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ON THE NATURE OF THE NONSTOICHIOMETRY DEFECTS IN $Cd_xHg_{1-x}Se$ ($x \leqslant 0.2$) SEMICONDUCTING ALLOYS. I

By R. J. Iwanowski and J. Bąk

Institute of Physics, Polish Academy of Sciences, Warsaw*

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The complex studies of a heat treatment and electrical properties of undoped $Cd_xHg_{1-x}Se$ ($x \leqslant 0.2$) mixed crystals have been done. The methods of a heat treatment, applied here, enabled us to obtain n-type crystals in the concentration range $7\times10^{16}-5\times10^{18}$ cm^{-3} with the controlled stoichiometry deviation (Hg-excess). A simplified model of the structure of native point defects has been proposed. Within this model the above nonstoichiometry is due to the interstitial Hg atoms which form both ionized (donors) and neutral (microprecipitations) centers in crystal lattice.

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1. Introduction

$Cd_xHg_{1-x}Se$ mixed crystals of the composition range $0 \leqslant x \leqslant 0.25$ belong to the group of small- and zero-gap semiconductors [1] because they are formed from semimetallic HgSe [2, 3] and semiconducting CdSe [4]. Latest measurements of magnetooptical [3, 5] and electron transport effects [6] point out that the energy gap, $E_0 = E_{\Gamma_6}-E_{\Gamma_8}$, changes linearly with composition x at 4.2 K from -0.274 eV in HgSe [3] to 1.90 eV for the cubic phase of CdSe [7]. $Cd_xHg_{1-x}Se$ solid solutions in the range up to $x = 0.77$ have a cubic zinc blende structure [8] with lattice constant which is almost independent of composition. In the region of our present interest, $x \leqslant 0.2$, $a_0 = 6.086$ Å [8].

Up to now, there has been only a little information concerning the structure of point defects in $Cd_xHg_{1-x}Se$ as well as their influence on the low temperature galvanomagnetic properties of these crystals. In fact, the literature devoted to this complex problem in small--gap II–VI compounds is not very wide. Early studies of the heat treatment of undoped $Cd_xHg_{1-x}Se$ ($x < 0.2$) mixed compounds [9, 10] enabled us to deduce that only n-type crystals of the concentrations similar to those of undoped HgSe could be obtained. It was suggested that the donor centers associated with native point defects existing in crystal lattice are responsible for this effect.

* Address: Instytut Fizyki PAN, Lotników 32/46, 02-668 Warszawa, Poland.

Semiconducting properties of a crystal strongly depend on the concentration of point defects which form donor or acceptor centers, on degree of their ionization and on the mobility of current carriers. Therefore this paper is devoted to the thermal treatment and some conclusions concerning the structure of native point defects in $Cd_xHg_{1-x}Se$ ($x \leqslant 0.2$). Also an effort to construct the simplest point defect model has been made for these crystals which could help us to explain the observed phenomena and which would be useful in further interpretation. The next paper [11] (for our purposes it will be denoted as a paper II, whereas for this work the index I will be used in the following text) will contain the analysis of the influence of point defects on the electron mobility in $Cd_xHg_{1-x}Se$ ($x \leqslant 0.2$) at 4.2 K. Hence, both papers (I and II) form an entirety.

2. *Material preparation*

Undoped $Cd_xHg_{1-x}Se$ ($x \leqslant 0.2$) crystals were grown from the melt by the Bridgman method [6]. The as-grown boules were compositionally homogeneous in the predominant part of their volume [6]. The homogeneity of material was studied using an electron microprobe and an energy dispersive X-ray device (EDAX). The real structure of the resulting ingots was typical for large grain polycrystal (i.e. for grains of linear dimensions from several to a dozen or so millimeters) or a monocrystal [6].

In $Cd_xHg_{1-x}Se$ crystals, obtained by this method, a slight systematic deviation from stoichiometry in Se deficit direction has been observed. The chemical analysis of a chosen set of samples enabled us to estimate this deviation (further on denoted by δ) below 0.5 mole %. It agrees well with the results of Schreiber–Pawlak [12] obtained earlier on similar ingots by use of the EDAX technique.

The studies with application of the X-ray dispersive spectrometry (EDAX) [13] and the spectral emission analysis have shown that the dominant trace impurities detected in undoped $Cd_xHg_{1-x}Se$ crystals were Si, Fe, Cu, As and Ag — the estimated impurity level was below 10 ppm [6].

For galvanomagnetic measurements, rectangular parallelepiped samples with approximate dimensions of $2.0 \times 2.5 \times 15$ mm^3 were cut from parts of previously tested Bridgman ingots. The composition of the specimens was determined from electron microprobe as well as from density measurements. This allowed us to determine the x value with an accuracy of ± 0.005.

The measurements of the electrical conductivity σ and the Hall coefficient R_H of the samples were carried out by the standard d.c. technique. Electron concentration and mobility were calculated from the formulae $n = 1/e|R_H|$ and $\mu = |R_H|\sigma$. All the as-grown samples had n-type conductivity, as in typical HgSe crystals, and their electron concentration ranged from 7×10^{17} to 2×10^{18} cm^{-3}, depending on the composition.

3. *Heat treatment of $Cd_xHg_{1-x}Se$ crystals*

In order to obtain undoped $Cd_xHg_{1-x}Se$ samples in the widest possible range of electron concentration, particularly the low concentration samples, they were subjected to various heat treatments. These included annealing the samples in dynamic vacuum, in selenium vapor, in conditions of Hg or Se saturation (i.e. annealing the crystal in equilibrium with the maximal Hg or Se partial pressure), and the heat treatment with controlled Hg partial pressure.

First of all it was necessary to determine the limits of the electron concentration range as a function of annealing temperature for the alloy of the fixed x (i.e. homogeneity range), just as for HgSe [14]. These studies have been done here for $Cd_{0.1}Hg_{0.9}Se$.

The experimental dependence of electron concentration n on annealing temperature for Hg — saturation was determined in the range 100–400°C. Samples were annealed in Hg vapor or equilibrated with a source (mixture) of the following composition: $Hg_{0.5}Se_{0.5}$, $Hg_{0.55}Se_{0.45}$ or $(Cd_{0.1}Hg_{0.9})_{0.55}Se_{0.45}$. The annealing time, τ_a, applied here, depended on annealing temperature — e.g. at 400°C τ_a was within 4–12 h, at 100°C $\tau_a \approx 400$ h. After annealing run the ampoule containing a sample with a source was taken out of the furnace and quenched in water bath. The measurements of R_H and σ for each sample were carried out at 300 and 77K just after the ampoule was open.

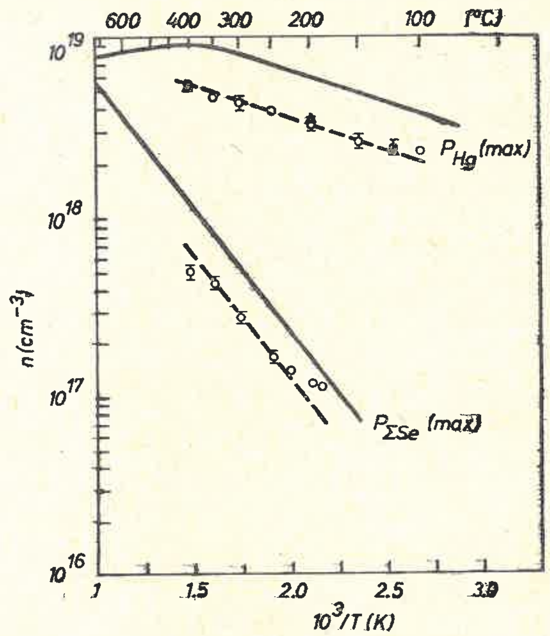

Fig. 1. Electron concentration (at 77K) in $Cd_{0.1}Hg_{0.9}Se$ vs reciprocal annealing temperature in the conditions of maximal P_{Hg} or $P_{\Sigma Se}$ partial pressure (experimental points and broken lines). Solid lines correspond to the analogous dependences for HgSe, taken from [14]

Also the experimental relation of electron concentration in $Cd_{0.1}Hg_{0.9}Se$ on annealing temperature in the range 190–400°C was determined for Se — saturation case. The samples were equilibrated with a source of the composition $Hg_{0.45}Se_{0.55}$ or $Hg_{0.4}Se_{0.6}$. Annealing time was fixed depending on annealing temperature — e.g. $\tau_a(400°C) \approx 12$ h, whereas at 190°C $\tau_a \approx 1000$ h.

Fig. 1 presents the electron concentration (measured at 77 K) in $Cd_{0.1}Hg_{0.9}Se$ vs reciprocal annealing temperature for both extremal cases: Hg and Se saturation. Subscript Σ Se (at the maximal Se partial pressure) indicates that selenium in gas phase has a structure of polyatomic particles [15]. Homogeneity range of HgSe (from [14]) has been drawn here for the comparison (solid lines). Experimental points which represent arithmetic averages of electron concentration for three or more different samples were marked with scatter of results. Points denoted by full triangles correspond to the samples equilibrated with the source of the composition $(Cd_{0.1}Hg_{0.9})_{0.55}Se_{0.45}$. For Hg — saturation branch, no discrepancies (within accuracy of the measurement) have been observed between the reached values of electron concentration in the samples annealed in the same temperature but with sources of different composition. It proves that in the temperature range $T \leqslant 400°C$ the maximal equilibrium partial pressure P_{Hg} over $Cd_{0.1}Hg_{0.9}Se$ solid solution is approximately equal to the saturated Hg vapor pressure, similarly as it has been found for HgSe [15] (compare also with $P-T-x$ diagram for $Cd_{0.2}Hg_{0.8}Te$ [16]). Broken line drawn between experimental points shows that for the case of P_{Hg}(max) the $\ln n(1/T)$ function changes linearly in the studied range of temperature, as in HgSe.

The analogous effect can be seen for $P_{\Sigma Se}$(max) branch, although the electron concentration rises here stronger with annealing temperature. Similarly as in HgSe [14], for the temperature $T > 350°C$ one can observe lower values of n then it could be deduced from the extrapolated linear $\ln n(1/T)$ dependence drawn for the range 230–350°C (a lower broken line). Brebrick and Strauss [14] suppose it is mainly due to formation of the Se microprecipitations in a crystal during quenching process. Also, like in HgSe [14], for the annealing temperature below 230°C the reached values of electron concentration are higher than the extrapolated ones. Probably, the applied annealing time was not long enough for the crystal to reach complete thermodynamic equilibrium with $P_{\Sigma Se}$(max).

The results presented in Fig. 1 show the qualitative similarity of the homogeneity range of $Cd_{0.1}Hg_{0.9}Se$ and HgSe. Only the boundaries of this range for $x = 0.1$ are lowered

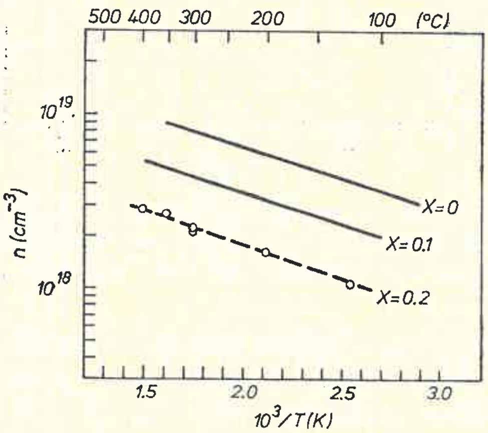

Fig. 2. Electron concentration (at 77 K) vs reciprocal annealing temperature for the case of P_{Hg}(max) in $Cd_{0.2}Hg_{0.8}Se$ (experimental points and broken line), $Cd_{0.1}Hg_{0.9}Se$ (from Fig. 1) and in HgSe [14]

on the concentration scale referring to those of HgSe. The intermediate values of n (with reference to the boundary ones) for a fixed value of annealing temperature have been reached by annealing the crystals in reduced and controlled P_{Hg}.

Fig. 2 presents the concentration vs annealing temperature dependence obtained for $Cd_{0.2}Hg_{0.8}Se$ in Hg-saturation condition in the range 120–400°C. It is referred to the analogous dependences of HgSe [14] and $Cd_{0.1}Hg_{0.9}Se$ (Fig. 1). The slope of $\ln n(1/T)$ is almost the same in all three cases. As it can be seen in the figure, the Hg-saturation boundary of the homogeneity range of undoped $Cd_xHg_{1-x}Se$ lowers with x; this is due to the decrease of the Hg-solubility limit in $Cd_xHg_{1-x}Se$ solid solutions.

For the case of $Cd_xHg_{1-x}Se$ crystals, the heat treatment in dynamic vacuum (5×10^{-6} Torr) has been also applied. Annealing temperature has been fixed in the range 200–260°C, depending on the composition of the sample. It has been observed that the annealing of the undoped $Cd_xHg_{1-x}Se$ ($x \leqslant 0.2$) crystals in dynamic vacuum is qualitatively equivalent to the Se-saturation — like in HgSe [17]. Both methods lead to decreasing in electron concentration and increasing in electron mobility in the crystal; the only difference lies in higher effectivity of the dynamic vacuum heat treatment [6, 10].

The so-called "passive annealing" effect (i.e. change of electron concentration for specimens stored at room temperature), previously reported for HgSe (see [2, 18]) was also noticed in $Cd_xHg_{1-x}Se$ ($x \leqslant 0.2$). It was observed, to a different extent, in as-grown as well as in annealed samples.

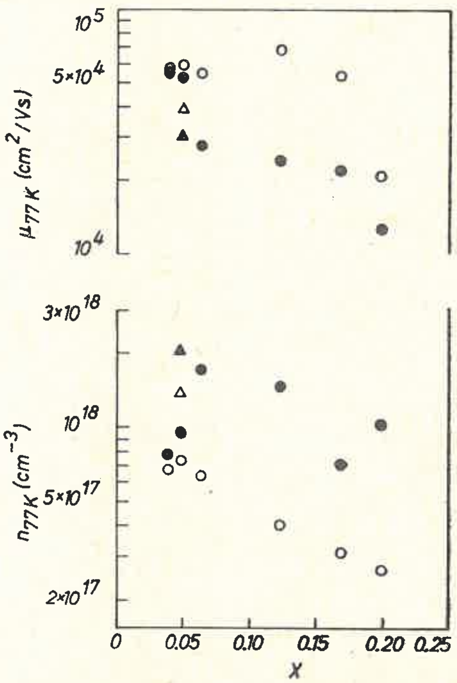

Fig. 3. Changes of the electron concentration and mobility (measured at 77K) in the investigated $Cd_xHg_{1-x}Se$ crystals due to passive annealing. ●, ▲ — electron concentration and mobility of the as-grown samples; ○, △ — n and μ in the same samples after 1.5–3 years of passive annealing

Fig. 3 illustrates the change of electron concentration and mobility in the as-grown $Cd_xHg_{1-x}Se$ ($x \leqslant 0.2$) samples due to passive annealing. This process produces a lowering of electron concentration in an as-grown crystal irrespectively of its composition. The decrease of electron concentration have been accompanied by the rise of electron mobility.

Similar changes have been observed in the Hg-saturated crystals, especially in those annealed at higher temperature (~400°C). Se-saturated samples (or annealed in dynamic vacuum) show also a slight decrease of electron concentration due to passive annealing. The effect depends on composition — for $x \geqslant 0.2$ the changes of n and μ even during a period of several years were within the experimental error.

It should be added that in some Se-saturated or dynamic vacuum annealed samples certain increase (up to 10%) of electron concentration on time accompanied by slight growth of μ or certain increase of μ with constant value of n have been observed.

4. Native point defects in $Cd_xHg_{1-x}Se$ ($x \leqslant 0.2$)

The results of previous paragraph show that the heat treatment conditions crucially influence the electrical properties of the undoped $Cd_xHg_{1-x}Se$ crystals. It would prove the dominant role of native point defects and insignificant influence of foreign atoms, i.e. trace impurities in crystal lattice. The above results also suggest the tight similarity of the native point defect structure of $Cd_xHg_{1-x}Se$ ($x \leqslant 0.2$) and that of HgSe. Therefore this problem should not be considered without referring to HgSe.

Blue and Kruse [17], who studied heat treatment of HgSe, reported that only n-type material could be obtained due to certain nonstoichiometric Hg-excess in crystal. They supposed this nonstoichiometry manifests itself in a form of Hg interstitials (Hg_I) or vacancies in Se sublattice (V_{Se}). Brebrick and Strauss [14] assumed a model of isolated and completely ionized donor point defects in HgSe, although they did not give any explanation of the origin of those centres. Kumazaki et al. [19] put forward a thesis, that Hg interstitials (doubly ionized) and Schottky-type defects ($V_{Hg}V_{Se}$) are the dominant point defects in HgSe. However, their analysis is not very complete and profound and it leaves some doubts.

It is obvious that a real structure of native point defects in crystal is very complex. The purpose of the present paper is to give the simplest model which could explain the up-to-now results of the heat treatment and galvanomagnetic properties of $Cd_xHg_{1-x}Se$ and would be useful in further interpretation. We should try to answer the following questions:
— what type of point defects dominates in the studied conditions?
— what type of point defects mainly influences the electrical properties of material?

4.1. Hagemark's theory in reference to $Cd_xHg_{1-x}Se$

HgSe and $Cd_xHg_{1-x}Se$ can be treated, in general, as MX type compound (where M = Hg, Cd and X = Se). In such binary (or pseudobinary) compound following types of native point defects could exist: cation and/or anion vacancies (V_M, V_X) and interstitials (M_I, X_I), misplaced atoms (M_X, X_M) and associated centres (e.g. Schottky and Frenkel defects). We shall use here Kröger and Vink [20] notation. Considering defect structure of $Cd_xHg_{1-x}Se$ ($x \leqslant 0.2$) one can neglect, in the first approximation, misplaced atoms defects because of high ionicity of HgSe and CdSe [21].

Hagemark [22] showed that for a semiconductor of the *MX* type, where considerable difference in temperature dependence on diffusion constants of the components *M* and *X* occurs, one should consider three temperature ranges (Fig. 4):

I — at temperatures $T > T_H$ the diffusion of both *M* and *X* is fast enough to allow a complete equilibrium. The system has two degrees of freedom, P_M and T.

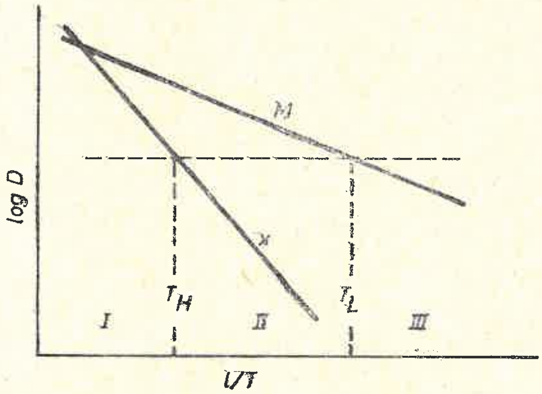

Fig. 4. Self-diffusion coefficient of the *M* and *X* atoms in the *MX* compound (from [22]). See explanation in the text

II — in the range $T_L \gtrsim T \gtrsim T_H$ the diffusion rate of *X* becomes too slow. *X* atoms are assumed to be frozen-in while the diffusion rate of *M* is still significant. For fixed *T* only a quasi-equilibrium is attained. The system has three degrees of freedom: P_M, T and $[V_X]$.

III — for $T < T_L$ both *M* and *X* atoms are frozen-in. Heat treatment of *MX* crystal in this range does not provide any change of the concentration of defects associated with *M* or *X*.

In our case heat treatment has been carried out in the temperature range 100–400°C and at the room temperature (passive annealing).

There is no information for $Cd_xHg_{1-x}Se$ mixed crystals about self-diffusion constants. The only data available concern self-diffusion coefficients of Cd and Se in CdSe [23] and Hg in HgSe [24]. For example, at 200°C D_{Hg}(HgSe) is nine orders of magnitude higher than D_{Se}(CdSe). The latter is six orders of magnitude higher than D_{Cd}(CdSe). Analogous disproportions in self-diffusion coefficients should be expected in $Cd_xHg_{1-x}Se$. Therefore only Hg-diffusion is practically important in the whole (or almost the whole) temperature range of heat treatment, whereas Se-diffusion and particularly Cd-diffusion should be neglected in this approximation. In fact, Brebrick and Strauss [14] noticed that the time to attain gas-solid phase equilibrium of Hg- or Se- saturated HgSe was relatively short; they connected it with high Hg diffusion rate. In other words, we can treat the studied range of annealing temperatures for $Cd_xHg_{1-x}Se$ ($x \leqslant 0.2$) as type II region (Fig. 4).

In this approximation we neglect completely all point defects associated with Cd atoms. In case of need we shall take into account Se-associated defects, mainly V_{Se} (due to the type of nonstoichiometry) which were frozen-in during the cooling process which followed crystal growth. In the investigated range of temperature $[V_{Se}]$ will be assumed constant (according to [23]) — it could be changed in Se-saturation process at higher temperatures ($T \gtrsim 400°C$).

In the range in question we should expect the dominant influence of the defects associated with Hg atoms, with their concentration depending on P_{Hg} partial pressure. Therefore, Hg interstitials (due to the stoichiometry deviation) and the Frenkel type defects ($Hg_I V_{Hg}$) should be taken into account. It is worth noticing that zinc blende type lattice allows, to certain degree, the creation of interstitials because its packing of atoms is not tight [25].

4.2. Ionized and neutral defects in $Cd_{0.1}Hg_{0.9}Se$

The hypothesis set forth in previous paragraph and concerning the defect structure of $Cd_xHg_{1-x}Se$ ($x \leqslant 0.2$) crystals should have been verified — for this purpose a combined experiment was carried out.

The lattice constant a_0 as a function of electron concentration was measured for $Cd_{0.1}Hg_{0.9}Se$. The measurements were performed for the chosen monocrystalline samples,

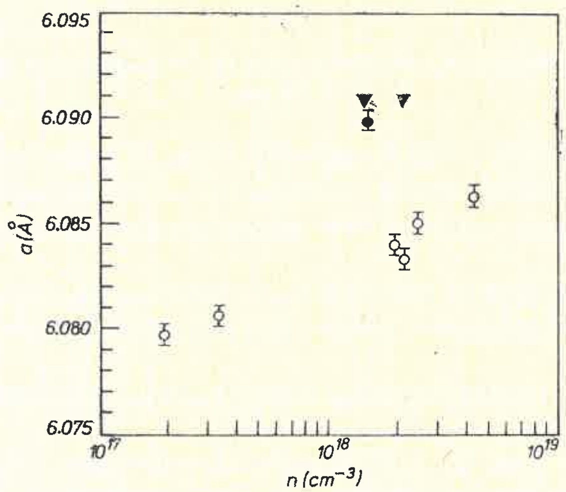

Fig. 5. Lattice constant a_0 vs electron concentration in the $Cd_{0.1}Hg_{0.9}Se$ crystals. ● (this paper), ▼ (taken from [27]) — a_0 values for the as-grown crystals; ○ — a_0 in the crystals subjected to the various heat treatments

before and after annealing process (Hg- or Se-saturation, dynamic vacuum annealing). Electron concentration was measured at 77 and 300 K. Precise measurements of a_0 at room temperature were carried out using the Bond method [26].

Fig. 5 presents the experimental $a_0(n)$ dependence in $Cd_{0.1}Hg_{0.9}Se$. The a_0 values for the as-grown samples are denoted by full symbols. Open symbols correspond to the lattice constant of annealed crystals. For the samples subjected to various heat treatments (where we can obtain the controlled stoichiometry deviation) lattice constant increases with electron concentration[1]. The above results prove that dominant defects in $Cd_{0.1}Hg_{0.9}Se$ are of the interstitials form. Taking into account previous considerations (§4.1), only Hg interstitials (Hg_I) are possible. It can be seen that a part of them is ionized and gives probably the main contribution to the electron concentration. Another conclusion is, that the relation $[Hg_I^{\cdot}]+[Hg_I] \gg N_F$ (N_F — concentration of Frenkel pairs, $Hg_I V_{Hg}$) should be valid — in the opposite case there should be $a_0(n)$ = const. However, the Frenkel type defects ($Hg_I V_{Hg}$) should be taken into account as minority ones when considering Se-saturation of a crystal. The concentration of Schottky type defects ($V_{Hg}V_{Se}$) or V_{Se} (prefered due to the stoichiometry deviation) which probably exist in a crystal should be constant in the studied annealing conditions and/or significantly lower than $[Hg_I^{\cdot}]$ $+[Hg_I]$. If not, the $a_0(n)$ dependence could have the reciprocal slope (as in CdTe [29]).

It can also be seen from Fig. 5 that the lattice constants of the as-grown crystals are higher than those measured after annealing process. It means that as-grown crystal contains more defects (higher concentration of the Hg interstitial atoms), however only a part of point defects is ionized. This is due to the fact that the crystal grown and cooled to the room temperature can contain more Hg atoms in its interstitials than it could result from the solubility limit of Hg in $Cd_{0.1}Hg_{0.9}Se$ solid solution at 300 K. Part of these Hg atoms could form neutral microprecipitations while the rest remains ionized giving the contribution to the value of n.

The obtained $a_0(n)$ dependence enables us to estimate the concentration of the neutral Hg atoms in the as-grown as well as in the annealed crystals.

(a) As-grown crystals

Within $a_0(n)$ measurements for $Cd_{0.1}Hg_{0.9}Se$ an additional experiment has been simultaneously performed to determine the change of material density, d_{exp}, which is due to the annealing process. From the chosen and tested part of the as-grown Bridgman ingot with $x = 0.1$ three specimens were cut: a standard sample for electrical measurements, a sample for density measurements (weighing about 6g) and a small sample for lattice constant measurements. Electron concentration at 77 K and 300 K and lattice constant before annealing were measured. Crystal density was obtained as an average of 30 independent measurements carried out with use of the standard density liquid (standard density about 2 g/cm^3).

Then the samples were subjected to the heat treatment in dynamic vacuum at 230°C during 90 h. Soon afterwards analogous measurements were made. It was found that electron concentration in the crystal (at 77 K) diminished from 1.50×10^{18} to 1.95×10^{17} cm^{-3}. The corresponding decrease of a_0 (see Fig. 5) was also observed. The detected decrease of density due to the annealing was equal $\Delta d_{exp} = 0.0022\pm0.0004$ g/cm^3 ($\Delta d_{exp} = d_{exp}^0 - d_{exp}^w$; where d_{exp}^0 and d_{exp}^w are initial and final density, respectively). On the other hand

$$\Delta d_{exp} = \Delta d_{def} + \Delta d_a, \tag{1}$$

[1] It should be added here that similar effect was also observed in HgSe [28].

where Δd_{def}, Δd_a are the contributions due to the change of point defect concentration and lattice constant, respectively. The change of a_0 gives $\Delta d_a = -0.0394\ \mathrm{g/cm^3}$, therefore using Eq. (1) we have $\Delta d_{\mathrm{def}} = 0.0416\ \mathrm{g/cm^3}$.

The sign of Δd_{exp} and Δd_{def} confirms the hypothesis assuming the dominant role of interstitials, namely Hg_I, as the main point defects in a crystal in the discussed conditions. Taking it into account we obtain the estimated value $\Delta[Hg_I] = 1.25\times10^{20}\ \mathrm{cm^{-3}}$. Comparing it with the mentioned change of electron concentration $\Delta n \simeq 1.3\times10^{18}\ \mathrm{cm^{-3}}$ it can be seen that the applied heat treatment of $Cd_{0.1}Hg_{0.9}Se$ as-grown crystal not only leads to the decrease of charged defects concentration ($[Hg_i^{\cdot}]$) but, first of all, reduces the concentration of the neutral defects, $[Hg_I]$.

It means that in the as-grown crystal the concentration of neutral Hg interstitial atoms can reach the approximate value $[Hg_I] \approx 10^{20}\ \mathrm{cm^{-3}}$ i.e. two orders of magnitude higher than the value of electron concentration. To simplify the interpretation, we have made an assumption (which seems reasonable) that in annealed $Cd_{0.1}Hg_{0.9}Se$ samples with low electron concentration ($n \gtrsim 2\times10^{17}\ \mathrm{cm^{-3}}$) the concentration of neutral native defects, $[Hg_I]$, does not exceed trace impurities level ($[Hg_I] \gtrsim 10^{18}\ \mathrm{cm^{-3}}$ — see § 2).

(b) Annealed crystals

Taking into account the previous assumption (§ 4.2a) one can make the analogous estimation for the case of Hg-saturated crystal, for example, by comparing the lattice constants of the samples with the highest ($n = 4.30\times10^{18}\ \mathrm{cm^{-3}}$) and the lowest ($n = 1.95 \times10^{17}\ \mathrm{cm^{-3}}$) electron concentration (see Fig. 5). We assume additionally that the total density of annealed crystal remains unchanged ($\Delta d_{\mathrm{exp}} = 0$) within the investigated range of n and a_0. In fact, it seems quite plausible because $|\Delta d_a| \gg |\Delta d_{\mathrm{exp}}|$, as it was shown in §4.2a. Therefore we obtain for this case $\Delta d_{\mathrm{def}} = -\Delta d_a = 0.0264\ \mathrm{g/cm^3}$, which gives the approximate value for the concentration of neutral Hg interstitial atoms $[Hg_I] \simeq 8\times10^{19}\ \mathrm{cm^{-3}}$. This value refers to the undoped $Cd_{0.1}Hg_{0.9}Se$ crystal with maximal electron concentration reached here in Hg-saturation process. One can also deduce from the $a_0(n)$ dependence for annealed $Cd_{0.1}Hg_{0.9}Se$ crystals (Fig. 5) that the magnitude [Hg should depend on n (due to the dependence of $[Hg_I]$ on P_{Hg}).

4.3. Approximate model of the structure of native point defects

The results and discussion presented in the previous paragraphs enable us to outline the simplified model of the structure of native point defects in $Cd_xHg_{1-x}Se$ ($x \leqslant 0.2$). It is based on the following assumptions:

(1) The defects associated with Hg atoms, first of all Hg_I, are dominant in a crystal within studied range of annealing temperature — existence of Frenkel type defects (Hg_IV_{Hg}) as minority ones is also possible.
(2) In the thermodynamic equilibrium of the crystal with the gas phase the above defects are completely isolated (interaction between them is neglected) and ionized.
(3) Donor ($Hg_i^{\cdot}$) and acceptor (V'_{Hg}) defects are singly ionized.
(4) Interaction between native point defects and impurities is neglected.

(5) The cooling process of the grown crystal down to the room temperature or quenching it after heat treatment (Hg-saturation) leads to the creation of the neutral Hg micro-precipitations in crystal lattice.

Two of the above assumptions need some comment.

Ad (3). In the II–VI compounds, due to the valency of the components, one could generally expect the twofold ionization of the native point defects like vacancy or interstitial atom, which act as donor or acceptor centers (see e.g. [4]). However, it appears sometimes that the defect, even at high temperatures, remains singly ionized (see [30]).

For the point defects in HgSe the problem of the ionization degree is still open. A similar situation can be observed in the case of HgTe and $Cd_xHg_{1-x}Te$, where V_{Hg} is a dominant acceptor defect (which mainly determines the type of low temperature conductivity), although the authors of different papers treat it as singly or doubly ionized [31–33]. On the other side $Hg_I^{\cdot}$ is supposed to be the main donor defect in HgTe [31, 33]. The authors of [33] have drawn this conclusion grom the diffusion studies of Hg in $Cd_xHg_{1-x}Te$ at the temperatures up to 560°C — however they do not exclude the possibility of twofold ionization of Hg_I at higher temperatures.

Taking into account the lack of information concerning this subject in reference to $Cd_xHg_{1-x}Se$ ($x \leqslant 0.2$) crystals the simplest variant was chosen — single ionization of Hg_I and V_{Hg} at the temperatures up to 400°C.

Ad (5). It should be added that interstitial Hg atoms, which are not ionized, can only exist in the lattice in the form of neutral microprecipitations. Otherwise, in the case of the isolated neutral Hg_I defects, the electron concentration in a crystal (which in our model is $n \simeq [Hg_I^{\cdot}]$) should depend strongly on temperature in the range 4.2 — 300 K, whereas in fact it remains constant [1, 9, 10]. Therefore the estimated values of $[Hg_I]$ for $Cd_{0.1}Hg_{0.9}Se$ calculated in previous paragraph should be regarded as concentrations of the neutral interstitial Hg atoms which form the above mentioned microprecipitations. The concentration of these microprecipitations is difficult to estimate; one can only suppose that it is at least two times lower than $[Hg_I]$.

We shall briefly discuss now, within the presented model, the two extremal cases of the thermodynamic equilibrium of the crystal with gas phase, i.e. Hg- and Se-saturation.

Firstly, the $Cd_xHg_{1-x}Se$ ($x \leqslant 0.2$) crystal in equilibrium with maximal P_{Hg} pressure will be considered. As had been stated before (see § 3), $P_{Hg}(\max)$ in the investigated range of annealing temperature ($T \leqslant 400$°C) practically equals to the Hg saturated vapor pressure. The corresponding quasichemical reactions and mass-law equations are as follows:

$$\mathrm{Hg}(g) \rightleftarrows \mathrm{Hg}_I^{\cdot} + e, \qquad \frac{[\mathrm{Hg}_I^{\cdot}]n}{P_{\mathrm{Hg}}} = K,$$

$$0 \rightleftarrows e + h, \qquad np = K_i. \tag{2}$$

Electron concentration is determined by neutrality condition:

$$n = [\mathrm{Hg}_I^{\cdot}] + p. \tag{3}$$

From (2) and (3) we obtain electron concentration vs P_{Hg}:

$$n = (K_i + KP_{\mathrm{Hg}})^{1/2}. \tag{4}$$

The above equation has not a unique solution because K remains unknown (K_i could be found from the intrinsic concentration extrapolated to the temperatures $T > 300$ K). The reaction constant K can be accurately determined from the experimental $n = f(P_{Hg})$ isotherms but on condition that n is the in situ measured electron concentration. If this condition is not fulfilled, the discrepancies between experimental results occur — it can be observed for HgSe when comparing the papers [14, 19, 34]. However, it becomes clear if we take into account the results and discussion in the paragraphs 4.1. and 4.2. In fact, the electron concentration in a crystal previously annealed and quenched depends on quenching rate and on the value of annealing temperature.

It can be shown that the excluding of influence of the intrinsic concentration ($K_i = 0$) reduces Eq. (4) to the dependence $n \sim P_{Hg}^{1/2}$, which is typical for singly ionized point defects. It should be emphasized that in zero- and small-gap $Cd_xHg_{1-x}Se$ semiconducting alloys the contribution of the intrinsic concentration could not be neglected as it was done e.g. in [19].

The case of thermodynamic equilibrium of the $Cd_xHg_{1-x}Se$ crystal with $P_{\Sigma Se}(\max)$ is more complex. Contrary to the previously discussed situation, we cannot neglect here the contribution of P_{Hg} to the total pressure of gas phase (see the P–T–x diagram of HgSe [15]). In our model the corresponding quasichemical reactions can be put down:

$$\mathrm{Hg}(g) \rightleftarrows \mathrm{Hg}_i^{\cdot} + e, \qquad \frac{[\mathrm{Hg}_i^{\cdot}]n}{P_{Hg}} = K,$$

$$0 \rightleftarrows e + h, \qquad np = K_i,$$

$$\tfrac{1}{2}\,\mathrm{Se}_2(g) \rightleftarrows V_{Hg}' + h + \mathrm{Se}_{Se}, \qquad \frac{[V_{Hg}']p}{P_{Se_2}^{1/2}} = K',$$

$$\mathrm{Cd}_x\mathrm{Hg}_{1-x}\mathrm{Se}(s) \rightleftarrows x\mathrm{Cd}(g) + (1-x)\mathrm{Hg}(g) + \tfrac{1}{2}\,\mathrm{Se}_2(g)$$

$$P_{Cd}^{x} P_{Hg}^{1-x} P_{Se_2}^{1/2} = K''. \tag{5}$$

The neutrality condition is new in the form:

$$n + [V_{Hg}'] = [\mathrm{Hg}_i^{\cdot}] + p. \tag{6}$$

From (5) and (6) the following formula for electron concentration can be obtained:

$$n = K_i^{1/2} \left(\frac{1 + P_{Hg}\dfrac{K}{K_i}}{1 + P_{Se_2}^{1/2}\dfrac{K'}{K_i}} \right)^{1/2}. \tag{7}$$

Certainly, for the case of $P_{Hg}(\max)$ formula (7) can be reduced to Eq. (4). Electron concentration cannot be determined from (7) because of two unknown reaction constants K and K'. Additional difficulty stands in the fact that partial pressure P_{Se_2} corresponding to $P_{\Sigma Se}(\max)$ also remains unknown (in the given range of temperature) — it is due to the previously mentioned polyatomic structure of the Se-vapor particles.

These qualitative considerations enable us to conclude that in $Cd_xHg_{1-x}Se$ ($x \leqslant 0.2$) crystal subjected previously to Se- saturation the electron concentration is determined by the contribution of donor defects ($Hg_i^{\cdot}$) and intrinsic concentration (in the region near 300 K) as well as by the contribution of acceptor defects (V'_{Hg}). The results presented in this paper suggest that $[Hg_i^{\cdot}] > [V'_{Hg}]$. Therefore for the samples in which relatively low electron concentration ($n \sim 10^{17}\,cm^{-3}$) has been reached by Se-saturation one can expect partial compensation by acceptor centers. We shall return to this problem in the analysis of low temperature electron mobility (see next paper — II).

The problem of passive annealing of $Cd_xHg_{1-x}Se$ crystals needs also some comment. It was shown in § 4.2 that in as-grown as well as in Hg-saturated crystals the interstitial Hg atoms could exist as ionized defects $Hg_i^{\cdot}$ and in the form of neutral microprecipitations. Owing to mentioned high diffusion coefficient of Hg in $Cd_xHg_{1-x}Se$ the $Hg_i^{\cdot}$ atoms, which are not frozen-in at room temperature, can diffuse across the crystal also towards the surface. Kumazaki [35] observed surface Hg microprecipitations in HgSe. The transition of Hg atoms from crystal surface to the gas phase is then possible. On the other hand, a competitive process can also occur — the $Hg_i^{\cdot}$ atoms can join themselves in neutral pairs, triplets etc.; i.e. the neutral microprecipitations in crystal lattice. Such Hg microprecipitations could be created e.g. at the dislocations [36]. Within both the processes the concentration of the charged centers (and hence electron concentration) decreases in time tending to attain certain thermodynamic quasiequilibrium between defects and lattice. Then the increase of mobility related with above effect (see § 3) is mainly due to decrease of concentration of the ionized scattering centers.

In the Se-saturated or dynamic vacuum annealed samples the above effect occurs similarly, although it is weakly observable due to the lower $[Hg_i^{\cdot}]$ value. The only modifications can be introduced here by the acceptor defects V'_{Hg} partially compensating $[Hg_i^{\cdot}]$. A part of the V'_{Hg} vacancies could be filled back by Hg atoms due to passive annealing This process produces certain increase of mobility in a sample together with slight increase of electron concentration or without any change of n (see § 3).

It is worth estimating, within the assumed model of native point defects structure, the stoichiometry deviation in the studied $Cd_xHg_{1-x}Se$ mixed crystals. Here, the stoichiometry deviation which points at the deficit of anion component (Se) is given by (compare with [32]):

$$\delta = \frac{N_I}{2(N+N_I)}, \tag{8}$$

where N_I is the total concentration of excessive interstitial Hg atoms (both neutral and ionized), whereas N is the concentration of lattice sites.

It results from our experiments carried out at $Cd_{0.1}Hg_{0.9}Se$ that in as-grown crystal N_I can reach the value $10^{20}\,cm^{-3}$, which corresponds to $\delta = 1.4 \times 10^{-3}$ (or 0.14 mole %). The latter value agrees well with the experimental data of δ given in § 2, especially with those of [12]. It should be underlined that this value of δ for $Cd_{0.1}Hg_{0.9}Se$ corresponds to the stoichiometry deviation at the melting point. For a comparison, we ought to add that the estimated δ value for the purest sample of $x = 0.1$, where the concentration $n = 7 \times 10^{16}$ cm^{-3} was reached, equals $\delta \simeq 10^{-6}$ (under the assumption that $n = [Hg_i]$ and $[Hg_I] = 0$).

5. Conclusions

The investigations of a heat treatment and the electrical properties of undoped $Cd_xHg_{1-x}Se$ ($x \leqslant 0.2$) mixed crystals have been performed. The main purpose was to get more specific information concerning the structure of native point defects in these alloys.

Undoped $Cd_xHg_{1-x}Se$ crystals, obtained by the Bridgman method, were characterized by certain slight stoichiometry deviation in the Se deficit direction — its estimated value was below 0.5 mole %. Trace impurities at the concentration level below 10^{18} cm^{-3} have been observed in the studied materials. The above stoichiometry deviation significantly influences the electrical properties of $Cd_xHg_{1-x}Se$ crystals. Only the n-type samples with $n \approx 10^{18}$ cm^{-3} could have been obtained.

Applied methods of heat treatment enabled us to get crystals with regulated stoichiometry deviation and with the controlled value of electron concentration in the range $7 \times 10^{16} - 5 \times 10^{18}$ cm^{-3}, depending on composition x. For $Cd_{0.1}Hg_{0.9}Se$ the homogeneity range within the investigated annealing temperatures for both Hg- and Se-saturation limits has been determined. The effect of passive annealing has been observed in $Cd_xHg_{1-x}Se$ ($x \leqslant 0.2$) mixed crystals.

The analysis of heat treatment, supplemented with additional studies of $a_0(n)$ dependence in $Cd_{0.1}Hg_{0.9}Se$, permits to give a simplified model of the point defects structure in $Cd_xHg_{1-x}Se$ ($x \leqslant 0.2$). Within this model, the above slight nonstoichiometry of the studied crystals is due to the existence of excessive interstitial Hg atoms in crystal lattice. Part of them remains ionized and gives the major contribution to the electron concentration, the other part forms neutral microprecipitations in a crystal. It has been proved, that in the as-grown crystals the concentration of the Hg atoms in such microprecipitations can even exceed 10^{20} cm^{-3}. It has also been shown that the concentration of both types of defects, $[Hg_I]$ and $[Hg_i]$, depends on the growth process and the heat treatment conditions of a crystal.

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