-gap semiconductor. In the case of HgTe, these components were calculated by Grynberg *et al.* [172] in the random phase approximation. It is clear from Fig. 16 that the frequency dependences of $\Delta\epsilon'$ and $\Delta\epsilon''$ exhibit a strong dispersion at low temperatures with maxima in the region of ω_F ($\hbar\omega_F = E_F$). When the temperature is increased, these maxima become flatter and shift toward higher frequencies but, even at room temperature, their contribution is considerable and, in particular, we find that $\Delta\epsilon' \approx 7$, whereas $\epsilon_\infty = 15$.

A correct interpretation of the infrared reflection spectra of HgTe is not possible without exact allowance for the term $\Delta\epsilon_{ie}(\omega)$ [172-174] (Fig. 17).

The anomalies of the static and dynamic permittivity of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ alloys decrease with increasing cadmium concentration, tending to zero in the region of the ZG-OS transition. [109, 130]

8. CONCLUSIONS

Considerable progress was made in the last decade in the understanding of the properties of mercury telluride, which is a member of a new class of substances—zero-gap semiconductors. The most important results obtained in investigations of mercury telluride were the verification of the inverted band structure model, development of a theory of resonance impurity states and

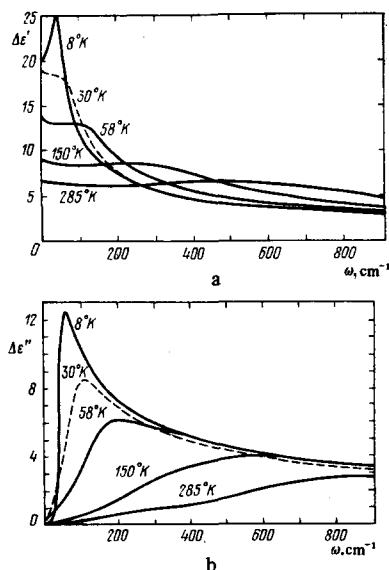


FIG. 16. Frequency dependences of the real (a) and imaginary (b) components of $\Delta\epsilon_{ie}(\omega)$ of HgTe. [172]

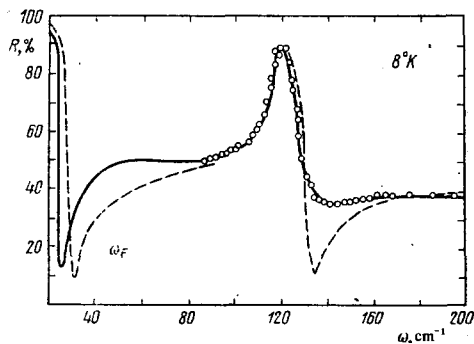


FIG. 17. Deflection coefficient of HgTe at 8°K.^[172] Circles represent the experimental results; the dashed curve is obtained without allowance for $\Delta\epsilon_{ie}(\omega)$, whereas the continuous curve is obtained allowing for $\Delta\epsilon_{ie}(\omega)$.

their experimental detection, modification of the band structure of HgTe under the influence of external agencies and, finally, the appearance of the first many-electron theoretical treatments which allow for the actual band structure of HgTe. Some of the propositions of the theory are of considerable physical interest and deserve deliberate experimental verification. This applies particularly to the determination of the principal parameters of the valence band in a wide range of temperatures, and of acceptor and donor concentrations. The problem of impurity states is not yet fully solved. In this case, we need studies of samples with controlled nature and concentration of impurities in the zero-gap and in the presence of a narrow forbidden band. It would be highly interesting to carry out comprehensive studies of the properties of HgTe at very low temperatures and in purer samples.

The preparation of the latter would require further improvements in the technology of this material.

Studies of the properties of HgTe are not only of academic interest. Mercury telluride is a promising material and devices made of it can operate at very low (amounting to a few millivolts or a few tens of millivolts) values of supply and control voltages. Moreover, HgTe is used as the base in the preparation of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ alloys which have extremely important practical applications. There are no naturally available substances with a forbidden band width below 0.12 eV, which is required in optical devices operating in far infrared. The value of E_0 of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ can be varied continuously and even reduced to zero by altering the alloy composition. Already, $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ photodetectors have been used successfully in the detection of infrared radiation of 1–35 μ wavelength^[72] so that the solution of the many problems mentioned above would also have immediate practical application.

Note added in proof. Several new theoretical and experimental papers on the subject of impurity states in zero-gap and narrow-gap semiconductors appeared recently^[175] but the problems treated in them (discussed in Sec. 6) have not yet been resolved. One should mention the paper of Gel'mont^[176] reporting an investigation of the influence of the nonlocality of the potential on the structure of the heavy-hole band in these materials.

- ¹There are many books which give detailed accounts of the band theory but for experimental physicists specializing in semiconductors the most convenient, in our opinion, are: I. M. Tsidil'kovskii, *Elektrony i dyrki v poluprovodnikakh* (Electrons and Holes in Semiconductors), Nauka, M., 1972 and J. M. Ziman, *Principles of the Theory of Solids*, Cambridge University Press, 1964.
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