

# FUNDAMENTAL CHARACTERISTICS OF A NEW $\text{Hg}_3\text{TeCl}_4$ CRYSTAL OBTAINED BY MEANS OF THE ELEMENTARY ENERGY BANDS CONCEPT BASED ON *AB INITIO* BAND STRUCTURE CALCULATIONS

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*Ab initio* band structure calculations of the orthorhombic  $\text{Hg}_3\text{TeCl}_4$  crystal of the symmetry  $D_{2h}^{15}$  were performed and the topology of its valence band was analyzed in the framework of the elementary energy bands concept. The effective masses of charge carriers were estimated. It was demonstrated that the anisotropy of the effective mass tensor components does not coincide with the mechanical one of the  $\text{Hg}_3\text{TeCl}_4$  crystal. A possible reason of this fact was proposed.

**Key words:** chalcogenides, *ab initio* calculations, electronic structure.

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## I. INTRODUCTION

Recently, phase diagrams of the  $\text{HgS-HgTe-HgCl}_2$  have been investigated by means of *X*-ray and differential thermal analysis [1]. It has been proved that a new rhombic  $\text{Hg}_3\text{TeCl}_4$  crystal exists with the symmetry  $Pbca$  ( $D_{2h}^{15}$ ) and the lattice constants  $a = 11.552(4)\text{Å}$ ,  $b = 12.140(4)\text{Å}$ ,  $c = 12.683(2)\text{Å}$ , containing 64 atoms in its unit cell. These atoms are arranged into two double layers perpendicular to the *y* axis.

Since there is no information about this compound in the literature, there arises a question, if its physical properties can be predicted based from its chemical composition, crystalline structure and symmetry. Moreover, whether this crystal is created from the structure elements of the  $\text{HgTe}$  and  $\text{HgCl}_2$  crystals and if so, whether this crystal inherits their physical properties.

The space symmetry group  $D_{2h}^{15}$  is at the same time the symmetry group of a known covalent  $\text{CdSb}$  semiconductor [2]. We have shown in the framework of the elementary energy bands concept [3–7] and the empty-lattice approximation that a chemical bonding present in this crystal should be covalent [2] since none of the atoms of this compound coincide with the so-called special Wyckoff position in the unit cell (A Wyckoff position  $W_G$  consists of all points *X* for which the site-symmetry groups  $S(X)$  are conjugate subgroups of the space symmetry group *G* describing a crystal. A point *X* is called special position with respect to *G* if there is at least one other symmetry operation of *G*, in addition to the identity operation that leaves *X* fixed). From the elementary energy bands (EEBs) concept it follows that the band structure of every semiconductor is composed of some smallest structure elements that create a topologically closed entirety throughout the Brillouin zone (BZ). The irreducible representations describing energy states of the elementary energy band in high-symmetry points in the BZ can be obtained by induction from the irre-

ducible representations of the site-symmetry groups of a Wyckoff position. Among all Wyckoff positions that are assigned to every space symmetry groups, there are the so-called actual Wyckoff positions which are responsible for the symmetry of the valence band of a crystal [8, 9]. The actual Wyckoff position can be found based upon the empty-lattice approximation, since the symmetry of energy states obtained in this approximation coincides with the symmetry of irreducible representations of the elementary energy band induced from the site-symmetry group of a strictly specified Wyckoff position. We have additionally shown that the actual Wyckoff position has a physical meaning, i. e. the maximum of the spatial valence electron density distribution can be found in this position [10].

Also none of the atoms of the  $\text{Hg}_3\text{TeCl}_4$  crystal coincide with the special Wyckoff positions  $a(0, 0, 0)$  and  $b(0, 0, 1/2)$  [11] in the unit cell, hence one may suppose that the bonding should be covalent in this crystal as well. This statement seems to be strange for a compound with an element having valency equal to 7. This issue will be solved in this paper by means of the EEBs concept.

## II. EEBs OF $\text{Hg}_3\text{TeCl}_4$ AND $\text{HgCl}_2$ CRYSTALS IN THE EMPTY-LATTICE APPROXIMATION

There are 320 valence electrons in the unit cell of the  $\text{Hg}_3\text{TeCl}_4$  crystal (*d*-electrons are not taken into account). Therefore its valence band is composed of 160 bands. The closed valence band of  $\text{Hg}_3\text{TeCl}_4$  obtained in the empty-lattice approximation is composed of two sets of states in the  $\Gamma$  point:

$$20(\Gamma_1, \Gamma_3, \Gamma_5, \Gamma_7) + 20(\Gamma_2, \Gamma_4, \Gamma_6, \Gamma_8). \quad (1)$$

These two sets of states represent at the same time two kinds of the 4-branch EEBs which are characteristic for the  $D_{2h}^{15}$  space group and therefore they are identical with

those of CdSb crystal [2]. They correspond to the special Wyckoff positions  $a(0, 0, 0)$  and  $b(0, 0, 1/2)$  [11]. Since there are the same numerical coefficients in Eq.(1), one can also interpret the above sets as one set of the symmetry:  $\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4, \Gamma_5, \Gamma_6, \Gamma_7, \Gamma_8$  that represents another 8-branch EEB, characteristic for the  $D_{2h}^{15}$  space group, corresponding, however, to the general Wyckoff position  $c(x, y, z)$ . The coordinates of this position are free, hence they can point to atomic positions in a unit cell or to places between atoms. Therefore we can conclude that the valence electron density of the  $\text{Hg}_3\text{TeCl}_4$  crystal can be focused both on the atoms (this points to the ionic bonding) and on places between atoms (points to the covalent bonding). Then the space symmetry group  $D_{2h}^{15}$  describing the symmetry of  $\text{Hg}_3\text{TeCl}_4$  does not impose a covalent bonding for this compound as it takes place in the case of CdSb crystal [2].

A formula unit of the  $\text{Hg}_3\text{TeCl}_4$  crystal can be presented as a sum of the formula units of  $\text{HgTe}$  and  $2\text{HgCl}_2$  which, in turn, are the formula units of  $\text{HgTe}$  ( $T_d^2, F\bar{4}3m$  and  $\text{HgCl}_2$  ( $\text{Pnma}, D_{2h}^{16}$ ) crystals. Therefore we present also the results of the empty-lattice approximation for the  $\text{HgCl}_2$  crystal (lattice constants  $a = 12.776(4) \text{ \AA}$ ,  $b = 5.986(3) \text{ \AA}$ ,  $c = 4.333(2) \text{ \AA}$  [12]). The symmetry of the closed valence band of the  $\text{HgCl}_2$  crystal assigned in this approximation for the  $\Gamma$  point is as follows:

$$6(\Gamma_1, \Gamma_4, \Gamma_5, \Gamma_8) + 2(\Gamma_2, \Gamma_3, \Gamma_6, \Gamma_7). \quad (2)$$

Hence, the valence band of  $\text{HgCl}_2$  crystal is composed of 4-branch EEBs with the symmetry presented in Eq.(2). These EEBs correspond to the Wyckoff position  $c(x, 1/4, z)$  of  $D_{2h}^{16}$  space group that represents a plane coinciding with the atomic layer in the  $\text{HgCl}_2$  unit cell.

### III. BAND STRUCTURE OF $\text{Hg}_3\text{TeCl}_4$

The *ab initio* band structure of  $\text{Hg}_3\text{TeCl}_4$  has been calculated in the framework of the DFT by means of the full-potential nonorthogonal local-orbital minimum basis FPLO-3 program [13]. The following configuration has been chosen as a minimum basis set, Hg:  $6s 6p 5d$  (with  $4f 5s 5p$  as semicore states), Te:  $5s 5p 4d$  ( $4s 4p$  semicore states), Cl: ( $3s 3p 3d$ ). The exchange-correlation potential of Perdew and Wang [14] has been used and integration in the  $\mathbf{k}$ -space has been conducted by means of  $3 \times 2 \times 2$   $\mathbf{k}$ -mesh providing 8 irreducible  $\mathbf{k}$ -points. A part of the band structure near the energy gap and the total density of states is presented in Fig. 1. The minimal forbidden energy gap is situated in the  $\Gamma$  point and equals 2.49 eV. The expected experimental one should be larger  $\sim 3$  eV. We have fitted parabolic dependencies to the  $E(k)$  functions corresponding both to the conduction band minimum and the valence band maximum. Hence the following values of the effective masses were obtained:  $m_x^* = 0.55m_0$ ,  $m_y^* = 0.44m_0$ ,  $m_z^* = 0.38m_0$  for the conduction band electrons and  $m_x^* = 7.86m_0$ ,  $m_y^* = 2.01m_0$ ,  $m_z^* = 0.92m_0$  for the valence band holes. It can be seen that the electron effective masses do not exhibit anisotropy, while the anisotropy of the hole effective masses is strong but does not correspond to that of the  $\text{Hg}_3\text{TeCl}_4$  crystal structure. The crystalline structure of  $\text{Hg}_3\text{TeCl}_4$  exhibits layers in the direction perpendicular to the  $y$  axis. An analogous situation was observed in a layered  $\gamma$ -InSe crystal [15]. It has been interpreted in such a way that the overlap integral between some wave functions of atoms in the crystalline layer is smaller than that one between the functions of atoms in the neighboring layers. These wave functions are responsible for the creation of the valence band top.

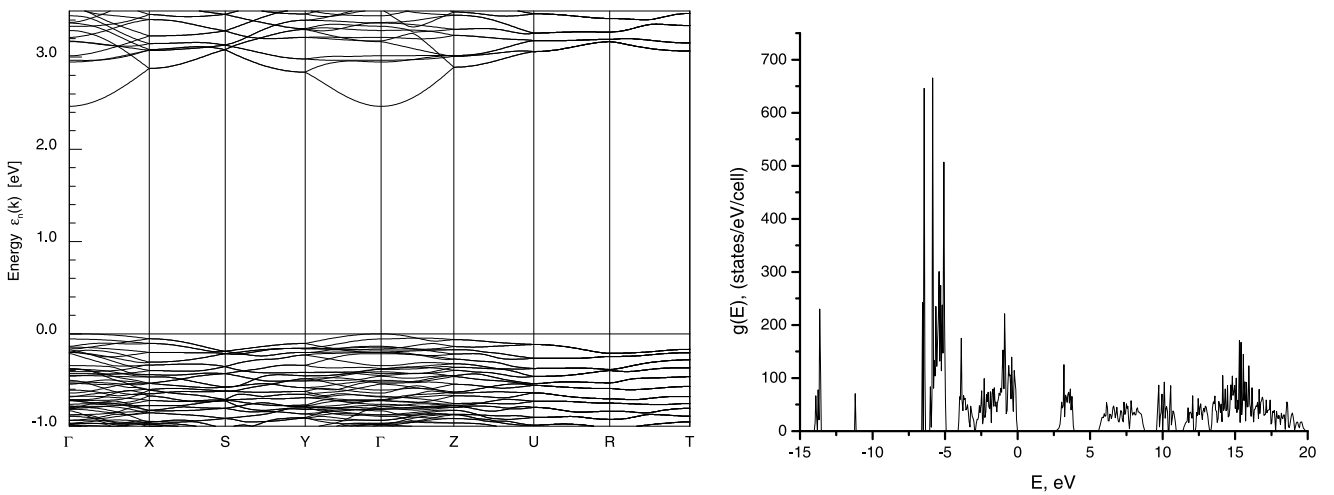


Fig. 1. Band structure and total density of states of the  $\text{Hg}_3\text{TeCl}_4$  crystal.

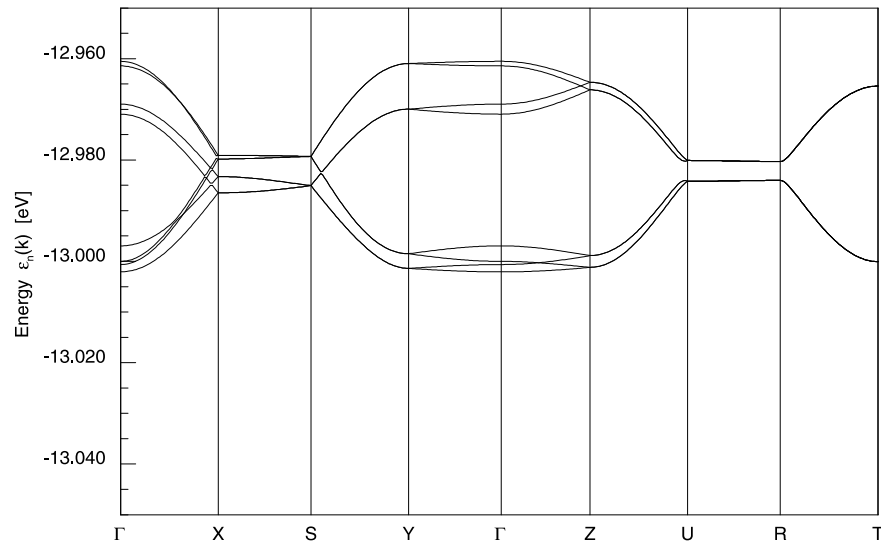


Fig. 2. 8-branch elementary energy band of the  $\text{Hg}_3\text{TeCl}_4$  crystal selected at the bottom of its valence band.

Therefore, regardless of the layered structure of the  $\text{Hg}_3\text{TeCl}_4$  crystal, we do not observe an essential anisotropy in its band structure and this testifies to the presence of a prevailing ionic bonding in this crystal (see Fig. 3).

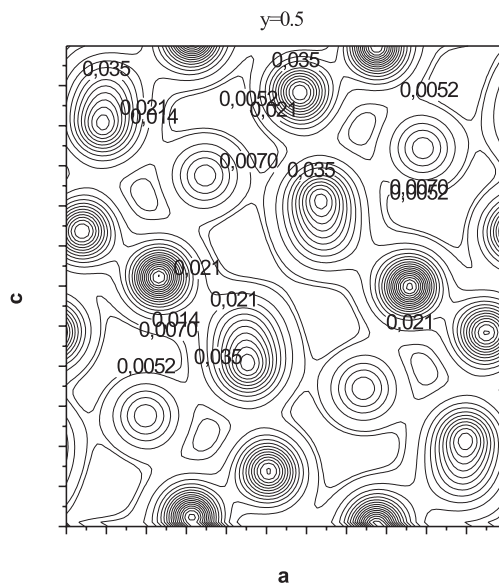


Fig. 3. Section of the spatial valence electron density distribution with the plane  $y = 0.5$  corresponding to the middle of the double translationally non-equivalent layer in the unit cell.

The whole valence band of  $\text{Hg}_3\text{TeCl}_4$  is composed of 8-branch EEBs which cross and overlap in the whole energy range  $(-14, 0)$  eV. Only at the bottom of the valence band  $(-14, -11)$  eV one can observe not overlapping EEBs having 8 branches. Based upon this topology we conclude that the actual Wyckoff position for  $\text{Hg}_3\text{TeCl}_4$  is  $c(x, y, z)$  which was predicted proceeding from the empty-lattice approximation. From the calculation of a partial density of states functions it follows that

the most essential contribution to the formation of the valence band top has  $3p$  Cl electrons with a smaller share of  $3p$  Te electrons. The contribution of  $6s$  and  $6p$  Hg electrons in this energy range is very small.  $6s$  Hg electrons contribute to the energy range  $(-4, -3)$  eV. An essential share of  $5d$  Hg electrons can be seen in  $(-7, -5)$  eV. The contribution of  $5p$  Te and  $3p$  Cl electrons is 3 times smaller in this energy range. Deep valence band states are created by  $3s$  Cl electrons. The obtained results confirm the statement following from the paper [1] about the presence of the prevailing ionic bonding in the  $\text{Hg}_3\text{TeCl}_4$  crystal with a share of covalent bonding between Te-Te and Hg-Te atoms due to  $sp$  hybridization. The bottom of the conduction band of  $\text{Hg}_3\text{TeCl}_4$  is formed by  $6s$  Hg and  $5p$  Te electrons which indicates also the presence of  $sp$  hybridization.

An issue of a layered composition of this crystal can be solved by analyzing stages of the splittings in its energy spectrum, assuming in advance an anisotropy of the inter- and intralayer bonding. If the interaction between atoms inside the double layer in a unit cell is stronger than that one between layers, then the sequence of energy states in the elementary energy band of the crystal is obtained which points to the Davydov splitting. Such Davydov splitting can be observed in the EEB in a chosen energy range, presented in Fig. 2.

We demonstrate now that the topology of the energy spectrum of this crystal is related to the energy spectrum of  $\text{HgCl}_2$ . This indicates that the process:  $\text{Hg}_3\text{TeCl}_4 = \text{HgTe} + 2\text{HgCl}_2$  can be understood as a participation of separate crystalline structure elements of HgTe and  $\text{HgCl}_2$  in the formation of the  $\text{Hg}_3\text{TeCl}_4$  crystal. At the same time, this process makes some physical properties of these two crystals (e. g. layered composition of  $\text{HgCl}_2$ ) are transferred to  $\text{Hg}_3\text{TeCl}_4$ . We assume that a framework in the creation of  $\text{Hg}_3\text{TeCl}_4$  is the  $\text{HgCl}_2$  crystal with the symmetry  $D_{2h}^{16}$  (Pnma). Its lattice constants have been enlarged as follows:  $c' = 3c$ ,  $b' = 2b$ ,  $a' = a$ . To obtain 320 valence electrons in the unit cell of such supercrystal one should utilize electrons of 4 and

8 formula units of  $\text{HgCl}_2$  and  $\text{HgTe}$ , respectively. The EEBs of the supercrystal  $\text{Hg}_3\text{TeCl}_4$  with the symmetry  $D_{2h}^{16}$  result from the following symmetry of the valence band of this crystal in the  $\Gamma$  point

$$25(\Gamma_1, \Gamma_4, \Gamma_5, \Gamma_8) + 15(\Gamma_2, \Gamma_3, \Gamma_6, \Gamma_7). \quad (3)$$

It can be seen that Eq. (1) can be also presented as two sets having the symmetry identical to that of Eq. (3) with the numerical coefficients 20 at both sets. We obtain at the same time that the origin of the energy spectrum of  $\text{Hg}_3\text{TeCl}_4$  follows from the energy spectrum of a  $\text{HgCl}_2$  crystal which undergoes an essential rearrangement of states described by Eq. (3) due to the presence of the  $\text{HgTe}$  formula units. As was mentioned above, in the formation of the bottom of the conduction band  $s$  and  $p$

electrons of Hg and Te take part, respectively. This is why an essential dispersion of the  $E(k)$  dependence can be observed for the first conduction band leading, regardless of a big  $E_g$  value, to relatively small values of the electron effective masses.

#### IV. CONCLUSIONS

The obtained values of the effective mass tensor components for electrons as well as a large value of the direct energy gap of the  $\text{Hg}_3\text{TeCl}_4$  crystal suggest that this crystal could be used in optoelectronics, on condition that experimental investigations show its stability under the influence of light.

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### ФУНДАМЕНТАЛЬНІ ХАРАКТЕРИСТИКИ НОВОСИНТЕЗОВАНОГО КРИСТАЛУ $\text{Hg}_3\text{TeCl}_4$ , ОДЕРЖАНІ ШЛЯХОМ ВИКОРИСТАННЯ КОНЦЕПЦІЇ МІНІМАЛЬНИХ КОМПЛЕКСІВ ЗОН ТА З ПЕРШОПРИНЦИПНИХ РОЗРАХУНКІВ ЗОННОЇ СТРУКТУРИ

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У межах концепції мінімальних комплексів зон та теорії функціонала густини з використанням *ab initio* розрахунків досліджено симетрію та топологію енергетичного спектра нового кристала  $\text{Hg}_3\text{TeCl}_4$  з просторовою групою  $D_{2h}^{15}$ . Виявлено, що валентна зона цього кристала складається з мінімальних комплексів із 8 гілок, які пов'язуються з так званою загальною позицією Викоффа, що підтверджує наявність у ньому йонно-ковалентного зв'язку. Показано, що топологія енергетичного спектра орторомбічного кристала  $\text{Hg}_3\text{TeCl}_4$  походить від зонної структури шаруватого діелектрика  $\text{HgCl}_2$ , деформованої наявністю структурних елементів  $\text{HgTe}$ . Цей результат підтверджує той факт, що в утворенні кристала  $\text{Hg}_3\text{TeCl}_4$  беруть участь структурні елементи кристалів  $\text{HgCl}_2$  і  $\text{HgTe}$  і, відповідно,  $\text{Hg}_3\text{TeCl}_4$  повинен проявляти фізичні властивості, які походять від указаних матеріалів. Оцінено компоненти тензора ефективних мас для носіїв заряду. Виявлено, що ефективні маси для електронів не проявляють анізотропії, тоді як анізотропія ефективних мас для дірок є сильною, однак їх анізотропія не корелює з анізотропією кристалічної структури  $\text{Hg}_3\text{TeCl}_4$ . Запропоновано пояснення такої поведінки, яке полягає в меншому перекритті хвильових функцій атомів у кристалічному шарі порівняно з перекриттям хвильових функцій атомів сусідніх шарів. У низькоенергетичній області валентної зони в мініальному комплексі з 8 гілок кристала  $\text{Hg}_3\text{TeCl}_4$  спостерігаємо давидівське розщеплення, притаманне шаруватим кристалом з трансляційно-нееквівалентними структурними одиницями. Одержані параметри (значення ефективних мас електронів та величина прямого забороненого проміжку в точці  $\Gamma$   $E_g=2.49$  eV) роблять кристал  $\text{Hg}_3\text{TeCl}_4$  перспективним для сучасної оптоелектроніки.