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Effect of annealing on activation of native acceptors in narrow-gap *p*-HgCdTe crystals

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Abstract. Hall effect, resistivity and *p-n*-junction characteristics were investigated on high pure and perfect *p*-type $Hg_{1-x}Cd_xTe$ crystals ($x \sim 0.2$) versus temperature, doping, and a way of heat treatment. It was shown, that activation energy of extrinsic acceptors does not depend on conditions of the crystal heat treatment, while the first native acceptor level increases monotonically from 10 meV in the Hg-saturated crystal up to 15.4 meV in the Te-saturated one. The experimentally observed energy of the first level of the native acceptor in Te-saturated crystals (15.4 meV) is in a good agreement with the value 16 meV, obtained by calculation carried out in the framework of the effective mass approximation. The difference between the crystals, saturated by Hg or Te, has an essential effect for reverse dark current through a *p-n*-junction at T = 77 K. It should be taken into account when manufacturing the photodiodes.

Keywords: native acceptor, ionization energy, heat treatment.

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1. Introduction

Narrow-gap *p*-$Hg_{1-x}Cd_xTe$ (MCT) is a base material for manufacturing photodiods for the wavelength range 8-13 μm. Often, the undoped material contained certain number of native acceptors ($\sim 10^{16}$ cm^{-3}) is used for this purposes. Electrical properties of such crystals have been studied intensely in 70-80-th, but the main interest was excited by galvano-magnetic anomalies of various kinds observed there (see, for example, [1, 2]). Now it is clear that imperfections of a technology of growth, treatment, and preparation of MCT were the causes of such anomalies [2].

Energy level of an isolated electrically active center is a principal characteristic of any such defect. But it is just the problem that is not soluted completely for acceptor states in narrow-gap MCT crystals up to date, despite an abundance of experimental data. For example, the values from 3 meV [3] up to 15 meV [4] are obtained for the first acceptor level of mercury vacancy (V_M), and no reliable value was obtained for energy of the second level of V_M.

There are some reasons for this situation. One of them is that a defect energy level depends on the defect concentration. Another one is that activation energy of the Hall effect and resistivity depends on a compensation degree of the semiconductor.

A trivial imperfection of the investigated material could be also a cause of such dispersion of the experimental data. However, special researches show, that mercury vacancies exhibit exotic properties in rather perfect crystals too. It has become clear after such samples were obtained due to successes in a technology of MCT crystal growth, reached last years. In this paper outcomes of researches of the Hall effect and resistivity of narrow-gap *p*-type MCT crystals, studied as a function of temperature, conditions of a preannealling, and doping by donors and acceptors are presented. Voltage-current characteristics of p-n-junctions depending on conditions of preparation of the initial crystals were measured too. The results demonstrate an appreciable influence of conditions of heat treatment of MCT crystals on activation energy of V_M. The experimental data is compared with results of calculations of acceptor levels.

2. Experimental procedure

Uniform and perfect in their structure monocrystalline MCT ingots of $x \approx 0.20 \div 0.24$ were taken for our study. The ingots were grown by a vertical directed crystallization from a melt and then sectioned on wafers of thicknesses about 0.1mm. The wafers were annealed in saturated vapors of Hg below 300 °C. The undoped crystals contained less than $2 \cdot 10^{14}$ cm^{-3} of extrinsic electrons after such annealing. Electron mobilities were there more than $2 \cdot 10^5$ cm^{2}V^{-1}s^{-1}, and lifetimes – more than $2 \cdot 10^{-6}$ s at T =77 K. A small part of crystals was intentionally doped with indium from a melt and, thus, contained from $1 \cdot 10^{15}$ up to $2.2 \cdot 10^{16}$ cm^{-3} of extrinsic electrons at low temperatures. Density of dislocations in the wafers did not exceed $3 \cdot 10^5$ cm^{-2}.

One from such wafers containing about $1 \cdot 10^{15}$ cm^{-3} of In was doped with copper by diffusion from a powdered source of surface copper density about $3 \cdot 10^{15}$ cm^{-2}. The diffusion was carried out during 72 hrs in Hg-saturated conditions at 200 °C. In accord with [5], such annealing is enough for obtaining uniform distribution of copper in the wafer.

As-grown MCT wafers contain a lot of Te precipitates. In the course of annealing in Hg-saturated conditions below ~ 500 °C they interact with diffusing mercury, and extended dislocation defects arise on the sites of the precipitates [6]. For elimination of such defects the undoped wafers of MCT were subjected to pre-annealing within one week at 600 °C under Hg vapor pressure of 0.2 MPa. Accumulations of impurities were dissolved during annealling too.

All the wafers were sectioned on samples to sizes about 0.10×0.3×1.2 cm^3 after the annealling, and the samples were annealed then in different conditions within the MCT existence region (see Tab.1). Some samples were annealed at 240 °C in the atmosphere of own vapors in ampoules with minimum of free volume. Under these conditions mercury diffusion from the vapor had no time to take place, and the equilibrium in Te-saturated conditions was reached due to Te precipitates arising there. In all these cases, Hg vacancies were generated in the samples in the same amount close to $1.8 \cdot 10^{16}$ cm^{-3}. The duration of the annealing was enough for reaching equilibrium conditions.

The crystals doped with indium up to $2.2 \cdot 10^{16}$cm^{-3} were annealed in Hg-saturated conditions at 445 °C or in Te-saturated conditions at 255 °C. The concentration of mercury vacancies in the samples was identified with concentration of them in the undoped samples-satellites annealed in the same ampoules, and was equaled approximately $2.5 \cdot 10^{16}$ cm^{-3}. Thus, these crystals were obviously compensated ($K \approx 0.9$).

For measuring voltage-current characteristics of *p-n*-junctions, three undoped *n*-type MCT wafers of composition $x = 0.206 \pm 0.003$ or $x = 0.240 \pm 0.002$ were annealed at 407 °C and Hg pressure 0.24 MPa or at 350 °C and Hg vapor pressure 0.01 MPa (see Tab.1). Some wafers (samples 10, 12, 14, and 16) contained low-angle grain boundaries (LAGB), but the others (samples 11, 13, 15, and 17) were free of them.

The crystals were etched, and diffusion of mercury into them was carried out in Hg-saturated conditions at 160 °C within ~ 1. Thus, *p-n*-junction was formed in the crystals on a depth of 7-10 microns from the surface.

The samples were slightly etched after the annealling, and indium was deposited on to one of the wafer surfaces by evaporation in vacuo. Sites with *p-n*-junction by area of $A = 0.035$ cm^2 were etched then, and gold contacts to the p-areas were made up. Voltage-current characteristics were measured at T = 77 K using leads, pressed to the *n*-type sites and *p*-type bases.

3. Experimental results

3.1. Galvano-magnetic measurements

The Hall coefficients of the samples in the magnetic field of 2T were measured at T = 77 K after the heat treatment and chemical etching of them; a concentration of uncompensated acceptors in crystals was estimated from these data as N_A-$N_D = r_H/eR_H$. The total Hall factor r_H of holes was close to 1.07 under such condition [7].

Then temperature dependences of the Hall coefficient R_H in the low magnetic field ($B = 0.03$ T) and resistivity ρ were measured in the temperature range 4.2÷120 K.

Fig. 1 shows the data of ρ measurements depending on 1/T in the region of freeze-out of extrinsic conduction

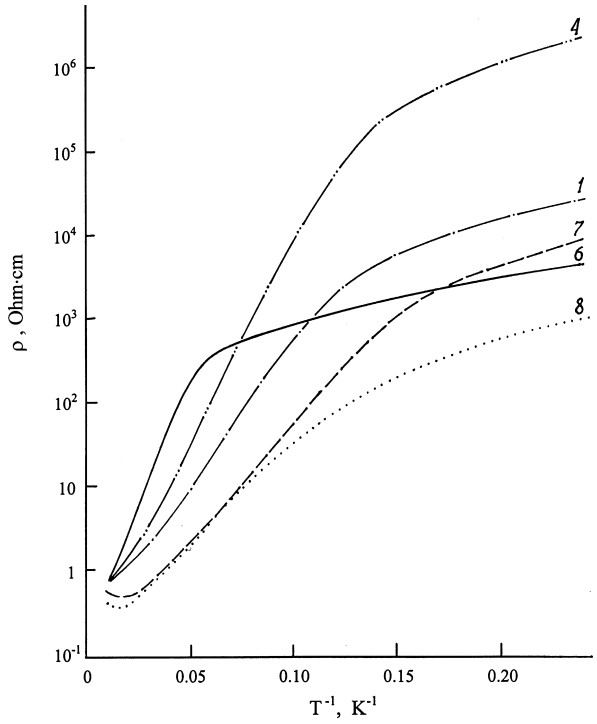

Fig. 1. Temperature dependence of resistivity for *p*-type $Hg_{0.79}Cd_{0.21}Te$ crystals (the curves numbers correspond to the samples numbers in Tab.1).

Table 1. The main characteristics of the investigated samples.

Sample	LAGB	x	T, ∘C	P_{Hg}, MPa	$[V_M]$, cm^{-3}	N_{Cu}, cm^{-3}	N_{In}, cm^{-3}	E_A, meV	$R_0.A$, Ohm.cm^2	j, A/cm^2
1	yes	0.216	420	0.28	$1.8.10^{16}$	-	-	10	-	-
2	yes	0.212	420	0.26	$1.7.10^{16}$	-	-	12	-	-
3	yes	0.218	360	0.01	$1.7.10^{16}$	-	-	13.5	-	-
4	yes	0.215	240	Te-saturated	$1.8.10^{16}$	-	-	15.4	-	-
5	yes	0.207	445	0.35	$2.5.10^{16}$	-	$2.2.10^{16}$	14	-	-
6	yes	0.220	255	Te-saturated	$2.5.10^{16}$	-	$2.2.10^{16}$	12	-	-
7	yes	0.215	200	Hg-saturated	-	3.10^{16}	-	5.5	-	-
8	yes	0.212	420	0.26	$1.8.10^{16}$	3.10^{16}	-	5.5	-	-
9	yes	0.214	240	Te-saturated	$1.8.10^{16}$	$3.5.10^{16}$	-	5.5	-	-
10	yes	0.205	407	0.24	$1.0.10^{16}$	-	-	-	<0.4	0.70
11	no	0.206	407	0.24	$1.0.10^{16}$	-	-	-	<0.4	0.42
12	yes	0.208	350	0.01	$1.1.10^{16}$	-	-	-	<0.4	0.31
13	no	0.203	350	0.01	$1.1.10^{16}$	-	-	-	~0.4	0.12
14	yes	0.24	407	0.24	$1.0.10^{16}$	-	-	-	0.7	0.150
15	no	0.24	407	0.24	$1.0.10^{16}$	-	-	-	5.0	0.040
16	yes	0.24	350	0.01	$1.1.10^{16}$	-	-	-	1.2	0.055
17	no	0.24	350	0.01	$1.1.10^{16}$	-	-	-	10	0.005

for some from the investigated samples. At rather high temperatures up to T ~ 100 K, conduction caused by free holes of valence band (ε_1-conduction) is dominant in all the crystals. At certain temperature (namely, at 5.5÷8.5 K for the copper doped stoichiometric samples; 7÷12 K for the uncompensated non-stoichiometric samples both with copper and without it; 16÷30 K for the high-compensated samples) hopping conduction due to jumps of bound holes on the acceptors states competes with ε_1-conduction. And at the lowest T only the hopping mechanism provides charge transport in the samples.

In the range of hopping conduction resistivity of the crystals containing a great number of V_M increases with decrease in temperature in accordance with the Mott law [8], i.e., as $\exp[(T_0 / T)^{1/4}$. On the contrary, the activation energy of hopping conduction is independent of T and equals to ~ 1 meV for the copper doped samples without V_M (ε_3-conduction). The hopping conductivity of the samples, doped with copper and contained a great number of V_M at the same time, is much more than conductivity of the samples, containing only one kind of the acceptors.

The Hall coefficient is positive in the temperature field, where free holes of valence band dominate the total conduction, increasing with decrease in T (Fig. 2). In the field of transition to hopping conduction, R_H is pos-

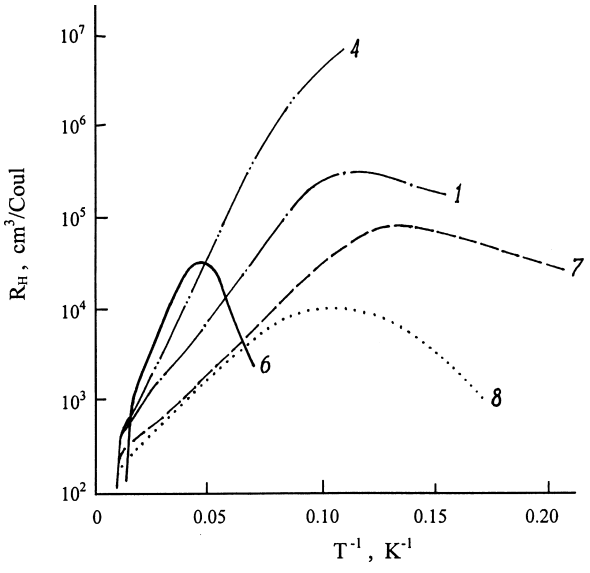

Fig. 2. Temperature dependence of the low-magnetic-field Hall coefficient for $Hg_{0.79}Cd_{0.21}Te$ crystals (the curves numbers correspond to the samples numbers in Tab.1).

itive too, but decreases with decreasing T. A maximum of R_H corresponds to temperature at which contributions of these mechanisms of charge transport are close in sizes. At the lowest temperatures, where ε_1-conduction is freezed out completely, the Hall effect it was not possible to register because of the lowest mobility of the carriers.

Declinations of the R_H(T) and ρ(T) curves in the field of ε_1-conduction are noticeably different for the crystals, prepared by different ways. It is minimum for the copper doped samples (curve 7) and maximum for the samples compensated with In (curve 6). However, strong influence of hopping conduction, exhibited in Hall effect in MCT, and dependence of the Hall factor of holes on temperature do not allow to apply a usual procedure of determination of ionization energy for acceptors immediately using a declination of the Hall-effect curve. For correct and reliable determination of the ionization energy a contribution of free holes only must be allocated in the range of the mixed conduction.

3.2. Voltage-current measurements

Fig. 3 shows the results of measurements of the voltage-carrent characteristics at T = 77 K on the structures obtained here. One can see that the revers dark current is essentially less for the crystals prepared far from Hg-saturated conditions (curves 16, 17), especially in lack of low-angle grain boundaries (curve 17).

For the samples of $x \approx 0.24$, the difference in R_0A product is quite clear. It increases from the value $R_0A \sim$ ~ 0.7 Ohm·cm^2 for Hg-saturated sample 14 up to $R_0A \sim$ ~ 10 Ohm·cm^2 for sample 17. Dark current density j at reverse voltage of -0.2 V decreases, respectively, from 0.15 A/cm^2 down to 0.005 A/cm^2.

For the more narrow-gap samples the difference in R_0A product is expressed poorly because of effect of series resistance of p-type body (about 3-5 Ohm). In the best case (sample 13) an estimation R_0A~0.4 Ohm·cm^2 can be obtain. Dark current density j at reverse voltage of -0.2V decreases from 0.7 A·cm^2 for sample 10 down to 0.12 A·cm^2 for sample 13.

The results can be treated as a corollary of presence of additional channels of charge leakage along low-angle grain boundaries, channel capacities of which essentially depend on a way of heat treatment of initial crystals.

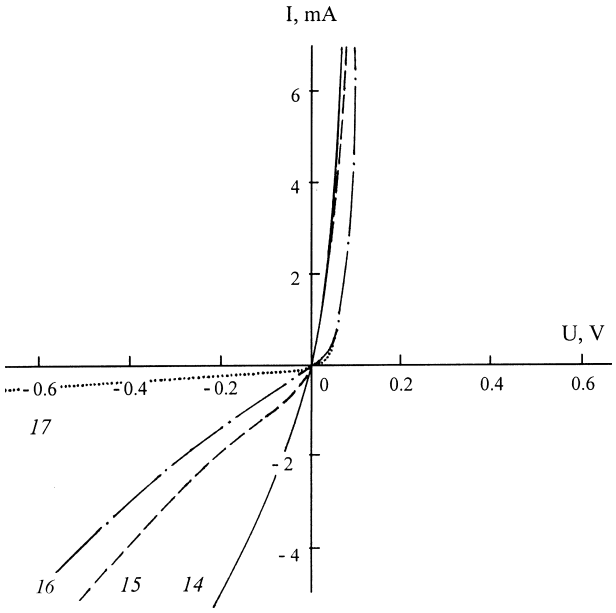

Fig. 3. Voltage-carrent characteristics of *p-n*-junction at T = = 77K for $Hg_{0.76}Cd_{0.24}Te$ crystals (the curves numbers correspond to the samples numbers in Tab.1).

4. Calculation

Ionization energy of a single acceptor in a narrow-gap semiconductor with degenerate valence band was calculated numerically in [9]. In a limit $m_{lh} / m_{hh} \to 0$ it is given by the next relationship:

$$E_A = \frac{4}{9} \cdot \frac{m_{hh} e^4}{2\varepsilon^2 \hbar^2} \qquad (1)$$

Just the same relationship is found in [10] in the identical approximation, using the direct variational method (detail description of this method can be found, for example, in [11]).

The effective mass ratio $m_{lh} / m_{hh} \sim 10^{-2}$ for MCT, hence, approximation (1) is quite acceptable. Substituting into (1) values of static dielectric constant ε = 17.3 [12] and $m_{hh} = 0.385 m_0$ [7], we shall obtain the value $E_A \approx$ ≈ 8 meV for MCT.

Calculations of levels E_{A1} and E_{A2} of a double acceptor were not made earlier for diamond-like crystals. Therefore, E_{A1} and E_{A2} is calculated here with the help of the variational method [11]. Pursuant to this method, a system of two holes, bound on an acceptor with a nucleus charge of Ze, is examined, and the averaged value of a Hamiltonian of the system is calculated in a state with a wave function of a kind:

$$\psi(x_1, x_2) = \varphi_1(x_1) \cdot \varphi_2(x_2). \qquad (2)$$

Here, $\varphi(x)$ is a wave function of a hole, bound on an acceptor with effective nucleus charge Z^*e.

In the framework of the effective mass method, a bound hole wave function has the next from for diamond-like semiconductors [9]:

$$F_{jM}(r, \vartheta, \varphi) =$$

$$= \sqrt{2j+1} \sum_l (-1)^{l-3/2+M} R_{j,l}(r) \sum_{m,\mu} \begin{pmatrix} l & 3/2 & j \\ m & \mu & -M \end{pmatrix} Y_{lm}(\vartheta, \varphi) \chi_\mu \; ; \quad (3)$$

Here, Y_{lm} stands for spherical functions; χ_μ is the spinor for a particle with effective spin of 3/2, corresponding to a proper value μ; j is a proper value of a total angular momentum operator (with M as its projection). The ground state corresponds to the value j = = 3/2 [10]; this state is degenerated with multiplicity of $\beta_0 = 4$.

Ideal mathematical expressions for $R_{j,l}(r)$ have not been obtain in a general form in [9] because of the obtained there equations are too complicated. However, in [10] it is shown that the next trial functions:

$$R_{3/2,0}(r) = \frac{\sqrt{2}}{a^{3/2}} e^{-r/a}, \tag{4}$$

$$R_{3/2,2}(r) = \frac{\sqrt{2}}{a^{3/2}} \left(\frac{a}{r}\right)^3 \times \times \left\{6 - e^{-r/a}\left[\left(\frac{r}{a}\right)^3 + 3\left(\frac{r}{a}\right)^2 + 6\left(\frac{r}{a}\right) + 6\right]\right\} \tag{5}$$

can be effectively used instead of the ideal functions for calculation of energy level of the ground state of a single acceptor in a limit $m_{lh}/m_{hh} \to 0$. Here $a = 3\varepsilon\hbar^2/(2m_{hh}e^2)$.

Using functions (3)-(5) as φ(x) and supposing there $a^* = a/Z^*$ instead of a [11], we shall obtain after minimization on Z^* the following evaluation for energy of a ground state of a double acceptor in a diamond-like crystal with small light holes effective mass:

$$E_{AZ} \approx -1.95(Z^*)^2 E_A \tag{6}$$

$$Z^* \approx 1.01Z - 0.27 \tag{7}$$

Here, E_A is an ionization energy (1) of a single acceptor in the same limit.

In the case of the neutral vacancy Z = 2, therefore, the value $Z^* \approx 1.75$ is obtained from (7). Accordingly, an energy of the ground state of the neutral vacancy is equal to $\mathcal{E}_{AZ} \approx -6.0E_A$. This energy is equal to a sum E_{A1} and E_{A2} to within a sign. Taking into account that $E_{A2} = 4E_A$ in the adopted approximation, it can be obtained:

$$E_{A1} \approx 2.0E_A, \tag{8}$$

i.e., $E_{A1} \approx$ 16 meV and $E_{A2} \approx$ 32 meV for narrow-gap MCT crystals.

5. Discussion

Contribution of hopping conduction into the Hall effect can be estimated by the joint analysis of temperature dependencies of σ and $R_H \cdot \sigma^2$. The low-magnetic-field Hall coefficient, as it is well known, is not additive value at presence of several types of carriers, but is equal to:

$$R_H = \sum_j \frac{r_{Hj}\,\mu_j^{\,2} p_j e_j}{\sigma^2} \tag{9}$$

(here, $\sigma = \sum e_j \mu_j p_j$ is a conductivity). Therefore, it is very difficult to separate contributions of different carriers using data of the Hall coefficient measurements only.

On the contrary, contributions of different carriers are added in σ and $R_H \cdot \sigma^2$ in additive manner. If we take into consideration only the light (j = l) and heavy ($j = h$) holes of the valence band, and holes, bound on acceptors ($j = a$), it is easy to transform (9) in to the next form:

$$R_H\sigma^2 = R_{H1}\sigma_1^2 + R_{Ha}\sigma_a^2, \tag{10}$$

where R_{H1} and R_{Ha} are the Hall coefficients due to band and hopping conduction; σ_1 and σ_a are contributions of band and hopping conduction, respectively, and:

$$R_{H_1} = e\frac{p_l\mu_l^{\,2} + p_h\mu_h^{\,2}}{\sigma_1^{\,2}}; \quad \sigma_1 = e\mu_l p_l + e\mu_h p_h; \tag{11}$$

Effect of hopping conduction on the $R_H \cdot \sigma^2$ values can be easily found from the kind of temperature dependence of $R_H \cdot \sigma^2$. One can see (Fig. 4) that in all the cases no segments with low activation energy are observed, i.e., $R_H \cdot \sigma^2$ was limited there only by free holes.

In the copper doped crystals and in the crystal annealed far from the boundaries of the existence region, a crook of temperature dependence of $R_H \cdot \sigma^2$ accompanied by increase in declination is observed with decrease in T. Calculation shows that this crook is caused by a change in Fermi energy. Different declinations correspond to different kinds of solutions of the electroneutrality equation:

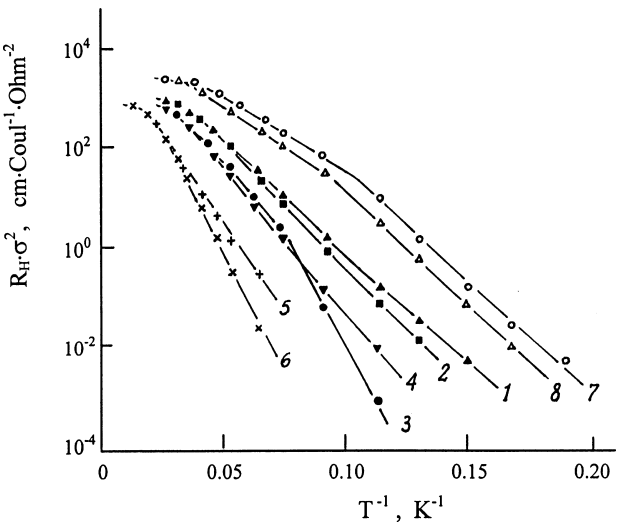

Fig. 4. Temperature dependence of product $R_H \cdot \sigma^2$ for p-type $Hg_{0.79}Cd_{0.21}Te$ crystals (the curves numbers correspond to the samples numbers in Tab.1).

$$p_h + p_l + N_D^+ = N_A^- + \left[V_M^-\right] + 2\left[V_M^{2-}\right] \qquad (12)$$

in the cases, when $p_h + p_l > N_D$ and when $p_h + p_l < N_D$. Here, N_D, N_A are concentrations of the extrinsic donors and acceptors, respectively; $[V_M]$ is a concentration of mercury vacancies.

For the doped crystals, where V_M are neutral at low temperatures and free holes concentration is determined only by extrinsic acceptors, the declination varies at T ≈ ≈ 10K, when $p_h + p_l \sim N_D$ (curves 7 and 8). On the contrary, all the shallow extrinsic centers are ionized in the undoped crystals at $N_D > N_A$, therefore, the crook is observed, when $p_h + p_l \sim N_D - N_A \sim 10^{14}$cm^{-3} (curve 3). For the compensated crystals the declination of curves 5 and 6 is constant, as it was necessary to expect.

For the crystals, saturated either by Hg or Te, the crook of the temperature dependence of $R_H \cdot \sigma^2$ has an opposite direction. This appearance is not connected to the contribution of hopping conduction, so as activation energy is too great for this purpose. It also fails to connect with effect of uncontrollable extrinsic acceptors predominating over residual donors, because the course of R_H(T) curves before the crook corresponds just to the contrary case $N_D > N_A$ (namely, $N_D - N_A \approx 10^{14}$ cm^{-3}).

Most likely, the course of the dependence of $R_H \cdot \sigma^2$ on T in the material annealed at boundary pressure of Hg or Te testifies to the presence of extended coherent clusters of *p*-type in a matrix of the crystals. The contribution of these clusters to the Hall effect at low temperatures predominates above the contribution of the matrix, whereas their contribution to conductivity is small. It is quite possible, so far as the hopping Hall effect is anomalously small [13]. Such supposition is suggested with the data of research of the voltage-current characteristics of *p-n*-junctions, obtained here.

Thus, hopping conduction practically does not create any visible Hall voltage in the *p*-type MCT crystals, but it shunts the effect caused by free holes. It allows calculating the band Hall coefficient R_{H1} from the data of ρ and R_H measurements extrapolating the ρ(T) dependence into the area of mixed conduction from the next sections and using then relationship (10). For samples 1, 2, and 4 such procedure is not correct at T < 10 K because of the effect of shunting by the charge leakage channels there.

The R_{H1}(T) curves obtained in such a way are shown in Fig. 5. It is clearly visible that in the case of the undoped crystals the activation energy perceptibly increases with removal from the Hg phase boundary limits (curves 1-4). In the samples compensated with In (curves 5 and 6) R_{H1} grows with decrease in T much faster, than in the uncompensated samples, which demonstrates a qualitatively higher degree of compensation of the In-doped crystals. It confirms that the concentration of the uncontrollable donors was small in the investigated material ($N_D << 10^{16}$ cm^{-3}).

The double native acceptors have higher ionization energy in comparison with copper dopants, therefore,

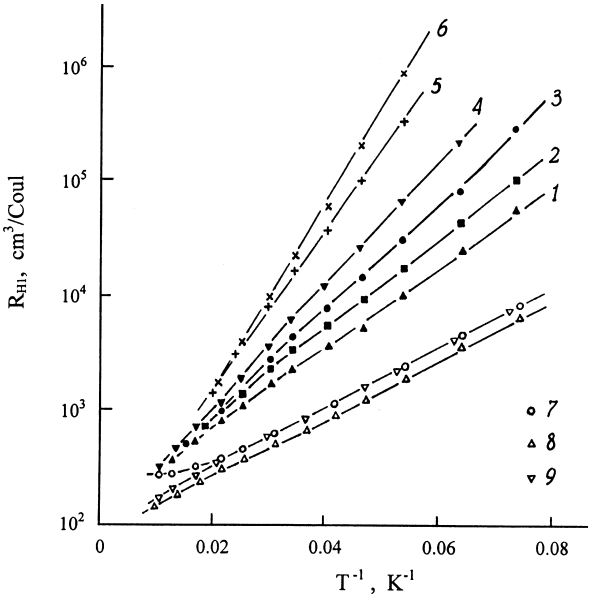

Fig. 5. Temperature dependence of valence band holes contribution into the low-magnetic-field. Hall coefficient for *p*-type $Hg_{0.79}Cd_{0.21}Te$ crystals (the curves numbers correspond to the samples numbers in Tab.1).

the Fermi energy is determined by the shallowest of them (i.e., by copper) in presence of those and others simultaneously. Adding of the vacancies does not change the value R_{H1} at low temperatures. It allows to estimate a degree of annealing effect on copper ionization energy, despite the presence of a significant amount of vacancies. As follows from Fig. 5, activation energy of copper dopants does not depend on a way of heat treatment of the crystals.

Ionization energy of acceptors was estimated from temperature dependence of R_{H1} at T < 35 K, where the heavy holes Hall factor is limited due to scattering on charged impurities only and, hence, it can be considered as equal to its theoretical value r_{Hh} = 1.93. Account of the light holes contribution was made empirically using the data of the field dependence $R_H(B)$ with the additional factor $r_1(B)$. According to [7], $r_1(0) = 1.35 \pm 0.05$ at T = 77 K in MCT crystals ($x \sim 0.2$). The special researches showed that r_1 (0) practically does not vary with decreasing in temperature from 77 K down to 4.2 K, therefore it was considered to be equal to 1.35 for all these temperatures.

The concentration of charged acceptors was calculated depending on temperature pursuant to the Gauss distribution:

$$V_M^- = V_M \times \frac{g_1(N_V/p)\cdot exp(-E_{A1}/k_BT)}{g_0 + g_1(N_V/p)exp(-E_{A1}/k_BT) + g_2(N_V/p)^2 exp[-(E_{A1}+E_{A2})/k_BT]}; \quad (13)$$

$$V_M^{2-} = V_M \times \frac{g_2(N_V/p)^2 \cdot exp[-(E_{A1}+E_{A2})/k_BT]}{g_0 + g_1(N_V/p)exp(-E_{A1}/k_BT) + g_2(N_V/p)^2 exp[-(E_{A1}+E_{A2})/k_BT]}; \quad (14)$$

$$N_A^- = N_A \cdot \frac{\beta_1(N_V/p)\cdot exp(-E_A/k_BT)}{\beta_0 + \beta_1(N_V/p)\cdot exp(-E_A/k_BT)}. \quad (15)$$

Here, E_A is an ionization energy of extrinsic acceptor; E_{A1}, E_{A2} are energies of the first and the second acceptor levels of mercury vacancy, respectively. The values of the degeneration factors of the acceptors states were believed to be equal as follows: $\beta_0 = 4$; $\beta_1 = 1$; $g_0 = 6$; $g_1 = 4$; $g_2 = 1$.

The effective density of states in the heavy hole band was chosen in the kind found in [7] by taking into account some non-parabolicity of this band:

$$N_V = 2\left(\frac{m_{hh}k_BT}{2\pi\cdot\hbar^2}\right)^{3/2}\left[1+\frac{T}{T_1}+\left(\frac{T}{T_2}\right)^2\right] \quad (16)$$

($m_{hh} = 0.385m_0$; $T_1 = 329$ K; $T_2 = 102$ K). The account of the non-parabolicity reduces the determined value of the ionization energy by about 1 meV.

In an outcome, it was found, that the ionization energy of copper dopant in the studied MCT crystals was 5.5 ± 0.2 meV irrespective of the heat treatment conditions. On the contrary, the first acceptor level (E_{A1}) of the vacancy depends on annealing conditions. In the uncompensated crystals 1-4 it monotonically increases from 10 meV up to 15.5 meV in accordance with removal from the Hg phase boundary limit (see Tab.1). In the case of the In-compensated crystals E_{A1}= 14 meV for the Te-saturated sample 6 and E_{A1} = 12 meV for the Hg-saturated sample 5. That does not differ almost from E_{A1} values for the uncompensated crystals. Filling the second acceptor level of the vacancy begins only at higher temperatures T > 35 K, therefore E_{A2} was not determined.

The obtained data were compared to the values of ionization energy of acceptors, calculated in approach of the effective mass method.

The observed value $E_A \approx 5.5$ meV is noticeably less than the calculated one $E_A \approx 8$ meV. Most likely, it is connected to the known effect of decrease in activation energy of dopant with increase in concentration of them. Really, the Mott metal-insulator transition in copper doped uncompensated MCT crystals of composition $x \approx 0.21$ was observed by the author at $N_A \approx 3.8\cdot10^{17}$ cm^{-3}. If one accepts, that $E_A \approx 0$ at the transition, and the ionization energy linearly decreases with increase in $N_A^{1/3}$, the value $E_A \approx 9.5$ meV could be obtained by extrapolation of the experimental data in the limit $N_A = 0$. It coincides with the data [14] for the lowest Cu concentrations and will be not bad agreed with the results of calculations made within the framework of the effective mass approximation [9,10].

The calculated value $E_{A1} \approx 16$ meV for the first level of a double shallow acceptor is close to the value E_{A1} = =15.4 meV obtained experimentally for Hg vacancies in the undoped Te-saturated crystal. But it is essentially higher than in the Hg-saturated material. It means that the Te-saturated MCT crystals have more perfect microstructure than the Hg-saturated samples.

6. Conclusion

Thus, the results obtained here confirm the essential dependence of an ionization energy of the native acceptors in narrow-gap MCT crystals on conditions of annealing the crystals, that explains the divergence of the literary data on energies of Hg vacancy ionization. Observed ionization energy of native and extrinsic acceptors in Te-saturated narrow-gap MCT crystals are in a good agreement with results of calculations. Activation energy of mercury vacancies in Hg-saturated crystals is visibly less. One from the possible reasons of this phenomenon is a difference of a microstructure of Hg-saturatied material and Te-saturatied one. Such difference appears to be very essential for IR photodiodes based on use of undoped MCT crystals. It should be taken into account when manufacturing them.

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