# Narrow-gap semimagnetic semiconductors

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The good solubility of Mn atoms in a matrix based on gapless semiconductors HgTe, HgSe makes it possible to reconstruct smoothly the band structure of solid solutions  $Hg_{1-x}Mn_x$  Te and  $Hg_{1-x}Mn_x$  Se from the inverted gapless structure to the usual semiconductor structure with a finite energy gap between the valence band and the conduction band. The presence in solid solutions of substitution atoms (Mn) with an uncompensated magnetic moment leads to a significant change in the band spectrum in a magnetic field, which depends on the state of the magnetic subsystem of the impurity ions. All this gives rise to a very specific behavior of the kinetic coefficients in charge-transport phenomena in the region of strong magnetic fields and of magnetooptical phenomena at low temperatures. Such "anomalous" properties as the splitting of the peaks of the Shubnikov-de Haas oscillations as the temperature is increased, the nonmonotonic temperature dependence of the amplitudes of these peaks, the sensitivity to temperature of the spectra of magneto-absorption and other phenomena can be successfully explained only by taking into account the magnetization of the band charge carriers by the molecular field of the localized electrons of the Mn ions. The magnetic properties of semimagnetic semiconductors have also turned out to be quite unique. Thus, in these crystals a concentration transition is observed from a paramagnetic phase into a spin-glass phase. The review presents the most important and significant results of the investigations of gapless and narrow-gap semimagnetic semiconductors obtained recently.

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## **1. INTRODUCTION**

In recent years considerable attention has been attracted to a new class of materials—dilute magnetic semiconductors, or, as they have been called, semimagnetic semiconductors (SMS). Of particular interest are the narrow-gap SMS which are solid solutions of mercury chalcogenides (HgTe, HgSe) and the transition or rare-earth elements (MnTe, MnSe, EuTe and others). Mercury chalcogenides are gapless semiconductors, manganese, europeum and other chalcogenides are magnetic semiconductors. The possibility of varying over wide limits the composition of the solid solutions enables one to alter smoothly the electron band structure from a gapless inverted band spectrum for which the energy gap between the closest bands of the s-type ( $\Gamma_6$ ) and ptype ( $\Gamma_8$ ) is negative ( $\varepsilon_g = \varepsilon(\Gamma_6) - \varepsilon(\Gamma_8) < 0$ ), to a direct spectrum usual for semiconductors with  $\varepsilon_g > 0$ , i.e., to convert a gapless semiconductor into a semiconductor with a gap.<sup>1</sup>

Below we shall consider the main features of only the gapless and narrow-gap SMS which contain atoms of transition elements with unfilled d-shells and we shall not touch upon the SMS with a wide energy gap of the type of  $Cd_{1-x} Mn_x$  Te. We shall restrict ourselves to a description of the properties of the gapless and narrow-gap SMS that have

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been more intensively investigated, specifically—the solid solutions of mercury and manganese chalcogenides  $Hg_{1-x}Mn_xTe$  and  $Hg_{1-x}Mn_xSe$ .

Different aspects of the physics of SMS were discussed at a number of international conferences on semiconductors (Warsaw, 1977; Edinburgh, 1978; Kyoto, 1980; Linz, 1981; Grenoble 1982<sup>2-7</sup>). Interest in these materials is determined by their specific properties. Firstly, in contrast to traditional magnetic semicondcutors the band structure of the basic crystal of SMS (HgTe or HgSe) is well known. Secondly, the high mobility of band electrons in SMS which exceeds by many orders of magnitude the mobility in ordinary magnetic semiconductors enables one to utilize practically the whole arsenal of modern methods of investigating physical properties of solids. In particular, the possibility appears of determining quite reliably the values of exchange integrals. Finally, in SMS a nontrivial concentration transition is observed from the gapless state to the semiconductor state which is of independent interest in itself.

In the absence of a magnetic field or at high temperatures the properties of gapless SMS are similar in many respects to the properties of solid solutions of gapless semiconductors  $Hg_{1-x}Cd_xTe$  whose electron spectrum is well described by the Groves-Paul inverse band scheme. Pidgeon and Brown<sup>9</sup> have utilized for the calculation of the inverse band structure the well known Kane approximation in which the interaction between the  $\Gamma_6$ ,  $\Gamma_7$ , and  $\Gamma_8$  bands is treated exactly, while the effect of the other bands is treated as a perturbation. Such an approach is sometimes referred to as the Pidgeon-Brown model. This model gives a good explanation of the majority of electronic properties of gapless semiconductors of the type of HgTe. However, in the case of SMS within the framework of this model it is not possible to interpret a number of features of transport phenomena in the range of strong magnetic fields and magneto-optic phenomena at low temperatures. For example, such "anomalous" properties, as the splitting of the peaks of the Shubnikov-de Haas oscillations as the temperature is raised, the nonmonotonic dependence on the temperature of the amplitudes of these peaks, the sensitivity of the magneto-absorption spectra to temperature and others9-11 can be successfully explained only when magnetization of the band charge-carriers by the molecular field of d-electrons of the Mn ions is taken into account<sup>1)</sup>. The exchange interaction between valence electrons and d-electrons localized on the impurity ions leads to a radical restructuring of the energy spectrum of the band charge-carriers in a magnetic field, and this change depends on the state of the magnetic subsystem and is proportional to the average values of the magnetic moment M(H, T) of the impurity ions. The Pidgeon-Brown model which in addition includes the exchange interaction between the band electrons and the electrons localized on the impurity ions has made it possible to explain the observed "anomalies" and to predict new effects characteristic only of SMS.

The magnetic and thermodynamic properties of the SMS turned out to be quite unique. Investigations of magnetic susceptibility, specific heat and electron paramagnetic resonance have shown that in these crystals there is a concentration transition from the paramagnetic phase into a spin-glass phase.<sup>12</sup>

The state of investigations of SMS can be characterized in the following manner. A clear insufficiency of experimental data is experienced. Some results are contradictory. A number of experimental facts require explanation, and on the whole there is a lot that remains unclear. It is just because of this that we have decided to give at least a brief description of the most interesting and important papers (references to most of them are given) in order to clarify, as far as we are able, the present state of affairs. We are quite conscious of the fact that the investigation of SMS has not yet reached a level which could be considered satisfactory. New work can and must extend, make more precise, and in a number of cases alter the interpretation of experimental data given below. At the same time quite a bit has been achieved alreadymany essential specific features of the properties of SMS have been brought to light-and it is reasonable to draw some conclusions.

# 2. ENERGY SPECTRUM OF BAND CHARGE CARRIERS a) Energy bands in the absence of a magnetic field

The basis for the solid solutions of SMS discussed below are the gapless semiconductors HgTe and HgSe. Therefore, it is useful to recall certain specific properties of the band structure of solids in which the gapless state is realized (cf., Ref. 13). The anomalously small forbidden band was first found at the end of the 1950's-beginning of 1960's in HgTe<sup>14</sup> and  $\alpha$ -Sn.<sup>15</sup> S. P. Shubin and S. V. Vonsovskiĭ have pointed out the possibility in principle of the existence of dielectrics with a continuous energy spectrum without a gap already in the 1930's.<sup>16</sup> At the present time a number of gapless semiconductors are known with an identically zero direct energy gap between the conduction band and the valence band. They differ from semiconductors by the absence of a threshold energy required to produce an electron-hole pair. They differ from metals by the significantly lower density of the electron gas which under external conditions can vary over wide limits down to arbitrarily low values. The gapless state in the case of gapless semiconductors of HgTe type is due to the symmetry of the crystal lattice. It can disappear only under the action of a perturbation which lowers the symmetry of the lattice (uniaxial deformation, magnetic field, etc.).

The order of arrangement of energy bands in the case of gapless semiconductors (for example, HgTe) is opposite to the one which occurs in ordinary semiconductors (for example, InSb) with the same symmetry of the crystal lattice (Fig. 1). It is therefore said that gapless semiconductors have an inverted band structure. In crystals with an inverted band structure of the type of HgTe the band of light holes is described in the neighborhood of the maximum (for a momentum fik = 0) by wave functions of s symmetry (the irreducible representation  $\Gamma_6$ ) and is situated below the valence zone for heavy holes which is described at the edge by functions of **p**-symmetry (irreducible representation  $\Gamma_8$ ). The states in the valence band are classified in terms of the total angular momentum j = 3/2 (j = l + s; l is the orbital angular momentum



FIG. 1. The band diagram for semiconductors with zinc blende structure. a—The inverted scheme of bands of HgTe ( $\varepsilon_g = \varepsilon(\Gamma_6) - \varepsilon(\Gamma_8) < 0$ ); b—the band diagram for InSb ( $\varepsilon_g > 0$ ).

tum while s is the spin angular momentum). Two bands correspond to the value j = 3/2, each of which is doubly degenerate for  $\mathbf{k} \neq 0$ . For  $\mathbf{k} = 0$  the bands with j = 3/2 are four-fold degenerate. As a result of the inversion the curvature of one of the bands with j = 3/2 turns out to be positive, while of the other band it is negative. In such a structure the energy gap is identically equal to zero with a split  $\varepsilon_g = \varepsilon(\Gamma_6) - \varepsilon(\Gamma_8) < 0$ . The value j = 1/2 in gapless semiconductors corresponds to the valence band which is split off from the two  $\Gamma_8$  bands by the value of the energy of the spinorbital interaction  $\Delta$ .

X-ray investigations have shown that the solid solutions  $Hg_{1-x} Mn_x Te$  up to  $x \approx 0.35$ ,<sup>17</sup> and  $Hg_{1-x} Mn_x Se$  up to  $x \approx 0.37^{18}$  have the structure of zinc blend just as the gapless semiconductors HgTe and HgSe. The Te and Se atoms form one fact-centered cubic lattice, while the Hg and Mn atoms are distributed more or less randomly over another sublattice. The gapless state in SMS, and also in HgTe and HgSe is due to the symmetry of the crystal lattice. The substitution of Hg atoms by Mn atoms leads to a smooth restructuring of the band spectrum analogous to the one which occurs in solid solutions  $Hg_{1-x} Cd_x Te$ . The  $\Gamma_6$  band in SMS is formed from  $6s^2$ -electrons of Hg and  $4s^2$ -electrons of Mn, while  $\Gamma_8$  and  $\Gamma_7$  bands are formed by the valence p-electrons of Te or Se.

The dependence of the value of the energy gap  $\varepsilon_{g}$  on the content of Mn in SMS has been determined by different methods.<sup>9,11,17-22</sup> It turned out that for  $0 < x \le 0.2\varepsilon_g(x)$  varies practically linearly with the concentration of manganese (Fig. 2). The deviation of  $\varepsilon_g(x)$  from linearity for x > 0.2 is apparently a consequence of the fact that the crystallographic structures of gapless semiconductors HgTe and HgSe and magnetic semiconductors MnTe, MnSe are different.<sup>2)</sup> It should be noted that the value of the energy gap  $\varepsilon_{g}$  varies with the composition x in the case of  $Hg_{1-x}Mn_x$  Te considerably faster than in the case of solid solutions  $Hg_{1-x}Cd_xTe$ , i.e., a definite value of  $\varepsilon_g$  is attained in the case of SMS for considerably lower values of x. Thus for example in  $Hg_{1-x}Cd_xTe$  with a Cd content x = 0.22 we have  $\varepsilon_g = 100 \text{ meV} (T = 4.2 \text{ K})$ , while in  $\text{Hg}_{1-x} \text{Mn}_x \text{Te}$ such a gap corresponds to the composition x = 0.11. The

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FIG. 2. Dependence of the energy gap  $\varepsilon_g$  on Mn content in SMS Hg<sub>1-x</sub>  $n_x$  Te: 1-4, 2-3, 3-18, 4-21, 5-62; Hg<sub>1-x</sub> Mn<sub>x</sub> Se: 6-16, 7-17, 8-

conversion of a gapless semiconductor into a semiconductor with a gap occurs in the case of  $Hg_{1-x}Mn_x$  Te at x = 0.07while in the case of  $Hg_{1-x}Mn_x$  Se it occurs at x = 0.065(T = 4.2 K). The change of the gap  $\varepsilon_g$  as a function of the temperature and composition for SMS is described well by the following empirical formulas<sup>17-21,24</sup>:

$$Hg_{1-x}Mn_{x}Te \begin{cases} e_{g}(x) = -0.305 + 0.55T + 4.4x \quad (eV), \\ \frac{de_{g}}{dT} = 5.2 \cdot 10^{-4} eV/K. \end{cases}$$
(1)  
$$Hg_{1-x}Mn_{x}Se \begin{cases} e_{g}(x) = -0.27 + 4.4x \quad (eV), \\ \frac{de_{g}}{dT} = 8 \cdot 10^{-4} eV/K. \end{cases}$$

#### b) Energy spectrum of band electrons in a magnetic field

For the calculation of energy levels of gapless semiconductors in a magnetic field a good approximation is the Pidgeon-Brown model<sup>8</sup> in which the interaction between the closely situated,  $\Gamma_6$ ,  $\Gamma_7$ , and  $\Gamma_8$  bands is treated exactly, while the effect of the distant bands is taken into account up to terms quadratic in k.

In this calculation both Luttinger effects for the  $\Gamma_8$  band, and also the nonparabolicity arising as a result of strong  $\mathbf{k} \cdot \mathbf{p}$  interaction between the s and p states are taken into account.

The energies of the Landau levels of the  $\Gamma_6$  and  $\Gamma_8$ bands are the solutions of the secular equation corresponding to the matrix of the Hamiltonian D [8×8].<sup>1</sup> If the inverse asymmetry and anisotropy of the  $\Gamma_8$  band is neglected the matrix D in the case of the propagation vector  $k_z = 0$  (the magnetic field is directed along the z axis) breaks up into two [4×4] matrices  $D_a$  and  $D_b$ :

$$D = \begin{bmatrix} D_a & 0\\ 0 & D_b \end{bmatrix} \,. \tag{2}$$

The eigenvalues of the Hamiltonian  $D_a$  and  $D_b$  are the energies of the electronic levels of the  $a_n$  and  $b_n$  series which differ in spin  $(b_n$  corresponds to levels with spin  $\sigma = 1/2$ , while for  $a_n$ -levels  $\sigma = 1/2$ ).<sup>3)</sup> The level energy in a magnetic field in this case turns out to depend on 6 parameters:  $\varepsilon_g$ , P the matrix element of the momentum operator between the  $\Gamma_6$  and  $\Gamma_8$  states,  $\Delta$ —the energy of the spin-orbit interaction and  $\gamma$ ,  $\overline{\gamma}$ , k—the Luttinger parameters which take into account the influence of distant bands.

In SMS the band carriers in s and p states can interact through the exchange coupling with d electrons localized on the manganese ions. Therefore, phenomena which depend on spin must in SMS have specific features compared with the corresponding phenomena in the semiconductor of the type  $Hg_{1-x} Cd_x Te$ .

The exchange interaction between the band and the localized 3d electrons of the manganese ions is described by a Hamiltonian of the Heisenberg type

$$H_{\rm ex} = \sum_{\rm R} J \left( {\bf r} - {\bf R} \right) \, \hat{s} \hat{S}_{\rm R}, \tag{3}$$

where  $J(\mathbf{r} - \mathbf{R})$  is the exchange interaction integral between band carriers and the magnetic moment of the Mn ion,  $\hat{s}$  and  $\hat{S}$  are the spin operators of the band and localized electrons respectively.

Since the range of the exchange potential is of the order of atomic dimensions, i.e., much smaller than the radius of the electron wave function in a magnetic field (the magnetic length)  $\lambda = \sqrt{c\hbar/eH}$ , then in calculating the energy spectrum of the band carriers in the SMS the interaction (3) can be regarded as a contact interaction. In this approximation the correction to the unperturbed Landau levels for the  $\Gamma_6$ and  $\Gamma_8$  bands can be represented in the form<sup>9</sup>:

$$\Delta \varepsilon_{N,\sigma} = \sum_{\mathbf{R}} f_{N}^{*}(\mathbf{R}) f_{N}(\mathbf{R}) \hat{S}_{\mathbf{R}} \int_{\underline{\Omega}_{0}} d\Omega u_{J}^{*}(m) J(\mathbf{r}) \hat{s} u_{J}(m); \qquad (4)$$

here  $u_i(m)$  are the Bloch amplitudes for the  $\Gamma_6$  and  $\Gamma_8$  bands:

$$u_{1/2}\left(\frac{1}{2}\right) = |S\uparrow\rangle, \ u_{1/2}\left(-\frac{1}{2}\right) = |iS\downarrow\rangle,$$

$$u_{3/2}\left(\frac{3}{2}\right) = \left|\frac{1}{\sqrt{2}}X^{+}\uparrow\rangle, \quad u_{3/2}\left(-\frac{3}{2}\right) = \left|\frac{i}{\sqrt{2}}X^{-}\downarrow\rangle,$$

$$u_{3/2}\left(\frac{1}{2}\right) = \left|\frac{i}{\sqrt{6}}(X^{+}\downarrow - 2Z\uparrow)\rangle,$$

$$u_{3/2}\left(-\frac{1}{2}\right) = \left|\frac{1}{\sqrt{6}}(X^{-}\uparrow + 2Z\downarrow)\rangle,$$
(5)

the arrows indicate spin functions corresponding to the two directions of spin;  $X^{\pm} = X \pm iY$ , and S, X, Y, Z are periodic functions which transform as the functions s,  $p_x$ ,  $p_y$ ,  $p_z$  under transformations of the tetrahedral group  $T_d$ . The quantities  $f_N(\mathbf{R})$  are harmonic oscillator eigenfunctions. Integration in (4) is carried out over the volume of an elementary cell  $\Omega_0$ .

For Bloch amplitudes (5) the contribution of the exchange interaction (3) to the energy of the Landau levels of the band electrons is described by two parameters

$$\boldsymbol{\alpha} = \langle S \mid \boldsymbol{J}(\boldsymbol{r}) \mid S \rangle, \quad \boldsymbol{\beta} = \langle X \mid \boldsymbol{J}(\boldsymbol{r}) \mid X \rangle, \tag{6}$$

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corresponding to the  $\Gamma_6$  and  $\Gamma_8$  bands. In calculating the exchange correction to the energies of the electronic levels  $\Delta \varepsilon_{N,\sigma}$  the localized spin operator  $\hat{S}$  is replaced by the average value  $\langle \hat{S} \rangle$  (the brackets  $\langle \cdots \rangle$  denote both the thermodynamical average and averaging over the random distribution of the Mn ions in the crystal). As a result of averaging over the direction of the magnetic field  $\mathbf{H} || z$  there remains only the z-component  $\langle \hat{S} \rangle = \langle S \rangle^z$ , ( $\langle S^{\alpha} \pm i S^{\gamma} \rangle = 0$ ), which is directly related to the magnetization of the SMS:

$$M^{z} = -N_{\rm m} g \mu_{\rm B} \langle S^{z} \rangle; \tag{7}$$

here  $N_m = N_0 x$  is the concentration of the manganese atoms in the SMS,  $N_0$  is the number of elementary cells per unit volume,  $\bar{g} = 2$  is the spectroscopic splitting factor of the d electrons of manganese,  $\mu_B$  is the Bohr magneton.

Within the framework of the three-band model ( $\Gamma_6$ ,  $\Gamma_7$ ,  $\Gamma_8$ ) the explicit expressions for the exchange energy of the electrons of the  $\Gamma_8$  band have the form<sup>11</sup>

$$\Delta \varepsilon_{N, +1/2} = N_{\rm m} \langle S^z \rangle \left( \frac{\beta}{6} \frac{8N-1}{4N+1} \frac{|e_{\rm g}| + e_{N, +1/2}}{|e_{\rm g}| + 2e_{N, +1/2}} + \frac{\alpha \varepsilon_{N, +1/2}}{|e_{\rm g}| + 2e_{N, +1/2}} \right),$$

$$\Delta \varepsilon_{N, -1/2} = N_{\rm m} \langle S^z \rangle \left( \frac{\beta}{6} \frac{8N+9}{4N+3} \frac{|e_{\rm g}| + e_{N, -1/2}}{|e_{\rm g}| + 2e_{N, -1/2}} + \frac{\alpha \varepsilon_{N, -1/2}}{|e_{\rm g}| + 2e_{N, -1/2}} \right);$$
(8)

here  $\varepsilon_{N, +1/2}$  are the unperturbed values of the energy of the band electrons in a magnetic field, N = 0, 1, 2... is the quantum number characterizing the number of the Landau level.

For a quadratic dispersion law which is not a bad approximation for the electrons with large values of the gap  $|\varepsilon_g|$ , the exchange energy is described by simple expressions<sup>10,25</sup>:

$$\Delta \boldsymbol{\varepsilon}_{N,\sigma} = \frac{\beta N_{\rm m}}{3} \sigma \langle S^7 \rangle \times \begin{cases} \frac{8N-1}{4N+1}, & \sigma = +\frac{1}{2}, \\ \frac{8N+9}{4N+3}, & \sigma = -\frac{1}{2}. \end{cases}$$
(9)

From formula (9) it follows that for N = 0 the signs of the exchange corrections  $\Delta \varepsilon_{N,\sigma}$  to energy  $\varepsilon_{N,\sigma}$  are the same for  $\sigma = \pm 1/2$ , and for  $N \ge 1$  the signs are opposite. For  $N \ge 1$ the exchange correction evidently does not depend on the number of the Landau level.

In SMS with a finite gap  $(\varepsilon_g > 0)$  the addition to the energy of the electrons of the  $\Gamma_6$  band in the approximation of the quadratic dispersion law has the form

$$\Delta \varepsilon_{N,\sigma} = \alpha N_{\rm m} \sigma \langle S^z \rangle \qquad \left( \sigma = \pm \frac{1}{2} \right). \tag{10}$$

The exchange interaction affects also the g-factor of the band electrons, which characterizes the spin splitting of the levels in a magnetic field. The energy of the spin splitting of the Landau levels is, by definition,

$$\varepsilon_{\rm sp} (N) = \varepsilon_{N, -1/2} - \varepsilon_{N, +1/2} = g\mu_{\rm B}H. \qquad (11)$$

For the Kane nonparabolic band the *g*-factor of the electrons in a semiconductor with the gap  $\varepsilon_g > 0$  [for  $\varepsilon_g < 0$  the term  $3\varepsilon_g$  is absent from the denominator in (12)]

$$g = 2\left\{1 + \left[\left(1 - \frac{m_0}{m_n}\right) \frac{\Delta}{2\Delta + 3\epsilon_g + 3\epsilon_F}\right]\right\},\tag{12}$$

where  $m_0$  is the mass of a free electron,  $\varepsilon_F$  is the Fermi energy,  $m_n$  is the effective mass of the electron at the bottom of the band. In case of small effective mass  $(m_n < m_0)$ , which usually holds in the case of semiconductors with a small value of the direct gap  $\varepsilon_g = |\varepsilon(\Gamma_6) - \varepsilon(\Gamma_8)|$ , the g-factor for the band electrons is negative, in contrast to the g-factor of a free electron which by definition is equal to +2.

The exchange interaction in the SMS leads, as can be seen from formulas (8) and (11), to a renormalization of the gfactor for the band electrons, which becomes a function of the magnetic field and temperature. For a quadratic dispersion law the renormalized g-factor is

$$g^* = g + \frac{\delta N_{\rm m} c \langle S^z \rangle}{\mu_{\rm B} H}, \qquad (13)$$

where  $\delta \equiv \alpha$  or  $\delta \equiv \beta$  for the  $\Gamma_6$  and  $\Gamma_8$  bands respectively,  $c \approx 1$ .

It follows from formula (13) that if the signs of g and  $\delta$ are the same, then the spin splitting of the Landau levels under the action of the exchange interaction can only increase. For sufficiently great exchange correction degeneracy can be initiated and even an inversion of the spin sublevels corresponding to the different Landau levels. However, in this case the temperature dependence of  $|g^*(T)|$  will be monotonic, since  $\langle S^z \rangle$  for any magnetic systems decreases with increasing temperature. A more curious situation can arise when the signs of g and  $\delta$  are opposite. In this case the spin splitting of the Landau levels decreases as a result of the exchange correction. In such a case in actually attainable magnetic fields degeneracy of spin sublevels related to a single Landau level ( $g^* = 0$ ) can occur. A further increase in the contribution of the exchange interaction to the energy will lead to an inversion of the spin sublevels and to an increase of the effective  $g^*$ -factor. In such a case the evolution of spin sublevels must, evidently, lead to a nonmonotonic dependence of  $|g^*(T)|$ .

This exchange interaction also exerts a strong influence on the restructuring of the energy levels of the heavy holes of the valence band. Fig. 3 shows the results of calculation of the dependences of the energy of the Landau levels for  $k_z = 0$  on the magnetic field for two temperatures for Hg<sub>0.96</sub> Mn<sub>0.04</sub> Te crystals.<sup>10</sup> From calculations it follows that the exchange interaction affects particularly strongly the variation of the lowest electronic  $\varepsilon_{\rm C}$  and the upper valence  $\varepsilon_{\rm v}$  energy levels. As the magnetic field is increased the levels  $\varepsilon_{\rm C}$  and  $\varepsilon_{\rm V}$  can cross. The overlap energy of these levels will increase until the addition to the energy of the valence level  $\varepsilon_{\rm v}$  which is proportional to  $\langle S^{\rm z} \rangle$  reaches saturation  $(\langle S^z \rangle \sim S)$ . The further motion of the  $\varepsilon_v$  level as the magnetic field is changed is determined by the dependence on the field of the cyclotron energy of the hole  $\hbar \omega_p = e H / m_p c (m_p \text{ is the}$ effective mass of the heavy hole), which in the final analysis leads to a decrease in the overlap of the levels  $\varepsilon_{\rm V}$  and  $\varepsilon_{\rm c}^{4}$ . In a certain magnetic field  $H = H_{\rm cr}$  the overlap  $\varepsilon_0 = \varepsilon_{\rm V} - \varepsilon_{\rm C}$ becomes equal to zero ( $H_{cr} = 37$  kOe for x = 0.004 at T = 2 $K^{10}$ ; H = 80-100 kOe for  $x \le 0.06$  for T = 4.2 K.<sup>26</sup>

The same effect also results from an increase of the





FIG. 3. Dependence of the energy of Landau levels in the  $\Gamma_8$  band for  $k_z = 0$  on the magnetic field for  $Hg_{1-x}Mn_xTe$  of different compositions.<sup>9</sup> The arrows  $\uparrow,\downarrow$  denote the spin state, V is the top of the valence band.

manganese content in  $Hg_{1-x} Mn_x$  Te at a constant magnetic field and fixed temperature. As the manganese content is increased in  $Hg_{1-x} Mn_x$  Te the energy of the valence level  $\varepsilon_v$ increases so rapidly that for certain values  $x = x_{cr}$  the upper valence level  $\varepsilon_v$  also turns out to be placed higher in energy than the lowest level of the conduction band  $\varepsilon_c$ . In this case the SMS becomes a semimetal (Fig. 4). The magnitude of the overlap of the energy levels  $\varepsilon_v$  and  $\varepsilon_c$  ( $\varepsilon_0 = \varepsilon_v - \varepsilon_c$ ) depends on the external magnetic field, the temperature and the concentration of the transitional element (Mn) in the SMS. Such an unusual evolution of the energy levels of band carriers leads to a number of special features of the thermogalvanomagnetic coefficients in the SMS some of which will be discussed below.

#### **3. MAGNETIC PROPERTIES**

The magnetic properties of gapless semiconductors HgTe and HgSe on the one hand and the magnetic semiconductors MnTe and MnSe on the other hand differ appreciably. Manganese telluride and selenide are typical antiferromagnetic substances.<sup>23 5)</sup>

Evidently, as the manganese content is increased in the solid solutions  $Hg_{1-x} Mn_x$  Te and  $Hg_{1-x} Mn_x$  Se the nature of the exchange interaction between the localized angular moments must change, and this will lead to a change in the magnetization of SMS. The kinetic and magneto-optic phenomena in the SMS are quite sensitive to the state of the magnetic subsystem of the crystal. Therefore, a knowledge of the nature of the exchange coupling between the localized magnetic moments is required, in particular, in order to interpret the kinetic and magneto-optic properties of the SMS



FIG. 4. The evolution of the electron  $(0^+ \text{ and } 0^-)$  and the upper valence b(-1) energy levels as the Mn content is varied in Hg<sub>1-x</sub> Mn<sub>x</sub> Te. H = 30 kOe, T = 2 K; the horizontal lines correspond to positions of the edges of the energy bands.

and, moreover, to understand the special features of the behavior of disordered magnetic material.

In order to obtain a general picture of the magnetic properties of SMS numerous measurements of the magnetic susceptibility, specific heat, paramagnetic resonance and other effects were made in a number of laboratories. Results of the measurements showed that in narrow-gap SMS as the content of manganese is increased a continuous transition is observed from the paramagnetic phase to the spin-glass phase. In the SMS with a wide forbidden band  $Cd_{1-x}Mn_x$  Te and with a high manganese content ( $x \ge 0.70$ ) a magnetically ordered phase was observed which is not present in the narrow-gap SMS.

#### a) Paramagnetic phase

Experimental investigation of the magnetic properties of the SMS<sup>30-40</sup> showed that a magnetization M different from zero appears, in the case of the solid solutions  $Hg_{1-x}Mn_x$  Te and  $Hg_{1-x}Mn_x$  Se and begins to increase as an external magnetic field is switched on and its intensity is increased. In the temperature range 10–60 K the magnetization of the SMS with a manganese content  $x \leq 0.16$  increases up to magnetic fields  $H \sim 60$  kOe, as in the case of typical paramagnetic substances in direct proportion to the intensity of the magnetic field<sup>41</sup>:

$$\mathbf{M} = \mathbf{\chi}\mathbf{H}.$$
 (14

The paramagnetic susceptibility  $\chi$  does not depend on the magnetic field, but depends strongly on the temperature and on the content of the Mn<sup>2+</sup> ions in solid solution.

An analysis of measurements of the temperature dependence of the magnetic susceptibility showed that for a sufficiently low content of manganese ions in the SMS ( $x \le 0.005$ ) the magnetic susceptibility is well described by the Curie law<sup>31</sup>

$$\chi = \frac{N_{\rm m} S(S+1) \, (\bar{g} \mu_{\rm B})^2}{3 k_B T},$$
(15)

where  $k_{\rm B}$  is the Boltzmann constant.

This experimental fact can be explained by the extreme-

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ly weak exchange interaction between the  $Mn^{2+}$  ions the distance between which is great when their concentration is so low. The magnetic moment of the ion introduces in this case an additional contribution to the total magnetization of the SMS. The average value of the localized spin which enters into the expression for the magnetization (7) is determined by the expression

$$\langle S^{z} \rangle = -SB_{s} \left( \frac{\bar{g}\mu_{B}SH}{k_{B}T} \right), \qquad (16)$$

where the Brillouin function is given by

$$B_{S}(y) = \frac{2S+1}{2S} \operatorname{cth}\left(\frac{2S+1}{S}y\right) - \frac{1}{2S} \operatorname{cth}\frac{y}{2S}.$$
 (17)

For comparatively low temperatures or strong magnetic fields when  $\bar{g}\mu_B SH \gg k_B T$ , the linear relationship between M and H breaks down and according to (7) as H increases the magnetization approaches saturation at which  $M = -N_m \bar{g}\mu_B$ .

As the concentration of manganese in the SMS increases above  $x \sim 0.005$  the magnetic susceptibility of solid solutions is no longer described by the Curie law (15). In the region of high temperatures and for x > 0.005 it obeys the Curie-Weiss law

$$\chi = \frac{N_{\rm m} S \, (S+1) \, (\bar{s}_{\rm \mu} \mu_{\rm B})^2}{3k_{\rm B} \, (T-\Theta)} \,, \tag{18}$$

where the characteristic temperature  $\Theta$  is negative. The existence of a characteristic temperature which is different from zero indicates the appearance of exchange interaction between manganese ions, and the negative sign of  $\Theta$  indicates that this interaction is antiferromagnetic. The dependence of  $\Theta$  on the content of  $Mn^{2+}$  ions at concentrations  $x \leq 0.3$  is practically linear.<sup>9,38</sup>

At low temperatures the relationship  $\chi^{-1}(T)$  deviates from a linear one and as the temperature is decreased  $\chi^{-1}$ tends to zero. Such a behavior of the magnetic susceptibility can be explained within the framework of a model in which the formation in SMS of magnetic clusters is assumed which consist of several closely situated  $Mn^{2+}$  ions. Between the magnetic moments of the manganese ions forming the cluster there is a direct exchange interaction of an antiferromagnetic nature, and this is what determines the sharper variation of the magnetic susceptibility  $\chi$  as the temperature is lowered. The magnetic susceptibility in the presence of magnetic clusters in a crystal can be represented in the form

$$\chi = \chi_1 + \chi_2 + \chi_3 + \dots,$$
 (19)

where  $\chi_1$  is the susceptibility of the isolated  $Mn^{2+}$  ions which form a cluster of type O. The value of  $\chi_1$  is determined by expression (15). The value of  $\chi_2$  is the contribution to the susceptibility of clusters consisting of two magnetic  $Mn^{2+}$ ions (clusters of type D). According to Ref. 30

$$\chi_2 = \frac{C_2 N_2}{T}; \tag{20}$$

here  $N_2$  is the concentration to type D clusters, while

t

$$C_{2} = \frac{(\bar{g}\mu_{\rm B})^{2} \sum_{S=0}^{5} S(S+1) (2S+1) \exp\left[-J_{1}S(S+1)/2k_{B}T\right]}{3k_{B} \sum_{S=0}^{5} (2S+1) \exp\left[-J_{1}S(S+1)/2k_{B}T\right]}; (21)$$



FIG. 5. Probability of finding the  $Mn^{2+}$  magnetic ion in a cluster of a definite kind in the case of a random distribution of manganese in SMS.<sup>38</sup>

 $J_1$  is the exchange integral describing the exchange interaction between magnetic moments within the cluster D. The values of the exchange integral obtained from measurements of the magnetization of  $Hg_{1-x}Mn_x$  Te crystals are equal to:  $J_1 = 0.7$  meV for x = 0.02 according to Ref. 9 and  $J_1 = 0.84$ meV for x = 0.05 according to Ref. 39. The susceptibility  $\chi_3$ characterizes the contribution of clusters consisting of three  $Mn^{2+}$  ions.

The probability P(x) of the formation of magnetic clusters of different configuration as a function of the manganese content in SMS on the assumption that the  $Mn^{2+}$  ions are randomly distributed along the sublattice, are shown in Fig. 5. For clusters consisting of three manganese ions a distinction is made between open (TO) and closed (TC) clusters. In TO clusters the first of the magnetic  $Mn^{2+}$  ions interacts with the second, the second with the third, and there is no coupling between the third and the first ions. In TC clusters each magnetic  $Mn^{2+}$  ion interacts with the other two. The probability of formation of a cluster of a definite kind is shown in Table I.

An analysis of the probabilities of formation of magnetic clusters of different configurations under the assumption of a random distribution of  $Mn^{2+}$  ions in the sublattice has shown that in a SMS with a Mn content  $x \leq 0.03$  it is sufficient for the description of magnetization to take into account only clusters of type O and D. The average value of the localized spin appearing in the expression for magnetization (7) in this case takes the form

#### TABLE I

Type of cluster	P (x)
• 0	$(1-x)^{12}$
•• D	12 x (1-x) <sup>18</sup>
•• 70	18 x <sup>2</sup> (7-x) (1-x) <sup>28</sup>
•• TC	24 x <sup>2</sup> (1-x) <sup>22</sup>

where  $P_1(x)$  is the probability of formation of a cluster of type O, while  $P_2^{(1)}$  and  $P_2^{(2)}$  are the probabilities for the formation of D clusters with the distances between the  $Mn^{2+}$  ions equal to  $a_0\sqrt{2}$  and  $a_0$  respectively ( $a_0$  is the lattice constant),  $\langle S_i^z \rangle$  is the average value of the localized spin in a cluster of type i.

Within the framework of the above cluster model Bastard *et al.*<sup>37</sup> obtained the following expression for the magnetic susceptibility in the limit  $\bar{g}\mu_{\rm B}SH < k_{\rm B}T$ :

$$\chi = \frac{(g\mu_{\rm B})^2 S (S+1) N_{\rm eff} (T)}{3k_B (T-\Theta (T))};$$
(23)

here  $N_{\text{eff}}(T)$  is the concentration of those localized magnetic moments which make a contribution to the magnetization of SMS at a temperature T;  $\Theta(T)$  is the effective Curie-Weiss temperature. The analysis carried out by the authors of Ref. 37 showed that the quantities  $N_{\text{eff}}$  and  $\Theta$  are very sensitive to temperature. Thus, at low temperatures  $(T \rightarrow 0)$  we have

$$N_{ett} (T \rightarrow 0) = \Omega^{-1} N_m P_1 (x),$$
  

$$\Theta (T \rightarrow 0) = -\frac{S (S+1) x P_1 (x)}{3} \sum_{\mathbf{R}_{ij} \alpha} J (\mathbf{R}_{ij}), \qquad (24)$$

where  $\Omega$  is the volume of the crystal,  $J(\mathbf{R}_{ij})$  is the exchange integral which describes the interaction between the localized spins  $S_{\mathbf{R}_i}$  and  $S_{\mathbf{R}_i}$ ;

In the high temperature range  $(T \rightarrow \infty)$ 

$$N_{\rm eff} (T \to \infty) = \Omega^{-1} N_{\rm m},$$

$$\Theta(T \rightarrow \infty)$$

$$= -\frac{S(S+1) x \left[P_1(x) + P_2^{(1)}(x) + P_2^{(2)}(x)\right]}{3} \sum_{\mathbf{R}_{ij} > \mathbf{a}_{\bullet}} J(\mathbf{R}_{ij}). \quad (25)$$

Thus, at low temperatures the contribution to the magnetization of SMS is made only by single clusters of type O, while the contribution of clusters of type D is practically equal to zero. In the range of high temperatures the magnetization of the SMS is determined both by clusters of type O, and clusters of type D. The expression (23) gives a good description of the experimental curves of the magnetization M(T) for the Hg<sub>1-x</sub> Mn<sub>x</sub> Te crystals with  $x \le 0.03$ .<sup>31</sup> However, the neglect in the calculation of clusters greater than pairs did not allow the authors of Ref. 37 to describe the magnetization of crystals with a manganese content x > 0.03.

In samples of  $Hg_{1-x} Mn_x$  Te with manganese content exceeding 3% the number of clusters containing a large number of  $Mn^{2+}$  ions increases sharply. Therefore it is necessary to take into account the contribution to the magnetization from triple and even larger clusters. In such a situation the exchange interaction is significant not only between the nearest neighbor  $Mn^{2+}$  but also between more distant ions. A quantitative treatment in this case is practically impossible to realize due to the excessively great mathematical difficulties.

However, another method is possible for the description of the magnetization of SMS which is free from such difficulties. We assume that the distribution of the  $Mn^{2+}$ 

TABLE II

Type of cluster	<i>x</i> =	x = 0,03 $x = 0,05$			x = 0,03		0,05
		P <sub>m</sub> (x)	P (x)	$P_m(x)$			
0 D TC TO	0,72 0,20 0,04 0,05	0,23 0,59 0 0	0,40 0,24 0,02 0,05	0,46 0,47 0 0,07			

ions in the SMS lattice does not obey the statistical laws, so that the concentrations of clusters of types O, D, TO, TC calculated according to the Poisson distribution P(x) does not correspond to their actual distribution in the crystal. One can introduce a certain modified distribution  $P_m(x)$  according to which the process of formation of clusters must begin at significantly lower manganese concentrations than in the case of the Poisson distribution. Selecting by an empirical method contributions to the magnetization of the SMS from clusters of types O, D, TO and TC one can attempt to describe the dependence of the magnetization on the temperature and the magnetic field. Such a procedure was carried out by authors of Refs. 38, 39 who investigated experimentally the magnetization of Hg<sub>1-x</sub> Mn<sub>x</sub> Te crystals with a manganese content  $x \approx 0.03$  and  $x \approx 0.05$ . The results of this work are illustrated in Table II. It gives for comparison the probabilities of formation of magnetic clusters in the case of a random P(x) and modified  $P_m(x)$  distributions. Utilizing the values of  $P_m(x)$  the authors of Refs. 35, 38 could describe quite satisfactorily the experimental curves of the magnetization of  $Hg_{1-x}Mn_x$  Te and  $Hg_{1-x}Mn_x$  Se over a wide range of temperatures and magnetic fields.

However, it is clear that the problem of the adequacy of the obtained empirical distribution of the  $Mn^{2+}$  ions and their actual distribution in a SMS requires a further thorough investigation.

In the domain of low temperatures and strong magnetic fields the magnetization of the  $Hg_{1-x}Mn_x$  Te and  $Hg_{1-x}Mn_x$  Se crystals with a manganese content of x > 0.05, as it turned out, can be well described by the semiempirical formula

$$\langle S^{z} \rangle = -S_{0}B_{5/2} \left( \frac{\tilde{g}\mu_{B}SH}{k_{B}(T+T_{0})} \right), \qquad (26)$$

where  $S_0$  and  $T_0$  are adjustable parameters which can be determined from a comparison of expression (26) and the experimentally obtained dependence of the susceptibility on

TABLE III

			Hg <sub>1-x</sub>	Mn <sub>x</sub> Te		Hg <sub>1-x</sub> Mn <sub>x</sub> Se			
	т. к	x =	0,1	x = 0, 12		x = 0, 14		x = 0,145	
			T <sub>0</sub>	<i>S</i> 0	T <sub>0</sub>	S <sub>0</sub>	T <sub>0</sub>	$S_0$	$T_0$
:	1,7 4,2 10 20	1,02 1,02 0,83 1,14	9,9 8,6 8,6 23,4	0,87 0,89 0,94 1,18	11,7 11,0 14,1 22,7	0,77 0,79 0,85 1,03	12,1 11,2 12,9 18,5	0,67 0,70 0,74 0,86	9,9 9,4 10,7 14,9

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FIG. 6. The dependence of the magnetization of  $Hg_{1-x}Mn_x$  Te and  $Hg_{1-x}Mn_x$  Se crystals with different content of Mn on magnetic field and temperature.<sup>41</sup> 1—Hg<sub>0.855</sub> Mn<sub>0.145</sub> Se, 2—Hg<sub>0.865</sub> Mn<sub>0.14</sub> Te, 3—Hg<sub>0.9</sub> Mn<sub>0.1</sub> Te (solid lines are the results of calculations, the symbols denote experimental data).

the temperature. The values of  $S_0$  and  $T_0$  determined from the measurements of magnetic susceptibility<sup>41</sup> are shown in Table III.

The correspondence between the experimental curves and the theoretically calculated values of the magnetization for  $Hg_{1-x}Mn_x$  Te and  $Hg_{1-x}Mn_x$  Se is shown in Fig. 6.

#### b) The spin-glass phase

Investigating the temperature dependence of the magnetic susceptibility of the  $Hg_{1-x}Mn_xTe$  crystals with  $0.12 \le x \le 0.20$  the authors of Ref. 42 have demonstrated a nonmonotonic variation of the magnetic susceptibility in the range of temperatures 2-10 K for samples with a manganese content of  $x \ge 0.13$ . A similar behavior of the magnetic susceptibility was found for Hg<sub>0.65</sub> Mn<sub>0.35</sub> Te in the temperature range  $8 \leq T \leq 12$  K.<sup>38</sup> The appearance of a characteristic break in the  $\chi(T)$  curve and its shape, as the investigations of Ref. 38 have shown, depend in an essential manner on whether the sample was cooled in a magnetic field or in its absence (Fig. 7). Such a behavior of the magnetic susceptibility is characteristic for substances which have been given the name of spin-glasses (for example, CuMn, AuFe).43 The transition from a paramagnetic phase into the spin-glass phase was also found in studying the specific heat of SMS.35

Spin-glasses are characterized by having a definite temperature  $T_s$  below which a magnetic moment different from



FIG. 7. Dependence of the magnetic susceptibility of  $Hg_{1-x}Mn_x$  Te on the temperature.<sup>38</sup> 1—x = 0.012, 2—x = 0.036, 3—x = 0.35.

zero is present at the *i*th node of the lattice  $(\langle S_i \rangle \neq 0$  for  $T < T_S$  and  $\langle S_i \rangle = 0$  for  $T > T_S$ ) which is "frozen in" along a certain arbitrary axis. The distribution of these axes in space is random, so that the configuration average  $\langle \overline{S}_i \rangle = 0$  for all temperatures. It is important to note the radical difference of the spin-glass phase from the paramagnetic phase: in the latter the directions of the magnetic moments fluctuate in time continually and randomly. In a spin-glass for  $T < T_S$  the directions of the magnetic moments are "frozen" and do not change further with passage of time. The distribution of magnetic moments arising in the spin-glass phase is not the only one possible, it represents one of many almost degenerate ground states of the system.

The values of the critical concentration of manganese  $x_{cr}$  which separates the paramagnetic phase and the spinglass phase in  $Hg_{1-x}Mn_x$  Se is  $x_{cr} \approx 0.16^{.35}$  This value agrees well with the values which follow from the flow theory:  $x_{ci} = 0.17^{44}$ ,  $x_{cr} = 0.20.^{45}$  The existence of the spinglass phase for SMS with  $\varepsilon_g < 0$  has been demonstrated by the authors of Refs. 46, 47 who investigated  $Hg_{1-x}Mn_xTe$ with a manganese content of  $0 < x \le 0.075$ . The concentration of manganese in the investigated samples was significantly less than the flow concentration  $x_{cr}$ . It appeared that at such a low content of Mn<sup>2+</sup> the SMS must remain a paramagnetic substance right down to the very lowest temperatures. However, as is well known, in semiconductors an indirect exchange is possible between the magnetic ions  $Mn^{2+}$  as a result of the virtual transitions of electrons from the valence band into the conduction band. This mechanism is relatively weak in semiconductors with a finite value of the forbidden band ( $\varepsilon_g > 0$ ), since the indirect interaction is proportional to  $\exp[-\alpha m_n \varepsilon_g \mathbf{R}_{ij}/\hbar]$  ( $\mathbf{R}_{ij}$  is the distance between magnetic ions). At the same time in gapless SMS  $(\varepsilon_{e} < 0)$  the role played by virtual transitions in establishing the interaction between the  $Mn^{2+}$  ions (we shall return to this topic below) is sufficiently great as a result of which the formation of the spin-glass phase becomes possible.

With the aim of determining the possibility of a correlation between the magnitude of the gap  $\varepsilon_g$  and the temperature  $T_s$  of the transition to the spin glass the authors of Ref. 47 carried out a number of experiments using  $Hg_{1-x} Mn_x$  Te crystals for which a study was made of the influence on the value of  $\varepsilon_g$  of pressure acting on all sides. As the pressure is increased the value of  $|\varepsilon_g|$  decreases, becomes zero at a certain pressure  $\mathscr{P} = \mathscr{P}_c$ , at which the  $\Gamma_6$  and  $\Gamma_8$  terms are inverted, and later for  $\mathcal{P} > \mathcal{P}_c$  a direct gap  $\varepsilon_g = \varepsilon(\Gamma_6) - \varepsilon(\Gamma_8) > 0$  opens up in the SMS. The results of these measurements shows that the transition of the SMS into the spin-glass phase occurs only in the region of the gapless state. After the inversion of the  $\Gamma_6$  and  $\Gamma_8$  terms such a transition was not observed. This, apparently, indicates that the existence of the spin-glass state for  $\varepsilon_g < 0$  is due to the exchange interaction of the  $\mathrm{Mn}^{2+}$  ions which is brought about with the aid of virtual interband transitions of electrons through the zero forbidden band. The spin-glass behavior in this case is the result of the random distribution of the magnitude and the sign of the integral of the indirect exchange interaction between neighboring magnetic moments.

At sufficiently high concentrations of Mn, when the SMS crystals have a finite gap, the indirect exchange due to the virtual transitions cannot be responsible for the occurance of the spin-glass phase. One might think that in this case the frustration mechanism<sup>50,51</sup> is responsible for the transition to the spin-glass phase. The essence of this mechanism is as follows. In an SMS with a gap the  $Mn^{2+}$  ions form, as has been established, a large number of magnetic clusters. The minimum in the energy of the magnetic ferro- or anitferromagnetic interaction between the Mn<sup>2+</sup> ions within the limits of each cluster corresponds to a certain "optimum" ferro- or antiferromagnetic orientation of magnetic moments within the cluster. As the temperature is lowered the magnetic moments of the clusters do not form a magnetically ordered phase: The minimum of the energy of the crystal below a certain critical temperature  $T = T_s$  characteristic for the crystal corresponds to the spin-glass phase in which the magnetic moments of the clusters turn out to be "frozen" and form a frustrated<sup>6)</sup> system in a random manner. We note that the location of the magnetic moments of  $Mn^{2+}$  in the ground state of a frustrated system is not unique: a large number of equivalent states of the system is possible.

Fig. 8 shows phase diagrams for the SMS  $Hg_{1-x}Mn_x$  Te and  $Hg_{1-x}Mn_x$  Se obtained by means of magnetic measurements. For  $Hg_{1-x}Mn_x$  Te two regions of the spin-glass phase can be seen. However, if one takes into account the tendency towards the formation of clusters even for a relatively low content of manganese in SMS, and also the data from the investigations of SMS with a wide forbidden band (Cd<sub>1-x</sub>Mn<sub>x</sub> Te<sup>52</sup>), according to which the spin-glass phase is realized for crystals with a manganese content



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FIG. 8. Phase (T-x) diagrams of the magnetic state of an SMS. *p*-region of the paramagnetic phase *S*-region of the spin-glass. a—the SMS Hg<sub>1-x</sub> Mn<sub>x</sub> Te (the inset shows data from Ref. 47; open circles are from Ref. 39, solid circles are from Ref. 38); b—the SMS Hg<sub>1-x</sub> Mn<sub>x</sub> Se (circles are from Ref. 35).

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of x = 0.01 and x = 0.05 at  $0.01 \le T \le 0.1$  K, it is not possible to disregard the probability of existence on the phase diagram of a single region of the spin-glass phase. It is clear that it is necessary to investigate the SMS  $Hg_{1-x} Mn_x$  Te with an intermediate content of manganese from x = 0.05 to x = 0.10 (cf., Fig. 8).

## c) The indirect interaction in the gapless crystals $Hg_{1-x}Mn_x$ Te

With a low content of manganese in the SMS the orbits of the strongly localized d electrons of the manganese ions overlap very little. In this case the direct exchange interaction between the localized moments, which is due to the overlap of the wave functions of the electrons of neighboring ions, becomes negligibly small. Nevertheless the exchange coupling between magnetic moments localized on ions can arise even in the absence of a direct exchange as a result of the indirect exchange through the band charge carriers (RKKI interaction)<sup>7)</sup>. However at low temperatures the concentration of band charge carriers in gapless SMS of the type of  $Hg_{1-x}Mn_xTe$  ( $x \le 0.07$ ) is relatively not very great ~ $10^{15}$ - $10^{16}$  cm<sup>-3</sup>. As estimates in Ref. 24 have shown this number of charge carriers turns out to be insufficient to ensure effective RKKI interaction between localized magnetic moments. The absence of an energy gap in  $Hg_{1-x}Mn_xTe$ crystals with  $x \leq 0.07$  results in the fact that the indirect exchange coupling between  $Mn^{2+}$  ions can be brought about by virtual electrons excited from the valence band into the conduction band. Such a mechanism for the indirect exchange was discussed for the first time in the paper by Bloembergen and Rowland as applied to an antiferromagnetic dielectric substance.53 For semiconductors with different variants of mutual placing of the maximum of the valence band and several minima of the conduction band the mechanism of indirect exchange via the virtual electrons was studied in the papers of Abrikosov.54

Due to strong spin-orbit coupling of electrons in  $Hg_{1-x}Mn_x$  Te the indirect exchange interaction is no longer described by the simple expression in the Heisenberg form  $\sim S_1S_2$  but has a more complicated form<sup>49</sup>:

$$H_{\rm ex} = \sum_{\alpha\beta} \Delta^{\alpha\beta} \mathbf{S}_1 \mathbf{S}_2 \qquad (\alpha, \ \beta = x_1, \ y, \ z).$$
(27)

The tensor  $\Delta^{\alpha\beta}$  describing the indirect exchange coupling between manganese ions is characterized in the general case by nine independent constants. This number, generally speaking, can be decreased, if one takes into account the placing of a pair of Mn<sup>2+</sup> ions with respect to the atoms of the lattice.<sup>55</sup> The symmetric part of the  $\Delta^{\alpha\beta}$  tensor is the sum of the Heisenberg exchange interaction

$$H_{\rm ex}^{\rm I} = A \sum {\rm S}_{\rm i} {\rm S}_{\rm 2} \tag{28}$$

and the anisotropic pseudodipole interaction

$$H_{ex}^{II} = B \left[ \mathbf{S}_{1} \mathbf{S}_{2} - 3 \frac{(\mathbf{R}_{12} \mathbf{S}_{1}) (\mathbf{R}_{12} \mathbf{S}_{2})}{\mathbf{R}_{12}^{2}} \right];$$
(29)

here  $\mathbf{R}_{12} = \mathbf{R}_1 - \mathbf{R}_2$ , and the constants A and B are expressed in terms of the diagonal components of the  $\Delta^{\alpha\beta}$  tensor.<sup>49</sup>

Estimates of the exchange integrals made in Refs. 56, 57

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on the assumption that the valence band is completely filled, and the conduction band is empty (the case corresponds to T = 0) have shown that the pseudodipole interaction (29) introduces a greater contribution to the exchange coupling of (Mn - Mn) than the isotropic interaction (28).

Therefore the estimate of the temperature of magnetic ordering which was earlier made by Bastard and Lewiner,<sup>57</sup> who considered only the isotropic interaction (28), is incorrect: The presence of a large anisotropic interaction must lead to the "freezing" of localized moments, i.e., to the formation of a spin glass. Investigations of the magnetic susceptibility of gapless semiconductors  $Hg_{1-x}Mn_xTe^{47}$  indeed showed that at low temperatures a spin-glass phase is realized.

## 4. MAGNETO-OPTICAL PROPERTIES

A study of intraband and interband transitions executed by band charge carriers on absorbing light in a magnetic field enables one to obtain information on the energy spectrum, the effective masses and the g-factor of the charge carriers.

Experiments on investigations of magneto-optical transitions in SMS were carried out both for the Faraday configuration (**k**||**H**) and for the Voigt configuration (**k**⊥**H**) (**k** is the wave vector of the electromagnetic wave). The energy of the radiation utilized by different investigators to excite both intraband (transitions between Landau levels within the limits of the same band  $\Gamma_8 \rightarrow \Gamma_8$ ) and also interband (transitions of the type  $\Gamma_6 \rightarrow \Gamma_8$ ) transitions amounted to several meV (3.68<sup>58</sup>, 6.36<sup>59</sup>, 10.45<sup>19</sup>) to hundreds of meV (230–370)<sup>60,61</sup>, 600.<sup>19</sup> All the experiments were carried out in the temperature range from 4.2 K to 80 K. The concentration of manganese in the SMS crystals that have been investigated was varied over quite a wide range  $x \le 0.001^{-59}$ ,  $x \le 0.02^{-62}$ ,  $x \le 0.15^{-3}$ ,  $^{63}$ ,  $x \le 0.27^{-63}$ . In other words, both gapless ( $\varepsilon_g < 0$ ), and semiconducting ( $\varepsilon_g > 0$ ) SMS samples were investigated.

#### a) Magneto-optical transitions in gapless SMS

Selection rules which were satisfied by the magnetooptical transition in the gapless SMS that were investigated are shown in Table IV: here  $\varepsilon''$  corresponds to the longitudinal, and  $\sigma^{\pm}$  corresponds to the right and left circular polarizations of the electromagnetic wave.

The first characteristic feature discovered in the absorption spectral of gapless SMS turned out to be their strong temperature dependence in the temperature range 2– 4 K.<sup>9</sup> As the manganese concentration was increased the position of the observed absorption maxima was shifted in the direction of lower magnetic fields.

TABLE	IV
TADLL	Τ.

Polariza- tion	Transition
σ+	$b_{\Gamma_8}(N+1) \rightarrow b_{\Gamma_8}(N)$
σ-	$\boldsymbol{a}_{\Gamma_6}(N) \to \boldsymbol{a}_{\Gamma_8}(N+1)$
ε″	$a_{\Gamma_{\mathfrak{g}}}(N) \to b_{\Gamma_{\mathfrak{H}}}(N+1)$



FIG. 9. Dependence of the energy of the spin splitting  $\varepsilon_{sp}(N = 1)$  on the magnetic field for  $Hg_{1-x}Mn_x Te$  and  $HgTe^9$ .

Compared to the energies of transitions observed in gapless  $Hg_{1-x}Mn_x$  Te crystals at a temperature of 4.2 K with corresponding transitions in  $Hg_{1-x}Cd_xTe$  crystals with the same value of the energy gap  $\varepsilon_{g} = \varepsilon(\Gamma_{6}) - \varepsilon(\Gamma_{8})$ , the authors of Ref. 10 have established that these transitions for the case of  $\varepsilon''$  polarization practically coincide for both types of crystals while for the  $\sigma^-$  polarization the position of the corresponding transitions in  $Hg_{1-x}Mn_x$  Te is shifted in the direction of the lower and for the  $\sigma^+$  polarization is shifted in the direction of greater energies compared with the position of the corresponding transitions in  $Hg_{1-x}Cd_xTe$ . This fact indicates that the energy of the spin splitting  $\varepsilon_{sp}(N)$  in SMS increases. An analysis of the magneto-optical spectra showed that the energy of the spin splitting in SMS depends both on the composition x, and on the temperature. A typical dependence of the energy of the spin splitting  $\varepsilon_{sp}(N=1)$ on the magnetic field found for  $Hg_{1-x}Mn_xTe$  from the difference in the energies between the transitions  $(2^+ \rightarrow 1^+)$  for the  $\sigma^+$  polarization and  $(2^- \rightarrow 1^-)$  for the  $\varepsilon''$  polarization is shown in Fig. 9.

Figure 10 illustrates the dependence of the energy of spin splitting on the magnitude of the energy gap  $\varepsilon_g$  i.e., on the content of Cd or Mn in  $Hg_{1-x}Cd_xTe$  and  $Hg_{1-x}Mn_xTe$  crystals in a magnetic field of H = 20 kOe. We note that the change in the energy of spin splitting in SMS with temperature and with composition leads to a different dependence of the difference in the energies of the transitions  $\delta = \varepsilon(1^+ \rightarrow 2^+) - \varepsilon(1^- \rightarrow 0^-)$  on the value of the energy gap  $\varepsilon_g$  than in the case of the gapless semiconductors of the type  $Hg_{1-x}Cd_xTe$ . Thus, if for the  $Hg_{1-x}Cd_xTe$  crystals with  $\varepsilon_g < 0$  the value of  $\delta$  increases as the temperature and the Cd content increase, then for the SMS the value



FIG. 10. Dependence of the energy of spin splitting for  $Hg_{1-x} Cd_x Te(1)$ and  $Hg_{1-x} Mn_x Te(2)$  on the value of the energy gap  $\varepsilon_g^{9}$ .



FIG. 11. Dependence on the magnetic field of the energy of the  $\Gamma_6 \rightarrow \Gamma_8$ Hg<sub>0.99</sub> Mn<sub>0.01</sub> Te at T = 2 K.<sup>9</sup> Dotted lines—theory, symbols—experiment.

of  $\delta$  decreases and becomes negative. Thus, for the SMS  $Hg_{1-x}Mn_x$  Te with  $\varepsilon_g = -270$  meV the value of  $\delta$  is negative.<sup>65,60</sup>

In contrast to spectra of gapless semiconductors of the type  $Hg_{1-x} Cd_x$  Te in the magneto-optical absorption spectra of gapless SMS an interchange between the magnetoabsorption curves for  $\sigma^+$  and  $\sigma^-$  polarizations was observed. Thus, as the manganese content in  $Hg_{1-x} Mn_x$  Te with  $x \le 0.02$  was increased, the curve corresponding to the  $1^- \rightarrow 0^-$  transition turns out to be situated higher in energy than the curve which corresponds to the  $1^+ \rightarrow 2^+$  transition in Fig. 11.<sup>10</sup>

We have already noted that in gapless SMS the energy of the valence level at low temperatures increases as the magnetic field is increased so strongly that the level b (-1) turns out to be higher in energy than the lowest electronic level of the conduction band. It is evident that in this case one should expect in the magnetoabsorption spectrum the appearance of additional lines associated with the transitions of band electrons to this level. Such transitions have been actually identified in Hg<sub>1-x</sub> Mn<sub>x</sub> Te crystals with a manganese content in the range  $0.004 \le x \le 0.08$  at a temperatures of T = 2 K (Fig. 11).

Finally, in Hg<sub>1-x</sub> Mn<sub>x</sub> Te with x > 0.04 a transition was observed in magneto-optical spectra from the Landau levels of the  $\Gamma_6$  band to an acceptor level lying in the  $\Gamma_8$  band. As the analysis of Ref. 10 has shown the energy of the transitions  $\varepsilon_{\Gamma_6} \rightarrow \varepsilon_A$  as the magnetic field is made to approach zero tends to the value  $\varepsilon_g + \varepsilon_A$  while for the transitions  $\varepsilon_{\Gamma_6} \rightarrow \varepsilon_{\Gamma_8}$ it tends to the value  $\varepsilon_g$ . The value of  $\varepsilon_A$  found in this manner turned out to be equal to 2–3 meV for Hg<sub>1-x</sub> Mn<sub>x</sub> Te crystals with  $\varepsilon_g \approx 150$  meV.<sup>11</sup>

#### b) Magneto-optical transitions in SMS with a finite gap

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We examined briefly the magneto-optical phenomena in SMS with a finite value of the energy gap ( $\varepsilon_g > 0$ ). The selection rules which are obeyed by the magneto-optical transitions are the same as in ordinary semiconductors<sup>66</sup>

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TABLE V

Polariza- tion	Transition				
σ•	$a_{\Gamma_8}(N) \rightarrow a_{\Gamma_6}(N+1),$	$b_{\Gamma_8}(N) \rightarrow b_{\Gamma_6}(N+1)$			
σ	$a_{\Gamma_8}(N) \rightarrow a_{\Gamma_8}(N+1),$	$b_{\Gamma_8}(N) \rightarrow b_{\Gamma_6}(N+1)$			
8″	$a_{\Gamma_8}(N-1) \to b_{\Gamma_6}(N),$	$b_{\Gamma_6}(N+1) \rightarrow a_{\Gamma_6}(N)$			

(Table V).

The analysis of transition probabilities shows that for the  $\sigma^+$  polarization the contribution from the transitions from the heavy-hole band is considerably weaker than for the  $\sigma^-$  and  $\varepsilon''$  polarizations. For the  $\varepsilon''$  polarization the transitions

$$a_{\Gamma_{\bullet}}(N+1) \rightarrow b_{\Gamma_{\bullet}}(N), N \ge 0$$

are the dominant ones from the heavy-hole band, while for the  $\sigma^-$  polarization the principal transition is one of the type of

$$b_{\mathbf{F}} (N-1) \rightarrow b_{\mathbf{\Gamma}_{\bullet}}(N), N \ge 0.$$

In this case the transitions from the bands of heavy and light holes are equivalent.<sup>66</sup>

In accordance with the selection rules stated above and the transition probabilities the magnetoabsorption spectra for  $\sigma^-$  and  $\varepsilon''$  polarizations turn out to be considerably richer than spectrum for the  $\sigma^+$  polarization, where only a very weak structure has been observed.<sup>60</sup>

The temperature dependence of the magnetoabsorption spectra in the case of SMS with a gap is considerably weaker than in the gapless semiconductors.<sup>65,60</sup> This is due, as has been noted, to the increase in the probability of formation of large magnetic clusters as the manganese content in SMS is increased. The contribution to the magnetization made by the cluster can in this case turn out to be smaller than in the case of individual manganese ions. Thus, for example, if the localized spins of the Mn<sup>2+</sup> ions in a cluster are situated in an antiparallel fashion, then the magnetic moment of the cluster will be lower than in the case of an individual Mn ion.<sup>41</sup> A confirmation of an increase in the role of magnetic clusters as the concentration of manganese ions is increased is provided by the increasing deviation of the experimental magnetization curves from the Brillouin curve for  $Hg_{1-x}Mn_x Te.^{61}$ 

Just as in the case of gapless SMS, in the magneto-optical spectra of  $Hg_{1-x}Mn_x$  Te with a finite energy gap  $(0.12 \le x \le 0.17)^{61}$  a transition was observed from an acceptor level to the level b(1) of the conduction band. The dependence of the energy of the acceptor level  $\varepsilon_A$  on the magnetic field found by the authors of Ref. 61 at T = 2 K, is shown in Fig. 12.

An analysis of the magneto-optical spectra in SMS with a gap showed that the energy of the transition  $\varepsilon_{\Gamma_{s}}(-1) \rightarrow \varepsilon_{\Gamma_{s}}(0)$  decreases as the magnetic field is increased. This effect is evidently due to the fact that just as in the case of gapless SMS the exchange correction to the energy of the valence level b(-1) shifts it upward in energy, and



FIG. 12. Dependence of the energy of an acceptor level on the magnetic field in Hg<sub>0.87</sub> Mn<sub>0.13</sub> Te ( $\varepsilon_g = 219$  meV) at T = 2 K.<sup>61</sup>

this leads to a decrease in the energy of the transition.

All the above "anomalous" magneto-optical properties of SMS can be interpreted if one takes into account the exchange interaction of the band charge carriers with the localized d electrons of the manganese ions. Indeed, a change in the temperature and the manganese content leads to a change in the magnetization of the sample, which in turn determines the change in the energy of the band carriers. Evidently the values of the magnetic fields corresponding to the magneto-optical transitions also change in this case both with temperature and with the manganese content in SMS.

### 5. KINETIC PROPERTIES

In this section we examine the effect on the kinetic properties of the SMS of the renormalization of the electron energy spectrum due to the exchange interaction of band electrons with the ions of transition elements.

## a) Shubnikov-de Haas (ShH) oscillations

One of the methods of studying the energy spectrum of charge carriers that provides the most information is the ShH effect. The ShH oscillations of the longitudinal and transverse magnetoresistance were studied in SMS in steady state (up to 60 kOe) and in pulsed (up to 300 kOe) magnetic fields in the temperature range of 1.7-77 K.<sup>9,18,69-73</sup> In both the gapless SMS and those with a gap special features of the ShH oscillations were found which do not occur in semiconductors which do not contain magnetic ions. We list these special features.

1. In the quasiclassical region of magnetic fields, where the ShH oscillations are determined by the Landau levels with high quantum numbers N, the harmonic picture of oscillations in the case of gapless SMS breaks down—beats and nodes appear (Fig. 13).<sup>69</sup>

2. The amplitudes of the peaks in the oscillations change with temperature in a nonmonotonic fashion (Fig. 14).<sup>9,69</sup> A similar character of the dependence on the temperature of the amplitude of the de Haas-van Alfven oscillations was observed earlier in the case of the Cu:Mn alloys.<sup>72</sup> It is clear that similar changes in the amplitudes of oscillations in the case of gapless SMS do not allow one to use the usual method for determining the effective mass of electrons based on the temperature dependence of the amplitudes at a fixed value of the magnetic field. As the analysis of Ref. 69 has shown, the ratio of amplitudes at two temperatures can take on values both greater than and less than unity for different oscillation



FIG. 13. Formation of oscillation nodes (indicated by arrows) in  $Hg_{1-x}Mn_x Se (x = 0.013; n = 9 \cdot 10^{18} \text{ cm}^{-3})$  at different temperatures.<sup>69</sup>

peaks. Negative masses would correspond to the latter case.

3. Investigation of the ShH oscillations over a wide temperature range showed that the positions of the oscillation peaks are shifted considerably with temperature. As the temperature is increased some of the peaks are shifted in the direction of higher magnetic field. But usually as a result of the partial lifting of the degeneracy of the electron gas by the magnetic field the peaks are shifted in the direction of lower fields. Moreover, as the temperature is increased, some of the peaks are split (Fig. 15).<sup>69</sup> The appearance of a doublet structure of the peaks is associated with the spin splitting of the Landau levels. However, in contrast to usual semiconductors where the splitting of the levels as the temperature is increased is smeared out, in the case of SMS it appears and is increased. The special features of the ShH oscillations in the case of SMS, just as the effects found in the investigations of the magneto-optical spectra, are due to the effect of the exchange interaction on the energy spectrum of the band charge carriers.

Let us analyze the oscillation picture in the range of magnetic fields where peaks that are not split according to spin are observed. In the quasiclassical limit  $N \ge 1$  the oscillating part of the magnetoresistance is

$$\frac{\Delta \rho_{xx}}{\rho_0} = \sum_{r=1}^{\infty} A_r \cos\left(2\pi r \,\frac{\varepsilon_{\rm F}}{\hbar \omega_{\rm c}} - \frac{\pi}{4}\right),\tag{30}$$

where the amplitude of oscillations is given by



FIG. 14. Temperature dependence of the amplitude of the oscillation peak for  $Hg_{1-x}$  Mn<sub>x</sub>Se (x = 0.013, n = 3 · 10<sup>17</sup> cm<sup>-3</sup>).<sup>69</sup>

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FIG. 15. Effect of temperature of the spin splitting of oscillation maxima in  $Hg_{1-x}Mn_x Se^{69}$ 

$$A_{r} = \sqrt{\frac{\hbar\omega_{c}}{\varepsilon_{F}}} \frac{(-1)^{r} y}{\sqrt{r} \operatorname{sh}(ry)}} \exp\left(-\frac{2\pi^{2} r k_{B} T_{D}}{\hbar\omega_{c}}\right) \cos\left(\pi v^{*} r\right),$$
(31)

here  $y = 2\pi^2 k_B T / \hbar \omega_c$ ,

$$v^* = \frac{g^*m}{2m_0} = \left( - |g| + \frac{\beta N_0 x \langle S^z \rangle}{\mu_{\rm B} H} \right) \frac{m}{2m_0}$$

 $T_{\rm D}$  is the Dingle temperature, which characterizes the nonthermal smearing of the Landau levels. The factor  $\cos(\pi v^* r)$  appears as a result of the spin splitting of the Landau levels.

Electrons of the two spin sublevels  $\sigma = + 1/2$  make an additive contribution to the magnetoresistance which can be represented in the form of harmonics with the same period but displaced in phase. If  $v^*$  does not depend on the magnetic field H, as is the case in usual semiconductors, then the superposition of each pair of harmonics with a given value of r leads to a decrease of the total amplitude of the oscillations  $A_r$ . Thus, for example, for  $v^* = 1/2$  the amplitudes of the first and all the odd harmonics are identically equal to zero. As is well known, this is manifested by the doubling of the period of oscillations.

If  $v^*$  varies weakly with the field over the range of periodicity of the function  $\cos(2\pi\varepsilon_F/\hbar\omega_c)$ , the factor  $\cos(\pi v^*r)$ modulates the amplitude of the oscillations and describes beats of the fundamental harmonic with i = 1. In fields  $H_0$ that satisfy the condition  $v^* = (2l + 1)/2(l = 0, 1, 2...)$ , the amplitude of the first harmonic vanishes, while the amplitude of the second harmonic (r = 2) is in this case a maximum. Under such conditions no sharply expressed node is observed, but in a certain neighborhood of the field  $H = H_0$  a "disruption" of oscillations occurs. Along the oscillation curve an appearance of whole series of nodes becomes possible, corresponding to different values of l = 0, 1, 2.... However, according to estimates that have been made, nodes with l = 2, 3, 4... must be situated at very low magnetic fields,

where the oscillations are poorly resolved, and the node with l = 0, on the contrary, must be situated in the region of strong magnetic fields where the description of the oscillation picture with the aid of harmonic formulae is no longer reasonable. Therefore, in the experiments of Ref. 69 only nodes with l = 1, 2 were successfully observed.

#### b) g-factor of band electrons

As is well known, the position of the zero peak of the ShH oscillations in a magnetic field is associated with the *g*-factor of the electrons:

$$H_{0}^{-} = \frac{\hbar c}{e} \left[ \frac{4\pi^{4} n^{2} m_{0}}{|s^{*}| m} \right]^{1/3} .$$
(32)

In studying the evolution of the first (from the side of higher magnetic fields) oscillation peaks as the temperature is varied, it is possible to analyze the effect of the exchange interaction on the energy of the band charge carriers in SMS.<sup>73</sup> It has been established experimentally that as the temperature increases the zero peak is shifted noticeably into the region of higher magnetic fields. The values of the *g*-factor have been determined by the authors of Ref. 73 from the positions of the zero peak taking into account the corrections for the incomplete degeneracy of the electron gas:

$$|g^*| = \frac{2m_0}{m} \left( \frac{\sqrt{\pi} n\lambda^3}{2} - 0.535 \sqrt{\frac{k_B T}{\hbar \omega_c}} \right)^2.$$
(33)

The results for  $Hg_{1-x}Mn_x$  Se with  $x = 0.01(n = 3 \cdot 10^{17} \text{ cm}^{-3})$  and  $x = 0.12(n = 1.3 \cdot 10^{17} \text{ cm}^{-3})$  are shown in Table VI.

From Table VI it can be seen that for the gapless SMS as the temperature is lowered from 77 to 4.2 K the exchange correction leads to an increase in the energy of the spin splitting  $\varepsilon_{sp} = |g^*|\mu_B H$ . The anomalously large values of  $|g^*_{T_s}|$  at low temperatures indicate that the exchange integral  $\beta N_0$ for electrons of the  $\Gamma_8$  band is negative. As the temperature increases  $|g^*_T s|$  decreases monotonically approaching the value of |g| given by the Kane theory (12).

For SMS with a finite energy gap the situation is different. In view of the fact that

$$|g_{\Gamma_{\bullet}}^{\star}| = |g_{\Gamma_{\bullet}}| + \frac{\alpha N_0 x \langle S^2 \rangle}{\mu_{\mathrm{B}} H} < |g_{\Gamma_{\bullet}}|$$
  
and  $g_{\Gamma_{\bullet}} < 0$ ,

the exchange integral  $\alpha N_0$  for electrons of the  $\Gamma_6$  band must be positive. Since as the temperature is increased the spectroscopic splitting factor decreases monotonically then, evi-

TABLE VI

	g*(T)			
Т, К	$\varepsilon_{g}^{x=0,01}$ , $\varepsilon_{g}^{z=-220}$ meV	$\varepsilon_{g} \stackrel{x=0,12,}{=+260 \text{ meV}}$		
1,7 3,5 4,2 14 25 64 77	35 35 35 31 27 18 16	4,0 3,7 3,6 2,4 1,6 0 0		





FIG. 16. Effect of exchange interaction on the energy spectrum of band charge carriers in narrow-gap (a) and gapless (b) SMS (qualitative representation).

dently, the exchange interaction leads to the inversion of the Landau spin sublevels, i.e.,  $\varepsilon_0 \uparrow > \varepsilon_0 \downarrow$  (Fig. 16). With a further increase of temperature in a certain magnetic field  $H = H_1$  evidently a degeneracy of spin sublevels  $(g^* = 0$  for  $\varepsilon_{0\downarrow}(H_1) = \varepsilon_{0\uparrow}(H_1)$ ) must evidently occur, after which  $|g^*(T)|$  will again increase, and  $\varepsilon_0 \downarrow > \varepsilon_0 \uparrow$ . In the sample of Hg<sub>0.88</sub> Mn<sub>0.12</sub> Se investigated by the authors in Ref. 73 this corresponds to a region of temperatures where the ShH oscillations, unfortunately, have not been resolved. Apparently, such an effect should be expected in the case of SMS with a lower concentration of manganese ( $x \leq 0.10$ ). Thus, for SMS with a finite gap the temperature dependence of  $|g^*_{\Gamma_0}|$  must be nonmonotonic, in contrast to gapless SMS.

#### c) ShH oscillations in the quantum limit

It is well known that the dependence of the Fermi energies of the electrons on the magnetic field in the case of usual semiconductors (for example, in the case of InSb) does not alter the period of the ShH oscillation, but is manifested only in the positions of the peaks i.e., in the values of the magnetic field at which the peaks are situated.<sup>1</sup> The first peak from the side of the high magnetic fields (0<sup>-</sup>-peak) corresponds to the crossing of the Fermi level with the spin sublevel  $\varepsilon_{0, -1/2}$ , while the next peak (1<sup>+</sup>-peak) corresponds to the equality  $\varepsilon_F = \varepsilon_{1, +1/2}$ .

For a SMS with a finite gap  $(\varepsilon_g > 0)$  quite a different situation is possible. Indeed, in the case  $\varepsilon_g > 0$  in magnetic fields

$$H \supset H_1 = \frac{\alpha N_0 x}{|g| \mu_B}$$
(34)

an inversion of the Landau spin sublevels occurs, and this under the conditions of the quantum limit when only the lower Landau level is populated ( $\varepsilon_g < (3/2)\hbar\omega_c$ ), leads to additional nonmonotonic behavior in the dependence of the Fermi energy on the magnetic field. The main special feature of this additional lack of monotonic behavior of the curve of  $\varepsilon_F(H)$  consists of the fact that at electron concentrations  $n \leq 2.7 \cdot 10^{17}$  cm<sup>-3</sup> the Fermi level crosses the Landau sublevel (bottom of the sub band)  $\varepsilon_{0, +1/2}$  twice in magnetic fields  $H < H_i$ , crosses the Landau sublevel  $\varepsilon_{0, -1/2}$  at  $H > H_i$  and



FIG. 17. Variation of the Fermi energy  $\varepsilon_{\rm F}(H)$  and of the Landau levels for different concentrations of the conduction electrons in Hg<sub>0.9</sub> Mn<sub>0.1</sub>Se.  $n({\rm cm}^{-3}) = 1.3 \cdot 10^{17} (1)$ ,  $2.0 \cdot 10^{17} (2)$  and  $3.5 \cdot 10^{17} (3)$ . On curve 2 arrows indicate the crossing of the curves for  $\varepsilon_{0, +1/2}$  and  $\varepsilon_{\rm F}(H)$  where appearance of zero oscillation peaks is possible.

only then, in stronger fields, tends to the sublevel  $\varepsilon_{0, +1/2}$  (Fig. 17).

From Fig. 17 it is clearly seen that, as a result of the inversion of Landau sublevels  $\varepsilon_{0, -1/2}$  and  $\varepsilon_{0, +1/2}$  in the field  $H_i$  additional peaks can rise in stronger magnetic fields together with the  $0_1^+$  peak observed in the case of usual semiconductors, which is due to the coincidence of the Fermi level with the upper Landau sublevel  $\varepsilon_{0, +1/2}$ .

The results of calculating the transverse conductivity  $\sigma_{xx}$  for different values of the collision broadening of the Landau level  $\Gamma^{78}$  confirm the qualitative considerations that in the region of magnetic fields  $H \approx H_i$  two additional maxima of the magnetoresistance arise (at  $\Gamma \approx 3$  K) ( $0_2^+$  and  $0_1^-$ ) which correspond to the intersection of the Fermi level with the spin sublevels  $\varepsilon_{0, +1/2}$  (for  $H < H_i$ ) and  $\varepsilon_{0, -1/2}$  (for  $H > H_i$ ). Calculations show that the resolution of the  $0_2^+$  and  $0_1^-$  peaks depends to a considerable extent on the collisional broadening parameter  $\Gamma$ . For large values of  $\Gamma$  ( $\Gamma \approx 5$  K) the  $0_2^+$  and  $0_1^-$  peaks are smeared out into a single maximum situated in the magnetic field  $H \approx H_i$ .

An analysis of the ShH oscillations of the longitudinal magnetoresistance  $\rho_{zz}(H)$  has shown<sup>78</sup> that, just as in the case of the transverse magnetoresistance it is possible for three oscillation peaks to appear in magnetic fields satisfying the condition  $\varepsilon_F(H) = \varepsilon_{0, + 1/2}$ . However, in contrast to the transverse magnetoresistance the longitudinal magnetoresistance  $\rho_{zz}(H)$  can lack oscillation maxima in fields  $H \approx H_i$  when  $g^* = 0$  and the energy of the spin splitting is less than  $\Gamma$ . Under these conditions one of the maxima in the fields  $H < H_i$  or  $H > H_i$  can also disappear.

Thus, an analysis of the ShH oscillations in the quantum limit in the case of SMS points to the essential role played by the dependence of the Fermi energy on the magnetic field. However, as a rule, in interpreting the results of measuring the magnetoresistance of the  $Hg_{1-x} Mn_x$  Te and  $Hg_{1-x} Cd_x$  Te crystals it was assumed<sup>17,80</sup> that the Fermi level does not depend on the magnetic field and remains constant even in very strong fields. Possibly it is just because of this that the authors of Ref. 80 could not explain the reason for the appearance of additional peaks of  $\rho_{xx}(H)$  in  $Hg_{0.89} Mn_{0.11}$  Se in magnetic fields 100–200 kOe.

SMS	x	aNo, eV	β <b>Ν</b> 0, eV
Hg <sub>1-x</sub> Mn <sub>x</sub> Te, 4,2 K Hg <sub>1-x</sub> Mn <sub>x</sub> Se, 10 K	$\begin{array}{c} 0,09\\ 0-0,16\\ 0-0,09\\ 0,02\\ 0,01\\ 0,026\\ 0-0,12^{12}\\ 0,01\\ 0,12\\ \end{array}$	$1,4^{75},7^{4},4^{59},7^{5},65^{79},7^{5},9^{18},35^{76},7^{5},7$	$\begin{array}{c} -2,3 & 75 \\ -1,4 & 77 \\ -0,7 & 62, & -0,65 & 53 \\ -1,4 & 75, & -0,7 & 5 \\ -1,5 & 18 \\ -0,9 & 76 \\ -0,7 & 76 \\ -0,28 & 69 \end{array}$

#### d) Estimate of the values of exchange integrals

The values of the exchange integrals  $\alpha N_0$  and  $\beta N_0$  for  $Hg_{1-x}Mn_x$  Te and  $Hg_{1-x}Mn_x$  Se determined from the magneto-optical measurements and the ShH oscillations are shown in Table VII.

The noticeable differences in the values of the exchange integrals, both of  $\alpha N_0$ , and  $\beta N_0$ , obtained by different authors from the ShH oscillations are due, as analysis has shown, firstly, to the use of different methods of reducing the results of measurements; and secondly, and this is the determining factor, to the different form of recording the magnetization energy  $\Delta \varepsilon_{N,\sigma}$ . Thus, the authors of Refs. 18, 77 utilizing the procedure of fitting the parameters have calculated the dependence of the energy of the Landau levels  $\varepsilon_{N,\sigma}$  on the magnetic field and the temperature, and then have determined the position of the oscillation maxima of the magnetoresistance from the condition  $\varepsilon_{\rm F}(H) = \varepsilon_{\rm F}(0) = \varepsilon_{N,\sigma}$ . The dependence of the Fermi energy on the magnetic field in this case was not taken into account, i.e., it was assumed that  $\varepsilon_{\rm F}(H) = \varepsilon_{\rm F} = {\rm const.}$  The criterion for the correct choice of the parameters was the coincidence of the calculated and experimentally observed positions of the peaks in the magnetoresistance. We note, however, that in the region of magnetic fields close to the quantum limit it is extremely important to take into account the dependence of the Fermi energy on the magnetic field. The function  $\varepsilon_{\rm F}(H)$  without appreciably distorting the periodicity of the oscillations not only significantly affects the position of the oscillation peaks, but also, as was mentioned in Sec. 5c can give rise to the appearance of new additional ShH oscillations in SMS.

In order to estimate the parameters of the exchange interaction the authors of Ref. 69 took into account the fact that for Hg<sub>0.97</sub> Mn<sub>0.03</sub> Se with a concentration of the conduction electrons of  $n \approx 3.2 \times 10^{17}$  cm<sup>-3</sup> at  $T \leq 4$  K the Landau levels  $\varepsilon_{2, +1/2}$  and  $\varepsilon_{1, -1/2}$  merge in the magnetic field of 80 kOe. The values of the exchange parameter calculated under these conditions should, evidently, be regarded as more reliable than the values found without taking into account the dependence of the Fermi energy on the magnetic field.

The apparent differences in the numerical values of the exchange parameters  $\beta N_0$  in Table VII are due to the fact that the different authors in interpreting the experimental data utilized different forms of recording the magnetization energy  $\Delta \varepsilon_{N,\sigma}$ . Thus, in Refs. 18, 75, 77 it was assumed that the charge carriers in the  $\Gamma_8$  band are classified, just as in the

 $\Gamma_6$  band according to the value of the spin. In this case the expression for  $\Delta \varepsilon_{N,\sigma}(N \ge 1)$  has the form

$$\Delta \varepsilon_{N,\sigma} = \frac{1}{6} \beta N_0 x \sigma \langle S^z \rangle, \qquad (35)$$

while the values of the exchange parameters found from the ShH oscillations and magneto-optical measurements turned out to be equal to 1.4–1.5 eV. In Refs. 62, 58, 76 values of  $\beta N_0$  have been obtained that are lower by a factor of two, specifically 0.65–0.75 eV. One can only assume that the authors of these articles utilized for determining the energy  $\Delta \varepsilon_{N,\sigma}$  the expression (35) where the coefficient is 1/3 instead of 1/6. The authors of Ref. 69, starting from the fact that in the case of a degenerate  $\Gamma_6$  band the states should be classified not according to the spin but according to the total angular momentum *j*, have ascribed to the electrons of the band an "effective spin" of j = 3/2. In this case  $\Delta \varepsilon_{N,\sigma}$  for  $N \ge 1$  is determined by the expression

$$\Delta \varepsilon_N \gg 1, \sigma = \beta N_0 x \sigma \langle S^z \rangle_{i}$$

while for  $\beta N_0$  values are obtained of (0.25–0.30) eV. The values of  $\beta N_0$  calculated with such a classification of the states coincide with the exchange parameter  $\alpha N_0 = 0.28$  eV,<sup>73</sup> obtained from the ShH oscillations for Hg<sub>0.88</sub> Mn<sub>0.12</sub> Se crystals with a finite value of the forbidden band. The values of  $\alpha N_0$  calculated by other authors turned out to be (cf., Table VII) lower by a factor of two than the parameters  $\beta N_0$  that have been obtained.

# e) Special features of magnetoresistance in gapless $Hg_{7-x}Mn_xTe$ crystals

In contrast to the gapless  $Hg_{1-x}Mn_x$ Se crystals for which the concentration of band electrons usually amounts to ~10<sup>17</sup>-10<sup>18</sup> cm<sup>-3</sup> in the case of  $Hg_{1-x}Mn_x$  Te crystals, unless they are specially doped, the concentration, as a rule, is lower:  $n \sim 10^{15}-10^{16}$  cm<sup>-3</sup>. At the same time the Fermi energy of gapless  $Hg_{1-x}Mn_x$  Te turns out to be comparable with the energy of an acceptor level  $\varepsilon_A$ , which lies in the conduction band. The contribution to the conductivity of charge carriers of the impurity acceptor band gives rise to many unique features of transport phenomena in  $Hg_{1-x}Mn_x$  Te.

Thus, in the case of  $Hg_{1-x} Mn_x$  Te crystals of the p type with  $0.02 \le x \le 0.06n \sim (2-13) \times 10^{15}$  cm<sup>-3</sup> a maximum has been observed on the curves of the transverse magnetoresistance  $\rho_{xx}(H)$ ,<sup>67,68</sup> which as the temperature is increased is broadened and is shifted in the direction of high magnetic fields (Fig. 18). On the curves of the longitudinal magnetoresistance  $\rho_{zz}(H)$  in magnetic fields corresponding to the maximum of  $\rho_{xx}(H)$  there either are no special features, or a very weak maximum in  $\rho_{zz}$  is observed. In the case of  $Hg_{1-x} Cd_x$  Te crystals which in their parameters are close to the  $Hg_{1-x} Mn_x$  Te crystals that are being described (but which do not contain ions with an uncompensated magnetic moment!) a similar decrease in the transverse magnetoresistance as a function of the field is not observed.

The observed special features of  $\rho_{xx}(T,H)$  were explained<sup>68</sup> within the framework of a model according to which the contribution to conductivity is made by the holes of the acceptor band  $\sigma_{xx}^{\rho}$  together with the band electrons



FIG. 18. Variation of the transverse  $\rho_{xx}$  (T = 2.9, 4.2 and 6.5 K) and longitudinal  $\rho_{xx}$  (T = 1.6 K) magnetoresistances with the magnetic field for Hg<sub>1-x</sub> Mn<sub>x</sub> Te (x = 0.03,  $n = 1.2 \cdot 10^{15}$  cm<sup>-3</sup>).<sup>67</sup>

 $\sigma_{xx}^n$ .

A decrease in  $\sigma_{xx}^n$  as the magnetic field is increased gives rise to a significant increase in  $\rho_{xx}(H)$  in fields of H < 5 kOe. In strong magnetic fields (H > 7 kOe), as estimates have shown, the contribution of band electrons to  $\sigma_{xx}$  becomes vanishingly small. From this it is clear that a decrease in  $\rho_{xx}(H)$  for H > 7 kOe can be brought about only by a change in the contribution to the conductivity of the charge carriers of the impurity band. One might think that a decrease in  $\rho_{xx}(H)$  in strong magnetic fields for samples for which the Hall coefficient does not change significantly, is due to an increase in the mobility of the holes. The point is that as the magnetic field is increased ordering occurs in the system of the manganese magnetic ions whose magnetic moments become oriented along the field. This evidently leads to a decrease in the efficiency of the scattering of holes by them and, therefore, to a decrease in the resistance. As far as the longitudinal magnetoresistance is concerned, in this case the electrons which do not undergo a Larmor deflection are the principal charge carriers since their mobility greatly exceeds the mobility of the holes. But for electrons the wavelength  $\lambda_e = h / m_e \overline{v}$  ( $\overline{v}$  is the average electron velocity) is greater than the average interimpurity distance  $(\mathbf{r}_i)$  between the Mn<sup>2+</sup> ions while for the acceptor holes with an effective mass  $m_h \gg m_e$  the wavelength is  $\lambda_h = h / m_h \bar{v} \sim r_i$ . Therefore, the system of Mn<sup>2+</sup> ions is not an efficient source for the scattering of electrons.

Naturally, one should keep in mind that in investigating the processes of charge transfer along the impurity band which in essence is a disordered system, in which the conductivity is of a diffusion nature, it is not possible, strictly speaking to utilize all the concepts that are useful for periodic structures. It is also not clear how justified it is to consider the magnetic moments of the manganese ions of which a crystal contains  $\sim 10^{20}$  cm<sup>-3</sup>, as sources for scattering charge carriers of the impurity band.

It is well known that in gapless semiconductors of the type of  $Hg_{1-x} Cd_x Te$  an energy gap appears<sup>13</sup> in a magnetic field between the terms of the  $\Gamma_8$  valence band and the conductivity band. In this case the acceptor level associated with the top of the valence band can land in the gap that is formed. An analysis of experimental data has shown<sup>68</sup> that in gapless SMS  $Hg_{1-x} Mn_x Te$ , just as in the case of  $Hg_{1-x} Cd_x Te$  in a magnetic field there also occurs the effect of "freezing out"

of electrons onto acceptors which fall into the energy gap that has been formed. In particular, this can be clearly seen in investigating the change in the magnetoresistance  $\rho_{zz}$  and  $\rho_{xx}$  as the magnetic field is varied in the case of samples with x > 0.065. Thus, the longitudinal and transverse magnetoresistance in a sample with  $x \approx 0.073$  (the value of  $\varepsilon_g$  is close to zero) increases sharply already for H < 1 kOe. As the magnetic field is increased further  $\rho_{zz}(H)$  and  $\rho_{xx}(H)$  practically coincide and this, as is well known, is characteristic for conduction along an impurity band. And this means, that the conductivity is brought about only by the carriers of the impurity band, while the electrons in the conduction band in fields H > 1 kOe have already been "frozen out".

# f) Anomalies of the specific resistance of $Hg_{\tau-x}Mn_xTe$ at low temperatures

Investigations of the temperature dependence of specific resistance  $\rho(T)$  and the Hall coefficient R(T) allow one, as is well known, to obtain information on the nature of the scattering of the charge carriers. Of particular interest in the study of transport phenomena in SMS are the ultralow temperatures when the thermal activation of electrons from the valence band becomes insignificant and one can expect that the special properties of the galvanomagnetic effects which are manifested for  $T \gtrsim 1.7$  K must become apparent more clearly. Such investigations were carried out by the authors of Ref. 47 at low temperatures down to  $T \sim 0.04$  K using  $Hg_{1-x}Mn_x$  Te crystals of the p type with manganese content of  $0 < x \leq 0.07$ . The concentration of donors in crystals that have been investigated amounted to  $(1-4) \cdot 10^{15}$  cm<sup>-3</sup>. The measured dependence of the Hall coefficient on the magnetic field in the temperature range  $1.7 \le T \le 4.2$  K indicates that in the  $Hg_{1-x}Mn_x$  Te crystals that have been investigated the conductivity  $\sigma$  is realized by two types of charge carriers with strongly differing mobilities: electrons with a mobility of  $10^5 - 10^6$  cm<sup>2</sup>/V  $\cdot$  s and the less mobile carriers of the impurity acceptor band (which overlaps with the conduction band) giving a positive contribution to the Hall coefficient.

An analysis of the experimental dependence of the specific resistance  $\rho(T)$  and Hall coefficient R(T) on the temperature enable the authors of Ref. 47 to divide all the specimens that have been investigated into two groups. The first group includes specimens for which the Hall coefficient practically does not change in the temperature range from 0.1 to  $\sim 5$  K while the specific resistance increases by a factor of 5-7 as the temperature increases. For this group of specimens  $\sigma_n \gg \sigma_p$  ( $\sigma_n$  is the conductivity for which the band electrons are responsible,  $\sigma_{\rm p}$  is the conductivity along the impurity band). The second group comprises specimens for which  $\sigma_n \sim \sigma_p$ . The value of the specific resistance for the specimens increases by a factor of 2-5 as the temperature increases from 0.1 to 4.2 K, while the Hall coefficient measured in fields of 20-50 Oe in the same temperature range decreases sharply (by a factor of 5-70). Typical dependences of  $\rho(T)$  and R(T) for both types of specimens are shown in Fig. 19.

In all the specimens that have been investigated well-



FIG. 19. Temperature dependence of the specific resistance  $\rho$  and the Hall coefficient R on the temperature for Hg<sub>1-x</sub> Mn<sub>x</sub> Te.<sup>47</sup> a—x = 0.065; b—x = 0.036.

defined ShH oscillations are seen whose period and, consequently, also the concentration of band electrons in the range  $0.1 \le T \le 4.2$  K is practically independent of temperature. Therefore it is natural to assume that the changes in  $\rho(T)$  and R(T) observed experimentally are associated with the change in the mobility  $\mu_n$  of the band charge carriers. What can then explain the anomalous decrease in  $\mu_n$  in the temperature range where the thermal energy  $k_B T$  is lower than the Fermi energy by a large factor? One succeeds in explaining this decrease if one assumes that as the temperature increases the number of charged centers changes which for  $k_B T \le \varepsilon_F$  limit the magnitude of the mobility  $\mu_n$ .

The explanation proposed in Ref. 47 of the anomalous behavior of  $\rho(T)$  and R(T) is based on the following assumptions. Donors in GS do not form bound states even at  $T \approx 0$  K and are therefore positively charged centers (their concentration is  $N^+{}_D$ ). The electrons that have left the donors fill the conduction band and partially the impurity band formed by the acceptors. As a result of this a fraction of the acceptors becomes negatively charged (their concentration is  $N^-{}_A$ ). These acceptors correspond to the states in the impurity band occupied by electrons. In contrast to ordinary semiconductors, where the charged acceptors arise only as a result of thermal excitation of electrons from the valence band, in GS they can (with a sufficiently high concentration of donors and acceptors) exist at the very lowest temperatures down to  $T \rightarrow 0$ .

As a result of the Coulomb interaction between charged donors and acceptors donor-acceptor pairs can be formed. If the wavelength of a band electron in such a case is much greater than the average distance between a donor and an acceptor forming a complex (just such a situation is realized in the samples of Hg<sub>1-x</sub> Mn<sub>x</sub> Te that have been investigated with N<sub>A</sub>  $\approx 3 \cdot 10^{16}$ -1  $\cdot 10^{17}$  cm<sup>-3</sup>), then the scattering of an electron by this complex will be ineffective. Electrons will be scattered primarily by charged donors not bound into pairs. It is evident that not all charged centers participate in forming donor-acceptor complexes, since *n* electrons from their total number are in the conduction band. A decrease in the mobility  $\mu_n$  will be the greater, the greater is the fraction of neutral complexes that decays and forms individual charged centers  $N_D^+ + N_A^-$ . Therefore for those specimens in which the conductivity along the impurity band is  $\sigma_{\rm p} \sim \sigma_{\rm n}$ , the decrease in the mobility  $\mu_n$  is considerably greater than for specimens for which  $\sigma_n \gg \sigma_p$ . As the temperature is increased



FIG. 20. Dependence of the specific resistance and the Hall coefficient upon the magnetic field for  $Hg_{0.87}Mn_{0.13}$  Te.<sup>78</sup> 1—T = 1.7 K, 2—T = 4.2 K.

an electron from an acceptor can move over to another acceptor near which there is no donor (in the GS crystals that have been investigated the concentration of acceptors is always higher than the concentration of donors). Thus, donoracceptor pairs will start breaking up as the temperature is increased, and this is accompanied by a considerable increase in the number of charged centers. As a result the mobility of band electrons must be decreased.

It should be emphasized that the observed special behavior of  $\rho(T)$  and R(T) are apparently not related directly to the presence in  $Hg_{1-x}Mn_x$  Te crystals of localized magnetic moments, since similar anomalies were found also in the case of the gapless semiconductor  $Hg_{1-x}Cd_x$  Te. At the same time, in contrast to the usual GS in the case of an SMS there is an additional factor which facilitates the stabilization of an excess electron on an acceptor: a large number (in comparison with the number of acceptors) of uncompensated magnetic moments. Therefore in  $Hg_{1-x}Mn_x$  Te crystals of the p type at sufficiently low temperatures the exchange interaction of an excess electron with the magnetic moments of the manganese ions must lead to polarization of the latter and as a result of this to its self-localization on an acceptor.

# g) Characteristic features of the magnetoresistance of narrow-gap p-Hg<sub>1 -x</sub>Mn<sub>x</sub>Te crystals

The presence of acceptors in  $Hg_{1-x}Mn_x Te$  crystals with a finite forbidden band exerts a significant influence on transport phenomena, in particular in a magnetic field. Figure 20 shows characteristic dependences on the magnetic field of the longitudinal  $\rho_{zz}(H)$  and the transverse  $\rho_{xx}(H)$ magnetoresistances and the Hall coefficient R(H) for  $Hg_{1-x}Mn_x Te^{78}$  at low temperatures (T = 1.7 K and 4.2 K). Similar behavior of  $\rho_{zz}(H)$  and  $\rho_{xx}(H)$  was observed for  $Hg_{1-x}Mn_x$  Te crystals with a manganese content of  $0.12 \le x \le 0.17^{79}$  and with x = 0.19 and x = 0.14.<sup>80</sup>

In contrast to the narrow-gap semiconductors p  $Hg_{1-x}Cd_x$  Te with closely similar parameters in the case of p  $Hg_{1-x}Mn_x$  Te crystals a large negative magnetoresistance is observed both in the case of the transverse as well as longitudinal orientation of the magnetic field with respect to the crystallographic axes. The resistance of the specimens falls by one to three orders of magnitude as the magnetic field increases to ~40 kOe. At the same time the transverse mag-

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netoresistance in all the specimens that have been studied in the temperature range  $1.8 \le T \le 25$  K turns out to be lower than the longitudinal one. In the ranges of temperatures  $1.8 \le T \le 25$  K and of magnetic fields  $H \le 40$  kOe that have been investigated the Hall coefficient decreases as the magnetic field is increased and this usually occurs if carriers of two types participate in charge transfer. From the nature of the variation of R(H) one can conclude that the charge carriers are light and heavy holes presumably belonging to the valence and impurity bands (or to the valence band and the tail of the density of its states, if the concentration of acceptors is higher than the critical concentration of Mott transition, when the impurity and the valence bands merge.

An analysis of the temperature dependence of the resistance in the absence of a magnetic field<sup>78-80</sup> showed that the conductivity of the p Hg<sub>1-x</sub> Mn<sub>x</sub> Te crystals in the temperature range  $5 \le T \le 25$  K is of an activating nature, with the different temperature ranges corresponding to different activation energies.

In the temperature range  $10 \le T \le 25$  K the conductivity of p Hg<sub>1-x</sub> Mn<sub>x</sub> Te is determined primarily by the valence holes with an activation energy  $\varepsilon_1$ . The quantity  $\varepsilon_1$  represents an energy gap between the acceptor and valence bands (with a very low concentration of acceptors this is the ionization energy for an isolated acceptor).

In all the specimens of p  $Hg_{1-x}Mn_x$  Te investigated in Refs. 78–80 a decrease in the activation energy  $\varepsilon_1$  was found as the magnetic field was increased. In the case of narrowgap semiconductors which do not contain atoms of transition elements the nature of the change in the activation energy  $\varepsilon_1$  as a function of the magnetic field is significantly different. For weak magnetic fields  $\hbar\omega_p \ll \hbar^2/m_p a_p^2$ , or, what is the same,  $a_p \ll \lambda (\omega_p = eH/m_p c, a_p = \hbar^2 \varkappa/m_p e^2$  is the Bohr radius,  $m_{\rm p}$  is the effective mass of heavy holes,  $\varkappa$  is the static dielectric permittivity) the activation energy practically does not change. In the case of strong fields  $a_p > \lambda$  the magnetic field compresses the wave functions of the impurity electrons in the transverse direction. As a result of this the overlap of wave functions of electrons on neighboring acceptors decreases with increase in field, the impurity band narrows down to a discrete narrow level, while the activation energy  $\varepsilon_1$  increases up to the value of the ionization energy of an isolated acceptor. As a result the specific resistance of the crystal increases. Therefore one may think that the decrease in the resistance and in the energy  $\varepsilon_1$  observed for p  $Hg_{1-x}Mn_x$  Te crystals as the magnetic field is increased is associated with the special features of the spectrum of the valence band of an SMS which differs from the spectrum of the valence band of an ordinary semiconductor due to the effect of the p-d exchange interaction.

Before discussing the question of the dependence of activation energy  $\varepsilon_1$  in an SMS on the magnetic field we shall examine briefly the effect of the exchange interaction on the energy spectrum of the degenerate valence band  $\Gamma_8$  in an SMS with a finite energy gap. For simplicity we shall assume that the dispersion laws for heavy and light holes in the absence of an exchange interaction are isotropic and quadratic with effective masses  $m_p$  and  $m_l$  ( $m_p > m_l$ ).

We now examine the range of magnetic fields for which

the cyclotron energy of the charge carrier is small in comparison with the exchange energy  $\hbar \omega_p \ll \hbar \omega_l \ll A$ ,  $A = (1/6)\beta N_0 x \langle S^z \rangle$ ,  $\omega_l = eH/m_l c$ . Taking into account the exchange interaction leads to the splitting of the  $\Gamma_8$  band with j = 3/2 into four sub-bands with  $j_z = \pm 3/2, \pm 1/2$  with the splitting energy being  $j_z |A|$  for k = 0.

The dispersion laws for light  $[\varepsilon_{\pm 1/2}(\mathbf{k})]$  and heavy  $[\varepsilon_{\pm 3/2}(\mathbf{k})]$  holes can be found, as usual, from the secular equation obtained from the Schrödinger equation. For the wave vectors  $\mathbf{k} || \langle S^z \rangle$  and  $\mathbf{k} \perp \langle S^z \rangle$  the dispersion laws for light and heavy holes are obtained in the form of simple analytic expressions. The value of the shift of the energy levels for k = 0, due to the exchange p-d interaction depends in an essential manner on the modulus of the wave vector and on its orientation with respect to the magnetization of the crystal  $\mathbf{M} (M^z \sim \langle S^z \rangle)$ .

For  $k \perp \langle S^z \rangle$  the dispersion laws for the holes have the form<sup>81</sup>

$$\varepsilon_{\pm 3/2} (\mathbf{k}) = -\frac{\hbar^{2}}{2} \left[ \left( \frac{3}{4m_{l}} + \frac{1}{4m_{p}} \right) (k_{x}^{2} + k_{y}^{2}) + \frac{1}{m_{p}} k_{z}^{3} \right] \\ \pm 3 \mid A \mid,$$

$$\varepsilon_{\pm 1/2} (\mathbf{k}) = -\frac{\hbar^{2}}{2} \left[ \left( \frac{1}{4m_{l}} + \frac{3}{3m_{p}} \right) (k_{x}^{2} + k_{y}^{2}) + \frac{1}{m_{p}} k_{z}^{3} \right] \\ \mp \mid A \mid.$$
(37)

From formulas (37) it may be seen that the exchange interaction affects the band of heavy holes more than the band of light holes. The isoenergetic surfaces that are spherical in the absence of the exchange interaction are deformed as a result of exchange and are converted into ellipsoids of revolution with significantly different values of the effective masses along and perpendicular to the direction of the magnetic field. In the case under consideration  $(m_1 \ll m_p)$  the effective mass in the transverse direction  $m_1$  is close to the mass of the light holes  $m_1$ . The band with  $\varepsilon_{-3/2}(\mathbf{k})$  turns out to be the highest in energy.

Analysis shows (cf., for example,<sup>9</sup>), that in the case when the energy of orbital motion is comparable with exchange energy the splitting of the  $\Gamma_8$  band and the shift of levels in the magnetic field are of the same nature for gapless and narrow-gap SMS. The level with  $j_z = -3/2$  corresponds to the highest energy state of the valence band:

$$\varepsilon_{b(-1)} = -\frac{\hbar^2 k_z^2}{2m_p} - \frac{\hbar\omega_{\perp}}{2} + \frac{3}{2} \hbar\omega_0 k + 3 |A|, \qquad (38)$$

where k is the Luttinger parameter,  $\omega_0$  is the cyclotron frequency of a free electron, while  $\omega_{\perp}$  is the cyclotron frequency corresponding to the transverse effective mass  $(m_{\perp} = m_0/(\gamma_1 + \overline{\gamma}))$  of the  $\varepsilon_{-3/2}(\mathbf{k})$  band (37).

The energies |A| and  $\hbar\omega_{\perp}$ , which determine the position of the level b (-1), under actual conditions of an experiment can turn out to be comparable in magnitude with the activation energy  $\varepsilon_1$  in zero magnetic field  $\varepsilon_1^0 = \hbar^2/2m_p a_p^2$ . Therefore the problem of finding the activation energy in a magnetic field  $\varepsilon_1^H$  can be solved analytically only in some special cases when it turns out to be possible to introduce a small parameter.

Thus, in the region of weak fields

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$$\varepsilon_1^0 \gg |A|, \quad \hbar \omega_{\perp}$$
 (39)

the energy of the exchange interaction |A| can be regarded as a perturbation. In this case the activation energy decreases in a magnetic field:<sup>82</sup>

$$\varepsilon_1^H = \varepsilon_1^0 - 0.8 \mid A \mid \tag{40}$$

(we recall that |A| in weak magnetic fields increases as the field increases).

The other limiting case in which it also turns out to be possible to obtain an analytic expression for  $\varepsilon_1^H$  is the range of magnetic fields for which

$$\hbar\omega_{\perp}, \quad |A| \gg \varepsilon_1^0. \tag{41}$$

As a result of the p-d exchange interaction the valence level b(-1) moves quite far away from the other levels of the valence band. Therefore their effect on the acceptor level situated above the level b(-1) is relatively small and the ground state of this acceptor level will be determined largely by the wave functions of the highest valence level b(-1).<sup>83</sup>

In ordinary narrow-gap semiconductors such a situation is realized in the range of strong magnetic fields for which the magnetic length  $\lambda$  is considerably smaller than  $a_p$ . However, in the case of an SMS the approximation being considered corresponds to a relatively wide interval of magnetic fields which also includes the region of weak fields for which  $\lambda \gg a_p$ . Under these conditions there is a small parameter  $a_p/\lambda$ , and this enables one to obtain an approximate analytic expression for  $\varepsilon_1^{H,83}$ 

$$\varepsilon_{1}^{H} \approx \frac{\sqrt{\pi} \, \epsilon^{2}}{2\kappa\lambda} \left[ 1 - 0.73 \left( \frac{a_{\mathrm{p}}}{\lambda} \right)^{1/3} \right]. \tag{42}$$

From formula (42) it may be seen that in the zero order of approximation in terms of the parameters  $a_p/\lambda$  the energy  $\varepsilon_1^H$  does not depend on the effective mass  $m_p$ . As the magnetic field is increased  $\varepsilon_1^H$  also increases. If one compares the quantity  $\varepsilon_1^H$  (42) with  $\varepsilon_1^0 = \hbar^2/2m_p a_p^2$ , then it turns out that in magnetic fields for which  $\lambda \gg a_p$  the energy  $\varepsilon_1^H$  is still lower than the activation energy in zero field  $\varepsilon_1^0$ . Thus, the energy  $\varepsilon_1^H$  decreases in weak (39) and increases in strong (41) magnetic fields.

A numerical calculation which also includes the interval of intermediate magnetic fields  $(0 \le H \le 40 \text{ kOe})^{84}$  has confirmed that the function  $\varepsilon_1^H$  is indeed nonmonotonic. As the magnetic field is increased the activation energy  $\varepsilon_1^H$  at first decreases in accord with the results of Ref. 82 and then beginning with a certain field  $H = H_1$  (for p-Hg<sub>1-x</sub> Mn<sub>x</sub> Te with  $x = 0.155 H_1 = 25 \text{ kOe})^{84} \varepsilon_1^H$  begins to increase. Estimates have shown that for band parameters Hg<sub>1-x</sub> Mn<sub>x</sub> Te in the field H = 25 kOe the ratio  $a_p/\lambda \approx 0.1$  and, consequently, the condition for the applicability of formula (42) is satisfied.

The increase in  $\varepsilon_1^H$ , in accordance with the theory of Yafet, as has been mentioned already, begins in the region of magnetic fields for which the magnetic length  $\lambda$  is comparable with the Bohr radius of the charge carrier. In the case under consideration  $\lambda \ge a_p$ , but at the same  $\varepsilon_1^H$  increases as the field is increased. If, however, one takes into account the anisotropy of the isoenergetic surface of the holes it is not

difficult to convince oneself that in the region of magnetic fields  $\lambda \gg a_p$  the magnetic length can turn out to be comparable with some effective Bohr radius  $a_p^*$  which is determined by the combination  $(m_p^*)$  of the longitudinal  $m_p$  and transverse  $m_1$  effective masses. If one starts from the relation  $\lambda = a_p^* = \hbar^2 \varkappa / m_p^* e^2$ , then for a magnetic field of  $H_1 = 25$  kOe we obtain  $m_p^* \approx 0.04 m_0$ . This value is close to the value of the effective mass of the density of states for an isoenergetic surface having the form of an ellipsoid of revolution:  $m^* = (m_p m_1^2)^{1/3} \approx 0.06 m_0$ . In the region of the fields  $H > H_1(\lambda < a_p^*)$  the compression of the wavefunctions of the impurity electrons leads, just as in the case of ordinary semiconductors, to an increase in  $\varepsilon_1^H$ .

For all the specimens that have been investigated it was established that the activation energy  $\varepsilon_1^H$  diminishes as the magnetic field is increased. According to Ref. 80 the rate at which  $\varepsilon_1^H$  falls off with the magnetic field amounts to (-0.16) meV/kOe.

The values of the activation energy  $\varepsilon_1^0$  for different compounds p-Hg<sub>1-x</sub> Mn<sub>x</sub> Te are shown in Table VIII.

It should be noted that the value of  $\varepsilon_1^0$  which is given by the authors of Ref. 79 (x = 0.155) differs appreciably from the value of  $\varepsilon_1^0$  for Hg<sub>1-x</sub> Mn<sub>x</sub> Te crystals with x = 0.13 and x = 0.19 used by other authors (i.e., the data of Refs. 78-80 for crystals with manganese content from 13 to 19% clearly do not agree among themselves).

The measurements of magnetoresistance using Hg<sub>0.91</sub>  $Mn_{0.09}$  Te crystals showed that in a magnetic field of  $H_0 = 20$  kOe the activation energy is  $\varepsilon_1^{H_0} = 0$ . As the field increases further  $(H > H_0)$  the resistance continues to decrease. The same holds also for crystals with x = 0.11: In a field of  $H_0 = 50$  kOe we have  $\varepsilon_1^{H_0} = 0$ , while the resistance continues to decrease.

In order to explain the decrease of the resistance as the field increases for  $H > H_0$  the authors of Ref. 78 assumed that the valence level b(-1) crosses in fields  $H > H_0$  with an acceptor level which thus becomes a resonance level. The concentration of holes at the b(-1) level with increasing magnetic field must increase until a complete exhaustion of acceptors is attained which will occur when the acceptor level crosses with the Fermi level situated deep within the valence band. The intersection of the valence b(-1) level with an acceptor level was also noted in the case of the narrow-gap Hg<sub>1-x</sub> Mn<sub>x</sub> Te crystals with x = 0.125 by the authors of Refs. 60,61 who investigated magneto-optical transitions in SMS. According to Refs. 60,61 the b(-1) level in a field of H = 40 kOe is situated above the acceptor level by 12 meV. Here it is assumed that this is not the ground acceptor level, but one of the excited ones. At the same time, with the aid of a variational calculation the authors of Ref. 84 arrived at the conclusion that the activation energy is  $\varepsilon_1^H > 0$  and that its minimum value amounts to  $\approx$  (3-5) meV. Thus, according to the calculation, the ground acceptor level must not cross with the valence level b(-1). Therefore another explanation for the decrease in the resistance  $\rho(H)$  seems to us to be more likely also for  $H > H_0$ . There is no doubt that for an impurity concentration of  $(N_A \sim 2 \cdot 10^{17} \text{ cm}^{-3})$  the acceptors form not a discrete level, but an impurity band of finite TABLE VIII

*	From Ref. 78			From Ref. 79	From Ref. 80
	0,09	0,11	0,13	0,155	0,19
$\epsilon_1^0$ , meV	0,5	1,4	3,2	8,2	3,5

width. Then for  $H = H_0$  and  $\varepsilon_1^{H_0} = 0$  the acceptor band only begins to overlap with the valence band and the conductivity is due to holes of both bands. As the magnetic field is increased in the range  $H > H_0$  the acceptor band merges increasingly with the valence band, and holes of the acceptor band are converted into valence ones whose mobility is considerably higher-the resistance continues to decrease. And only when all the acceptor holes have been converted into valence holes, i.e., when the acceptor states are completely exhausted (this usually occurs when the center of gravity of the acceptor band submerges into the valence band to a depth of  $\varepsilon_1^0$ ), the decrease in resistance with increasing magnetic field should cease. According to the experimental data of Ref. 78 for p-Ag<sub>0.89</sub> Mn<sub>0.11</sub> Te with  $N_A \sim 2.5 \cdot 10^{17} \, \mathrm{cm}^{-3}$ the resistance ceases to decrease in magnetic fields  $H \approx 110$ kOe. Thus, the explanation of the decrease in  $\rho(H)$  for  $H > H_0$ which takes into account the formation of an acceptor band removes the contradiction between the results of the calculation of Ref. 84 and the experimental data of Ref. 78.

In the temperature region  $T \le 10$  K the conductivity in p-Hg<sub>1-x</sub> Mn<sub>x</sub> Te changes by jumps with an activation energy  $\varepsilon_3^H$ . For all the specimens that have been investigated it was established that the activation energy  $\varepsilon_3^H$  decreases as the magnetic field is increased. According to Ref. 80 for crystals of Hg<sub>0.81</sub> Mn<sub>0.19</sub> Te  $\varepsilon_3(H=0) \approx 2$  meV and  $\varepsilon_3(H=24$  kOe)  $\approx 1$  meV.

Qualitatively the effect of the decrease in  $\varepsilon_3^H$  as the magnetic field is increased can be explained in the following manner. As we have already stated, the b(-1) level continues to move away from the other levels of the valence band  $\Gamma_8$  due to the strong influence of the exchange interaction on this level compared with others. Here also there is an increase in the contribution of the cyclotron energy  $\hbar\omega_1(m_1 \ll m_0)$  to the energy of the b(-1) level [cf., (38)]. Therefore the effective Bohr radius of the charge carriers in the acceptor band in a magnetic field becomes larger: It is determined not by the effective mass  $m_p$ , but by the mass  $m_p^*, \ll m_p$  which is close to the mass of the light holes  $m_1$ . This leads to an increase in the overlap of the wave functions of the electrons of neighboring acceptors, and this must lead to a decrease in the activation energy  $\varepsilon_3^H$  for the hopping conductivity along the acceptors. A considerable overlap of the wave functions can lead to a complete disappearance of the hopping conductivity  $(\varepsilon_3^H = 0)$  and to a transition to metallic conductivity along the impurity band.

We have noted above that in the region of hopping conductivity the transverse magnetoresistance is lower than the longitudinal one. We suppose that the reason for this fact, unusual for "normal" semiconductors, lies in the fact that, as has been stated already, the exchange interaction leads to an anisotropy of the isoenergetic surface: The spherical surface is converted into an ellipsoidal one with effective masses  $m_p$  and  $m_{\perp}$ . The effective mass in the transverse direction  $m_{\perp}$  is considerably smaller than the longitudinal mass  $m_p$  and, consequently, the overlap of the wave functions in the transverse direction is greater. Since the hopping conductivity in a given direction is determined primarily by the hopping of charge carriers specifically in this direction, the probabilities of hops in the transverse and longitudinal directions must differ.

According to Ref. 85, in this case we have

$$\frac{\rho_{xx}(H)}{\rho_{zz}(H)} \sim \frac{m_{\perp}}{m_{\rm p}}.$$

#### h) Temperature oscillations of magnetoresistance

The increment to the energy of the band charge carriers of an SMS made by the energy of the exchange interaction which depends on the temperature can, generally speaking, lead to the appearance of oscillations of kinetic coefficients as the temperature is varied at a fixed magnetic field.<sup>86</sup> This effect must to some extent be analogous to the ShH effect: the Landau levels cross the Fermi level as the temperature is changed (in the ShH effect as the magnetic field is changed). The temperatures at which such thermal oscillations should occur are determined from the condition  $\varepsilon_{\rm F}(H) = \varepsilon_{N,\sigma_{\rm c}}$  if one neglects the weak dependence of the Fermi energy on the temperature. In the region of magnetic fields which satisfy the inequalities  $\hbar \omega_c > k_B T$  and  $\bar{g} \mu_B SH \leq k_B T$ , the expression for the temperature  $T_{N,\sigma}$  which corresponds to the crossing of the Landau levels with the Fermi level on the assumption of  $M_n^{2+}$  ions which do not interact with one another can be written in the form

$$T_{N,\sigma} = \frac{\beta N_0 x_{\bar{k}} \mu_{\rm B} H S (S + 1)}{2k_{\bar{B}} B_{N,\sigma}} \begin{cases} \frac{8N - 1\frac{3}{4}}{4N + 1}, & \sigma = -\frac{1}{2}, \\ \frac{8N + 9}{4N + 3}, & \sigma = +\frac{1}{2}, \end{cases}$$

$$B_{N,\sigma} = \left(N + \frac{1}{2}\right) \hbar \omega_{\rm c} - \sigma |g| \mu_{\rm B} H - \varepsilon_{\rm F} (H).$$
(43)

Figure 21 shows the dependences of the transverse magnetoresistance for  $Hg_{1-x} Mn_x$  Te crystals with  $x = 0.009^{86}$ on the temperature for several values of the intensity of the magnetic field. The authors of Ref. 86 interpreted the two maxima that have been observed as thermal oscillations. An analogous maximum at  $T \leq 5$  K (H > 7 kOe) was found in studying  $Hg_{1-x} Mn_x$  Te crystals with x = 0.02.<sup>67</sup> A careful analysis of the measurements made by the authors of Ref. 67 showed, however, that the maximum of the transverse magnetoresistance observed for  $T \leq 5$  K cannot be regarded as due to thermal oscillations. Indeed, the aforementioned maximum is also observed in samples of  $Hg_{1-x}Mn_x$  Te in which the position of the peaks of the ShH oscillations does not depend on the temperature at all. Moreover, the change in the magnetoresistance at its maximum is considerably greater than the amplitude of the largest (first) Shubnikov peak at the lowest temperature. An additional argument against the assumption that the aforementioned maximum is due to thermal oscillations is also the fact that the maximum at  $T \lesssim 5$  K is not present on curves of longitudinal magnetor-



FIG. 21. Variation of the transverse magnetoresistance  $\rho_{xx}$  with temperature for Hg<sub>1-x</sub>Mn<sub>x</sub> Te (x = 0.009, n = 6.25 \cdot 10<sup>15</sup> cm<sup>-3</sup>).<sup>86</sup>

esistance. A more likely reason for the origin of the maximum in the magnetoresistance at low temperatures appears to be the change in the contribution to the conductivity of band electrons and impurity holes as the temperature changes.<sup>67</sup>

In all the samples that have been investigated the amplitudes of the ShH oscillations sharply decrease as the temperature is raised above 4.2 K. Therefore it is difficult to expect thermal oscillations to appear at all at high temperatures  $25 \le T \le 40$  K, as the authors of Ref. 86 suppose. Moreover, at T > 25 K for all the specimens that have been investigated<sup>86,71</sup> the condition for the degeneracy of an electron gas is poorly satisfied (for these samples  $(\varepsilon_{\rm F}/k_{\rm B}T) \sim 1.5$ ) which is needed for a more or less clear manifestation of the ShH oscillations. Therefore a maximum in the region of high temperatures<sup>86</sup> evidently also is not due to thermal oscillations. The special feature observed at T > 25 K can be due, for example, to the change in the mobility of electrons as a result of their being scattered by optical phonons.<sup>87</sup> The effect of thermal oscillations should, apparently, be sought in the region of sufficiently low temperatures  $\leq 1$  K. Due to the fact that in the gapless SMS  $Hg_{1-x}Mn_x$  Te there is an impurity acceptor band into which the Fermi level is most frequently "frozen in" ( $\varepsilon_{\rm F} - \varepsilon_{\rm A}$ ), these crystals are not convenient objects for the observation of the effects due to the temperature dependence of the energy of the exchange interaction. The SMB  $Hg_{1-x}Mn_x$  Se for which  $\varepsilon_F \gg \varepsilon_A$  appear to be more suitable materials for the study of thermal oscillations.

#### i) Threshold scattering of band electrons

We have already mentioned that in the case of SMS the upper level of the valence band  $\varepsilon_{\rm V}$  can in a sufficiently high magnetic field turn out to lie higher in energy than the lowest level of the conduction band  $\varepsilon_{\rm C}$ . The amount of overlap of the energy levels  $\varepsilon_{\rm V}$  and  $\varepsilon_{\rm C}$  attains at a certain magnetic field a maximum value, and then begins to decrease as the field is increased until an inversion of the levels  $\varepsilon_{\rm V}$  and  $\varepsilon_{\rm C}$  occurs and a gap opens up. Such an unusual evolution of the energy

levels in the case of SMS must open a new channel for the scattering of electrons brought about by their transition from a conduction band into the valence abnd. Such scattering will, evidently, be of a threshold nature: The channel will be open as long as  $\varepsilon_{\rm th} = \varepsilon_{\rm V} - \varepsilon_{\rm C} > 0$ .

The effectiveness of the threshold mechanism of scattering was estimated in Ref. 88 on the assumption that the band charge carriers are scattered by charged centers. It turns out that threshold scattering can even exceed intraband scattering in the range of magnetic fields where the valence band and the conduction band overlap. In this case, according to Ref. 88, the dependence of the Longitudinal magnetoresistance  $\rho_{zz}(H)$  on the magnetic field is determined by the function

$$\Phi(T, H) = \sqrt{-\frac{\hbar\omega_{\perp}}{2} - \frac{3}{2}\hbar\omega_{0}k + \frac{\beta N_{0}x}{2}\langle S^{z}\rangle - \varepsilon_{\rm F}}.$$
 (44)

Since the average value  $\langle S^z \rangle$  tends to saturation as the magnetic field is increased, while the first term in the expression for  $\Phi(T,H)$  increases monotonically with magnetic field, the longitudinal magnetoresistance as a function of the concentration of manganese ions can either decrease, or remain unchanged in the range of magnetic fields where  $\varepsilon_{\rm th} > 0$ . Such a variation in  $\rho_{zz}(H)$  was observed experimentally,<sup>68</sup> although so far it is not clear whether it is associated with threshold scattering of electrons.

## 6. CONCLUSION

One can distinguish three main directions of research on SMS. The first is associated with the progress in the technique of preparing semimagnetic materials. Success has already been achieved in the synthesis of SMS not only on the basis of the elements of II and VI groups (ZnMnTe), but also on the basis of elements of groups IV and VI (PbMnTe) and II and V groups ((CdMn)<sub>3</sub>As<sub>2</sub>). SMS are being produced with other magnetic ions (HgFeTe,HgEuTe). It is to be expected that the SMS "family" will continually increase.

Progress in understanding the magnetic properties of SMS will undoubtedly turn out to be useful also for investigating the more general problem of the physics of disordered magnetic materials. Therefore the second important direction is the detailed study of the physical properties of SMS over a wide range of magnetic fields, temperatures and concentrations of magnetic ions.

The range of variation of the properties of semimagnetic crystals is even wider than in the case of narrow-gap semiconductors (for example, in the case of  $Hg_{1-x} Cd_x Te$ ) which have already found wide application in electronic technology.<sup>89</sup> Therefore the third direction in the study of SMS is associated with the possibility of their practical application. First reports have appeared on the use of SMS as generators of electromagnetic radiation. It is evident that it is of the utmost importance to achieve progress in the technology of preparing semimagnetic materials with stable parameters.

Among the purely physical problems which await solution one can enumerate the following:

1. Elucidation of the mechanism responsible for the formation of a spin-glass phase, in particular at low concentrations of a transition element. 2. Investigation of the physical properties of SMS at ultralow temperatures, where among other distinctive features one might expect the manifestation of thermal oscillations.

3. Study of the effect of magnetic excitations which must occur in SMS with a concentration of the transition element exceeding 10-15% on the galvanomagnetic, magneto-optical and other properties.

4. Investigation of properties of semimagnetic thin films which until now have been studied neither experimentally nor theoretically.

<sup>1)</sup>For convenience we shall refer to ions of transition elements as impurity ions, although, being substitution atoms, they are not impurities in the generally accepted sense (but nevertheless they still distort the crystalline potential).

<sup>4)</sup>Such a strong effect of the exchange correction on the energy of the valence level is due to the relatively low value of the orbital energy of heavy holes which have a large effective mass  $m_{a} > m_{a}$ .

tors, Edinburgh, 1978, p. 133.

<sup>8</sup>C. R. Pidgeon and R. N. Brown, Phys. Rev. **146**, 575 (1966).

<sup>&</sup>lt;sup>21</sup>The magnetic semiconductor MnTe crystallizes in a hexagonal lattice, while MnSe crystallizes in the rock salt lattice.<sup>23</sup>

<sup>&</sup>lt;sup>3)</sup>For gapless semiconductors of the type of HgTe, in contrast to ordinary semiconductors, the electron states  $\varepsilon_a$  and  $\varepsilon_b$  are, strictly speaking, not characterized by different spins, since in gapless semiconductors the conduction band  $\Gamma_8$  is degenerate, and therefore the wave functions of the electrons are a superposition of functions with spin values of  $\sigma = + 1/2$ .

heavy holes which have a large effective mass  $m_p > m_n$ . <sup>5)</sup>The Néel temperature for MnTe is  $T_N = 307 \text{ K}^{28}$ , while for MnSe  $T_N = 223 \text{ K}^{29}$ 

<sup>&</sup>lt;sup>6</sup>The term frustration refers to destruction or derangement in the present case of magnetic order.

<sup>&</sup>lt;sup>7)</sup>The exchange interaction between band electrons and electrons localized at a node may become the reason for the appearance of effective exchange coupling between localized electrons even in the absence of a direct exchange between them. This type of indirect exchange through the conduction electrons is called the Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction.<sup>48</sup>

<sup>&</sup>lt;sup>1</sup>I. M. Tsidil'kovskiĭ, Zonnaya struktura poluprovodnikov (Band Structure of Semiconductors), Nauka, M., 1978, p. 328.

<sup>&</sup>lt;sup>2</sup>R. R. Galazka, In: Proc. of 4th Intern. Conf. on Physics of Narrow Gap

Semiconductors, Linz, Austria, 1981, p. 294. <sup>3</sup>G. Bastard, In: Proc. of 3rd Intern. Conf. on Physics of Narrow Gap

Semiconductors, Warszawa, 1977, p. 63. <sup>4</sup>R. R. Galazka, In: Proc. of 14th Intern. Conf. on Physics of Semiconduc-

 <sup>&</sup>lt;sup>5</sup>R. R. Gałazka and J. Kossut, In: Proc. of Intern. Summer School on the Physics of Narrow Gap Semiconductors, Nimes, France, 1979, p. 245.
 <sup>6</sup>J. A. Gaj, In: Proc. of 15th Intern. Conf. on Physics of Semiconductors,

Kyoto, 1980. J. Phys. Soc. Jpn. **49**, Suppl. A, 797 (1980).

<sup>&</sup>lt;sup>7</sup>J. Mycielski, In: Proc. of Intern. Sympos. Applic. High Magnetic Fields in Semiconductor Physics, Grenoble, France, 1982, p. 431.

<sup>&</sup>lt;sup>9</sup>M. Jaczynski, J. Kossut and R. R. Galazka, Phys. Status Solidi **B88**, 73 (1978), cited in Ref. 3, p. 325.

<sup>&</sup>lt;sup>10</sup>G. Bastard, C. Rigaux, Y. Guldner, J. Mycielski and A. Mycielski, J. Phys. (Paris) **39**, 87 (1978).

<sup>&</sup>lt;sup>11</sup>G. Bastard, C. Rigaux and A. Mycielski, Phys. Status Solidi **B79**, 585 (1977).

<sup>&</sup>lt;sup>12</sup>S. Nagata, R. R. Galazka, C. D. Khattak, C. D. Amarasekara, J. K. Furdyna and P. H. Keesom, Physica **B107**, 311 (1981).

<sup>&</sup>lt;sup>13</sup>B. L. Gel'mont, V. I. Ivanov-Omskiĭ and I. M. Tsidil'kovskiĭ, Usp. Fiz. Nauk **120**, 337 (1976) [Sov. Phys. Usp. **19**, 879 (1976)].

<sup>&</sup>lt;sup>14</sup>I. M. Tsidil'kovskiï, Zh. Tekh. Fiz. 27, 1744 (1957) [Sov. Phys. Tech. Phys. 2, 1622 (1958)].

<sup>&</sup>lt;sup>15</sup>S. Groves and W. Paul, Phys. Rev. Lett. 11, 194 (1963).

<sup>&</sup>lt;sup>16</sup>S. P. Schubin and S. Wonsowsky, Proc. R. Soc (London) A145, 159 (1934).

<sup>&</sup>lt;sup>17</sup>M. Dobrowolski, W. Dobrowolski, M. Otto, T. Dietl and R. R. Galazka, J. Phys. Soc. Jpn. 49, Suppl. A, 815 (1980).

<sup>&</sup>lt;sup>18</sup>S. Takeyama and R. R. Galazka, Phys. Status Solidi B96, 413 (1979).

<sup>&</sup>lt;sup>19</sup>S. W. McKnight, P. M. Amirtharaj and S. Perkowitz, Solid State Com-

mun. 25, 357 (1978).

- <sup>20</sup>J. Stankiewicz, W. Giriat and M. V. Bien, Phys. Status Solidi B68, 485 (1975).
- <sup>21</sup>J. Kaniewski and A. Mycielski, Solid State Commun. 41, 959 (1982).
- <sup>22</sup>G. Bastard, C. Rigaux, Y. Guldner, A. Mycielski, J. K. Furdyna and D. P. Mullin, Phys. Rev. B24, 1961 (1981).
- <sup>23</sup>É. L. Nagaev, Fizika magnitnykh poluprovodnikov (Physics of magnetic semiconductors), Nauka, M., 1979, p. 432.
- <sup>24</sup>C. Lewiner and G. Bastard, J. Phys. C13, 2347 (1980); Phys. Rev. B 22, 2132 (1980).
- <sup>25</sup>I. I. Lyapilin and V. V. Karyagin, Fiz. Tverd. Tela (Leningrad) 22, 2859 (1980) [Sov. Phys. Solid State 22, 1670 (1980)].
- <sup>26</sup>A. B. Davydov, B. B. Ponikarov and I. M. Tsidil'kovskii, Fiz. Tekh. Poluprovodn. 15, 881 (1981) [Sov. Phys. Semicond. 15, 504 (1981)].
- <sup>27</sup>V. I. Ivanov-Omskiĭ, B. T. Kolomiets, V. M. Mel'nik and V. K. Ogorodnikov, Fiz. Tverd. Tela (Leningrad) 11, 2563 (1969) [Sov. Phys. Solid State 11, 2067 (1969)].
- <sup>28</sup>K. Ozawa, S. Anzai and Y. Hamaguchi, Phys. Lett. 20, 132 (1966).
- <sup>29</sup>T. Ito, K. Ito and M. Oka, Jpn. J. Appl. Phys. **17**, 371 (1978).
   <sup>30</sup>H. Savage, J. J. Rhyne, R. Holm, J. R. Cullen, C. E. Carroll and E. P. Wohlfarth, Phys. Status Solidi B58, 685 (1973).
- <sup>31</sup>D. G. Andrianov, F. A. Gimel'farb, P. I. Kushnir, I. E. Lopatinskiĭ, M. V. Pashkovskii, A. S. Savel'ev and V. I. Fistul', Fiz. Tekh. Poluprovodn. 10, 111 (1976) [Sov. Phys. Semicond. 10, 66 (1976)].
- <sup>32</sup>R. T. Delves and B. Lewis, J. Phys. Chem. Solids 24, 549 (1963).
   <sup>33</sup>U. Sondermann and E. Vogt, Physica B86-88, 419 (1977).
- <sup>34</sup>U. Sondermann, J. Magn. Magn. Mater. 13, 113 (1979).
- <sup>35</sup>G. D. Khattak, C. D. Amarasekara, S. Nagata, R. R. Galazka and P. H. Keesom, Phys. Rev. B23, 3553 (1981).
- <sup>36</sup>A. B. Davydov, L. M. Noskova, B. B. Ponikarov and L. A. Ugodnikova Fiz. Tekh. Poluprovodn. 14, 1461 (1980) [Sov. Phys. Semicond. 14, 869 (1980)].
- <sup>37</sup>G. Bastard and C. Lewiner, J. Phys. C13, 1469 (1980).
- <sup>38</sup>S. Nagata, R. R. Galazka, D. P. Mullin, H. Akbarzadeh, G. D. Khattak, J. K. Furdyna and P. H. Keesom, Phys. Rev. B22, 3331 (1980).
- <sup>39</sup>P. Byszewski, A. Mongird-Gorska, and A. M. Sandauer, In: Proc. of 10th Conference on Physics of Semiconductor Compounds, Jaszowiec, Poland, 1980, p. 245
- <sup>40</sup>U. Sondermann and E. Vogt, J. Magn, Magn. Mater. 6, 223 (1977).
- <sup>41</sup>W. Dobrowolski, M. von Ortenberg, A. M. Sandauer, R. R. Galazka, A. Mycielski and R. Pauthenet, cited in Ref. 2, p. 302.
- <sup>42</sup>M. Otto, T. Dietl, A. Mycielski, M. Dobrowolska and W. Dobrowolski, cited in Ref. 39, p. 225.
- <sup>43</sup>J. L. Tholence and R. Tournier, J. Phys (Paris) 35, C4-229 (1974).
- <sup>44</sup>R. A. Tahir-Kheli, Phys. Rev. B6, 2826 (1972).
- <sup>45</sup>M. F. Sykes and J. W. Essam, J. Math. Phys. (N.Y) 5, 1117 (1964).
- <sup>46</sup>N. B. Brandt, V. V. Moshchalkov, L. Skrbek, A. N. Taldenkov and S. M. Chudinov, Pis'ma Zh. Eksp. Teor. Fiz. 35, 326 (1982) [JETP Lett. 35, 401 (1982)].
- <sup>47</sup>N. B. Brandt, V. V. Moshchalkov, A. O. Orlov, L. Skrbek, I. M. Tsidil-'kovskii and S. M. Chudinov, Zh. Eksp. Teor. Fiz. 84, 1050 (1983) [Sov. Phys. JETP 57, 614 (1983)]; N. B. Brandt, I. M. Tsidil'kovskii, V. V. Moshchalkov, B. B. Ponikarov, L. Skrbek, A. N. Taldenov and S. M. Chudinov, Fiz. Nizk. Temp. 8, 653 (1982) [Sov. J. Low Temp. Phys. 8, 326 (1982).].
- 48C. Kittel, Solid State Phys. 22, 1 (1968).
- <sup>49</sup>J. Ginter, J. Kossut and L. Swierkowski, Phys. Status Solidi B96, 735 (1979).
- <sup>50</sup>L. de Seze, J. Phys. C10, L353 (1977).
- <sup>51</sup>G. Toulence, Commun. Phys. 2, 115 (1977).
- <sup>52</sup>B. H. Verbeek, G. J. Nieuwenhuys, H. Stoker and J. A. Mydosh, J. Phys. (Paris) 39, C6-917 (1978).
- <sup>53</sup>N. Bloembergen and T. J. Rowland, Phys. Rev. 97, 1679 (1955).
- <sup>54</sup>A. A. Abrikosov, Adv. Phys. 29, 869 (1980); J. Low Temp. Phys. 39, 217 (1980).
- <sup>55</sup>M. Kurzynski, Acta Phys. Pol. 36, 571 (1969).

- <sup>56</sup>C. Lewiner and G. Bastard, Phys. Rev. B22, 2132 (1980).
- <sup>57</sup>G. Bastard and C. Lewiner, Phys. Rev. B20, 4256 (1979).
- 58K. Pastor, M. Grynberg and R. R. Galazka, Solid State Commun. 29, 739 (1979).
- <sup>59</sup>M. Dobrowolska, W. Dobrowolski, M. Otto, T. Dietl and R. R. Galazka, J. Phys. Soc. Jpn. 49, Suppl. A, 815 (1980).
- <sup>60</sup>G. Bastard, C. Rigaux, Y. Guldner, A. Mycielski, J. K. Furdyna and D. P. Mullin, Phys. Rev. B24, 1961 (1981).
- <sup>61</sup>C. Rigaux, G. Bastard, Y. Guldner, G. Rebmann, A. Mycielcki, J. K. Furdyna and D. P. Mullin, J. Phys. Soc. Jpn. 49, Suppl. A, 811 (1980).
- <sup>62</sup>M. Dobrowolska and W. Dobrowolski, J. Phys. C14, 5689 (1981).
- <sup>63</sup>M. Grynberg, G. Martinez and L. C. Brunel, Solid State Commun. 43, 153 (1982).
- <sup>64</sup>P. M. Amirtharaj, F. H. Pollak and J. K. Furdyna, Solid State Commun. 39. 35 (1981).
- <sup>65</sup>M. Dobrowolska, W. Dobrowolski, R. R. Galazka and A. Mycielski, Phys. Status Solidi B105, 477 (1981).
- <sup>66</sup>Y. Guldner, C. Rigaux, A. Mycielski and Y. Couder, Phys. Status Solidi 81, 615 (1977).
- <sup>67</sup>A. B. Davydov, B. B. Ponikarov and I. M. Tsidil'kovski, Phys. Status Solidi B101, 127 (1980).
- <sup>68</sup>A. B. Davydov, B. B. Ponikarov and I. M. Tsidil'kovskii, Fiz. Tekh. Poluprovodn. 15, 881 (1981) [Sov. Phys. Semicond. 15, 504 (1981)].
- <sup>69</sup>I. I. Lyapilin, A. I. Ponomarev, G. I. Kharus, N. P. Gavaleshko and P. D. Mar'yanchuk, Zh. Eksp. Teor. Fiz. 85, 1638 (1983) [Sov. Phys. JETP 58, 953 (1983)].
- <sup>70</sup>M. Jaczynski and W. Dobrowolski, Phys. Status Solidi **B102**, 195 (1980).
- <sup>71</sup>A. M. Sandauer and P. Byszewski, Phys. Status Solidi B109, 167 (1962).
- <sup>72</sup>P. T. Coleridge and I. M. Templeton, Phys. Rev. Lett. 24, 108 (1970).
- <sup>73</sup>N. P. Gavaleshko, I. I. Lyapilin, P. D. Mar'yanchuk, A. I. Ponomarev and G. I. Kharus, Fiz. Tekh. Poluprovodn. 18, 990 (1984) [Sov. Phys. Semicond. 18, 617 (1984)].
- <sup>74</sup>I. I. Lyapilin and Kh. M. Bikkin, Fiz. Tekh. Poluprovodn. 19, (1985) [sic].
- <sup>75</sup>P. Byszewski, K. Szlenk, J. Kossut and R. R. Galazka, Phys. Status Solidi B95, 359 (1979).
- <sup>76</sup>P. Byszewski, M. Z. Cieplak and A. Mongird-Gorska, J. Phys. C13, 5383 (1980).
- <sup>77</sup>R. T. Holm and J. K. Furdyna, Phys. Rev. B15, 844 (1977).
- <sup>78</sup>A. V. Germanenko, L. P. Zverev, V. V. Kruzhaev, G. M. Min'kov, O. É. Rut, N. P. Gavaleshko and V. M. Frasunyak, Fiz. Tverd. Tela (Leningrad) 26, 1754 (1984) [Sov. Phys. Solid State 26, 1062 (1984)].
- <sup>79</sup>A. Mycielski and J. Mycielski, J. Phys. Soc. Jpn. 49, Suppl. A, 807 (1980).
- <sup>80</sup>J. R. Anderson, W. B. Johnson, and D. R. Stone, J. Vac. Sci. Techn. A1, 1761 (1983)
- <sup>81</sup>J. A. Gaj, J. Ginter and R. R. Galazka, Phys. Status Solidi B89, 655 (1978).
- <sup>82</sup>J. Mycielski, Recent Dev. Condens. Mat. Phys. 1, 725 (1981).
- <sup>83</sup>J. Mycielski, Cited in Ref. 39, p. 217.
  <sup>84</sup>T. R. Gawron and J. Trylski, Cited in Ref. 2, p. 312.
- <sup>85</sup>B. I. Shklovskiĭ and A. L. Éfros, Elektronnye svoistva legirovannykh poluprovodnikov, Nauka, M., 1979, p. 416 [Engl. Transl. Electronic Properties of Doped Semiconductors, Springer-Verlag, Berlin, 1984].
- <sup>86</sup>M. Dobrowolska, W. Dobrowolski, R. R. Galazka and J. Kossut, Solid State Commun. 30, 25 (1979).
- <sup>87</sup>W. Walukiewicz, Phys. Rev. Lett. 33, 650 (1974).
- <sup>88</sup>I. I. Lyapilin, Fiz. Tekh. Poluprovodn. 16, 1942 (1982) [Sov. Phys. Semicond. 16, 1253 (1982)].
- <sup>89</sup>N. N. Berchenko, V. E. Krevs and V. G. Sredin, Poluprovodnikovye tverdye rastvory i ikh primenenie (Semiconductor Solid Solutions and Their Applications) Voenizdat, M., 1982.

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