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Elementary energy bands in *ab initio* calculations of the $YAlO_3$ and SbSI crystal band structure

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The local density approximation has been implemented to determine the band structure of orthorhombic crystals $YAlO_3$ (YAP) and SbSI. The topology of the valence band structures was analyzed. It has been demonstrated that Zak's elementary energy bands in the band structure are distinguishable on the basis of the empty-lattice approximation. The calculated electron density distribution of YAP and SbSI crystals is related to particular Wyckoff positions. Moreover, there is a direct correspondence between the obtained elementary energy bands and the aforementioned Wyckoff positions characterized by electron density distribution.

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I. INTRODUCTION

Nowadays there are many possibilities to conduct the band structure calculations for crystals even with a large amount of atoms in the unit cell. Since an interest in such crystals is still great there arises a necessity to interpret the obtained energy spectra, in particular to analyze the topology of branches of spectra in the Brillouin zone (BZ). Such an analysis is lacking in the literature. However, one should remember that a theory of the elementary energy bands widely developed by Zak and Michel exists[1–3] (and references contained therein). The most important conclusion for solid state physics following from Zak's papers can be formulated as follows: The symmetry of a Wyckoff position in the Wigner-Seitz cell is reflected in the symmetry and the topology of the elementary energy bands in the inverse space.

The present paper is intended to show that the theory of the elementary energy bands has an excellent application in interpretation of the band structure calculation results. To do this, we have chosen for calculations crystals described by the same space symmetry group having, however, completely different chemical bonding, considerably different anisotropy as well as physical properties. In order to easily ilustrate an existence of the elementary energy bands in their band structures, it is convenient to choose a space symmetry group belonging to the low symmetry systems (e.g., the orthorhombic system where the irreducible representations in high-symmetry points of the BZ have the same dimension). An important issue in our discussion is a query if to all the Wyckoff positions known for the given space symmetry group correspond the elementary energy bands which indeed appear in the calculated energy spectra. The elementary energy bands introduced by Zak[1,2] were obtained using a connection between extended functions and localized orbitals. In this paper the elementary energy bands were obtained in the valence band on the basis of the empty-lattice approximation with the use of the general data concerning a semiconducting crystal, which are the existence of the forbidden energy gap, lattice constants, number of valence electrons in the unit cell, and space symmetry group. It should be emphasized that the method presented below does not require information about positions of atoms in the unit cell.

The present paper is divided into five sections: in the next one we introduce crystals which are the subject of our interest, in the third one we calculate the elementary energy bands in the empty-lattice approximation, the fourth section contains details of *ab initio* calculations of the crystal band structures, while the last one is devoted to a discussion on the elementary energy bands.

II. THE $YAlO_3$ AND SbSI CRYSTALS AND THEIR CRYSTALLINE STRUCTURE

The dielectric $YAlO_3$ (YAP) and semiconducting SbSI crystals described by the D_{2h}^{16} space symmetry group have been chosen for our considerations. The $YAlO_3$ crystals belong to a group of materials serving as the basic materials of the laser technique, scintillators, optical recording media and the substrate materials for thin films of high-temperature superconductors.[4–7] Thorough investigation of their physical properties as well as a range of phenomena connected with defects creation is impossible without information about their band structures. Investigations of YAP optical parameters (refractive index, band gap) have been already described. [8,9] Detailed experimental investigation of absorption and reflection spectra in the wide energy range (6.5–42 eV) was also presented.[10,11] The first calculations of the electronic structure of the YAP were reported.[12] The density-functional theory based orthogonalized linear combinations of atomic orbitals (OLCAO) method was used and a comparative analysis of the electronic structure of the Y–Al–O system was conducted in that publication. A particular emphasis was, however, placed on the analysis of the nature of

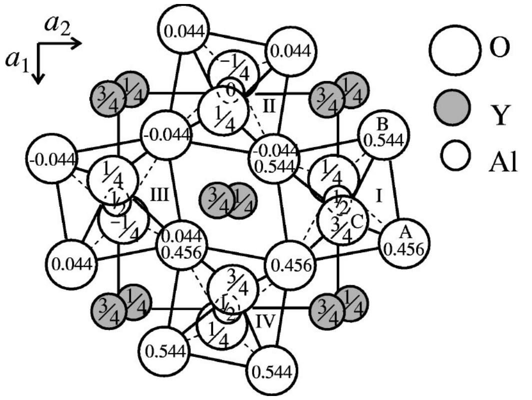

FIG. 1. Crystal structure of $YAlO_3$ (YAP).

interatomic bonds, the density of states, and the investigation of the electron density distribution, whereas the issues of the bands structure, its construction as well as symmetry aspects were exempt from the analysis.

The other crystal chosen for considerations is SbSI crystal. The chain SbSI crystal is, of course, not isomorphic to the YAP one, however it is describable in terms of the same space symmetry group D_{2h}^{16} (paraelectric phase).[13,14] This crystal belongs to the isomorphic $A^V B^{VI} C^{VII}$ group of crystals which possesses semiconducting properties. The discovery of ferroelectric properties[15] has caused intensive investigation of those crystals and other ferroelectric semiconductors.[16] According to the paper,[17] the width of the forbidden gap for SbSI is $E_g^{\perp}=1.95$ eV, $E_g^{||}=1.8$ eV, where $E_g^{\perp}$ and $E_g^{||}$ denote energies corresponding to polarizated light in the direction perpendicular and parallel to the direction of the spontaneous polarization vector, respectively.

The YAP crystal crystallizes in the orthorhombically distorted perovskite structure. The details of the YAP structure are given in the papers. [18,19] The space group D_{2h}^{16} describing the symmetry of the YAP crystal was chosen in the coordinate system of the Pbnm group since this group was utilized to describe the symmetry of the most isotypical ABO_3-type perovskite compounds. The YAP's structure can be conveniently presented as a grid of tilted AlO_6 octahedra with the Y ions occupying holes between them. A projection of the unit cell of the crystal is featured in Fig. 1 (four structurally equivalent Al^{3+} sites are denoted as I, II, III, and IV). [20] Lattice parameters are as follows: $a_1=5.180$ Å, $a_2=5.330$ Å, $a_3=7.375$ Å, whereas their atomic coordinates are presented in Table I. The Al cations are located in the centers of a practically regular octahedra. A mutual displacements of Y cations and oxygen anions cause a different distortion of the cation and anion environment of the oxygen atoms in the two nonequivalent positions O_I (4(c) site) and O_{II} (8(d) site). Y–O bond-lengths in YO_8 dodecahedra differ one from another [they vary from 0.2284 nm to 0.2597 nm for YAP–1% Nd (Ref. 19)]. Therefore, YO_8 dodecahedra can be said to be considerably distorted.

TABLE I. Atomic coordinates and positions of atoms of the $YAlO_3$ crystal (Ref. 18).

Ion	Position	x	y	z
Y^{3+}	4(c)	-0.0104	0.0526	0.25
Al^{3+}	4(b)	0.5	0	0
O_I^{2-}	4(c)	0.086	0.475	0.25
O_{II}^{2-}	8(d)	-0.297	0.293	0.044

TABLE II. Atomic coordinates of the SbSI crystal (Ref. 13).

Atom	Position	x	y	z
Sb	4(c)	0.118	0.124	0.25
S	4(c)	0.84	0.05	0.25
I	4(c)	0.508	0.827	0.25

The structure of the SbSI crystal which is, from the viewpoint of symmetry, related to the YAP crystal, was described[13] and the paraelectric phase of this crystal was assigned to the $Pnma$ (D_{2h}^{16}) space group. It should be noted that a better coordinate system to ilustrate the SbSI crystal is that of the $Pnam$ group, since this crystal exhibits a phase transition to the ferroelectric phase describable in terms of the $Pna2$ (C_{2V}^{9}) space group.[16] The $Pna2$ is a subgroup of the $Pnam$ group. There are 12 atoms is the unit cell of the SbSI crystal which create two translationally nonequivalent chains. Lattice constants of this crystal in the coordinate system of the $Pnam$ group are as follows: $a_1=8.52$ Å, $a_2=10.13$ Å, $a_3=4.10$ Å. The atomic coordinates are provided in Table II, whereas a projection of the crystal structure of the SbSI is illustrated in Fig. 2. Since the discussed crystals are described by the D_{2h}^{16} space symmetry group in different coordinate systems ($Pbnm$ and $Pnam$), the analysis of their band structure requires to take into account the mutual changes of points of the BZ. Table III presents mutual relations between high-symmetry points of groups $Pnma$ (International), $Pnam$, $Pbnm$.

The irreducible representations of groups of the wave vector for the $Pnma$ (I) group can be found in the book.[21] In order to determine characters of these representations for the

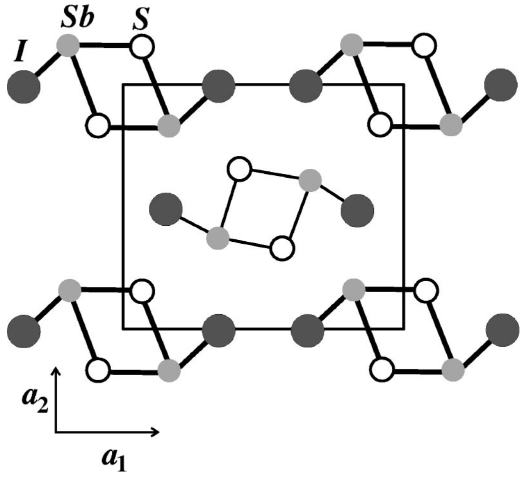

FIG. 2. Crystal structure of antimony sulfoiodide.

TABLE III. High-symmetry points in various coordinate systems of the D_{2h}^{16} space group.

$Pnma$ (I)	Γ	X	Y	Z	U	T	S	R
$Pnam$ (SbSI)	Γ	X	Z	Y	S	T	U	R
$Pbnm$ (YAP)	Γ	Y	Z	X	S	U	T	R

$Pnam$ and $Pbnm$ groups, it is necessary to take into account mutual transformations of the BZ's points and of the symmetry elements. As for the Γ point, as well as for the Σ, Δ, Λ directions, it is obligatory to retain the typical sequence of representations for the corresponding point groups.[21]

III. THE ENERGY SPECTRUM OF THE YAP CRYSTAL IN THE EMPTY-LATTICE APPROXIMATION

In the paper[22] which was specifically devoted to calculations of the band structure of the SbSI crystal by the semiempirical pseudopotential method, it was stated that even the calculations of this structure in the empty-lattice approximation enable one to draw conclusion about the construction of the valence band of the crystal and to provide a description of its symmetry. The empty-lattice approximation and the general data concerning the crystal allowed to fully describe the symmetry of branches of the valence band of the SbSI crystal (the term "branches" introduced in the paper[2] to designate an element of the band structure is used in the discussion below). The following irreducible representations in the order of increasing energies for the Γ point were described:

$$\Gamma_1,\quad \Gamma_4\Gamma_7,\quad \Gamma_6\Gamma_7,\quad \Gamma_4\Gamma_6\Gamma_7\Gamma_1,\quad \Gamma_1\Gamma_6,\quad \Gamma_6\Gamma_4\Gamma_1\Gamma_7,$$
$$\Gamma_1\Gamma_4,\quad \Gamma_4\Gamma_5,\quad \Gamma_1\Gamma_4\Gamma_6\Gamma_7,$$
$$\Gamma_1\Gamma_3\Gamma_6\Gamma_8,\quad \Gamma_2\Gamma_3\Gamma_6\Gamma_7,\quad \Gamma_1\Gamma_2\Gamma_3\Gamma_4\Gamma_5{\downarrow}\Gamma_6\Gamma_7\Gamma_8,\ \ldots . \tag{1}$$

The energy gap should arise at the position marked by the arrow when the pseudopotential is included. The valence band in the Γ point come into being as a result of the splitting of the eightfold degenerate state which is in the energy range of the predicted energy gap. As the result, the valence band is described by the following irreducible representations (in the Γ point):

$$7(\Gamma_1,\Gamma_4,\Gamma_6,\Gamma_7)+2(\Gamma_2,\Gamma_3,\Gamma_5,\Gamma_8). \tag{2}$$

Since the space symmetry group of the YAP crystal is identical with that of the SbSI crystal, we have also considered the creation of the valence band of the YAP crystal in the empty-lattice approximation. There are 96 valence electrons in a unit cell of the YAP crystal. Therefore, the valence band in the Γ point will be created from 48 nondegenerate states. For the coordinate system of the $Pbnm$ group the following energy states are obtained in the Γ point (in the order of increasing energies):

$$\Gamma_1,\quad \Gamma_3\Gamma_6,\quad \Gamma_4\Gamma_7,\quad \Gamma_6\Gamma_7,\quad \Gamma_2\Gamma_4\Gamma_5\Gamma_7,\quad \Gamma_1\Gamma_4\Gamma_5\Gamma_8,$$
$$\Gamma_1\Gamma_4\Gamma_6\Gamma_7,\quad \Gamma_1\Gamma_8,\quad \Gamma_1\Gamma_2\Gamma_3\Gamma_4\Gamma_5\Gamma_6\Gamma_7\Gamma_8,\quad \Gamma_2\Gamma_4\Gamma_5\Gamma_7,$$
$$\Gamma_2\Gamma_3\Gamma_6\Gamma_7,\quad \Gamma_1\Gamma_6,\quad \Gamma_1\Gamma_2\Gamma_3\Gamma_4\Gamma_5\Gamma_6\underline{\Gamma}_7\Gamma_8,\quad \underline{\Gamma}_1{\downarrow}\Gamma_4,$$
$$\Gamma_1\underline{\Gamma}_3\Gamma_6\underline{\Gamma}_8,\quad \Gamma_3\Gamma_6,\quad \Gamma_2\Gamma_3\Gamma_6\Gamma_7,\ \ldots . \tag{3}$$

The predicted energy gap should arise at the position marked by the arrow. It separates the first 48 states. Next, those irreducible representations to which representations describing the first 48 states are reduced can be found using the compatibility relations for characters of the irreducible representations in the Γ, *X*, *Y*, *Z* points, and in the points on the symmetry lines,

$$\text{in the } k_x \text{ direction}: 15\Sigma_1+9\Sigma_2+9\Sigma_3+15\Sigma_4,$$
$$\text{in the } k_y \text{ direction}: 15\Delta_1+10\Delta_2+8\Delta_3+15\Delta_4,$$
$$\text{in the } k_z \text{ direction}: 12\Lambda_1+13\Lambda_2+11\Lambda_3+12\Lambda_4. \tag{4}$$

States from (3) should be rearranged to obtain the closed valence band separated from the conduction band by the energy gap. Such a rearrangement can be carried out in the following way: the underlined states Γ_7 and Γ_1 from the set of the first 48 states pass to the conduction band, whereas the Γ_3, Γ_8 states pass from the higher energy ranges to the valence band. The following combinations of states on the symmetry lines are thus obtained:

$$\text{in the } k_x \text{ direction: } 14\Sigma_1+10\Sigma_2+10\Sigma_3+14\Sigma_4,$$
$$\text{in the } k_y \text{ direction:} 14\Delta_1+10\Delta_2+10\Delta_3+14\Delta_4,$$
$$\text{in the } k_z \text{ direction: } 12\Lambda_1+12\Lambda_2+12\Lambda_3+12\Lambda_4. \tag{5}$$

After such a rearrangement of states the valence band of the YAP crystal is already closed. In the k_x, k_y, k_z directions it is described by the set of irreducible representations (5). The following set of representations is obtained for the Γ point:

$$7(\Gamma_1,\Gamma_4,\Gamma_6,\Gamma_7)+5(\Gamma_2,\Gamma_3,\Gamma_5,\Gamma_8). \tag{6}$$

There is another possibility to carry out a rearrangement of states within the same energy interval leading to a closed valence band. This rearrangement includes states Γ_2, Γ_5, and Γ_4, Γ_6. As the result the following set describes the valence band of the YAP crystal in the Γ point:

$$8(\Gamma_1,\Gamma_4,\Gamma_6,\Gamma_7)+4(\Gamma_2,\Gamma_3,\Gamma_5,\Gamma_8). \tag{7}$$

A further discussion of the decompositon of the energy states (2) and (6), (7) can be found in Secs. IV and V. It is worthy noting that in order to obtain the closed valence band of the SbSI crystal in the empty-lattice approximation the significant rearrangement of states was not required. In that case the valence band in the Γ point arises as a result of the splitting of the eightfold degenerate state observable in the energy range of the predicted energy gap. Therefore, the symmetry description of the valence band of the SbSI crystal can be said to be unique. As for the YAP crystal, other variants of the rearrangement may be considered, i.e., the ones comprising states that belong to higher and lower energy ranges. However, as can be found in Sec. IV, calculations of the band structure and determining the symmetry of branches in the Γ point shows that such a deep rearrangement of states does not take place.

Our investigations of energy spectra of other crystals [$Sn_2P_2S_6$ (Ref. 23), In_4Se_3 (Ref. 24), CdSb (Ref. 25)] in the empty-lattice approximation have shown that the required rearrangement of energy states is quite small for the closed valence band to be created in a semiconducting crystal with the typical energy gap for semiconductors (up to 2.5 eV).

IV. DETAILS OF *AB INITIO* CALCULATIONS OF THE BAND STRUCTURES OF YAP AND SbSI CRYSTALS

Ab initio calculations of the band structures of the $YAlO_3$ and SbSI crystals were conducted. The nonlocal norm-conserving Troullier–Martins pseudopotentials[26] were used. To describe the exchange-correlation interaction the local density approximation was chosen. The Perdew–Zunger's analytic fit[27] to the results of Caperley and Alder[28] was used. Scalar relativistic effects were included in the pseudopotentials. The used pseudopotentials were tested by means of the fhi98PP program[29] to avoid nonphysical ghost states.[30] Calculations of the ground state and of the Kohn–Sham equation eigenvalues were done by means of the fhi98md (Ref. 31) and ABINIT (Ref. 32) package programs. The difference between the band structures obtained by means of these two programs is negligible (<0.01 eV). The special **k** points method[33] was used to carry out integration in the **k** space over the BZ. For both crystals the Monkhorst–Pack mesh $4\times4\times4$ was applied. The chosen parameters allowed to obtain a good convergence in calculations. We did not take into account the spin–orbit interaction. In the case of the YAP crystal the plane waves set was restricted by the kinetic energy cutoff 80 Ry. After comparison of the band structure caluculation results obtained at the kinetic energy cutoff 50 Ry, 70 Ry, and 80 Ry we conclude that the value 80 Ry is sufficient. The band structure of the SbSI crystal was calculated for the kinetic energy cutoff 24 Ry. Again, the comparison of the results of the band structure obtained at 40 Ry enables to claim that the value 24 Ry is already sufficient for the SbSI crystal. For both crystals differences between the band structures caluclated with the use of a denser integration mesh are negligible.

The calculated band structure of the $YAlO_3$ crystal is presented in Fig. 3. It can be seen that the band gap is an indirect one. The maximum of the valence band is located in the Γ point of the BZ, whereas the minimum of the conduction band can be observed along the $\Gamma-X$ direction. The smallest width of the energy gap equals 5.30 eV, i.e., approximately 2/3 of its experimental value ($E_g\simeq7.1$ eV) what is typical for the band structure calculations in the LDA.[34] The width of the valence band is equal to 17.9 eV with the internal gap equals 8.34 eV. Presented results are in agreement with the results of paper[12] which were obtained by means of the OLCAO method.

Figure 3 demonstrates that branches of the band structure are brought together in certain complexes consisting of 4 branches. Twelve of them can be distinguished in the valence band. Calculating the band structure of the YAP crystal we have determined additionally the symmetry of the valence band. The valence band in the Γ point can be represented by the following set of representations: $7(\Gamma_1,\Gamma_4,\Gamma_6,\Gamma_7)+5(\Gamma_2,\Gamma_3,\Gamma_5,\Gamma_8)$. It should be emphasized that we have predicted this result on the basis of calculations of the band structure of this crystal under consideration in the empty-lattice approximation [Eq. (6)]. The valence band branches touch in T and R points of the BZ. In these points the irreducible representations of groups of the wave vectors are united due to the extra degeneration under the time reversal. The states in T and R points are therefore fourfold degenerate (in the coordinate system of the $Pbnm$ group). The top valence band branches, starting from the forbidden energy gap, have the following symmetry in the Γ point: Γ_8, Γ_6 and Γ_4. States described by these representations are the $2p$ oxygen ions states. The bottom of the conduction band in the Γ point is described by the irreducible representation Γ_1. Probably, it corresponds to the $3s$ aluminum states. According to the selection rules the direct optical transitions occur at different energies in the Γ point for $\mathbf{E}\|\mathbf{a}_3$, $\mathbf{E}\|\mathbf{a}_2$, and for $\mathbf{E}\|\mathbf{a}_1$. Moreover, the transition with $\mathbf{E}\|\mathbf{a}_3$ takes place with the minimal energy. The experimental absorption spectra in the ultraviolet range [10] also exhibit the anisotropy of the optical transition energies. Unfortunately, our results cannot be compared with the experimental data[10] since this paper does not give us the information about the chosen coordinate system ($Pbnm$, $Pnma$).

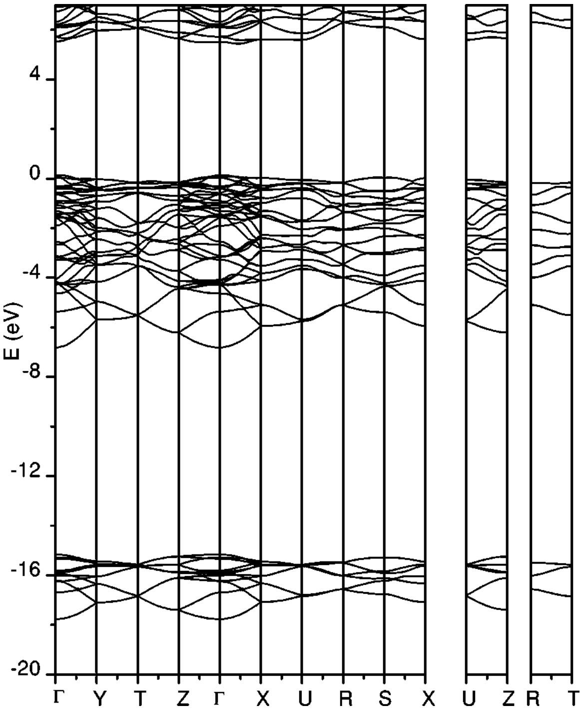

FIG. 3. Band structure of the $YAlO_3$ (YAP) crystal.

The band structure of the SbSI crystal is illustrated in Fig. 4. The $Pnam$ group's coordinate system was implemented in calculations. The obtained band structure of the SbSI crystal is similar to that of the YAP with respect of topology if mutual changes of the BZ points are taken into account (see Table III).

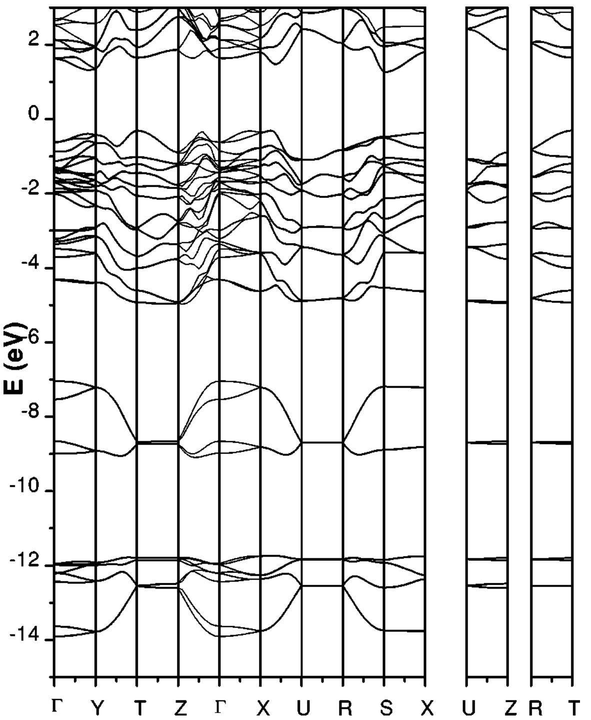

FIG. 4. Band structure of the SbSI crystal.

Since the SbSI crystal is strongly anisotropic, in the Z–T and R–U directions a small dispersion of branches is noticeable, especially for the deep branches of the valence band. The minimum of the conduction band is located in S point (1.24 eV) and along the $\Gamma - Y$ direction, near the Y point (1.30 eV). It should be noted that first band structure calculations of the SbSI crystal were conducted by means of the semiempirical pseudopotential method.[22,35,36] Our new results in general coincide with the data noted in papers[22,36] on condition that a change of the coordinate system is introduced. In the spectrum presented in Fig. 4 one can observe a small splitting of branches in T point arising as the result of a weak interaction between chains of the crystal. This behavior is predictable.[37] The width of the obtainded indirect band gap is equal to 1.5 eV, while the smallest experimental estimation of this value yields $E_{g\ \mathrm{min}} \simeq 1.8$ eV.[16] The most significant discrepancy between the band structure of the SbSI crystal arising as a result of the calculations conducted by the semiempirical pseudopotential method and that obtained by *ab initio* calculations can be specified as follows. The maximum of the valence band is not located in the Γ point, as is the case in calculations done by the semiempirical pseudopotential method. The distinct maxima of the valence band are observable along the $\Gamma - Z$, $\Gamma - X$, $\Gamma - Y$ directions as well as in T point (absolute maximum). It is evident enough that for low-energy values in the valence band there exist nine separate complexes consisting of 4 branches moreover, their symmetry in the Γ point is the same as the one calculated on the basis of the empty-lattice approximation, i.e., Eq. (2). In the $\Gamma - Z$ direction an intersection of branches can be found. The last two statements will be further elaborated on in the next section.

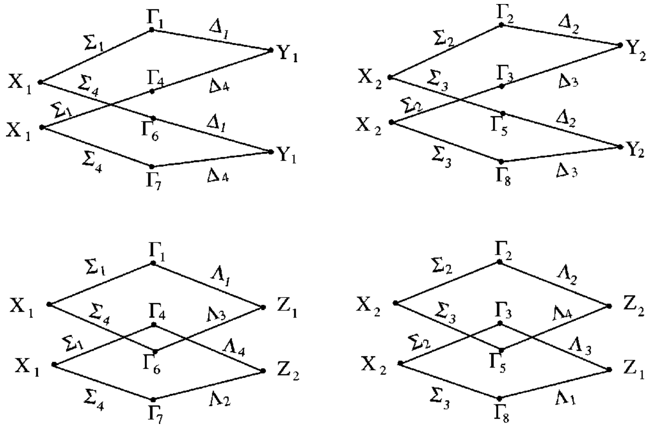

FIG. 5. Schemes of the elementary energy bands for the YAP crystal ($Pbnm$ space group). The sequence of states in the Γ point was chosen in an arbitrary way.

V. ELEMENTARY ENERGY BANDS IN THE BAND STRUCTURES OF THE YAP AND SbSI CRYSTALS

As was mentioned in the Introduction a concept of the elementary energy bands introduced by Zak has been widely developed in common publications of Zak and Michel. It should be emphasized that the elementary energy bands were obtained using a connection between extended functions and localized orbitals.

On the other hand, the authors of papers[37,22] considering an influence of the strong anisotropy of the SbSI crystal on its energy spectrum have reported that the band structure of this crystal is composed of the so-called minimal band complexes which reflect the Davydov splitting. It was also noted that the minimal band complexes have followed even from the empty lattice approximation which utilizes only the basic information concerning the semiconductor, its space symmetry group, and the existence of the forbidden gap. The localized Wannier functions do not appear in this approximation. To determine the aforementioned complexes the compatibility relations were used. The minimal band complex was defined as a set of the smallest number of connected bands in the certain high-symmetry points of the BZ obtained in accordance with the compatibility relations.

In spite of the above mentioned differences in the determining of the "elementary energy bands" and the "minimal band complexes," these two concepts are identical. Correspondingly, states of the energy spectrum, calculated in the empty-lattice approximation are contained in the elementary energy bands. A matter of primary importance is to assign a physical meaning to the introduced concepts.

Since the elementary energy bands correspond to the certain Wyckoff positions we check which positions can be attributed to those elementary energy bands which were obtained in Sec. III. Such analysis would remove ambiguity which appears when one of these positions has to be chosen. It is known that several kinds of Wyckoff positions are determined for every space symmetry group; in the case of the $Pnma$ group, there are 3 of them.[21,38]

Figures 5 and 6 present schemes of the elementary energy bands for the YAP and SbSI crystals constructed from states

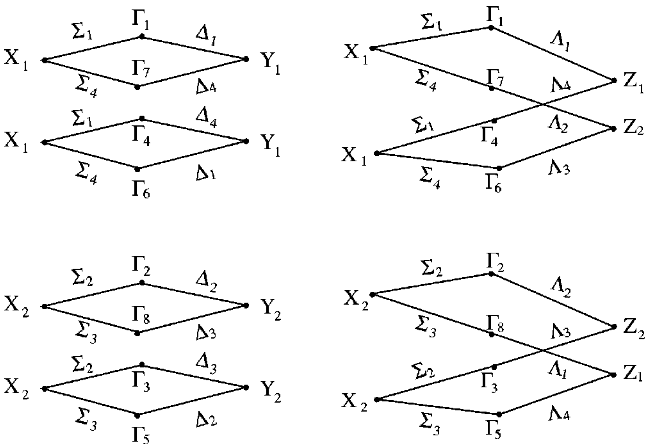

FIG. 6. Schemes of the elementary energy bands for the SbSI crystal (*Pnam* space group).

resulting from the calculations in the empty-lattice approximation (6) and (2) with the use of the compatibility relations for characters of irreducible representations for points located along the main directions in the BZ. It can be seen from these two figures that the elementary energy bands are composed of 4 branches for the symmetry group D_{2h}^{16} which describes the crystals under consideration. Moreover, the elementary energy bands are composed of 4 branches in all directions of the BZ. Constructing the elementary energy bands from four irreducible representations in the Γ point arising from calculations always shows an unavoidable crossing of branches in a certain direction of the BZ. As has been noted,[39] it is a direction which corresponds to a direction of the tight bond in strongly anisotropic crystals. In the case of the SbSI crystal, this is a direction along the chain of atoms of the crystal (the $\mathbf{a}_3$ direction).

The band structure of the SbSI crystal calculated in the previous section has demonstrated that the elementary energy bands ilustrated in Fig. 6 exist in the valence band of the crystal for low energy values. The unavoidable crossing of branches can be easily traced in the Γ–Z direction. The topology of the valence band branches for low energy values in the Γ–Y and Γ–Z directions agrees with predictions presented in Fig. 6. The elementary energy bands overlap for higher energies of the valence band, hence, analysis of the topology of branches is more difficult there. The YAP's crystalline structure does not exhibit a strong anisotropy of bondings, therefore, the intersections of branches appear in the electronic band structure along all the main directions of the BZ (Γ–X, Γ–Y, Γ–Z).

Now we shall turn to the discussion of Wyckoff positions for the D_{2h}^{16} group to which correspond the elementary energy bands from Figs. 5 and 6. The induced irreducible representations for all the little groups of the Wyckoff positions are described in the paper.[21] They are, however, specified for the D_{2h}^{16} group in the coordinate system of Pnma. Therefore, the representations in the Γ point contained in the elementary energy bands will be rewritten in this coordinate system. The representations (6) for the YAP crystal in the coordinate system *Pnma* are as follows:

$$7(\Gamma_1,\Gamma_8,\Gamma_4,\Gamma_5)+5(\Gamma_2,\Gamma_7,\Gamma_3,\Gamma_6). \tag{8}$$

By analogy, the representations for the SbSI crystal (2) can be represented in this system as

$$7(\Gamma_1,\Gamma_4,\Gamma_8,\Gamma_5)+2(\Gamma_2,\Gamma_3,\Gamma_7,\Gamma_6). \tag{9}$$

It can be found[21] that sets of irreducible representations (8) and (9) describing the elementary energy bands correspond to the initial Wyckoff position $c(x,1/4,z)$ (its multiplicity equals 4). In the coordinate systems of the YAP (*Pbnm*) and SbSI (*Pnam*) crystals, the coordinates of this initial position are $c(x,y,1/4)$. The coordinates of the all positions c for the symmetry group of the YAP crystal are as follows:

$$c_1(x,y,\tfrac{1}{4}),\quad c_2(x+\tfrac{1}{2},-y+\tfrac{1}{2},\tfrac{3}{4}),$$
$$c_3(-x+\tfrac{1}{2},y+\tfrac{1}{2},\tfrac{1}{4}),\quad c_4(-x,-y,\tfrac{3}{4}), \tag{10}$$

whereas for the symmetry group of the SbSI crystal,

$$c_1(x,y,\tfrac{1}{4}),\quad c_2(x+\tfrac{1}{2},-y+\tfrac{1}{2},\tfrac{1}{4}),$$
$$c_3(-x+\tfrac{1}{2},y+\tfrac{1}{2},\tfrac{3}{4}),\quad c_4(-x,-y,\tfrac{3}{4}). \tag{11}$$

A cross section of the valence electron density distribution which we have calculated for the $YAlO_3$ (YAP) crystal is presented in Figs. 7(a)–7(e). The positions of oxygen ions as well as dashed lines $z=1/4$ and $z=3/4$ corresponding to the Wyckoff position c are marked there, in addition to the remaining Wyckoff positions of the symmetry group *Pbnm*,

$$a_1(0,0,0),\quad a_2(\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}),\quad a_3(0,0,\tfrac{1}{2}),\quad a_4(\tfrac{1}{2},\tfrac{1}{2},0),$$
$$b_1(\tfrac{1}{2},0,0),\quad b_2(0,\tfrac{1}{2},\tfrac{1}{2}),\quad b_3(\tfrac{1}{2},0,\tfrac{1}{2}),\quad b_4(0,\tfrac{1}{2},0). \tag{12}$$

As can be seen from Figs. 7(a)–7(e), the electron density is concentrated only in those places which correspond to c_1, c_2, c_3, and c_4 positions. Hence, the existence of an apparent relation between a given Wyckoff position and the electron density distribution can be stated. On the other hand, a kind of elementary energy bands which is constructed on the basis of data following from the empty-lattice approximation with the account of the general data concerning a semiconductor corresponds to a given Wyckoff position. Therefore, the irreducible representations noticeable in the elementary energy bands correspond to the exactly determined Wyckoff position. It means that the former separate a given position from others. The considerations above demonstrate a deep relation between the elementary energy bands in the valence band and the general data concerning a crystal (semiconductor, dielectric).

With respect to the electron density distribution of the $YAlO_3$ crystal (Fig. 7) one can observe that oxygen ions attract electrons from outer shells of other atoms. Hence, the energy states of oxygen ions are responsible for creation of the valence band of the crystal. The results given in the paper[12] confirm this conclusion.

It is interesting to note that in a and b Wyckoff positions a concentration of the valence electron density is not ob-

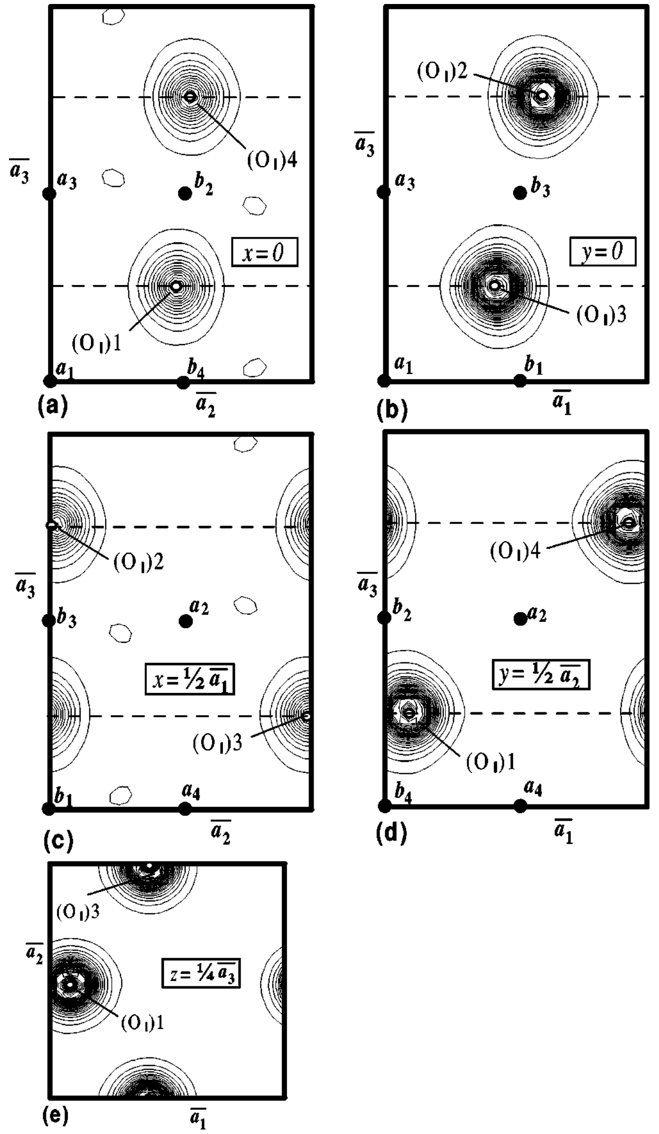

FIG. 7. Intersections of valence electron density distribution with planes (a) $x=0$; (b) $y=0$; (c) $x=\frac{1}{2}$; (d) $y=\frac{1}{2}$; (e) $z=\frac{1}{4}$ for the YAP crystal. Black dots denote the Wyckoff postions a_i and b_i, dashed lines correspond to the Wyckoff position *c*; circles denote oxygen atoms.

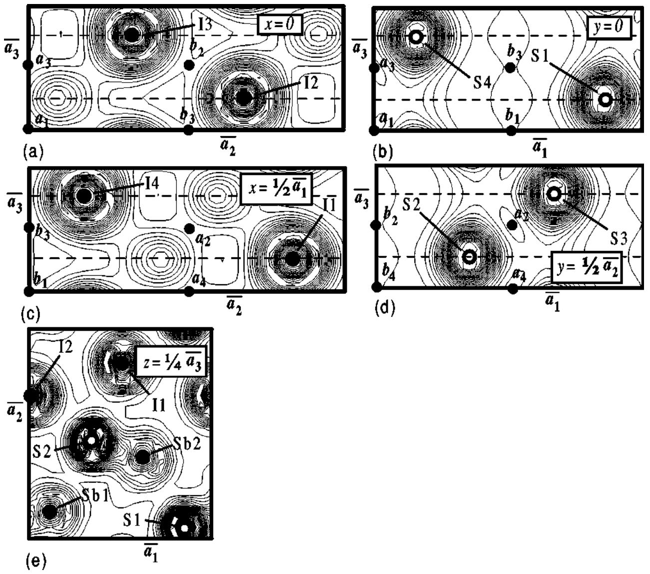

FIG. 8. Intersection of valence electron density distribution with planes (a) $x=0$; (b) $y=0$; (c) $x=\frac{1}{2}$; (d) $y=\frac{1}{2}$; (e) $z=\frac{1}{4}$ for the SbSI crystal. Positons of indium, sulfur, and antimony atoms are indicated.

served. These positions, in turn, relate to other sets of irreducible representations creating the elementary energy bands ($\Gamma_1,\Gamma_5,\Gamma_7,\Gamma_3$ and $\Gamma_2,\Gamma_6,\Gamma_8,\Gamma_4$) (Ref. 21) which do not result from calculations of the energy states in the empty-lattice approximation. Since four cations of aluminum are situated in the Wyckoff position *b*, it is possible that the elementary energy bands corresponding to this position may be located in the conduction band.

A similar analysis concerning the SbSI crystal was conducted in the paper. Figure 8 shows that the electron density distribution calculated for the SbSI crystal also coincides with the Wyckoff position *c*. In Figs. 8(a)–8(d) the dashed lines $z=1/4$, $z=3/4$ which correspond to this position are placed. Additionally, other Wyckoff positions a_i and b_i for the symmetry group $Pnam$ (of the SbSI crystal) are designated. Their coordinates are also given by Eq. (12). The largest contribution to the electron density distribution focused around *c* position is made by iodine and sulfur atoms.

The zth coordinate of all atoms which create the SbSI compound is equal to 1/4 or 3/4. Those atoms, therefore, occupy the positons in the unit cell which correspond to all mulitiplicities of the *c* (c_1, c_2, c_3, and c_4). In Fig. 8(e) the electron density distribution contributed by atoms situated in c_1 and c_2 positions is featured. This figure demonstrates that electrons of all atoms (Sb, S, and I) are involved in the creation of the valence band, though the contribution of electrons of the Sb atom is the smallest. This fact agrees with the first investigations on the bonding in the SbSI, from which it follows that the ionic-covalent bond between Sb and S is possible in this crystal. [40]

One should be aware that the elementary energy bands build every single-particle energy spectra. Therefore, they serve and are helpful to predict and to verify the topology of the band structure of crystals, e.g., with a large number of atoms in the unit cell. Accousto-optic family of crystals Tl_3AsS_4 belong also to the D_{2h}^{16} ($Pnma$) space symmetry group.[41] There are 32 atoms in the unit cell of these crystals. Using the empty-lattice approximation we have calculated that the valence band of these crystals is composed of the elementary energy bands with the following irreducible representations (in the Γ point),

$$12(\Gamma_1,\Gamma_4,\Gamma_5,\Gamma_8)+7(\Gamma_2,\Gamma_3,\Gamma_6,\Gamma_7). \tag{13}$$

They correspond to the Wyckoff position $c(x,1/4,z)$ in the unit cell where the structural unit AsS_4^{-3} is placed. The vibrational spectrum of this crystal has the following symmetry in the Γ point:

$$14(\Gamma_1(A_g)+\Gamma_4(B_{1u})+\Gamma_5(B_{2g})+\Gamma_8(B_{3u}))+10(\Gamma_2(A_u)$$
$$+\Gamma_3(B_{1g})+\Gamma_6(B_{2u})+\Gamma_7(B_{3g})). \tag{14}$$

As should be expected, the symmetry of the phonon spectrum is described by the representations which are present in the elementary energy bands Eq. (13).

The results of paper[42] confirm that the normal vibration of free complexes AsS_4^{-3} which were placed in the Tl_3AsS_4 crystal field split into two sets of vibrations with the symmetry: $(A_g, B_{2g}, B_{1u}, B_{3u})$ and $(B_{1g}, B_{3g}, A_u, B_{2u})$. These two sets were observed in the Raman or infrared spectra. Hence, we can conclude that the band structure of the Tl_3AsS_4 crystal which is yet unknown, will be composed of the elementary bands Eq. (13) and that the larges electron density distribution will be focused in the vicinity of the Wyckoff position c.

VI. CONCLUSIONS

The electronic band structure of the $YAlO_3$ (YAP) crystal calculated by means of the local density approximation (LDA) has been presented. The new calculations of the band structure of the SbSI crystal which is describable in terms of the same space symmetry group have been described. Our intention was not only to calculate the band structure but also to confirm our hypothesis that the main features of this structure can already be obtained on the basis of the general data concerning a crystal (semiconductor or dielectric).

The elementary energy bands can be obtained by a method differing from that of Refs. 1,2, namely, the empty-lattice approximation supplemented by the general data concerning a semiconductor. This method has been demonstrated in our analysis of the above mentioned crystals. It has been noticed that the elementary energy bands obtained in this way correspond to the exactly determined Wyckoff position in the unit cell. In this position an accumulation of the electron density originating from the selected anions of the considered compounds was observed.

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