Possibilities of the elementary energy bands concept to determine characteristics of crystals with phase transitions

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Abstract. It is demonstrated that the concept of the elementary energy bands can be used to predict a structural change of a crystal’s primitive cell during a phase transition without investigating this mechanism itself. Three examples of the phase transitions have been chosen: deformational phase transition occurring in GeTe (O\textsubscript{h}\textsuperscript{5}), pressure induced phase transition in ZnTe (T\textsubscript{d}\textsuperscript{2}) and induced by phonon-phonon interaction in SbSI (D\textsubscript{16h}). The discussed approach demands a knowledge about the space symmetry group of a crystal after phase transition.

1. Introduction

The concept of the elementary energy bands (EEBs), i.e. the smallest building bricks of the energy spectrum of a crystal has been obtained by means of two approaches. First, by induction of the band irreducible representations of the crystal’s symmetry group from the irreducible representations of the site-symmetry group of the Wyckoff position and taking into account the continuity property of \textbf{k} space \cite{1, 2, 3}. In the other approach the simplest solid state approximation for calculation of the crystal’s energy spectrum, i.e. the empty-lattice one, supplied by the symmetry description of the obtained energy states, has been used \cite{4, 5}. The latter approach led to the idea of ”minimal band complexes” that is identical with the ”elementary energy bands” concept. It has been demonstrated that the concept of the EEBs is useful to analyse the topologies of the valence band and of the phonon spectrum of semiconductors and their consequences on the physical properties of these crystals \cite{6, 7, 8}.

The background to apply this concept was a fact that, based upon the results of the empty-lattice approximation, one is able to distinguish the so-called ”actual” Wyckoff position among all Wyckoff positions assigned to the space group of a considered crystal. At the same time a hypothesis was presented that this actual Wyckoff position has a physical meaning, i.e. that the maximum of the spatial valence electron density distribution is focused in the unit cell of a crystal in the actual Wyckoff position. Owing to the idea concerning the physical meaning of the actual Wyckoff position, it has been demonstrated in particular, the way how to predict a type of chemical bonding for orthorhombic CdSb crystal described by the D\textsubscript{15h} space group \cite{7}.

The validity of such prediction has been confirmed for the classical Si semiconductor with the symmetry O\textsubscript{h}\textsuperscript{7}. It has been shown that for the A\textsuperscript{III}B\textsuperscript{V}-type crystals there exists the so-called itinerant Wyckoff position that is the actual one for all these crystals having T\textsubscript{d}\textsuperscript{2} symmetry and
mixed ionic-covalent bonding [9]. Further analysis of this issue showed that the concept of the EEBs can be applied also to the artificial periodic system like superlattices [9].

Since the relation between the reciprocal \( k \) and the direct \( r \) spaces that is contained in the EEBs concept is used also for the description of phase transitions which crystals undergo, we investigate in this paper if this concept can be used to describe structural changes caused by phase transitions of different natures. We analyse as an example the deformational phase transition in GeTe, the pressure induced one (ZnTe) and induced by phonon-phonon interaction (SbSI).

2. Evolution of the EEBs of crystals during phase transitions

In Ref. [10] we analysed a possibility to use the concept of the EEBs for the description of a change of the primitive cell’s volume of the GeTe crystal during the deformational phase transition. Below we report the most essential steps of this approach that will be the background for the further analysis.

It is known that at high temperatures the GeTe ferroelectric has an NaCl-type structure with the symmetry \( O_{h}^{5} (Fm\overline{3}m) \) space group [11, 12, 13, 14]. At lower temperatures, phase transitions to the ferroelectric rhomboedral – \( C_{3v}^{5} (R3m) \)– and antiferroelectric orthorhombic – \( D_{16}^{2h} (Pnma) \) modifications are observed in these compounds which are accompanied by a severe distortion of NaCl-structure, caused by electron-phonon coupling [15, 16]. The GeTe is the only representative of \( A_{IV}B_{VI} \)-type crystals that exists in both the rhombohedral and orthorhombic phases under normal pressure [17]. The orthorhombic phase of GeTe is stabilized by pressure and non-stoichiometric deficiency of Ge atoms, the latter leading to the existence of free carriers in the material. Various reasons for the origin of the orthorhombic phase in GeTe were proposed [17, 18] and it was suggested also that the transition from the cubic to the orthorhombic modification in GeTe is accompanied by a fourfold enlargement of the initial cubic cell [19]. We demonstrate that this conclusion can be drawn automatically by applying the EEBs concept.

Calculating the energy states of the cubic GeTe at high symmetry points \( \Gamma, X(0,0,\pi/a), L(\pi/a,\pi/a,\pi/a) \) \((a \text{ is the lattice constant})\) in the empty-lattice approximation, then applying the compatibility relations and taking into account that 10 valence electrons of GeTe will occupy 5 states in the closed valence band, we conclude that the resulting band representation of the dimensionality 5 that describes this valence band consists of the following three EEBs:

\[
X_{1} - \Gamma_{1} - L_{1}, \quad X_{1} - \Gamma_{1} - L_{4}, \quad X_{4} \oplus X_{10} - \Gamma_{10} - L_{1} \oplus L_{5}. \tag{1}
\]

From Ref. [20] follows that the EEB with \( X_{1} - \Gamma_{1} - L_{1} \) symmetry corresponds to the Wyckoff position \( a(0,0,0) \) of the space group \( O_{h}^{5} \), while two others with the symmetry \( X_{1} - \Gamma_{1} - L_{4} \) and \( X_{4} \oplus X_{10} - \Gamma_{10} - L_{1} \oplus L_{5} \) correspond to the Wyckoff position \( b(1/2,1/2,1/2) \). Therefore we regard these positions as the actual Wyckoff positions for the cubic GeTe phase. When the cubic GeTe crystal undergoes a phase transition to the orthorhombic modification with the symmetry \( D_{16}^{2h} \), then the band representation of dimensionality 5 describing the symmetry of the whole valence band of cubic GeTe is also transformed. If the primitive cell of cubic GeTe is \( n \)-times enlarged in the orthorhombic modification, then the number of valence states in the corresponding band structure is also \( n \)-times increased. Therefore, the number of valence states in the orthorhombic GeTe is equal to \( 5n \). Since the four-dimensional irreducible band representations correspond to all Wyckoff positions of the \( D_{16}^{2h} \) space group [20], one can conclude that these \( 5n \) states should create \( l \) EEBs having four branches, i.e.

\[
5n = 4l. \tag{2}
\]
In Eq. (2) \( n \) and \( l \) are integers, and hence the primitive cell is at least \( n = 4 \)-times larger in the orthorhombic phase than in the cubic one, and its valence band is composed of at least 5 EEBs having 4 branches. Calculations of the energy states in the empty-lattice approximation for orthorhombic GeTe with the experimental values of the lattice constants [15] show that its closed valence band is composed of five 4-branch EEBs with the following symmetry in \( \Gamma \):

\[
4(\Gamma_1 \oplus \Gamma_4 \oplus \Gamma_5 \oplus \Gamma_8) + 1(\Gamma_2 \oplus \Gamma_3 \oplus \Gamma_6 \oplus \Gamma_7).
\]

They correspond to the actual Wyckoff position \( c(x, 1/4, z) \) of the \( D_{2h}^{16} \) space group. Since this position is a plane perpendicular to the \( b \)-axis of the orthorhombic cell of GeTe, the ionicity of bonding in this modification should be lower than that of the cubic one, where the maximum of the valence electron density coincides with positions of each of the atoms in the unit cell, which are, at the same time, the actual Wyckoff positions \( a \) and \( b \).

Our \textit{ab initio} band structure calculations of cubic GeTe and rhombohedral GeS being a prototype of GeTe in its orthorhombic modification presented in [10] confirm the predicted symmetry of the corresponding valence bands described by Eqs. (1) and (3), and the resulting maxima of the spatial valence electron density distribution are observed at the actual Wyckoff positions \( a \) and \( b \) for the \( \Omega^b \) space group as well as at the \( c \) position for the \( D_{2h}^{16} \) space group.

Hence, we demonstrated that the concept of the EEBs discussed in the empty-lattice approximation allowed to predict the proper change of the volume of a primitive cell of the GeTe crystal during the deformaional phase transition. Below we discuss in an analogous way structural changes which take place in the ZnTe crystal described by the \( T_d^3 \) space group.

Experimental and theoretical investigations of ZnTe confirmed the existence of phase transitions: the zinc blende structure ZnTe-I (\( T_d^3 \)) \( \rightarrow \) the trigonal cinnabar structure ZnTe-II (\( D_{3h}^4 \)) at 8.06 GPa as well as ZnTe-I (\( T_d^3 \)) \( \rightarrow \) the orthorhombic structure ZnTe-III (\( D_{2h}^{17}; \text{Cmcm} \)) at 10.24 GPa [21, 22, 23]. We demonstrated in Ref. [9] that the actual Wyckoff position for \( T_d^3 \) symmetry crystals is the itinerant Wyckoff position \( e(x, x, x) \), to which corresponds the 3-branch EEB of the symmetry \( \Gamma_1 \oplus \Gamma_{15} - X_1 \oplus X_3 \oplus X_5 - 2L_4 \oplus L_3 \). The irreducible band representation corresponding to this EEB is 4-dimensional and 8 valence electrons of ZnTe occupy 4 valence bands. At the symmetry decrease of this crystal caused by a phase transition, one should consider first a relation at the \( \Gamma \) point between representations present in the EEB of \( T_d^3 \) as well as of \( D_{3h}^4 \) and \( D_{2h}^{17} \) space groups, respectively. The three-dimensional \( \Gamma_{15} \) representation, having as a basis \( x, y, z \) functions, transforms in the case of the \( D_3^4 \) group to the direct sum of two- and one-dimensional representations: \( \Gamma_3(x, y) \oplus \Gamma_2(z) \), where in parenthesis the corresponding basis functions are displayed, while \( \Gamma_1 \) from \( T_d^3 \) transforms into \( \Gamma_1 \left( D_{3h}^4 \right) \). Since 3-dimensional irreducible band representations creating the EEBs correspond to both Wyckoff positions \( a \) and \( b \) of the \( D_{3h}^4 \) space group, the following relation should be fulfilled at the \( n \)-fold enlargement of the unit cell to the cinnabar structure:

\[
4n = 3l, \tag{4}
\]

where \( l \) denotes the number of sorts of the EEBs in the valence band of the trigonal ZnTe-II phase. Eq. (4) is fulfilled only for the 3-fold enlargement of the primitive cell’s volume as compared to the ZnTe-I, at \( n \) and \( l \) being integer. Then the valence band of trigonal ZnTe-II with the cinnabar structure and \( D_{3h}^4 \) symmetry is composed of 4 EEBs.

At the symmetry decrease from \( T_d^3 \) up to \( D_{2h}^{17} \), the three-dimensional \( \Gamma_{15} \) representation transforms into \( \Gamma_4(x) \oplus \Gamma_6(y) \oplus \Gamma_8(z) \), and the one-dimensional \( \Gamma_1 \) representation transforms into an analogous one of the \( D_{2h}^{17} \) space group. Then, at least one EEB containing \( \Gamma_1 \) representation, being a representation of the ground state, should occur in the valence band of ZnTe-III, as well as other EEBs containing \( \Gamma_4, \Gamma_6, \Gamma_8 \). Table 1 presents the symmetry of the EEBs in the \( \Gamma \) point that correspond to the particular Wyckoff positions of the \( D_{2h}^{17} \) space group.

A relation between the corresponding irreducible band representations of the \( T_d^3 \) and \( D_{2h}^{17} \) space groups is as follows.
We demonstrated in Ref. [6] that the valence band of the SbSI para-phase (D16h) is composed of sets of the 4-branch EEBs with the following symmetry in the Γ point $7(\Gamma_1 \oplus \Gamma_4 \oplus \Gamma_6 \oplus \Gamma_7) + 2(\Gamma_2 \oplus \Gamma_3 \oplus \Gamma_5 \oplus \Gamma_8)$. The space symmetry group of ferro-phase after the phase transition is C2V, that is a subgroup of D16h, therefore, based upon the isomorphic relation between the corresponding representations in the Γ point, we can conclude that the valence band of the SbSI ferro-phase is composed of the EEBs with symmetry $7(\Gamma_1 \oplus \Gamma_4 \oplus \Gamma_3 \oplus \Gamma_2) + 2(\Gamma_2 \oplus \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_1)$. Three conclusions follow directly from this equation. Since the topology of the EEBs and their number remains the same, the number of valence electrons in the unit cell of the SbSI ferro-phase is also the same. Therefore, the number of atoms in the unit cell (as well as its size) do not change after the phase transition. If follows from the last statement that the considered phase transition should be accompanied by the presence of the soft mode at $k = 0$. The presence of such mode in the center of the Brillouin zone was investigated experimentally and reported in Refs. [25, 26, 27].

Table 1. The symmetry of the EEBs in the Γ point for the D172h space group. All representations are one-dimensional [20].

| Wyckoff position | Symmetry of the EEBs in the Γ point |
|------------------|-------------------------------------|
| a(0, 0, 0)       | $\Gamma_1 \oplus \Gamma_3$, $\Gamma_2 \oplus \Gamma_4$, $\Gamma_5 \oplus \Gamma_7$, $\Gamma_6 \oplus \Gamma_8$ |
| b(0, 1/2, 0)     | $\Gamma_1 \oplus \Gamma_3$, $\Gamma_2 \oplus \Gamma_4$, $\Gamma_5 \oplus \Gamma_7$, $\Gamma_6 \oplus \Gamma_8$ |
| c(0, y, 1/4)     | $\Gamma_1 \oplus \Gamma_6$, $\Gamma_2 \oplus \Gamma_5$, $\Gamma_3 \oplus \Gamma_8$, $\Gamma_4 \oplus \Gamma_7$ |
| d(1/4, 1/4, 0)   | $\Gamma_1 \oplus \Gamma_3 \oplus \Gamma_5 \oplus \Gamma_7$, $\Gamma_2 \oplus \Gamma_4 \oplus \Gamma_6 \oplus \Gamma_8$ |
| e(x, 0, 0)       | $\Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3 \oplus \Gamma_4$, $\Gamma_5 \oplus \Gamma_6 \oplus \Gamma_7 \oplus \Gamma_8$ |
| f(0, y, z)       | $\Gamma_1 \oplus \Gamma_3 \oplus \Gamma_6 \oplus \Gamma_8$, $\Gamma_2 \oplus \Gamma_4 \oplus \Gamma_5 \oplus \Gamma_7$ |
| g(x, y, 1/4)     | $\Gamma_1 \oplus \Gamma_4 \oplus \Gamma_6 \oplus \Gamma_7$, $\Gamma_2 \oplus \Gamma_3 \oplus \Gamma_5 \oplus \Gamma_8$ |

where, as before, $n$ denotes multiplicity of the enlargement of a initial unit cell, $l$ is the number of sorts of the EEBs in the obtained valence band, and $s$ is a dimension of the corresponding irreducible band representation. For the Wyckoff positions $a$, $b$, and $c$ $s$ is equal to 2 and from Eq. (5) follows that only for $n = 2$, i.e. for the twofold enlargement of the unit cell one obtains $l = 4$ EEBs that contain all necessary representations in the valence band of ZnTe-III, originating from representations $\Gamma_1$ and $\Gamma_{15}$ ($T_2^3$). Correspondingly, for the Wyckoff positions $d$, $e$, $f$, and $g$ the equation holds true

$$4n = 4l,$$

which again for $n = 2$ leads to the valence band composed of $l = 2$ EEBs. Hence, one can conclude that the twofold enlargement of the initial primitive cell is necessary at the phase transition of ZnTe-I involving the symmetry decrease from $T_d^3$ up to $D_{2h}^{17}$. This, as well as the former conclusion concerning the phase transition ZnTe-I → ZnTe-II, agrees with the recent theoretical calculations on stability of the ZnTe polymorphs conducted in the framework of the density functional theory under nonlocal approximation [24].

The last type of phase transition that is discussed here is the phase transition induced by phonon-phonon interaction occurring in a chain orthorhombic SbSI crystal with the symmetry D16h (Pnam) (para-phase). After the phase transition, ferroelectric phase of SbSI exhibits C2V, (Pna2) space-group symmetry. It follows from experimental data, that this phase transition takes place at $T = 22^\circ C$ without a change of the unit cell’s volume [25]. This fact can be easily explained by means of the EEBs concept.

We demonstrated in Ref. [6] that the valence band of the SbSI para-phase (D16h) is composed of sets of the 4-branch EEBs with the following symmetry in the Γ point $7(\Gamma_1 \oplus \Gamma_4 \oplus \Gamma_6 \oplus \Gamma_7) + 2(\Gamma_2 \oplus \Gamma_3 \oplus \Gamma_5 \oplus \Gamma_8)$. The space symmetry group of ferro-phase after the phase transition is C2V, that is a subgroup of D16h, therefore, based upon the isomorphic relation between the corresponding representations in the Γ point, we can conclude that the valence band of the SbSI ferro-phase is composed of the EEBs with symmetry $7(\Gamma_1 \oplus \Gamma_4 \oplus \Gamma_3 \oplus \Gamma_2) + 2(\Gamma_2 \oplus \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_1)$. Three conclusions follow directly from this equation. Since the topology of the EEBs and their number remains the same, the number of valence electrons in the unit cell of the SbSI ferro-phase is also the same. Therefore, the number of atoms in the unit cell (as well as its size) do not change after the phase transition. If follows from the last statement that the considered phase transition should be accompanied by the presence of the soft mode at $k = 0$. The presence of such mode in the center of the Brillouin zone was investigated experimentally and reported in Refs. [25, 26, 27].
3. Summary
By the discussion of three phase transitions of different nature that occur in the crystals chosen for consideration, we demonstrated that the application of the EEBs concept is a fast method for the prediction of the structural changes which unit cells of these crystals undergo during phase transitions, as well as for the prediction of changes in the topology of the corresponding band structures, without a necessity to consider the mechanisms of these transitions themselves. The only information necessary for this approach is the knowledge about the space symmetry group of the given crystal’s phases.

References
[1] Zak J 1980 Phys. Rev. Lett. 45 1025
[2] Zak J 1982 Phys. Rev. Lett. 25 1344
[3] Michel L and Zak J 1999 Phys. Rev. B 59 5998
[4] Bercha D M, Nebola I I and Bercha I V 1978 Fiz. Tverd. Tela 20 1320
[5] Bercha D M and Mitin O B 1987 Fiz. Tekh. Polup. 21 1508
[6] Bercha D M Rushchanskii K Z, Sznajder M, Matkovskii A and Potera P 2002 Phys. Rev. B 66 195203
[7] Bercha D M, Slipukhina I V, Sznajder M and Rushchanskii K Z 2004 Phys. Rev. B 70 235206
[8] Sznajder M, Rushchanskii K Z, Kharkhalis L Yu and Bercha D M 2006 Phys. Stat. Sol. (b) 243 592
[9] Bercha D M, Glukhov K E and Sznajder M 2007 Phys. Stat. Sol. (b) 244 1318
[10] Bercha D M, Kharkhalis L Yu, Slipukhina I V and Sznajder M 2007 Phase Transitions 80 39
[11] Korzhuev M A, Petrova L I, Demenskiy G K, Teplov O A 1981 Fiz. Tverd. Tela 23 3387
[12] Abrikosov N K, Korzhuev M A and Shelimova L E 1977 Neorg. Mater. 13 1757
[13] Karbanov S G Zlomanov V P and Novoselova A V 1968 Doklady AN SSSR 182 832
[14] Rabe K M and Joannopoulos J D 1987 Phys. Rev. B 36 3319
[15] Karbanov S G, Zlomanov V P and Novoselova A V 1969 Neorg. Mater. 5 1171
[16] Bigyava A D, Gabedava A A and Shvangiradze E D 1981 Neorg. Mater. 17 2162
[17] Khachaturyan K A 1987 Phys. Rev. B 36 4222
[18] Vengalis B Yu 1978 Fiz. Tverd. Tela 20 3621
[19] Volkov B A and Pankratov O A 1978 J. Exper. Teor. Fiz. 75 1362
[20] Kovalev O V 1993 Representations of the Crystallographic Space Groups. Irreducible Representations, Induced Representations and Correspresentations, ed H T Stokes and D M Hatch (Gordon and Breach, Amsterdam), p. 390
[21] Nelmes R J and Mc Mahon M I 1998 Semiconductors and Semimetals Vol. 54, ed R K Willardson and E R Weber (Academic, New York) p. 145.
[22] Lee G D and Ihm J 1996 Phys. Rev. B 53 7622
[23] Cote M, Zakharov O, Rubio A and Cohen M 1997 Phys. Rev. B 55 13025
[24] Franco R, Sanches P M and Recio J M 2003 Phys. Rev. B 68 195208
[25] Fridkin V M 1976 Ferroelectrics-Semiconductors (Nauka, Moscow), p. 408
[26] Pierrefeu A, Steigmeier E F, Dorner B 1977 Phys. Stat. Sol. (B) 80 167
[27] Pouget J P, Shapiro S M, Nassau K 1979 J. Phys. Chem. Sol. 40 267