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Density of heavy hole states of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ in an isotropic nonparabolic approximation by exact measurements of electron concentration

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Abstract. High precision measurements of intrinsic electron concentration n_i in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ crystals were made in broad ranges of compositions ($x = 0 \dots 0.31$) and temperatures ($T = 77 \dots 420$ K). It was found that effective mass of the integral heavy hole state density essentially depends on temperature. It can be explained using the conception of the non-parabolic band. The proposed model enabled to determine the differential state density $N_{hh}(\varepsilon)$ in the band being based on the results of $n_i(T)$ measurements. It was found that the heavy hole dispersion law at $\varepsilon < 0.15$ eV have the relativistic form $\hbar k = \sqrt{2m_{hh}\varepsilon(1 + \varepsilon/\varepsilon_0)}$ in the framework of the measurements accuracy, where $m_{hh} = 0.39m_0$ and $\varepsilon_0 = 0.096$ eV for all studied compositions x . It was also shown that intrinsic electron concentration in CdTe at high temperatures (higher than 800 K), calculated with the found heavy hole state density, agrees quantitatively with known experimental data.

Keywords: $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$, heavy holes, effective mass, density of states

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1. Introduction

The differential heavy hole state density $N_{hh}(\varepsilon)$ in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ crystals – one of the basic materials for IR photoelectronics – remains disputable till now. On the one hand, in the most of experimental studies the parabolic approximation believes to be quite sufficient for this band [1–5]. On the other hand, the theoretical calculation shows that the heavy hole band should become non-parabolic here already at energies $\varepsilon \sim kP$, as well as the light holes, because of nonlocality of exchange interaction [6]. As a result, according to [6], the heavy hole effective mass m_{hh}^* at $k = 0$ should depend on temperature and the sample composition, especially at $|E_g| \sim k_B T$ and less.

Apparently, these reasons cause considerable distinctions in values of m_{hh}^* , found by the different investigators. It is enough to mention that on magneto-optical measurements data the heavy hole mass depends on a direction and varies in limits $m_{hh}^* = 0.40 \dots 0.53 m_0$ [1] or $m_{hh}^* = 0.40 \dots 0.42 m_0$ [2–3], while the density of intrinsic carriers corresponds to $m_{hh}^* = 0.9 m_0$ [5].

Thus, there is a problem of the heavy hole state density $N_{hh}(\varepsilon)$ experimental determination in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ crystals.

Here, this problem is solved by high precision experimental studying intrinsic electron density versus temperature and composition in comparison with simulation results.

2. Model

At a choice of a model for the state density $N_{hh}(\varepsilon)$ in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$, it was supposed that the dispersion law is isotropic but non-parabolic here. In this case $N_{hh}(\varepsilon)$ can be presented in the following form:

$$N_{hh}(\varepsilon) = \frac{\sqrt{2m_{hh}^3\varepsilon}}{\pi^2\hbar^3} \cdot \varphi(\varepsilon). \quad (1)$$

Here, m_{hh} is the heavy hole effective mass at $\varepsilon = 0$; $\varphi(0) = 1$.

The function $\varphi(\varepsilon)$, defined by Eq. (1), have no singularities at small ε , including the point $\varepsilon = 0$. It is well known that such function can be approximated with a required exactness by a polynomial of some limited degree R in given energy range of $\varepsilon < \varepsilon_{\max}$:

$$\varphi(\varepsilon) \approx 1 + \sum_{r=1}^R (\varepsilon/\varepsilon_r)^r. \quad (2)$$

The coefficients ε_r in Eq. (2) are empirical parameters that can be uniquely determined, for example, using temperature dependence of the intrinsic electron concentration. The procedure of ε_r determination is found here as follows.

Holes in undoped $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ are not degenerate with a good accuracy. Accordingly, their density is defined by the formula of the same form as for a parabolic band:

$$p = N_V(T) \cdot \exp\left(\frac{E_V - F}{k_B T}\right) \equiv 2 \left[\frac{m_{hh}^* k_B T}{2\pi\hbar^2} \right]^{3/2} \exp\left(\frac{E_V - F}{k_B T}\right); \quad (3)$$

but here the heavy hole effective mass depends on temperature:

$$m_{hh}^*(T) = m_{hh} \cdot \left[\frac{2}{\pi} \int_0^\infty dx e^{-x} \sqrt{x} \cdot \varphi(x k_B T) \right]^{2/3}. \quad (4)$$

It is quite admissible that the coefficients ε_r in Eq. (2) are independent of T . This assumption is valid, if the deviations from the parabolic law are not limited by nonlocality of the exchange interaction. As it will be shown further, m_{hh}^* is practically independent both of x and E_g , that is a good reason for such assumption. Then after substitution Eq. (2) into Eq. (3), we shall obtain:

$$m_{hh}^*(T) = m_{hh} \cdot \left[1 + \sum_{r=1}^R (2r+1)!! \cdot \left(\frac{k_B T}{2\varepsilon_r} \right)^r \right]^{2/3}. \quad (5)$$

On the other hand, measuring $m_{hh}^*(T)$ in some temperature range $T < T_{\max}$, it is possible to obtain the next relation using regression error analysis:

$$\left[m_{hh}^*(T) \right]^{3/2} = \text{const} \cdot \left[1 + \sum_{r=1}^R \left(\frac{T}{T_r} \right)^r \right]. \quad (6)$$

Then, equating the relevant coefficients in Eqs. (5) and (6), we shall obtain both the effective mass m_{hh} in the band extreme and the coefficients ε_r in the range $\varepsilon < \varepsilon_{\max}$. Here, $\varepsilon_{\max} \approx (3..4) \cdot k_B T_{\max}$. Thus, the state density $N_{hh}(\varepsilon)$ will be completely determined in the noted above range.

3. Experiment

The electron concentration in undoped $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ crystals with low density of residual impurities was examined for $x = 0 \dots 0.30$ versus temperature. Homogeneous on x single crystal wafers of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ were chosen for this study. The wafers were cut out from different ingots. The composition variations for each of them did not exceed ± 0.002 , and the electron concentration at 77 K was more than $9 \cdot 10^{13}$ but less than $3 \cdot 10^{14} \text{ cm}^{-3}$.

For studying concentration of intrinsic electrons (n_i) at 77 K versus composition the $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ crystals were cut out from two ingots grown by the Bridgeman technique. The composition of the ingots smoothly varied along the growth axes in the range of x from 0.03–0.05 up to 0.21–0.22. The density of residual impurities was evaluated on the electron concentration at 77 K in the control samples cut out from the same ingots and having the composition of 0.21–0.22. It was low (about of $2 \cdot 10^{14} \text{ cm}^{-3}$), and then it was taken into account calculating n_i .

For measuring the Hall effect, the 6-contact method was used. The samples were cut out from the wafers in the shape of either long brick (12:3:1) or dumb-bell. Composition of the narrow-gap and gapless samples with $x < 0.175$ was determined using reflection spectra near the maximum E_1 . Composition of crystals with $x > 0.175$ was determined on the edge absorption spectra.

The direct current Hall coefficient R_H was measured using the standard procedure in the magnetic field 1 T that is strong for electrons. Therefore, the electron concentration n was calculated by using the expression $n = -1/eR_H$. To make negligible the influence of thermomagnetic effects, the samples were closely pressed to massive copper heat-conductor through a thin mica plate. Temperature of the samples was measured to within 0.1 K. Its oscillations during unit measuring R_H did not exceed ± 0.15 K, and the Hall voltage was calculated at maximal T .

For the semiconductor crystals with $x = 0.175 \dots 0.315$, the Hall effect was measured in the temperature range 100...420 K, and for the gapless samples ($x = 0 \dots 0.07$) – in the range 77...325 K. Under such conditions, the influence of thermomagnetic effects could be neglected. The resulting measurement error of R_H was about 1.5 %.

4. Energy gap versus temperature and composition

The method of measurements for the heavy hole effective mass, applied here, differs by rigid requirements to the accuracy of determination of the energy gap E_g depending on x and T . In particular, the value of the temperature coefficient dE_g/dT should be known with an exactness about of 1 %. Any known interpolation formulas have not such exactness (see, for example, [7–10]). Therefore, the revision of the experimental data [7–14] was carried out here concerning dependence $E_g(x, T)$ in this material. To reach the necessary exactness, the analysis was based on application of the new model for edge absorption in narrow-gap crystals,

developed in [15]. The model ensures a diminution of the absolute error of E_g determination up to magnitude ~ 0.1 meV by an evaluation of exact value of the factor before the exponent in the Urbach rule. Secondly, the value dE_g/dT was put in correspondence not to a composition x but to a value E_g at $T = 295$ K, which is determined much more precisely. In such approach, the composition x plays a role of an auxiliary intermediate parameter. Thirdly, the interlaboratory error that leads to an additional scattering the data [7–10] was eliminated. It was considered that this scattering is caused by a systematic error of direct measurements of x .

According to this procedure, for each sample and each value of temperature the rectified value E_g was evaluated on data, represented in [7–13], using the model [15]. The dependence $E_g(x)$ was built up further for $T = 295$ K separately for everyone of studies [7–10], and the interlaboratory error was determined by comparison of these dependences. It was considered that in [8], where x was measured by a microprobe with the best exactness ($\Delta x = \pm 0.003$), and E_g was determined using edge absorption spectra, the systematic error of $E_g(x)$ is absent. In Fig. 1, the data obtained after subtraction of the systematic error are shown. One can see that after such procedure they are in perfect agreement with each other. Interpolation of these data results in the following relation:

$$E_g(x, 295 \text{ K}) = -0.1226 + 1.5301x - 0.6773x^2 + 0.7703x^3 \pm 0.0012, \text{ eV} \quad (7)$$

Then, the new value $\partial E_g / \partial T$ was determined for each sample using the data [7–10] and the improved value x was evaluated applying Eq. (7). The magnitude $\partial E_g / \partial T$ for HgTe was determined by linear interpolation of the data set

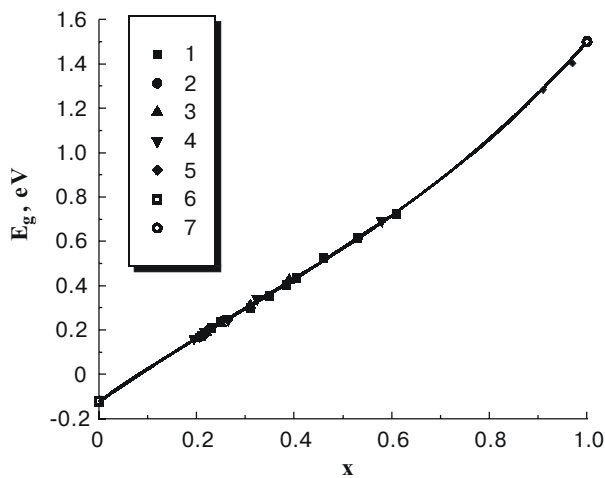


Fig. 1. Energy gap versus composition of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ crystals at 295 K.

Points 1–7 – accordingly, data of [7–14]; the curve is the result of interpolation.

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obtained by different authors and methods at different temperatures and represented in [13–14]. For CdTe , the spectra obtained in [12] as well as our own data were used.

The values $\partial E_g / \partial T$, found in the result, are plotted versus x in Fig. 2. It is quite clear that this dependence is non-linear, whereas earlier it was believed to be only linear [7–9]. Here, the next relation is obtained:

$$\frac{\partial E_g}{\partial T} = 6,345 \cdot 10^{-4} \times (1 - 2.195x + 0.309x^2 + 0.343x^3) \pm 2 \cdot 10^{-6}, \text{ eV/K.} \quad (8)$$

One can see that the relative error of $\partial E_g / \partial T$ represented by Eq. (8) really does not exceed 1 % for $x < 0.3$. Combining Eqs (7)–(8) we shall obtain:

$$E_g(x, T) = -0.3098 + 1.9409x - 0.7351x^2 + 0.7061x^3 + 6.345 \cdot 10^{-4}T \times (1 - 2.195x + 0.309x^2 + 0.343x^3), \text{ eV.} \quad (9)$$

Eq. (9) is usable for anyone x at $T > 25$ K and ensures a necessary exactness of determination of E_g in a wide range of temperatures, if the exact value E_g is known at the room temperature.

5. Results and discussion

The integrated effective mass m_{hh}^* was evaluated from Eq. (3) and the electrical neutrality condition:

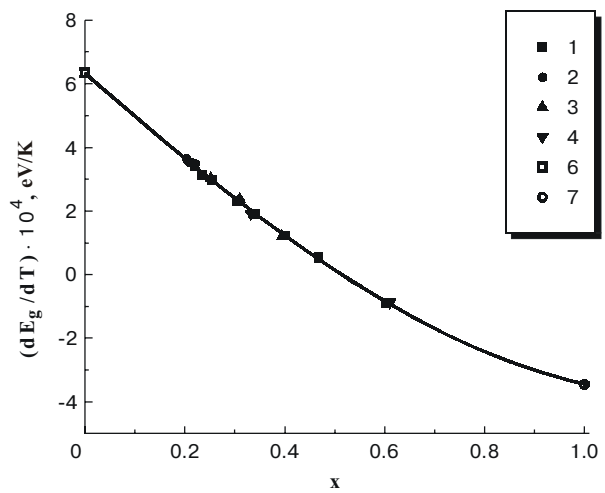


Fig. 2. Temperature coefficient of energy gap versus composition of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ crystals.

Points 1–7 – accordingly, data of [7–14]; the curve is the result of interpolation.

$$n - p = N_D - N_A \cdot \quad (10)$$

The Fermi level F was obtained by numerical solution of the equation:

$$n = \int_0^{\infty} N_e(\varepsilon) f(E_c + \varepsilon - F) d\varepsilon. \quad (11)$$

The state density in the conduction band $N_e(\varepsilon)$ was calculated within the framework of the model, proposed in [15], which accounts the influence of far bands. The values $P = 8.12 \cdot 10^{-8} \text{ eV} \cdot \text{cm}$ for the momentum matrix element and $\gamma_1 + 2\bar{\gamma} = 5.4$ for the sum of the modified Luttinger parameters were used. These values were found by the author [16] using the data set of exact measurements of Faraday rotation and optical absorption at $\lambda = 10 \mu$. Besides, it was assumed that $\gamma_S = 0.5$, where $\gamma_S = -1 - 2m_0A'/\hbar^2$ – an analog of the modified Luttinger parameters entered in [16] for convenience when accounting the influence of far bands on the dispersion law for electrons.

The results of evaluation m_{hh}^* are plotted in Fig. 3. One can see that m_{hh}^* essentially increase with increasing temperature and it does not depend on x in all studied range $x = 0 \dots 0.3$ at the chosen value γ_S . The interpolation of these data with a polynomial of the second degree gives the next expression:

$$m_{hh}^*(T)^{3/2} \approx m_{hh}^{3/2} \left[1 + \frac{T}{T_1} + \left(\frac{T}{T_2} \right)^2 \right]; \quad (12)$$

where $T_1 = 334 \text{ K}$; $T_2 = 594 \text{ K}$; $m_{hh} = 0.397 m_0$.

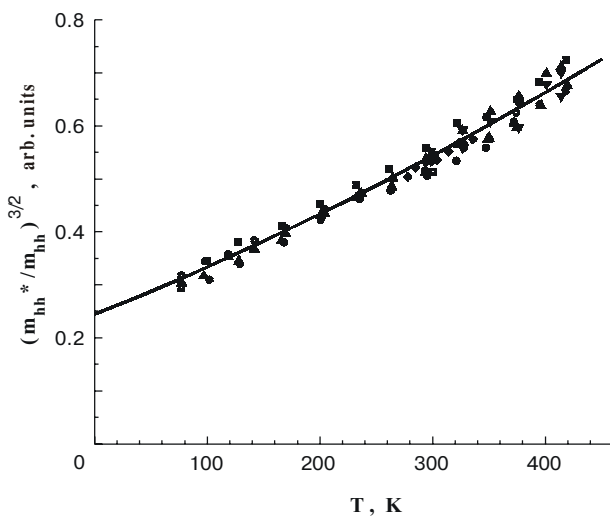


Fig. 3. Temperature dependence of the integrated heavy hole effective mass in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ crystals ($x = 0 \dots 0.315$).

Points represent the experimental data; the curve is the result of fitting with the relativistic-like heavy hole dispersion law.

Accounting errors of measurements and errors of adequacy to interpolation, we have obtained at $E < 0.15 \text{ eV}$:

$$m_{hh} = (0.40 \pm 0.01) m_0 \quad (13)$$

$$\varepsilon_1 = 0.0432 \text{ eV}; \quad \varepsilon_2 = 0.0992 \text{ eV}. \quad (14)$$

The found value m_{hh} coincides within the framework of errors with the data of magneto-optical measurements [2–3]. On the other hand, at $T = 300 \text{ K}$ Eq. (14) gives $m_{hh}^* \approx 0.66 m_0$, that is quite close to the data of cyclotron resonance measurements [4]. Thus, assuming that the heavy hole band is non-parabolic, it is possible to explain completely considerable distinctions in data of different methods of measuring m_{hh}^* in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ crystals.

It is necessary to note that correlation between ε_2 and ε_1 is characteristic for the relativistic-like dispersion law. Therefore, additional fitting the experimental data was carried out within the framework of such model:

$$N_{hh}(\varepsilon) = \frac{\sqrt{2m_{hh}^3}}{\pi^2 \hbar^3} \sqrt{\varepsilon(1 + \varepsilon/\varepsilon_0)} (1 + 2\varepsilon/\varepsilon_0). \quad (15)$$

The fitting has shown that calculated by using Eq. (15) dependence $m_{hh}^*(T)$ really perfectly coincides with the experimental data, if to assume $m_{hh} = 0.391 m_0$ and $\varepsilon_0 = 0.096 \text{ eV}$ (see Fig. 3). Thus, within the isotropic approximation, the heavy hole dispersion law is relativistic-like:

$$\varepsilon = -\frac{\varepsilon_0}{2} + \sqrt{\left(\frac{\varepsilon_0}{2} \right)^2 + \varepsilon_0 \frac{\hbar^2 k^2}{2m_{hh}}}. \quad (16)$$

In Fig. 4 the intrinsic electron concentration n_i measured at 77 K is shown versus composition of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ crystals. Comparison with results of the numerical n_i calculation (see the line in Fig. 4) shows that the calculated dependence $n_i(x)$ is in a good agreement with data of measurements for all $x < 0.2$. The calculations were carried out using formulas presented here assuming no composition and temperature dependences of $N_{hh}(\varepsilon)$ and P .

Hence, at $x < 0.3$ the heavy hole state density in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ practically does not depend on composition. It means that nonlocality of the exchange interaction considered in [6] is not the principal reason of deviations from parabolic dispersion law for the heavy hole band in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$.

It is possible to come to a similar conclusion by comparison of calculation of the temperature n_i dependence in CdTe with data of its direct measurements at $800 \dots 1000 \text{ K}$, carried out in [18] (Fig. 5). If one assumes $N_D - N_A = 6 \cdot 10^{15} \text{ cm}^{-3}$, that is typical impurity concentration in this material, then the calculated electron concentration will practically coincide with the experimental one. For comparison, results of the $n_i(T)$ calculations, carried out within the framework of an approximation of the parabolic heavy hole band with $m_{hh} = 0.4 m_0$. It is clear that a strong discrepancy is observed in this case.

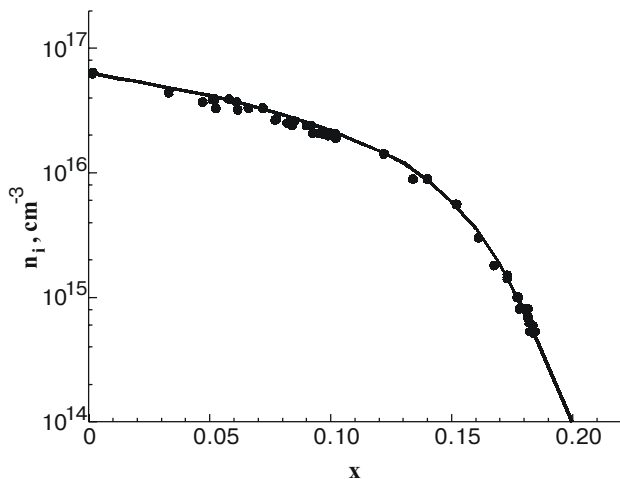


Fig. 4. Electron concentration at 77 K in the undoped $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ crystals versus composition.

Points represent the experimental data; the line is the result of calculation made at $N_D - N_A = 2 \cdot 10^{14} \text{ cm}^{-3}$.

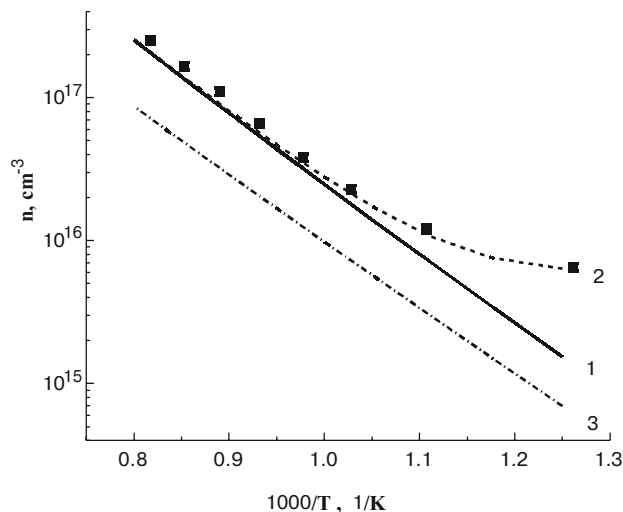


Fig. 5. Density of free electrons in CdTe at high temperatures.

1 – data of calculation of n_i for the nonparabolic heavy hole band; 2 – data of calculations of electron concentration for the nonparabolic heavy hole band at $N_A - N_D = 6 \cdot 10^{15} \text{ cm}^{-3}$; 3 – data of n_i calculations for a parabolic band of heavy holes;

Points represent experimental data [18].

Thus, the parameters of the heavy hole band depend neither on temperature nor on the composition of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ crystals. Hence, the structure of this band is determined, obviously, by the influence of far bands. The model of the state density, presented here, is applicable for a wide temperature range, including the range close to a point of the band inversion $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$.

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