

# Elementary energy bands in the band structure of the narrow-band-gap semiconductor CdSb

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Based upon the example of a narrow band gap covalent CdSb crystal ( $D_{2h}^{16}$ ), it is shown that a spatial electron density distribution in the unit cell is related to the Zak's elementary energy bands creating the valence band and to the corresponding Wyckoff positions. A role of particular electronic states in the creation of the elementary energy bands was analyzed by conducting *ab initio* band structure calculations of CdSb. The investigations of the topology of the elementary energy bands allows one to predict the nature of chemical bondings in rhombic crystals.

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## I. INTRODUCTION

In a series of papers by Zak, Michel,<sup>1,2</sup> and Bercha<sup>3-6</sup> it was shown that energy spectra of crystals are composed of some distinguished structural units called “elementary energy bands.” Zak has introduced in his first publications on this subject the concepts of band representation and then irreducible band representation<sup>1</sup> which contains energy states of high-symmetry points in the Brillouin zone (BZ). Following papers of Cloizeaux,<sup>7</sup> Burneika and Levinson,<sup>8</sup> as well as Kovalev,<sup>9</sup> he associated the elementary energy bands with a local symmetry of the specific Wyckoff positions.<sup>10</sup> Representations describing energy states of the elementary energy bands can be obtained by the inducing procedure applied to the representations of the local group of the Wyckoff positions.<sup>9,11</sup>

On the other hand, it was shown<sup>4,12-16</sup> that the closed valence band of a semiconducting crystal is composed of the elementary energy bands and the energy states that describe them can be obtained in the empty-lattice approximation with the use of some general data about a crystal (the existence of the forbidden energy gap, lattice constants, number of valence electrons in the unit cell, space symmetry group). The presence of a few Wyckoff positions in a unit cell, assigned to every space symmetry group (except for a few groups which have only one general Wyckoff position, of symmetry  $E$ ), leads to the fact that one cannot know which of those positions “induces” representations describing energy states of the elementary energy bands which create the real valence band of a given crystal.

We have recently shown<sup>15</sup> that in the case of orthorhombic crystals it is the position in a unit cell that is selected in the empty-lattice approximation (in the sense described above) and that it is at the same time characterized by the largest valence electron density. To summarize, it is possible to obtain information about a structure (symmetry and topology) of the valence band and about the spatial electron density distribution in a unit cell of wide band gap orthorhombic crystals, on the basis of the empty-lattice approximation supplemented by the general data concerning the crystal. This result was demonstrated on the basis of *ab initio* band structure calculations conducted for orthorhombic wide band gap  $YAIO_3$ ,  $SbSI$ ,<sup>15</sup>  $Tl_3AsS_4$ <sup>17</sup> crystals with a prevailing ionic bonding.

A problem arises. Can analogous information about the symmetry and topology of the valence band as well as about the spatial electron density distribution be obtained in the empty-lattice approximation for a narrow band gap semiconductor with predominant covalent bonding? Moreover, is the maximum electron density still observed in the Wyckoff positions selected by the empty-lattice approximation in the case when none of the atoms overlap with a Wyckoff position in the unit cell? Hence, in this paper we analyze these topics by performing *ab initio* band structure calculations as well as calculations of the spatial and energetic distribution of electron density in a narrow band gap CdSb semiconductor with the prevailing covalent character of bonding. For a comparison, we analyze a connection between the elementary energy bands and the valence electron density in a typical covalent crystal of silicon. In this crystal some of the Wyckoff positions overlap with positions of atoms. The CdSb crystal, on the other hand, gives an exceptional possibility to analyze the issue of the elementary energy bands and their connection with the spatial electron density distribution in a situation when none of the atoms of the compound overlap with the Wyckoff position.

## II. CRYSTALLINE STRUCTURE OF CdSb AND ITS PROPERTIES

Cadmium antimonide is an anisotropic semiconducting  $A^{II}B^V$  crystal which found wide practical application. Due to its thermoelectrical properties and specific topology of the forbidden band gap, it is a promising material for thermoelectrical devices as well as infrared sensors. Based on these crystals some thermoelements, converters of infrared radiation, and other electronic devices were created.<sup>18-20</sup> Owing to the approximately equal mobilities of electrons and holes as well as a small thermal conductivity, this crystal is a good material for an application in Nernst-Ettingshausen detectors.<sup>21</sup> Furthermore, a variety of interesting physical properties and effects were revealed in CdSb crystals: the existence of the magnetophonon resonance,<sup>22</sup> superconductive response near the localization threshold,<sup>23</sup> and the Shubnikov-de Haas effect.<sup>24-26</sup>

Single CdSb crystals without dopants are  $p$ -type crystals, while  $n$ -CdSb crystals can be obtained by doping with In and

TABLE I. Atomic coordinates of the CdSb crystal (Ref. 29).

Atom	$x$	$y$	$z$
Cd	0.5503(1)	0.6238(1)	0.63426(8)
Sb	0.13980(9)	0.07390(9)	0.10390(7)

Te.<sup>27</sup> CdSb crystallizes in the orthorhombic system and its symmetry is described by the  $D_{2h}^{15}$  ( $Pbca$ ) space group.<sup>28,29</sup> According to Ref. 29 the lattice constants are the following:  $a_1=6.469(1)\text{\AA}$ ,  $a_2=8.251(2)\text{\AA}$ ,  $a_3=8.522(2)\text{\AA}$ , whereas atomic coordinates are provided in Table I. According to Ref. 30 the minimal value of the forbidden energy gap is 0.44 eV which testifies to the low ionicity of the compound. The band structure of CdSb crystal has been calculated by the semi-empirical pseudopotential method so far.<sup>31–33,13</sup> Unfortunately, neither wave functions describing energy states nor information about the electron density distribution is provided in those papers. This information is necessary for our analysis. Except for Ref. 13, the valence band described in the aforementioned papers was not treated as the one composed of the elementary energy bands. It is known that the absolute maximum of the valence band is located in the direction of  $\Sigma(k_x, 0, 0)$  axis, near point  $X(\pi/a, 0, 0)$  in the BZ. The minima of the conduction band are nonequivalent ellipsoidal valleys, localized along  $\Delta(0, k_y, 0)$  and  $\Lambda(0, 0, k_z)$  axes.

It should be noted that a model of nonequivalent ellipsoidal valleys was proposed in Ref. 34 devoted to the investigation of piezoresistivity anisotropy effect. The presence of ellipsoidal valleys in the CdSb spectrum was confirmed experimentally by the cyclotron resonance,<sup>35</sup> Shubnikov–de Haas effect,<sup>24–26</sup> and negative magnetoresistance phenomenon in  $p$ -CdSb crystals.<sup>36</sup>

### III. ELEMENTARY ENERGY BANDS IN THE CdSb BAND STRUCTURE

The elementary energy bands can be composed of a various number of branches, depending on the space group of a crystal. In some cases one can trace a topologically unavoidable crossing (degeneracy) of branches. This peculiarity of the rhombohedral system was mentioned by Tovstyuk and Korolyshin.<sup>37,38</sup> From Ref. 5 follows that a number of the elementary energy bands with the topologically unavoidable degeneracy (in particular, a double one for the  $D_{2h}^{15}$  space group) is limited for the orthorhombic system. The  $D_{2h}^{15}$  space group describes the symmetry of the discussed CdSb crystal.

This group was also discussed recently by Zak<sup>39</sup> as an illustration of the topologically unavoidable degeneracy of branches in the elementary energy bands. He introduced two laws for this degeneracy to exist in spectra of orthorhombic crystals.

$D_{2h}^{15}$  space symmetry group has two specific Wyckoff positions of a multiplicity  $m=4$  Ref. 10:

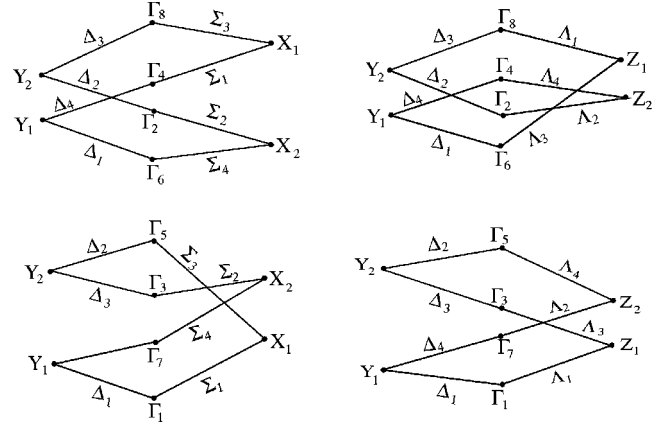


FIG. 1. Scheme of four-branch elementary energy bands of the  $D_{2h}^{15}$  space group.

$$\begin{aligned}
 & a_1(0,0,0), \quad a_2\left(\frac{1}{2}, \frac{1}{2}, 0\right), \quad a_3\left(0, \frac{1}{2}, \frac{1}{2}\right), \quad a_4\left(\frac{1}{2}, 0, \frac{1}{2}\right), \\
 & b_1\left(0, 0, \frac{1}{2}\right), \quad b_2\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right), \quad b_3\left(0, \frac{1}{2}, 0\right), \quad b_4\left(\frac{1}{2}, 0, 0\right).
 \end{aligned} \tag{1}$$

Inducing representations of the  $D_{2h}^{15}$  space group from irreducible representations of the local groups of the above positions we obtain the representations existing in the elementary energy bands and then, using the compatibility relations, we are able to draw their scheme. A scheme of the elementary energy bands consisting of 4 branches is presented in Fig. 1.

From Refs. 15 and 17 it follows that a symmetry of the representations existing in the elementary energy bands constituting the valence band is that one which is obtained in the empty-lattice approximation. It was demonstrated<sup>13</sup> on the basis of the empty-lattice approximation applied to CdSb crystal that 28 branches of the valence band in the  $\Gamma$  point of the BZ are described by irreducible representations of the symmetry

$$4(\Gamma_1, \Gamma_3, \Gamma_5, \Gamma_7) + 3(\Gamma_2, \Gamma_4, \Gamma_6, \Gamma_8). \tag{2}$$

It follows from Fig. 1 that a double, forced crossing of branches exists in  $D_{2h}^{15}$  space group. This crossing can be obtained also for other directions in the BZ if the sequence of the energy states in the  $\Gamma$  point is changed.

We have done calculations of the band structure of a CdSb crystal using the full-potential nonorthogonal local-orbital minimum basis FPLO<sup>®</sup>-3 scheme<sup>40</sup> within the local spin density approximation. In these scalar relativistic calculations we used the exchange and correlation potential of Perdew and Wang.<sup>41</sup> We utilized the values of lattice constants and atomic positions presented in Sec. II. The following configuration as a minimum basis set for the valence states was chosen: Cd-4*d*, 5*s*, 5*p*, Sb-4*d*, 5*s*, 5*p*. All lower lying states were treated as core states. In the case of cadmium atom, 5*p* states were included in order to increase the quality of the basis set. A  $k$  mesh of 150 points in the BZ (36 in the irreducible part) was used. Since the full-electron

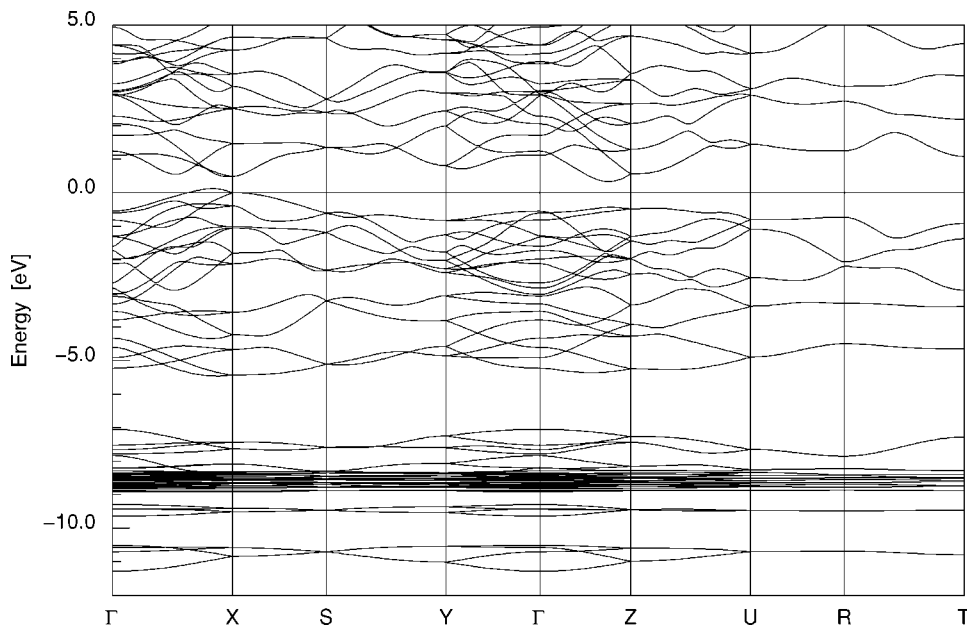


FIG. 2. Band structure of CdSb crystal with an account of  $d$  electrons.

method implemented in the FPLO<sup>®</sup>-3 scheme does not allow one to conduct calculations with “frozen” valence electron configurations, we have done additional calculations of the band structure by means of the ABINIT package.<sup>42</sup> A formalism of the pseudopotentials in the density-functional theory<sup>43</sup> is implemented there and it is based on an effective algorithm of a fast Fourier transformation of the wave functions. To calculate a self-consistent potential the method of conjugate gradients<sup>44,45</sup> is applied. We used the Troullier-Martins norm-conserving pseudopotentials in our calculations. The following configuration of Sb electrons was utilized:  $5s$ ,  $5p$ . In order to find pseudopotentials of Cd atoms we have chosen in the first case the configuration  $4d$ ,  $5s$  and then, the configuration  $5s$  by “freezing” cadmium’s  $d$  electrons in a pseudopotential core. The exchange-correlation effects were taken into account in the local approximation.<sup>41</sup> Integration in the BZ has been performed by means of 8  $k$  special points. A set of approximately 13 100 plane waves was restricted by the maximum kinetic energy of 40 Ry. Comparison of the band structure calculation results of both program packages (FPLO<sup>®</sup>-3 and ABINIT) shows a good agreement between the energy positions of bands. It testifies that the basis chosen for the calculations of the band structure and the electron density distribution is enough. The utilization of both packages enables to explain a role of  $s$ ,  $p$ , and  $d$  electrons of cadmium and antimony in the creation of the CdSb band structure. Figure 2 displays the band structure of a CdSb crystal with an account of  $d$  electrons. It can be seen that the upper part of the valence band is created by five elementary energy bands, each consisting of four branches. The band gap is an indirect one and the absolute maximum of the valence band is located near X point of the BZ, in the  $\Sigma(\Gamma-X)$  direction. The conduction band is a multivalley one, the absolute minimum appears in the  $\Lambda(\Gamma-Z)$  direction and the additional minima can be traced both in the  $\Delta(\Gamma-Y)$  and  $\Sigma(\Gamma-X)$  directions. Such a multivalley character of a top of the valence and a bottom of the conduction bands agrees qualitatively with the previous calculation results obtained by semiempir-

ical pseudopotential method. The value of the obtained indirect band gap equals 0.44 eV. The elementary energy bands overlap in the valence band and the most intersections (not conditioned by the symmetry and topology) can be seen in the  $Y-\Gamma-Z$  directions. Figure 3 presents the valence band in the energy range  $(-11 \text{ eV}, -7 \text{ eV})$ . The elementary energy bands existing there do not overlap, furthermore, one can trace double, unavoidable crossings of branches. On the basis of calculations of the energy density of states distribution and partial density of states we can state that ten elementary energy bands in the energy range  $(-9 \text{ eV}, -7 \text{ eV})$  are created by cadmium  $d$  electrons and hybridized cadmium  $4d$  and antimony  $5s$  states. Two lowest elementary energy bands in the valence band originate mainly from Sb  $5s$  states. Sb  $4d$  states do not take part in the creation of the CdSb valence band. The top of the valence band is constituted mainly by cadmium and antimony  $p$  states with a small admixture of  $s$  states of both atoms. In addition,  $s-p$  hybridized states of Cd and Sb atoms are responsible for the creation of the conduction band. The band structure calculation results show that if cadmium  $d$  electrons are not taken into account then the whole valence band of the CdSb crystal is composed of seven elementary energy bands and, furthermore, that the two lowest ones, which are separated from the others, are created by antimony  $s$  states. Cadmium  $d$  electrons make ten additional elementary energy bands of a small dispersion appear in the lowest energy ranges. Energy states of the elementary energy bands which arose without taking into account cadmium  $d$  electrons are moved then to even lower energy ranges.

By analyzing interatomic distances in CdSb crystal one can distinguish that  $\text{Cd}_2\text{Sb}_2$  is the smallest structural unit, moreover, that there are four such structural units in a unit cell of CdSb which surround the  $a_1$ ,  $a_2$ ,  $a_3$ , and  $a_4$  Wyckoff positions. The symmetry group of this unit is  $C_i$  which contains two elements: the identity element and inversion. This group coincide with the local group of the Wyckoff position  $a$ .

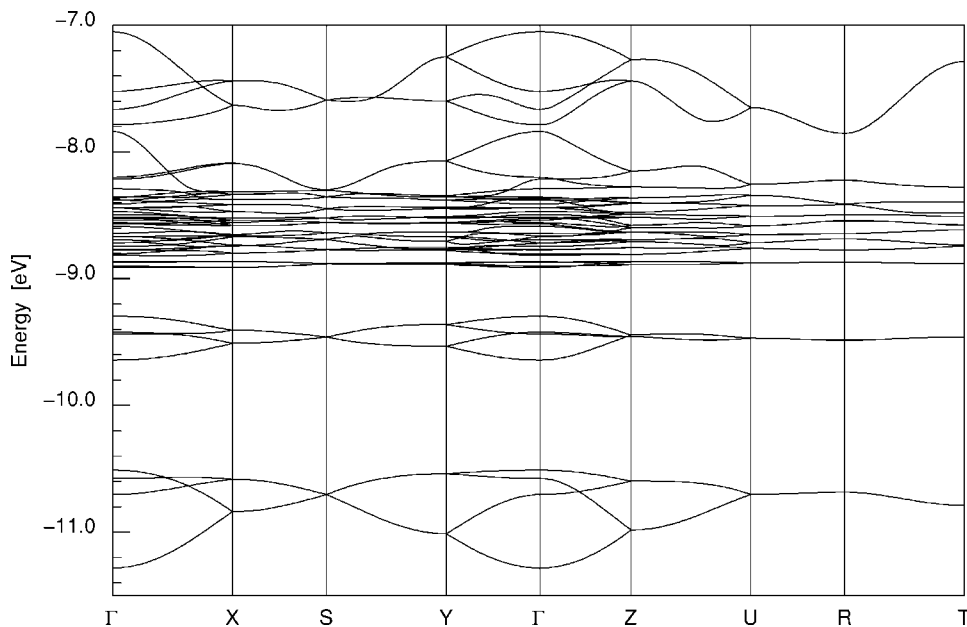


FIG. 3. Low energetic part of the valence band of CdSb crystal composed of the elementary energy bands.

Inducing representations of the  $D_{2h}^{15}$  space symmetry group from irreducible representations of the  $C_i$  group we obtain in the  $\Gamma$  point two sets of irreducible one-dimensional representations: a symmetrical set of  $\Gamma_1, \Gamma_3, \Gamma_5, \Gamma_7$  and an antisymmetrical one  $\Gamma_2, \Gamma_4, \Gamma_6, \Gamma_8$ . (By symmetrical and antisymmetrical we understand such representations for which the character of the inversion element in the  $\Gamma$  point is equal to 1 and  $-1$ , respectively. The same character is obtained for irreducible representations of the local group  $C_i$  for both  $a$  and  $b$  Wyckoff positions.) These two sets describe the elementary energy bands and each of them is related to a function which is localized mainly on the  $\text{Cd}_2\text{Sb}_2$  structural unit. It should be noted further that the second Wyckoff position  $b$  ( $b_1, b_2, b_3, b_4$ ) relates to identical sets of representations  $\Gamma_1, \Gamma_3, \Gamma_5, \Gamma_7$  and  $\Gamma_2, \Gamma_4, \Gamma_6, \Gamma_8$ . Therefore, it appears that on the basis of the inducing procedure applied to the  $\Gamma$  point we are not able to determine which of these positions ( $a$  or  $b$ ) is “responsible” for the creation of the valence band of CdSb crystal. Unfortunately, the situation is analogous for other high-symmetry points of the BZ, except  $R(\pi/a_1, \pi/a_2, \pi/a_3)$  point. The symmetrical representation of the local group of the Wyckoff position  $a$  corresponds in the  $R$  point to the representation  $2R_1(2)$  which is reduced in the  $\Gamma$  point to four representations  $\Gamma_1, \Gamma_3, \Gamma_5$ , and  $\Gamma_7$ , while the antisymmetrical representation corresponds to the representation  $2R_2(2)$  which is reduced in the  $\Gamma$  point to the antisymmetrical set of representations  $\Gamma_2, \Gamma_4, \Gamma_6$ , and  $\Gamma_8$ .

A situation for the Wyckoff position  $b$  is opposite: the symmetrical representation corresponds to the representation  $2R_2(2)$  which is reduced to the set of  $\Gamma_1, \Gamma_3, \Gamma_5, \Gamma_7$ , while the antisymmetrical representation corresponds to the representation  $2R_1(2)$  which is reduced to the set  $\Gamma_2, \Gamma_4, \Gamma_6, \Gamma_8$ . A group-theoretical analysis shows that irreducible representations of the wave vector group for the  $R$  point are two-dimensional [ $2R_1(2)$ -dimension) or  $2R_2(2)$ ] and they are joined due to the time-inversion symmetry. Hence, four branches of the elementary energy bands are joined in the  $R$  point.

Let us now analyze which information about a choice of the Wyckoff position is obtained in the empty-lattice approximation applied to the  $R$  point. It appears that a sequence of identical, eightfold degenerate states described by the following representations is obtained in the order of increasing energies:

$$2R_1(2)2R_2(2), 2R_1(2)2R_2(2), 2R_1(2)2R_2(2), \\ 2R_1(2)\downarrow 2R_2(2), \dots \quad (3)$$

The energy gap arises due to a splitting of the fourth eightfold degenerate state. A position of the splitting is marked in Eq. (3) by an arrow. One can see that it is impossible to foresee which of fourfold degenerate states [ $2R_1(2)$  or  $2R_2(2)$ ] will stay in the valence band and which of them is moved to the created conduction band. In our opinion, the  $2R_2(2)$  state, described by representations which are antisymmetrical with respect to inversion, is moved to the conduction band. Such a situation takes place in the  $\Gamma$  point, in a typical covalent crystal, namely silicon. CdSb crystal is in a first case from a series of orthorhombic crystals discussed by us (having different space symmetry groups) for which the empty-lattice approximation does not distinguish unequivocally the “actual” Wyckoff position from two of them. If our suspicion that a degenerate state described by the antisymmetrical representation is moved to the conduction band is proper, than the “actual” Wyckoff position which is responsible for the creation of the valence band, will be the Wyckoff position  $a$ . A final answer to this problem give numerical calculation results of the wave functions calculated for the  $\Gamma$  and  $R$  points, presented below.

We calculated wave functions corresponding to  $\Gamma$  and  $R$  points in the BZ by means of the ABINIT program, both for configuration comprising  $d$  electrons and without them. A symmetry of the valence band calculated without  $d$  cadmium electrons is the following:

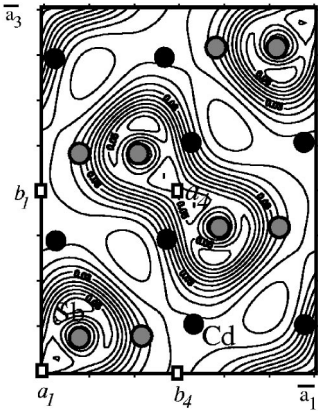


FIG. 4. Cross section of the spatial valence electron distribution of CdSb crystal with a plane  $y=0$ . ( $d$  electrons were not taken into account). Open squares denote the Wyckoff positions.

$\Gamma$  point

$$\begin{aligned} & \Gamma_1, \Gamma_7, \Gamma_3, \Gamma_5, \Gamma_6, \Gamma_4, \Gamma_8, \Gamma_2, \Gamma_4, \Gamma_5, \Gamma_7, \\ & \Gamma_3, \Gamma_6, \Gamma_2, \Gamma_1, \Gamma_8, \Gamma_7, \Gamma_3, \\ & \Gamma_2, \Gamma_5, \Gamma_4, \Gamma_8, \Gamma_5, \Gamma_6, \Gamma_1, \Gamma_3, \Gamma_7, \Gamma_1, \end{aligned} \quad (4)$$

$R$  point

$$2R_1, 2R_2, 2R_2, 2R_1, 2R_1, 2R_2, 2R_1. \quad (5)$$

As a consequence, the valence band consists of the elementary energy band of the symmetry in the  $\Gamma$  point

$$4\{\Gamma_1, \Gamma_3, \Gamma_5, \Gamma_7\} + 3\{\Gamma_2, \Gamma_4, \Gamma_6, \Gamma_8\} \quad (6)$$

and in the  $R$  point

$$4\{2R_1\} + 3\{2R_2\}. \quad (7)$$

Four symmetrical sets of representations  $\{\Gamma_1, \Gamma_3, \Gamma_5, \Gamma_7\}$  correspond to four sets of  $\{2R_1\}$ , while three antisymmetrical sets  $\{\Gamma_2, \Gamma_4, \Gamma_6, \Gamma_8\}$  correspond to  $3\{2R_2\}$ . Therefore, we are able to claim that the Wyckoff position  $a$  is responsible for the creation of the valence band of CdSb crystal. This conclusion is confirmed by a fact that the band representations of the  $D_{2h}^{15}$  space group which are induced from irreducible representations of the local group of the Wyckoff position  $a$ , contain identical representations in the  $\Gamma$  and  $R$  points. The same situation takes place when cadmium  $d$  electrons are taken into account.

From Refs. 15 and 17 it follows that the Wyckoff position which is responsible for the creation of the valence band is characterized by the largest valence electron density. Therefore we calculated a spatial electron density distribution in a unit cell of CdSb crystal which is displayed in Fig. 4. As can be seen, the largest valence electron density (without cadmium  $d$  electrons) is focused around  $a_1$  and  $a_4$  positions [Eq. (1)], in addition, the symmetry of that distribution is described by the  $C_i$  point group. Moreover, the electron density in every Wyckoff position  $a_i$  is significant; namely,  $0.057 e/\text{Bohr}^3$  what is almost 88% of the maximum of the whole distribution.

Now we compare this result with an analogous discussion for a covalent crystal of silicon. It is known that due to the covalent bonding the largest valence electron density is observed along the main diagonal of a unit cell,<sup>46</sup> in the point given by coordinates  $(a/8, a/8, a/8)$  (here  $a$  is the lattice constant). These coordinates point to the Wyckoff position  $c$ . According to our conception, this distinguished Wyckoff position is responsible for the symmetry and topology of the valence band. Inducing representations for the high-symmetry points in the BZ from the identity irreducible representation of the local group of this position, we obtain the elementary energy band whose symmetry and topology coincide with the respective one of the silicon valence band. Let us note further that the physical meaning of the distinguished Wyckoff position, noticed by us for rhombic crystals, i.e., an accumulation of the spatial electron density distribution, is also valid for crystals of the cubic system, e.g., silicon. The largest electron density, conditioned by a covalent bonding, appears in the distinguished Wyckoff position  $c$ , see, e.g., Ref. 46.

An interesting result can be obtained analyzing a cross section of a spatial distribution of  $|\psi|^2$  where  $\psi$  denotes the wave functions corresponding to the states of the lowest first two elementary energy bands in the valence band of CdSb crystal. It follows from Fig. 3 that those elementary energy bands do not overlap. The lowest elementary energy band is created from the symmetrical linear combination of localized functions formed from Sb  $s$  states, while the other one is created from the antisymmetrical combination of the same functions.

Figure 5(a) presents a cross section of  $|\psi|^2$  describing  $\Gamma_1$  state [belonging to the set of elementary energy bands  $(\Gamma_1, \Gamma_3, \Gamma_5, \Gamma_7)$ ], while that of Fig. 5(b) correspond to a  $\Gamma_6$  state [belonging to the set of  $(\Gamma_2, \Gamma_4, \Gamma_6, \Gamma_8)$ ]. The shape of the distribution in Fig. 5(a) is identical to that of the spatial distribution of the total electron density of CdSb crystal around the Wyckoff position  $a$ . However, a shape of the distribution corresponding to  $\Gamma_6$  state [Fig. 5(b)] is different. In this case the partial electron density is minimal in the Wyckoff position  $a$ . An analogous result is obtained for other states belonging to the symmetrical and antisymmetrical states of representations describing the elementary energy bands. These results are justified since functions localized on the  $\text{Cd}_2\text{Sb}_2$  structural unit are formed by antimony  $s$  states. It is known that the wave functions formed by atomic  $s$  orbitals, symmetrical with respect to inversion, describe bonding orbitals, while the antisymmetrical wave functions describe antibonding orbitals. Such a situation is not observed for partial electron density for energy states belonging to the energetically higher elementary energy bands, since wave functions describing those states originate from hybridized  $s$  and  $p$  states of cadmium and antimony. Moreover, the interaction between functions localized on the  $\text{Cd}_2\text{Sb}_2$  structural unit becomes stronger.

A shape of the partial electron density corresponding to the energy states creating the upper part of the valence band is similar to those presented in Figs. 5(a) and 5(b) (depending on if a representation belongs to the symmetrical or antisymmetrical set). Calculations of the wave functions of ten elementary energy bands, resulting in the case when cad-

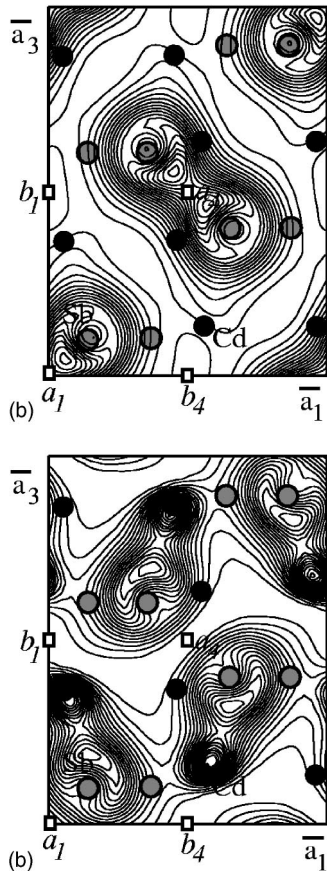


FIG. 5. Partial electron density distribution (cross section with plane  $y=0$ ) resulting from (a)  $\Gamma_1$  state belonging to the deepest symmetrical elementary energy band, (b)  $\Gamma_6$  state belonging to the deepest antisymmetrical elementary energy band.

mium  $d$  electrons were taken into account, show that the number of symmetrical and antisymmetrical states is the same. To symmetrical states correspond density distributions analogous to that of Fig. 5(a), while to antisymmetrical states the distributions of Fig. 5(b).

We shall show now that on the basis of the topology analysis of the elementary energy bands of a rhombic crystal from  $D_{2h}^{15}$  space group one can predict in an unambiguous way if this crystal is a layered one with a weak bonding, or not. As an illustration we utilize CdSb crystal. Two separated groups of atoms forming two translationally nonequivalent layers can be recognized in its unit cell. These layers are perpendicular to the  $x$  axis. The  $C_{2v}^5$  ( $Pca2_1$ ) space group which is a subgroup of  $D_{2h}^{15}$  can be assigned to every layer. If a weak van der Waals bonding exists between these layers then, by inducing representations of the space group of the crystal from irreducible representations of the space group of the layer, one can check that the nearby energy states described by representations ( $\Gamma_1$  and  $\Gamma_8$ ), ( $\Gamma_6$  and  $\Gamma_3$ ), ( $\Gamma_4$  and  $\Gamma_5$ ), as well as ( $\Gamma_7$  and  $\Gamma_2$ ) should exist in the  $\Gamma$  point. To achieve this, the valence band should contain in the  $\Gamma$  point an equal number both the symmetrical and antisymmetrical elementary energy bands with respect to inversion. Moreover, two sets of the elementary energy bands from Eq. (6) should overlap, forming a complex of eight branches. Such a

situation we observed for a layered  $\text{In}_4\text{Se}_3$  ( $D_{2h}^{12}$ ) crystal for which the elementary energy bands consist of two branches, while the real band structure is composed of overlapping elementary energy bands, having four branches. Their energy states reflect the Davydov splittings both in the electronic and phonon spectrum.<sup>14,47</sup>

In the case of a CdSb crystal, the representations of an eight-branch complex (two overlapping elementary energy bands) can be induced only from the general Wyckoff position, of the symmetry  $E$ . However, as we established in the empty-lattice approximation (2) and conducting numerical band structure calculations (6), the two aforementioned conditions are not fulfilled. As a consequence, the valence band of CdSb crystal must be composed of the elementary energy bands, having four branches. Hence, we can claim that a bonding between visible “layers” in the unit cell is not weak. This analysis allows to predict a nature of bonding in recently obtained, not investigated yet crystals of the  $D_{2h}^{15}$  space group (e.g.,  $\text{Hg}_3\text{TeCl}_4$ ,  $\text{Tl}_4\text{P}_2\text{S}_6$ ,  $\text{Tl}_3\text{AsS}_3$ ). Those crystals for which, in the empty-lattice approximation, an equal number of symmetrical and antisymmetrical representations is obtained for the elementary energy bands seem interesting. We can predict in the valence band of those crystals the overlapping elementary energy bands, the lack of maximum of the electron density in the Wyckoff positions  $a$  and  $b$ , and as a consequence, a different nature of chemical bonding than that of CdSb crystal. In order to overlap two sets of the symmetrical and antisymmetrical elementary energy bands, one should handle eight states described by all representations from  $\Gamma_1$  to  $\Gamma_8$ . A necessary condition for those overlapping elementary energy bands to create the valence band is that the total number of valence electrons can be divided by 16. The set of representations ( $\Gamma_1, \Gamma_2, \dots, \Gamma_8$ ) can be induced only from the general Wyckoff position, of the symmetry  $E$ . Therefore, the maximum electron density can be focused in any places in the unit cell of those crystals.

#### IV. CONCLUSIONS

Investigating the band structure of CdSb crystal we have confirmed that it is composed of the four-branch elementary energy bands which are obtained already in the empty-lattice approximation supplemented by general data about this crystal. Calculations of the total and partial density of states enabled us to check which atoms (and their electrons) are responsible for the creation of the particular elementary energy bands in the valence band of the crystal.

A physical meaning of the Wyckoff position noticed earlier by us for wide band gap rhombic crystals with prevailing ionic bonding was confirmed also for narrow band gap covalent CdSb crystal. We showed that for a covalent crystal of CdSb the specific Wyckoff position is a symmetry center around which a dominant valence electron density is placed. Since atomic positions in CdSb crystal do not coincide with any specific Wyckoff position therefore, the accumulation of electron density in those positions has no connection with a placement of atoms. Since both specific Wyckoff positions of the  $D_{2h}^{15}$  space group are situated in the corners, edges, and center of walls as well as in the unit center, we can claim that

a dominant covalent bonding can be traced in all those crystals from this space group whose atomic positions do not coincide with the specific Wyckoff positions. However, it happens only then, when the empty-lattice approximation gives a different number of the elementary energy bands described by symmetrical and antisymmetrical representations.

We confirmed that only selected Wyckoff positions, known from the International Tables for Crystallography, are responsible for the symmetry and topology of the valence band of rhombic crystals. Investigations of the topology of the elementary energy bands allows one to predict a nature of chemical bondings in those crystals.

Since irreducible representations of the local groups of the all Wyckoff positions for rhombic crystals are one dimensional, therefore, all the elementary energy bands corresponding to a particular Wyckoff position in a given group have the same topology. This particular feature of the orthorhombic system, that differentiates it from high-symmetry

systems, allows one to predict a topology of the real energy spectra already on the basis of the empty-lattice approximation.

The subject of a further analysis should be the explanation of the unavoidable double crossing of branches in the elementary energy bands (e.g., in the CdSb crystal) and of the character of overlapping energy bands (e.g., in the  $\text{In}_4\text{Se}_3$  crystal). In the case of a strongly anisotropic  $\text{In}_4\text{Se}_3$  crystal, which was discussed at the end of Sec. III, there exist the overlapping elementary energy bands in the whole electronic spectrum which create, for low-energy ranges, an isolated group of bands. Since the elementary energy bands introduced by Zak were obtained using a connection between extended functions and localized orbitals, it seems that in order to explain such a character of branches creating the elementary energy bands a theory of maximally localized Wannier functions<sup>48</sup> and its latest modification for entangled energy bands<sup>49</sup> will be particularly useful.

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- <sup>1</sup>J. Zak, Phys. Rev. Lett. **45**, 1025 (1980); Phys. Rev. B **25**, 1344 (1982); **26**, 3010 (1982).
- <sup>2</sup>L. Michel and J. Zak, Phys. Rev. B **59**, 5998 (1999).
- <sup>3</sup>D. M. Bercha, I. I. Nebola, and I. V. Bercha, Fiz. Tverd. Tela (Leningrad) **28**, 1320 (1978) [Sov. Phys. Solid State **20**, 759 (1978)].
- <sup>4</sup>D. M. Bercha and O. B. Mitin, Fiz. Tekh. Poluprovodn. (S.-Peterburg) **27**, 508 (1987) [Sov. Phys. Semicond. **21**, 919 (1987)].
- <sup>5</sup>D. M. Bercha and L. Yu. Kharhkalis, Ferroelectrics **192**, 113 (1997).
- <sup>6</sup>D. M. Bercha, A. A. Grabar, L. Yu. Kharhkalis, O. B. Mitin, and A. I. Bercha, Fiz. Tverd. Tela (S.-Peterburg) **39**, 1219 (1997) [Phys. Solid State **39**, 1081 (1997)].
- <sup>7</sup>J. Des Cloizeaux, Phys. Rev. **129**, 554 (1963); **135**, A685 (1964); **135**, A698 (1964).
- <sup>8</sup>I. P. Burneika and I. B. Levinson, Tr. Akad. Lit. SSR, Ser. B. **4**, 31 (1961).
- <sup>9</sup>O. V. Kovalev, Fiz. Tverd. Tela (Leningrad) **17**, 1700 (1975) [Sov. Phys. Solid State **17**, 1106 (1975)].
- <sup>10</sup>*International Tables for Crystallography, Space Groups Symmetry* (Reidel, Dordrecht, 1983), Vol. A.
- <sup>11</sup>O. V. Kovalev, in *Representations of the Crystallographic Space Groups. Irreducible Representations, Induced Representations and Corepresentations*, edited by Harold T. Stokes and Dorian M. Hatch (Brigham Young University, Provo, UT, 1993).
- <sup>12</sup>D. M. Bercha, O. B. Mitin, I. M. Rarenko, L. Yu. Kharhkalis, and A. I. Bercha, Fiz. Tekh. Poluprovodn. (S.-Peterburg) **28**, 1249 (1994) [Semiconductors **28**, 711 (1994)].
- <sup>13</sup>D. M. Bercha, O. B. Mitin, I. M. Rarenko, and B. N. Gritsyuk, Ukr. Fiz. Zh. (Russ. Ed.) **28**, 1523 (1983).
- <sup>14</sup>D. M. Bercha, M. Sznajder, and K. Z. Rushchanskii, in *Proceedings of the 6th International School on Theoretical Physics, Symmetry and Structural Properties of Condensed Matter, Myczkowce, 2000*, edited by T. Lulek, B. Lulek, and A. Wal (World Scientific, Singapore, 2001), p. 376.
- <sup>15</sup>D. M. Bercha, K. Z. Rushchanskii, M. Sznajder, A. Matkovskii, and P. Potera, Phys. Rev. B **66**, 195203 (2002).
- <sup>16</sup>K. Z. Rushchanskii, H. Haeuseler, and D. M. Bercha, J. Phys. Chem. Solids **63**, 2019 (2002).
- <sup>17</sup>M. Sznajder, D. M. Bercha, and K. Z. Rushchanskii, Phys. Status Solidi A **201**, 304 (2004).
- <sup>18</sup>S. G. Dremluzhenko, L. I. Konopatseva, S. M. Kulikovskaya, and Yu. P. Stetsko, Proc. SPIE **3890**, 104 (1999).
- <sup>19</sup>A. A. Ashcheulov, I. V. Gutsul, and V. S. Maevskii, Opt.-Mekh. Prom-st. **67**, 87 (2000) [J. Opt. Technol. **67**, 281 (2000)].
- <sup>20</sup>P. A. Bogomolov, A. N. Borets, T. S. Gertovich, N. V. Gorobets, I. M. Rarenko, and K. D. Tovstyuk, Opt.-Mekh. Prom-st. **39**, 64 (1972) [Sov. J. Opt. Technol. **39**, 645 (1972)].
- <sup>21</sup>G. P. Chuiko and N. M. Chuiko, Izv. Akad. Nauk SSSR, Neorg. Mater. **15**, 33 (1979) [Inorg. Mater. (USSR) **15**, 23 (1979)].
- <sup>22</sup>D. V. Smirnov, D. V. Mahovets, M. O. Safonchik, Yu. V. Roznovan, and J. Leontin, Fiz. Tekh. Poluprovodn. (S.-Peterburg) **30**, 543 (1996) [Semiconductors **30**, 297 (1996)].
- <sup>23</sup>V. F. Gantmakher, V. M. Teplinskii, V. N. Zverev, and O. I. Barkalov, Physica B **194-196**, 1083 (1994).
- <sup>24</sup>J. Cisowski, J. C. Portal, E. K. Arushanov, J. M. Broto, S. Huang, and L. L. Brunel, Phys. Status Solidi B **121**, 289 (1984).
- <sup>25</sup>E. K. Arushanov, A. V. Lashkul, V. I. Pruglo, S. I. Radautsan, and V. V. Sologub, Dokl. Akad. Nauk SSSR **263**, 71 (1982) [Sov. Phys. Dokl. **27**, 212 (1982)].
- <sup>26</sup>E. K. Arushanov, A. V. Lashkul, D. V. Mahovets, V. I. Pruglo, S. I. Radautsan, and V. V. Sologub, Dokl. Akad. Nauk SSSR **263**, 1112 (1982) [Sov. Phys. Dokl. **27**, 320 (1982)].
- <sup>27</sup>I. M. Rarenko, A. F. Semizorov, T. S. Gertovich, and B. N. Gritsyuk, Fiz. Tekh. Poluprovodn. (S.-Peterburg) **7**, 1595 (1973) [Sov. Phys. Semicond. **7**, 1062 (1974)].
- <sup>28</sup>K. E. Almin, Acta Chem. Scand. (1947-1973) **2**, 400 (1948).
- <sup>29</sup>K. J. Range, J. Pfauntsch, and U. Klement, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. **44**, 2196 (1988).
- <sup>30</sup>D. M. Bercha, A. N. Borets, T. S. Gertovich, I. M. Rarenko, and K. D. Tovstyuk, Fiz. Tverd. Tela (Leningrad) **12**, 2397 (1970).
- <sup>31</sup>Y. Yamada, J. Phys. Soc. Jpn. **35**, 1600 (1973).
- <sup>32</sup>Y. Yamada, J. Phys. Soc. Jpn. **37**, 606 (1974).

- <sup>33</sup>O. N. Manik and I. M. Rarenko, *Fiz. Tekh. Poluprovodn. (S.-Peterburg)* **20**, 1706 (1986) [*Sov. Phys. Semicond.* **20**, 1068 (1986)].
- <sup>34</sup>K. D. Tovstyuk, D. M. Bercha, Z. V. Pankevich, and I. M. Rarenko, *Phys. Status Solidi* **13**, 207 (1966).
- <sup>35</sup>A. I. Rarenko, A. V. Sirota, and D. D. Khalameida, *Fiz. Tekh. Poluprovodn. (S.-Peterburg)* **27**, 372 (1993) [*Semiconductors* **27**, 205 (1993)].
- <sup>36</sup>E. K. Arushanov, A. V. Lashkul, K. G. Lisunov, R. V. Parfen'ev, and S. I. Radautsan, *Fiz. Tverd. Tela (Leningrad)* **28**, 2386 (1986) [*Sov. Phys. Solid State* **28**, 1334 (1986)].
- <sup>37</sup>V. M. Korolyshyn and K. D. Tovstyuk, *Ukr. Fiz. Zh. (Russ. Ed.)* **17**, 1810 (1972).
- <sup>38</sup>K. D. Tovstyuk, *Science of Semiconductor Materials* (Naukova Dumka, Kiev, 1984), p. 246
- <sup>39</sup>J. Zak, *J. Phys. A* **35**, 6509 (2002).
- <sup>40</sup>FPLO<sup>®-3</sup> [scalar-relativistic, improved version of the original FPLO code by K. Koepernik and H. Eschrig, *Phys. Rev. B* **59**, 1743 (1999)].
- <sup>41</sup>J. P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13 244 (1992).
- <sup>42</sup>The ABINIT code is a common project of the Universite Catholique de Lovain, Corning Incorporated, and other contributors (URL: <http://www.pcpm.ucl.ac.be/abinit>).
- <sup>43</sup>W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- <sup>44</sup>M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, *Rev. Mod. Phys.* **64**, 1045 (1992).
- <sup>45</sup>X. Gonze, *Phys. Rev. B* **54**, 4383 (1996).
- <sup>46</sup>Y. W. Yang and P. Coppens, *Solid State Commun.* **15**, 1555 (1974).
- <sup>47</sup>D. M. Bercha, K. Z. Rushchanskii, and M. Sznajder, *Phys. Status Solidi B* **212**, 247 (1999).
- <sup>48</sup>N. Marzari and D. Vanderbilt, *Phys. Rev. B* **56**, 12 847 (1997).
- <sup>49</sup>I. Souza, N. Marzari, and D. Vanderbilt, *Phys. Rev. B* **65**, 035109 (2001).