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I.V. Gorichok

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Brookhaven National Laboratory
P.O. Box 5000
Upton, New York 11973
www.bnl.gov

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Compensation mechanism of bromine dopants in cadmium telluride single crystals

I. V. Gorichok[1*], P. M. Fochuk[2], Ye. V. Verzhak[2], T. O. Parashchuk[1], D. M. Freik[1], O. E. Panchuk[2]
A. E. Bolotnikov[3], and R. B. James[3]

[1]Physical-Chemical Institute, "Vasyl Stefanyk Precarpathian National University", Ivano-Frankivsk, Ukraine

[2]Department of Inorganic Chemistry, Yuriy Fed'kovych Chernivtsi National University, Chernivtsi, Ukraine

[3]Brookhaven National Laboratory, Upton, NY, 11973, USA

*Corresponding author: horichokihor@gmail.com

Annotation

We grew single crystals of cadmium telluride, doped with bromine by the Bridgman method, annealed them under a cadmium overpressure ($P_{Cd} = 10^2$-10^5 Pa) at 800-1100 K, and investigated their electrical properties at high- and low-temperature. The influence of impurities on the crystals' electrical properties were analyzed using the defect subsystem model; the model includes the possibility of the formation of point intrinsic defects (V_{Cd}^{2-}, Cd_i^{2+}, V_{Te}^{2+}, Te_i^{2-}), and substitutional ones (Br_{Te}^{0}, Br_{Te}^{+}), as well as complexes of point defects, i.e., $(Br_{Te}^{+}V_{Cd}^{2-})^{-}$ and $(2Br_{Te}^{+}V_{Cd}^{2-})^{0}$. We established the concentration dependence between free charge carriers and the parameters of the annealing process. Here, n(T) and n(P_{Cd}) are determined by two dominant defects – Br_{Te}^{+} and $(2Br_{Te}^{+}V_{Cd}^{2-})^{0}$. Their content varies with the annealing temperature and the vapor pressure of the component; the concentration of other defects is much smaller and almost does not affect the electron density.

Keywords: Computer simulation; Point defects; Bridgman technique; Semiconducting cadmium compounds.

1. Introduction

Among the elements of the VII Group of the Periodic Table that are used for doping CdTe, most attention has been given to chlorine due to the possibility of obtaining high ohmic crystals and the prospects of using it for manufacturing of uncooled highly sensitive detectors of X- and gamma-ray radiation [1]. The impact of other elements of the same group on the physical properties of cadmium telluride is less well studied, although they also exhibit self-compensation of impurities, but to a lesser extent than chlorine [2-3]. These findings suggested the possibility of obtaining a material with a controlled concentration of free charge carriers, which is essential for some electronics applications. However, for assuring the targeted growth of CdTe:Br single crystals with predetermined physical properties, it was necessary for us to first carry out additional studies of its defect subsystem due to 1) the critical influence of the type and charge state of the dominant point defects, and, 2) the lack of a unified point of view on self-compensation processes in CdTe:Br [2-8].

According to [1-8], during the doping of cadmium telluride by halogens, the impurity atoms replace tellurium in the anion sub-lattice, and create a shallow donor level in the crystal's bandgap. The electrical effects of ionized impurity atoms in cadmium telluride are compensated by the crystal's acceptor defects, or by complex associates, which include stoichiometric, impurity and dopant related defects [1-8]. The formation of complexes is due to a decrease in the system's free energy compared to the energy of the system with only single point defects. The main complexes we considered were the acceptor complex $(A^{+}_{Te}V^{2-}_{Cd})^{-}$ and the neutral complex $(2A^{+}_{Te}V^{2-}_{Cd})^{0}$, where (A = Cl, Br, I), the existence of which has been confirmed experimentally [8]. Moreover, several researchers [9-11] analyzed the possibility of the formation of neutral complexes and DX centers. Their formation is associated with a change in the lattice symmetry in the neighborhood of the substitution defect that deforms the atomic bonds and, consequently, the possibility of binding to or yielding free electrons, so, by this process, affecting the crystal's electrical properties. In contrast to complexes containing cadmium vacancies, there are no reliable data about the existence of large numbers of free vacancies.

In [12-13] a theoretical calculation of the concentration of free charge carriers in CdTe:Cl was carried out using a model of a crystal defect subsystem that takes into account the possibility of compensating for impurity defects in CdTe by cadmium vacancies with the formation of complexes of the $(A^{+}_{Te}V^{2-}_{Cd})^{-}$ type. Satisfactory agreement with the experimental data was obtained. This highlights the adequacy of this model. Given the expected similarity of the electronic structure of chlorine and bromine atoms, it also gives a reason to use a similar model to explain the influence of bromine impurities on the electrical properties of cadmium telluride.

2. Experimental

Single crystals were grown by the Bridgman method. Cadmium telluride was synthesized in quartz ampoules using cadmium and tellurium (6N purity), additionally purified by zone melting. The concentration of background impurities in the source component did not exceed 10^{-5} wt. %. The melt was maintained at 1393 K for 24 hours and then directionally solidified at a speed of 3 mm/h. The material was doped by adding $CdBr_2$ to the starting charge. The concentration of bromine in the melt was ~10^{19} at/cm^3.

The as-grown single crystals were cut by wire into 3-mm thick wafers. From their base we prepared rectangular shaped samples. High-temperature Hall effect measurements were carried out under two-temperature annealing conditions on samples placed in an evacuated ampoule in two-zone furnace, where the first zone governed the temperature of the sample, and the second controlled the temperature and pressure of the Cd vapor [14-15].

3. The experimental results: Analysis of, and thermodynamic model for the crystal's defect subsystem

The samples we investigated demonstrated n-type conductivity over the whole range of investigated temperatures, 200-900 °C. However, the values of the electron mobility were smaller than those observed in undoped CdTe (Fig. 1), especially at lower temperatures. For example, the mobility is about a factor of 3 smaller at room temperature. The reason is the high concentration of bromine in the samples. During the initial heating, we held the crystal at 300-, 400-, 500-, and 600-°C for 2-6 hours (Fig. 2) with the aim of observing the changes in electrical properties as mentioned before [2]. Indeed, a rapid increase in the conductivity and electron density happened at ~500 °C after 30 minutes of holding the material at this temperature (Fig. 2). However, the rise was not very steep, which can be explained by the high bromine content.

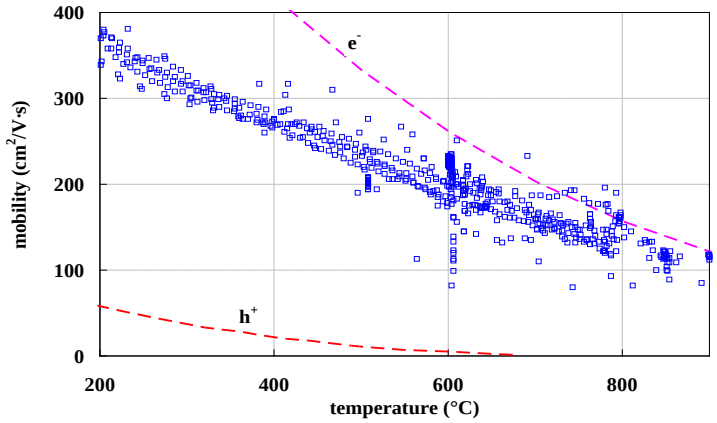

Fig. 1. The temperature dependence of the electron mobility in the CdTe:Br sample.

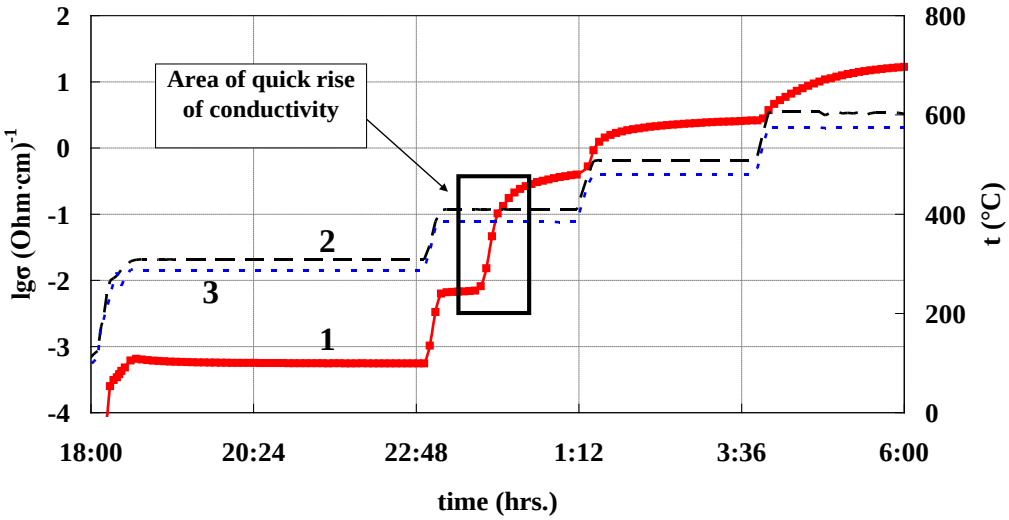

Fig. 2. Time dependence of the charge-carrier conductivity (thick solid red line 1), temperature of the CdTe:Br sample (dashed black line 2), and the Cd zone (dotted blue line 3)

The peculiarity of the perceived experimental dependences between electron density and technological parameters of annealing (Fig. 3) is that the value of n does not depend on the annealing temperature, T, but at the same time, it depends on the vapor pressure of cadmium P_{Cd}. Because the rate of change of carrier concentration with the change of vapor pressure for CdTe:Br differs from the magnitude of the rate change for pure crystals suggests that their defects are not dominant in the doped material. We explain the lack of dependence of n(T) by the fact that all impurities in the crystal are dissolved ones, and the carrier concentration is determined by ionized impurity atoms, the concentration of which does not change with temperature. Otherwise, if some of the impurities present in the sample are not dissolved, the temperature change would alter the amount of dissolved bromine and, therefore, the concentration of electrons too; however, we did not observe this. Also it is unlikely that the amount of dissolved impurities depends on the components of vapor pressure or on the temperature.

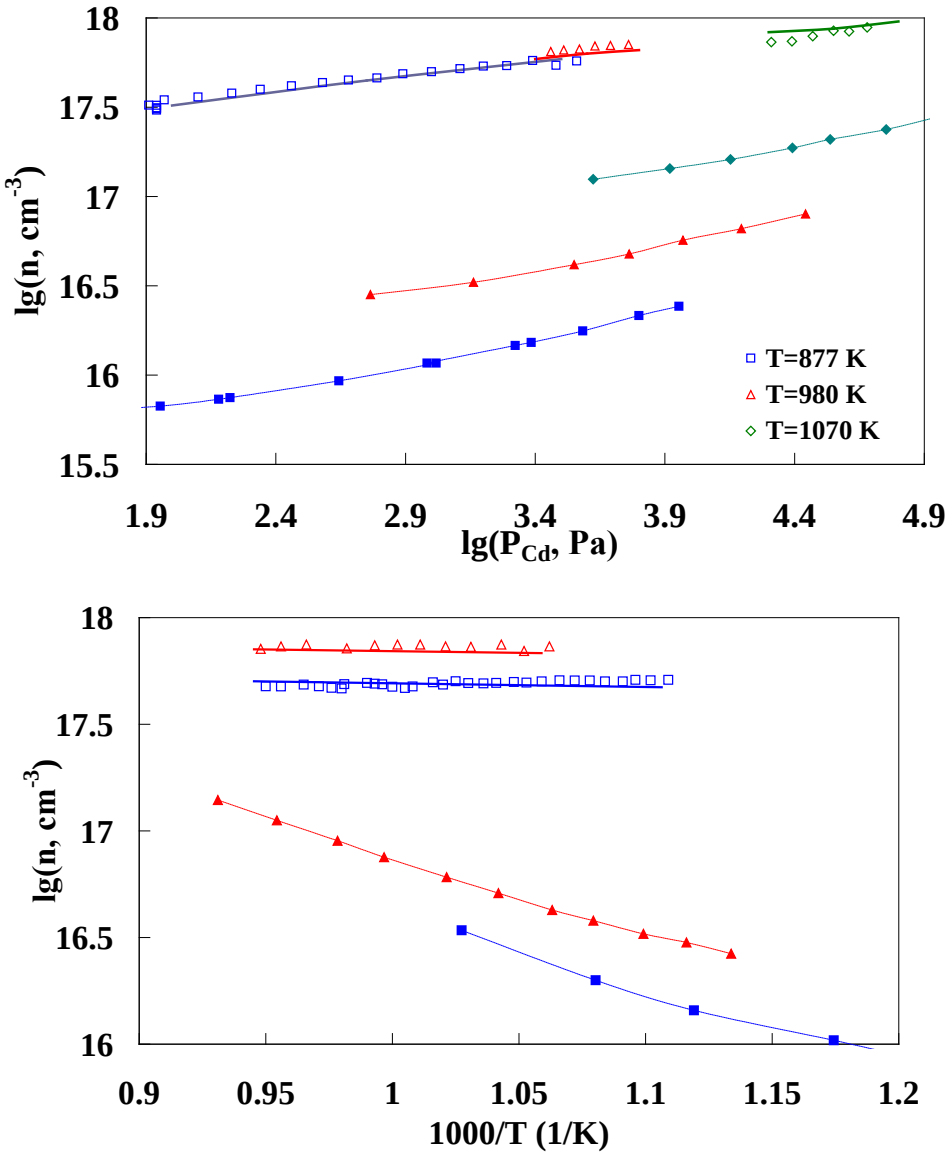

Fig. 3. Experimental and theoretically calculated isothermal dependences (above; □ - 870 K, Δ - 970 K, ◊ - 1070 K) and isobaric (below; □ - 1000 Pa, Δ - 10000 Pa) of the electron density in undoped- (closed symbols) and bromine-doped (open symbols) cadmium telluride crystal under conditions of both temperature annealing and cadmium overpressure.

Thus, we assume that the defect subsystem model can be implemented for CdTe:Br crystals. According to this model all introduced impurities at the studied range of technological parameters are completely dissolved and exist in the form of defects Br_{Te} (neutral and singly ionized), and their donor effects are compensated by acceptor defects in such a way that $n = f(P_{Cd})$ and $n \neq f(T)$. The highest probability is that the compensating defects are doubly ionized cadmium vacancies V_{Cd}^{2-}, which form acceptor $(Br_{Te}^{+} V_{Cd}^{2-})^{-}$ or neutral $(2Br_{Te}^{+} V_{Cd}^{2-})^{0}$ complexes. The concentration of intrinsic point defects should be significantly lower than the concentration of substitutional defects and point-defect complexes, however, knowledge of their content is required to complete the analysis. Taking into account the results of earlier work [16], the concentration of singly ionized and neutral defects in n-type conductivity material is assumed lower than the concentration of doubly ionized defects, so we can consider only the following point defects: (V_{Cd}^{2-}, Cd_{i}^{2+}, V_{Te}^{2+}, and Te_{i}^{2-}).

In two-temperature annealing terms for the system "doped crystal – vapor of component", the concentration of intrinsic point defects was determined from the equations of equality for the defects' chemical potential and of the components (μ_i) in the crystal "s" and vapor "g" [16]:

$$-\mu^{s}_{V^{2-}_{Cd}} = \mu^{g}_{Cd}, \qquad \mu^{s}_{Cd^{2+}_{i}} = \mu^{g}_{Cd}, \qquad -\mu^{s}_{V^{2+}_{Te}} = \mu^{g}_{Te}, \qquad \mu^{s}_{Te^{2-}_{i}} = \mu^{g}_{Te}. \tag{1}$$

The formation of complexes of equilibrium concentrations can be determined from the equilibrium conditions between intrinsic- and impurity-point defects:

$$\mu_{V^{2-}_{Cd}} + \mu_{Br^{+}_{Te}} = \mu_{(Br^{+}_{Te}V^{2-}_{Cd})^{-}}, \quad \mu_{V^{2-}_{Cd}} + 2\mu_{Br^{+}_{Te}} = \mu_{(2Br^{+}_{Te}\cdot V^{2-}_{Cd})^{0}} \tag{2}$$

If all introduced impurities in the crystal are dissolved, then the concentrations of singly ionized- and neutral unbound-atoms in the complexes can be determined from the equation:

$$\left[Br^{+}_{Te}\right] = \left(Br_{tot} - \left[(V^{2-}_{Cd}\ Br^{+}_{Te})^{-}\right] - 2\cdot\left[(V^{2-}_{Cd}\cdot 2Br^{+}_{Te})^{0}\right]\right)\cdot f\ ,$$

where

$$f = \left(1 + g_{A^{+}}/g_{A^{0}}\exp\left(-(\varepsilon-\mu)/kT\right)\right)^{-1}, \tag{3}$$

$$\left[Br^{0}_{Te}\right] = Br_{tot} - \left(Br^{+}_{Te} + \left[(Br^{+}_{Te}V^{2-}_{Cd})^{-}\right] + 2\cdot\left[(2Br^{+}_{Te}\cdot V^{2-}_{Cd})^{0}\right]\right), \tag{4}$$

Here, Br_{tot} is the full impurity concentration in the crystal, g is the degeneracy factor of energy level, ε is the impurity ionization energy, and μ is the chemical potential of the electrons.

In these last two expressions (3) and (4), the concentration of neutral defects and ionized-substitution defects is determined by accounting for the fact that the defects included in the composition of the associates already have been ionized. Hence, the number of unbound Br_{Te} defects will be equal to the general number of bromine atoms, Br_{tot}, minus those atoms that have been included in the complex.

The chemical potential of the vapor [17]:

$$\mu^{g} = kT\ln P + \mu_0. \tag{5}$$

For monatomic vapor of cadmium Cd:

$$\mu_0 = kT(-\ln(kT) + \ln(h^3/(2\pi mkT)^{\frac{3}{2}})). \tag{6}$$

For diatomic vapor of tellurium Te_2:

$$\mu_0 = kT(-\ln(kT) + \ln(h^3/(2\pi mkT)^{\frac{3}{2}}) + \ln(h^2/8\pi^2 IkT) + \ln(h\nu/kT)). \tag{7}$$

Here, m is the mass of the atom or molecule, $I = ml^2$ is the moment of inertia of the molecule, l is the distance between the nucleus of the molecule, and ν is the internal frequency of the molecules' vibrations.

Analytical expressions for the chemical potentials of point defects and their complexes are obtained by differentiating the Gibbs energy, G, on the concentration of crystal defects $\mu^{s}_{i} = \partial G/\partial\left[D_i\right]$. Here, the Gibbs energy is represented as follows:

$$G = G_0 + \sum\left(E + F_{vib}\right)[D] + \sum\left(E_K + F_{vib,K}\right)[K] + nE_C - pE_V - T(S_n + S_p + S_k), \tag{8}$$

where G_0 – Gibbs energy that does not depend on the presence of defects, E, E_K – defect formation energy and complex formation energy, F_{vib}, $F_{vib,K}$ – available vibrational energy of defect and complex, [D] – concentration of defects D, [K] – concentration of complexes K, n and p - concentration of electrons and holes, E_C, E_V – conduction band energy and the valence band energy, S_k – configuration entropy, and S_n, S_p – entropy of electrons in the conduction band and holes in the valence band. The summation is carried out on all sub-lattices and all defects in the sub-lattice.

The formation energy of singly and doubly ionized defects:

$$E_1 = E_0 - \frac{Z}{|Z|}\varepsilon_1, \qquad E_2 = E_2 - \frac{Z}{|Z|}(\varepsilon_1 + \varepsilon_2), \tag{9}$$

where E_0 – formation energy of neutral defect, Z – charge state of the defect, and ε_1 and ε_2 – energies of the first- and second-impurity level of the formed defect.

We note that the proposed model considered defects as a crystal system of non-interacting particles. Otherwise, all energy parameters should be a function of concentration, which greatly complicates the calculations.

One challenging task is to determine the free vibration defect energy, F_{vib}. The calculation of this value by "ab initio" methods requires a super-computer resource, which complicates the practicality of the approach; it is known today that the results of semi-empirical calculations of F_{vib}, in particular [18] and [19], may differ by more than twofold.

Taking into account that the measurements of the electrical parameters of the crystals were carried out at high temperatures (800-1100 K), much higher than the Debye temperature of cadmium telluride (200 K [20]), the value of the free vibration energy can be found on the basis of the Einstein model, which satisfactorily describes the heat capacity of substances. It is the principal feature that is most dependent on the characteristics of the phonon subsystem of the crystal, especially at high temperatures. Considering that the free energy of one oscillator in this approach [21] and that the formation of vacancies reduces the number of oscillators per volume unit in the crystal, while interstitial atoms increase this number, the change of free-vibration energy of the crystal during the defect formation can be represented as follows:

$$F_{vib} = \pm\left\{3kT\ln\left(\frac{T_\theta}{T}\right) - kT\right\} + x\cdot 3kT\ln\left(\frac{\omega}{\omega_0}\right), \tag{10}$$

where the first part of the sum takes into account the change of the number of oscillators in the system during the formation of the defects, and the second number accounts for changing the vibrational frequency of the oscillator in the vicinity of the defect. In (10), x is the number of atoms that changed their frequency of oscillation from ω_0 to ω. The value, ω/ω_0, was considered as a parametric variation of the model and was chosen so that the theoretical curves, n(T) and $n(P_{Cd})$, showed the best consistency with the experimental data. For intrinsic point defects, these values were obtained by calculations of the defect subsystem for undoped crystals [16, 22-24].

Entropy was determined by the Boltzmann law. For crystals where point defects can be grouped into complexes:

$$S_k = k\ln\left(\prod W_j \cdot \prod_K r_K P_K\right)\cdot \tag{11}$$

where W_j is thermodynamic probability of the j-th sublattice:

$$W_j = \frac{N_J!}{(N_J - \sum[D] - \sum[K])!\cdot\prod[D]!\prod[K]!}; \tag{12}$$

P_K is the probability of the complex formation K:

$$P_K = \prod_j\prod_i\left(\frac{[D_i]+K}{N_J}\right)^K\left(1-\frac{[D_i]+K}{N_J}\right)^{[D_i]}, \tag{13}$$

R_K - degeneration of the complex:

$$r_K = \frac{x_j!}{x_i!(x_j - x_i)!}. \tag{14}$$

In (12) – (14), N_J is the number of units in a sublattice, x_j is the number of units in the vicinity of the defect, where another defect that is included in a set can be formed, and x_i is the number of neighboring defects within the complex.

For electrons and holes, the thermodynamic probability is equal to the following:

$$W_n = \frac{N_C!}{(N_c - n)!n!},\ W_p = \frac{N_V!}{(N_V - p)!p!}. \tag{15}$$

In the absence of degeneracy of charge carriers, we get the following:

$$n = N_c e^{\frac{\mu}{kT}},\ p = N_V e^{-\frac{\mu+E_g}{kT}}, \tag{16}$$

N_C, N_V are, respectively, the density of states in the conduction band and the valence band, E_g is the band-gap, and, μ is the chemical potential of the electrons, which can be determined from the electro-neutrality equation:

$$\sum Z[D] = N_C e^{\frac{\mu}{kT}} - N_V e^{-\frac{E_g+\mu}{kT}}. \tag{17}$$

After substituting the above formulae, the expression for Gibbs energy (8) and the procedure of differentiation for the chemical potentials of defects take the form:

$$\mu^s_{Cd_i^{2+}} = E_{Cd_i^{2+}} + F_{vib,Cd_i^{2+}} - kT \cdot \ln\left(\frac{N_{tetr} - SS_{tetr}}{\left[Cd_i^{2+}\right]}\right) + A1_{Cd_i^{2+}}\left(Z_{Cd_i^{2+}}, SS, T\right) \tag{18}$$

$$\mu^s_{V_{Te}^{2+}} = E_{V_{Te}^{2+}} + F_{vib,V_{Te}^{2+}} - kT \cdot \ln\left(\frac{N_{an} - SS_{an}}{\left[V_{Te}^{2+}\right]}\right) + A1_{V_{Te}^{2+}}\left(Z_{V_{Te}^{2+}}, SS, T\right) \tag{19}$$

$$\mu^s_{Te_i^{2-}} = E_{Te_i^{2-}} + F_{vib,Te_i^{2-}} - kT \cdot \ln\left(\frac{N_{oct} - SS_{oct}}{\left[Te_i^{2-}\right]}\right) + A1_{Te_i^{2-}}\left(Z_{Te_i^{2-}}, SS, T\right) \tag{20}$$

$$\begin{aligned}\mu^s_{V_{Cd}^{2-}} &= E_{V_{Cd}^{2-}} + F_{vib,V_{Cd}^{2-}} - kT \cdot \ln\left(\frac{N_{cat} - SS_{cat}}{\left[V_{Cd}^{2-}\right]}\right) \\ &- kT \cdot \left(\frac{\left[\left(Br_{Te}^{+}V_{Cd}^{2-}\right)^{-}\right]}{\left[\left(Br_{Te}^{+}V_{Cd}^{2-}\right)^{-}\right] + \left[V_{Cd}^{2-}\right]} + \frac{\left[\left(2Br_{Te}^{+}V_{Cd}^{2-}\right)^{0}\right]}{\left[\left(2Br_{Te}^{+}V_{Cd}^{2-}\right)^{0}\right] + \left[V_{Cd}^{2-}\right]}\right) + A1_{V_{Cd}^{2-}}\left(Z_{V_{Cd}^{2-}}, SS, T\right)\end{aligned} \tag{21}$$

$$\mu^s_{Br_{Te}^{0}} = E_{Br_{Te}^{0}} + F_{vib,Br_{Te}^{0}} - kT \cdot \ln\left(\frac{N_{an} - SS_{an}}{\left[Br_{Te}^{0}\right]}\right) \tag{22}$$

$$\begin{aligned}\mu^s_{Br_{Te}^{+}} &= E_{Br_{Te}^{+}} + F_{vib,Br_{Te}^{0}} - kT \cdot \ln\left(\frac{N_{an} - SS_{an}}{\left[Br_{Te}^{+}\right]}\right) \\ &- kT \cdot \left(\frac{\left[\left(Br_{Te}^{+}V_{Cd}^{2-}\right)^{-}\right]}{\left[\left(Br_{Te}^{+}V_{Cd}^{2-}\right)^{-}\right] + \left[Br_{Te}^{+}\right]} + \frac{2\left[\left(2Br_{Te}^{+}V_{Cd}^{2-}\right)^{0}\right]}{\left[\left(2Br_{Te}^{+}V_{Cd}^{2-}\right)^{0}\right] + 2\left[Br_{Te}^{+}\right]}\right) + A1_{Br_{Te}^{+}}\left(Z_{Br_{Te}^{+}}, SS, T\right)\end{aligned} \tag{23}$$

$$\mu^{s}_{\left(Br^{+}_{Te}V^{2-}_{Cd}\right)^{-}} = E_{\left(Br^{+}_{Te}V^{2-}_{Cd}\right)^{-}} + F_{vib,\left(Br^{+}_{Te}V^{2-}_{Cd}\right)^{-}} - kT\cdot\ln\left(\frac{N_{cat}-SS_{cat}}{\left[\left(Br^{+}_{Te}V^{2-}_{Cd}\right)^{-}\right]}\right) - kT\cdot\ln\left(\frac{N_{an}-SS_{an}}{\left[\left(Br^{+}_{Te}V^{2-}_{Cd}\right)^{-}\right]}\right)$$

$$-kT\cdot\left(\begin{array}{l}\ln\left(\frac{\left[\left(Br^{+}_{Te}V^{2-}_{Cd}\right)^{-}\right]+\left[V^{2-}_{Cd}\right]}{N_{cat}}\right)+\frac{\left[\left(Br^{+}_{Te}V^{2-}_{Cd}\right)^{-}\right]}{\left[\left(Br^{+}_{Te}V^{2-}_{Cd}\right)^{-}\right]+\left[V^{2-}_{Cd}\right]}+\\ \ln\left(\frac{\left[\left(Br^{+}_{Te}V^{2-}_{Cd}\right)^{-}\right]+\left[Br^{+}_{Te}\right]}{N_{an}}\right)+\frac{\left[\left(Br^{+}_{Te}V^{2-}_{Cd}\right)^{-}\right]}{\left[\left(Br^{+}_{Te}V^{2-}_{Cd}\right)^{-}\right]+\left[Br^{+}_{Te}\right]}\end{array}\right)+A1_{\left(Br^{+}_{Te}V^{2-}_{Cd}\right)^{-}}\left(Z_{\left(Br^{+}_{Te}V^{2-}_{Cd}\right)^{-}},SS,T\right) \quad (24)$$

$$\mu^{s}_{\left(2Br^{+}_{Te}V^{2-}_{Cd}\right)^{0}} = E_{\left(2Br^{+}_{Te}V^{2-}_{Cd}\right)^{0}} + F_{vib,\left(2Br^{+}_{Te}V^{2-}_{Cd}\right)^{0}} - kT\cdot\ln\left(\frac{N_{cat}-SS_{cat}}{\left[\left(2Br^{+}_{Te}V^{2-}_{Cd}\right)^{0}\right]}\right) - kT\cdot\ln\left(\frac{N_{an}-SS_{an}}{\left[\left(2Br^{+}_{Te}V^{2-}_{Cd}\right)^{0}\right]}\right)$$

$$-kT\cdot\left(\begin{array}{l}\ln\left(\frac{\left[\left(2Br^{+}_{Te}V^{2-}_{Cd}\right)^{0}\right]+\left[V^{2-}_{Cd}\right]}{N_{cat}}\right)+\frac{\left[\left(2Br^{+}_{Te}V^{2-}_{Cd}\right)^{0}\right]}{\left[\left(2Br^{+}_{Te}V^{2-}_{Cd}\right)^{0}\right]+\left[V^{2-}_{Cd}\right]}+\\ \ln\left(\frac{\left[\left(2Br^{+}_{Te}V^{2-}_{Cd}\right)^{0}\right]+2\left[Br^{+}_{Te}\right]}{N_{an}}\right)+\frac{\left[\left(2Br^{+}_{Te}V^{2-}_{Cd}\right)^{0}\right]}{\left[\left(2Br^{+}_{Te}V^{2-}_{Cd}\right)^{0}\right]+2\left[Br^{+}_{Te}\right]}\end{array}\right)+ \quad (25)$$

$$+A1_{\left(2Br^{+}_{Te}V^{2-}_{Cd}\right)^{0}}\left(Z_{\left(2Br^{+}_{Te}V^{2-}_{Cd}\right)^{0}},SS,T\right)$$

The expression for the chemical potentials of defects introduced the expressions:

$$A1_{D_i}\left(Z_{D_i},SS,T\right)=\left[n\left(\frac{E_C}{kT}-\ln\left(\frac{N_C-n}{n}\right)\right)+p\left(\frac{E_V}{kT}+\ln\left(\frac{N_V-p}{p}\right)\right)\right]\times\frac{kT\cdot Z_{D_i}}{\sqrt{SS^2+4N_CN_V\exp\left(-E_g/kT\right)}}$$

$$SS=Z_{V^{2-}_{Cd}}\left[V^{2-}_{Cd}\right]+Z_{Cd^{2+}_{i}}\left[Cd^{2+}_{i}\right]+Z_{V^{2+}_{Te}}\left[V^{2+}_{Te}\right]+Z_{Te^{2-}_{i}}\left[Te^{2-}_{i}\right]+Z_{Br^{+}_{Te}}\left[Br^{+}_{Te}\right]+Z_{\left(Br^{+}_{Te}V^{2-}_{Cd}\right)^{-}}\left[\left(Br^{+}_{Te}V^{2-}_{Cd}\right)^{-}\right]$$

$$SS_{cat}=\left[V^{2-}_{Cd}\right]+\left[\left(Br^{+}_{Te}V^{2-}_{Cd}\right)^{-}\right]+\left[\left(2Br^{+}_{Te}V^{2-}_{Cd}\right)^{-}\right]$$

$$SS_{an}=\left[V^{2+}_{Te}\right]+\left[Br^{0}_{Te}\right]+\left[Br^{+}_{Te}\right]+\left[\left(Br^{+}_{Te}V^{2-}_{Cd}\right)^{-}\right]+2\left[\left(2Br^{+}_{Te}V^{2-}_{Cd}\right)^{0}\right]$$

$$SS_{tetr}=\left[Cd^{2+}_{i}\right]$$

$$SS_{oct}=\left[Te^{2-}_{i}\right]$$

So, for finding the equilibrium concentration of defects the system of equations (1) - (4) must be solved. This procedure is implemented numerically by minimizing the quadratic function of the absolute residuals values L_{MIN} of equations (1) and (2); the dependences (3) - (4) were taken into account as conditional residuals. The minimum was found by the random perturbations method, and initial (starting) values of coordinates were taken casually. The minimum coordinates,

$L_{MIN,}$ of the function are the equilibrium values of the concentration of defects at the set pressure P_{Cd}, the annealing temperature T, and the concentration of introduced impurities, Br_{tot}.

Tables 1 and 2 present the parameters of CdTe crystals and energy characteristics of the intrinsic point-defects that were used in the calculations

Table 1

Calculation parameters

Parameter	Value	Reference
Internal vibration frequency of the molecule, Te_2	$0.625102 \cdot 10^{13}$ s^{-1}	[25]
The distance between the nucleus in a molecule, Te_2	$2.59 \cdot 10^{-10}$ m	[25]
Constant $K = P_{Te_2} P_{Cd}^2$	$K = 10^{(-29475/T+18{,}923)} \cdot (101325)^3$, Pa^3	[26]
The effective mass of electrons	0.11 m_0	[19]
The effective mass of holes	0.40 m_0	[19]
Band gap	E_g = 1.65-0.000535 T, eV	[27]
Debye temperature	T_θ = 200 K	[20]

Table 2

Energy parameters of the intrinsic defects in CdTe crystals used in the calculations

	V_{Cd}	Cd_i	V_{Te}	Te_i
E, eB	3.6 [28]	2.04 [28, 29]	3.24 [28, 29]	3.41 [28, 29]
ε_1, eB	E_V+0.05 [30]	E_C-0.016 [32]	E_C-0.01 [34]	E_V+0.15 [30]
ε_2, eB	E_V+0.47 [31]	E_C-0.17 [33]	E_C-0.34 [33]	E_V+0.57 [35, 24]
x	4	5	4	5
ω/ω_0	3.75	0.25	1.60	0.20

4. Modeling results and discussion

In determining the dominant type of defects in doped crystals, taking into account the probability of an association of impurity atoms with cadmium vacancies, we considered three possible mechanisms: a) Cadmium vacancies are in a non-associated state with the other point defects; b) Cadmium vacancies form acceptor complexes $(Br_{Te}^{+} V_{Cd}^{2-})^{-}$; and, c) Cadmium vacancies form neutral complexes $(2Br_{Te}^{+} V_{Cd}^{2-})^{0}$. Each possible mechanism was discussed separately because the model, which considers several systems with unknown power characteristics, includes numerous variable parameters that, in our view, lower the reliability of the modeling results.

In the first case, for the model of the defect subsystem without complexes, the theoretical curve $n(P_{Cd})$ does not show the observed rate of change in the carrier concentration with the change of the vapor pressure of cadmium: The experimental curve $n(P_{Cd})$ is almost a straight line, while the theoretical line is curved upwards.

Similar results were obtained for the model of formation of acceptor complexes $(Br_{Te}^{+} V_{Cd}^{2-})^{-}$. Although the simulated results are less curved than in the previous model, it does not engender the desired agreement with the experimental results.

In the case of the model based on compensation impurity by cadmium vacancies with the formation of the complex, the calculated dependence $n(P_{Cd})$ is almost linear and both quantitatively and qualitatively consistent with the experimental data (Fig. 3). A satisfactory correlation was obtained for the temperature dependences n(T). The formation energy for the complex obtained by fitting the theoretical dependences, $n(T, P_{Cd})$, to the experimental values is 0.59 eV, which is very close to that proposed in [6] (0.6 eV), and the change in the oscillation frequency of the atoms in its vicinity $\omega / \omega_0 = 0.27$. Other parameters used in calculating impurity atoms and defect complexes

are the following: Concentration of dissolved impurities – $2\cdot10^{19}$ cm^{-3}; formation energy of substitutional defect – 0.62 eV [35]; change in the oscillation frequency of the atoms in the vicinity of the substitutional defect – 1.03; and ionization energy of the substitutional defect – (E_c – 0.025 eV) [5].

Therefore, according to the results based on the annealing temperature and vapor pressure of cadmium, the dominant defects related to the Br dopant are the singly ionized impurity point defect Br_{Te}^{+} and neutral $(2Br_{Te}^{+}V_{Cd}^{2-})^{0}$ complexes (Figs. 4-5). The concentration of neutral substitutional defects is smaller by one order of magnitude, and of intrinsic defects, by two-three orders-of-magnitude. Because the dominant complex is neutral, the concentration of free electrons is determined completely by the number of substitutional defects Br_{Te}^{+}. The presence of the material's own defects, donors and acceptors, does not affect the numerical value of n in practice. Changing the annealing temperature in the range 870-1070 K at a constant cadmium vapor pressure does not change the relation between Br_{Te}^{+} and $(2Br_{Te}^{+}V_{Cd}^{2-})^{0}$. That finding is an experimentally observed fact; viz., the absence of a dependence of the electron concentration on temperature over a wide range. The influence of Cd vapor pressure on the defect subsystem is significant: The growth of P_{Cd} causes a decrease in the concentration of complexes and the growth of substitutional defect concentrations. Probably this pattern is due to the fact that during an increase in the vapor pressure of the metal, the vacancies of metal V_{Cd}^{2-} are filled by cadmium atoms. It leads to a decrease in concentration of these vacancies and, therefore, to the decline in $[(2Br_{Te}^{+}V_{Cd}^{2-})^{0}]$ complexes.

We note that our model, used for interpreting the experimental data, denotes a large concentration of defect complexes at relatively high temperatures ($T \leq 1070$ K), which requires further research. However, taking into account the formation energy of $[(2Br_{Te}^{+}V_{Cd}^{2-})^{0}$ as 0.59 eV which is much higher than the value of kT, and the characteristic heat energy for dissolution of the complex at given conditions ($k\cdot1000$ K = 0.086 eV), we still consider the predicted result as reasonable.

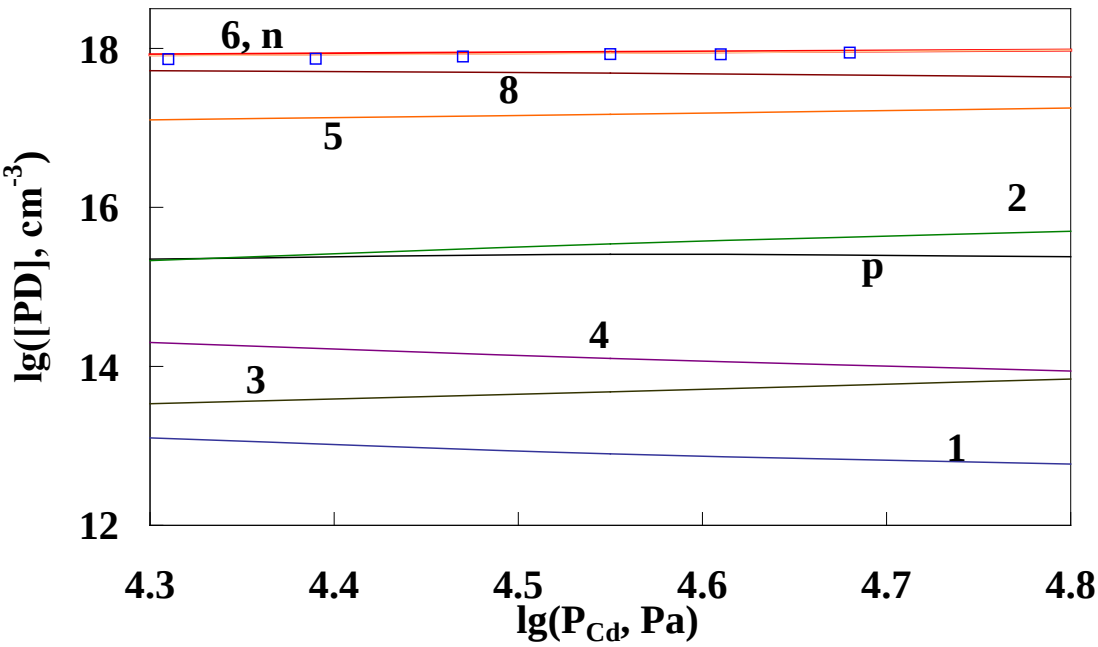

Fig. 4. Experimental (□) and theoretically calculated isothermal dependences of free charge carrier density (n, p) and point defects [D] (1 – $\left[V_{Cd}^{2-}\right]$, 2 – $\left[Cd_{i}^{2+}\right]$, 3 – $\left[V_{Te}^{2+}\right]$, 4 – $\left[Te_{i}^{2-}\right]$, 5 –

$\left[Br_{Te}^{0}\right]$, 6 – $\left[Br_{Te}^{1+}\right]$, 8 – $\left[\left(2Br_{Te}^{+}V_{Cd}^{2-}\right)^{0}\right]$) in CdTe:Br crystals under conditions of two-temperature annealing in a cadmium vapor at 1070 K.

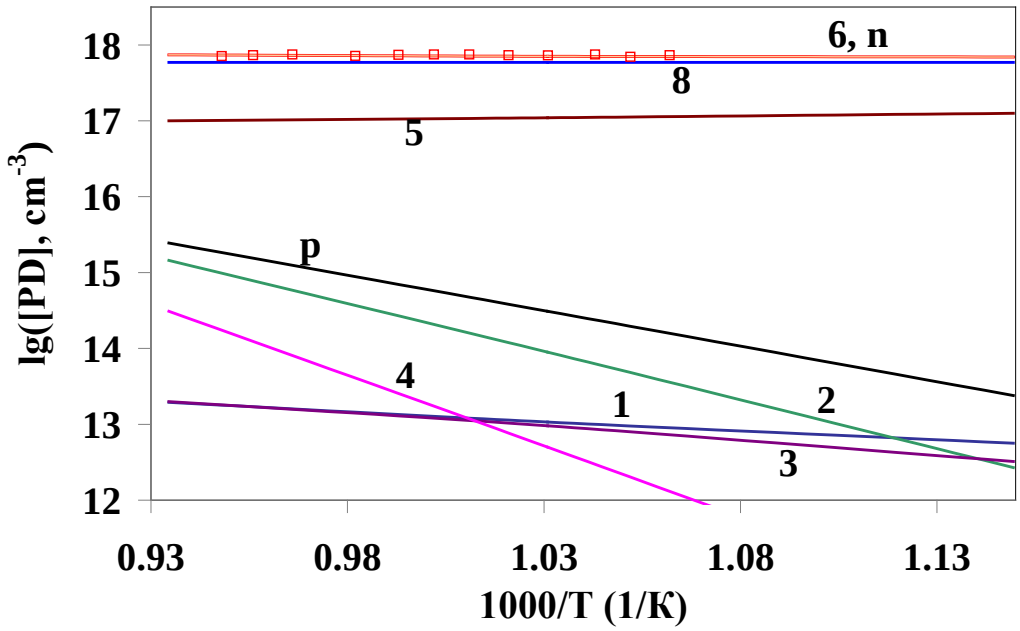

Fig. 5. Experimental- (□) and theoretically calculated-isobaric dependences of free charge carrier density (n, p) and point defects [D] (1 – $\left[V_{Cd}^{2-}\right]$, 2 – $\left[Cd_{i}^{2+}\right]$, 3 – $\left[V_{Te}^{2+}\right]$, 4 – $\left[Te_{i}^{2-}\right]$, 5 – $\left[Br_{Te}^{0}\right]$, 6 – $\left[Br_{Te}^{1+}\right]$, 8 – $\left[\left(2Br_{Te}^{+}V_{Cd}^{2-}\right)^{0}\right]$) in CdTe:Br crystals under conditions of two-temperature annealing in a cadmium vapor and pressure at 10000 Pa (b).

5. Conclusions

1. The introduction of bromine impurities in cadmium telluride crystals engenders a significant growth in the concentration of free electrons compared with undoped material.

2. During the two-temperature annealing of bromine-doped crystals in a cadmium vapor, changing of the temperature in the range, T = 870-1070 K, does not influence the concentration of free charge-carriers, while increasing the vapor pressure of the metal in the range 10^2-10^5 Pa leads to an almost linear increase of the free-electron concentration.

3. The donor action of bromine causes the dissolution of dopant atoms in the CdTe matrix as a substitutional defect Br_{Te}, the ionization of which leads to the formation of free electrons and defects Br_{Te}^{+}. The self-compensation of the donor-impurity defect leads to double-ionized acceptor cadmium vacancies, which are combined with substitutional atoms, forming electrically neutral complexes. The change of the cadmium vapor pressure in two-temperature annealing changes the ratio between the dominant point defects (Br_{Te}^{+} and $\left(2Br_{Te}^{+}V_{Cd}^{2-}\right)^{0}$), which affords the opportunity effectively to control the concentration of free charge-carriers for obtaining materials with the desired physical-electrical properties.

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6. References

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Highlights

- CdTe crystals, doped by bromine, were grown by the Bridgman method
- The samples were annealed under constant thermodynamic conditions
- Treatment conditions: ~500-1100 K under Cd overpressure
- Electrical properties were measured “in situ” using Hall-effect measurements
- A theoretical model is proposed for the point-defect structure of CdTe:Br crystals