SIMPLE INVERTED BAND STRUCTURE MODEL
FOR CADMIUM ARSENIDE (Cd₃As₂)

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The development of a simple Hamiltonian yielding the inverted band structure of Cd₃As₂ in the 4mm symmetry low-temperature phase is proposed. The presented theory takes into account the spin-orbit interaction and tetragonal distortion of lattice in the low symmetry. The authors obtain k-linear terms in the band structure and therefore a splitting in k-space of spin degenerate energy bands. The reported band model contains only one new crystal field parameter in addition to well-known Kildal’s set. The first evaluation of this shows that (0.028 < d < 0.072) eV using optical absorption edge data. The finite width of the anisotropic heavy and light hole bands is pointed out.

1. INTRODUCTION

Cd₃As₂ (alias cadmium arsenide, or tricadmium diarsenide), is a compound with extraordinary physical properties. First, it is a representative of the family of materials (α-Sn, HgTe, HgSe, CdₓHg₁-xTe solid solutions, etc.) with inverted band structure, i.e. where energy gap ε₉ < 0.

Only Cd₃As₂ (in ordered crystal modifications) belongs to tetragonal symmetry, in contrast to other compounds of this group. Hence, Cd₃As₂ is the only representative of these, which have the complete splitting of the valence band top at k=0.

The polymorphism of cadmium arsenide is well known [1, 2]. Its metallic sub-lattice contains exactly the quarter of vacant points. If the distribution of these vacancies is random, then we deal with disordered crystal, having cubic m₃m symmetry class. Whereas the different ways of ordering cause the lowering of crystal point symmetry to either 4/mmm or even 4mm tetragonal classes. These phases are different mainly due to the presence or absence of the symmetry center, respectively. Thereafter we shall use the short international notation for point symmetry classes.

Nevertheless, it should be noted that real tetragonal ordered crystals are not so far from cubic symmetry. The vacancies ordering process mainly affects the metallic sub-lattice, whereas the cubic face centered (FCC) sub-lattice of As is left almost undisturbed. The tetragonal distortion of the lattice is rather small: η = c/2a ≤ 1.006, here c, a - are lattice parameters. Therefore, the tetragonal cell of partly ordered crystals can be considered as a slightly stretched aggregate of few, almost identical cubic cells [1].

Bodnar [3] first suggested the adequate model of the energy band structure near k=0 for this compound. It did not take into account the structural peculiarities, mentioned above. Bodnar pointed out, that he dealt with 4mm symmetry tetragonal crystals. Nevertheless, his final approximations, which were caused by difficulties of calculations [3], led in fact to essential increasing of the symmetry of Bodnar’s Hamiltonian [4]. That is why the wide range of physical phenomena, caused by the symmetry center absence, e.g. oscillatory effects [5], combined resonance [6], circular photogalvanic effect [7], etc, cannot be described within limits of this model. Furthermore, Bodnar’s model completely ignores the tetragonal distortion of lattice. In spite of its small magnitude, the influence of this factor on the band structure may be clearly observable.

The main aim of presented paper is to obtain such a Hamiltonian and dispersion law, that correctly take into account the symmetry and real crystal structure of this material on the one hand and on the other hand contain some minimal set of parameters.
2. THEORY

The initial Hamiltonian in $kp$-approximation near $k=0$ has the following form [8]:

$$H = \frac{p^2}{2m} + V + H_{kp} + H_{so}, \quad (1)$$

where the operators of kinetic energy, crystal potential, $kp$-interaction and $k$-independent spin-orbit interaction are presented as separate parts of Hamiltonian respectively. Small part of spin-orbit interaction, which is dependent on wave vector $k$, is neglected. Following the Kildal’s approach [8], let us present the potential as $V = V_0 + V_{cr}$, where $V_0$ has cubic symmetry and $V_{cr}$ is the part of potential caused by the tetragonal distortion of the lattice as well as by the ordering of the vacancies. We assume the following Hamiltonian for the unperturbed problem:

$$H_0 = \frac{p^2}{2m} + V_0, \quad (2)$$

All the other terms of the Hamiltonian (1) are treated as perturbation given by

$$H' = V_{cr} + \frac{\hbar}{m} (k \cdot p) + \frac{\hbar}{4m^2 c^2} \left[ [V V \times p] \sigma \right]. \quad (3)$$

Eigenfunctions of $H_0$ can be written in the form: $S, X, Y, Z$ are periodic Kohn-Luttinger amplitudes, which are transformed like $s$ and $p$ atomic functions under operations of cubic $m3m$ symmetry, and $\alpha, \beta$ are spin quantum numbers.

In $m3m$ symmetry the function $S$ belongs to the irreducible representation $\Gamma_1$ whereas $X, Y, Z$ functions belong to $\Gamma_{15}$ (we shall use the notation [9] for irreducible representations of point groups). Since these functions are normalized on the volume of the cubic but not of the tetragonal unit cell, the next thing to do is the taking into account the difference between tetragonal and cubic coordinate systems, i.e. the tetragonal distortion of the lattice. Polubotko [10] described this procedure. It leads to appearing of term more in $H'$ operator (3). Assuming, that the main crystal axis is directed along Oz-axis, this new term can be written as $H_{cr} = (\eta^2 - 1)\frac{p_z^2}{2m}$. Moreover, it leads to some transformation of the $kp$- and spin-orbit interaction terms of the equation (3) too. In the first case we should substitute $\frac{\hbar}{m} k_z p_z$ by $\frac{\hbar}{m} \eta^2 k_z p_z$ and in the second case we should multiply the terms containing $\sigma_x$ and $\sigma_y$ by $\eta$.

We would like to work using first order perturbation theory and focus our attention to the transformational properties of $V_{cr}$ and $H_{cr}$ terms in the perturbed Hamiltonian $H'$. Primary, let us consider 4/mmm phase of this material. The potential $V_{cr}$ (hence and the total potential $V_0 + V_{cr}$) is transformed according to identical irreducible representation $\Gamma_1$ of the point symmetry group 4/mmm. Since the point symmetry group of unperturbed Hamiltonian $H_0$ is the cubic group $m3m$ we need the knowledge about the representation of this group, which according to the potential $V_0 + V_{cr}$ (and $V_{cr}$) is transformed. In other words, it is necessary to find the representation of $m3m$ group, which is induced by the identical representation $\Gamma_1$ of its subgroup 4/mmm, for this purpose. It may be shown that this reducible representation is direct sum of two irreducible representations: $\Gamma_1 \oplus \Gamma_{12}$ of $m3m$. The potential $V_0$, which has symmetry of scalar in cubic group $m3m$, is transformed according to the identical $\Gamma_1$ representation evidently. Hence, $V_{cr}$ is transformed in
accordance with two-dimensional irreducible representation $\Gamma_{12}$. It means that $V_{cr}$ can be decomposed into a linear combination of $d_1$ and $d_2$ basis functions of $\Gamma_{12}$ representation:

$$V_{cr} = j_1 d_1 + j_2 d_2, \quad (4)$$

where $j_1, j_2$ are coefficients of the combination. As far as the potential $V_{cr}$ has the symmetry of 4/mmm subgroup of m3m, it ought to be invariant regarding to all symmetry operators of this subgroup. Therefore, it must be:

$$D^{\Gamma_{12}}(g)V_{cr} = V_{cr} \quad (\forall g \in 4/mmm), \quad (5)$$

where $D^{\Gamma_{12}}(g)$ is matrix of symmetry operator $g$ in $\Gamma_{12}$ irreducible representation. Note also, that $D(g)d_i = \sum_j D_{ij}(g)d_j$, at $k,l = 1,2$.

As it was assumed above, the main crystal axis is directed along Oz-axis. This permits us to fix one of three 4/mmm subgroups, which are belonging to m3m parent group. If we additionally accept that the function $d_1$ is transformed like $2z^2 - x^2 - y^2$, whereas $d_2$ like $x^2 - y^2$ then one half of 4/mmm subgroup’s elements will be represented by the unit matrix 

$$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix},$$

while another half will be represented by the matrix 

$$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$ 

The substitution of the above matrix into expression (5) leads, taking into account equation (4), to the following conditions: $j_1 \neq 0, j_2 = 0$. Thus, $V_{cr} = j_1 d_1$.

Now we can find the matrix of $V_{cr} + H_{cr}$, using basis functions of the Hamiltonian $H_0$ mentioned above. The symmetry selection rules give only one non-zero matrix element of the operator $V_{cr}$:

$$\langle X | d_1 | X \rangle = \langle Y | d_1 | Y \rangle = -\langle Z | d_1 | Z \rangle / 2 = V_1 \quad (6)$$

Since the operator $H_{cr}$ is transformed like $z^2$, i.e. like the function $d_1$, conditions (6) are also true for matrix elements of this operator. If we introduce now the crystal-field splitting parameter (it is so-called Kildal’s parameter [8] obviously) in such a form:

$$\delta = \langle X | V_{cr} + H_{cr} | X \rangle - \langle Z | V_{cr} + H_{cr} | Z \rangle, \quad (7)$$

then the matrix of $V_{cr} + H_{cr}$ based on $S, X, Y, Z$ functions with the identical spin quantum numbers will be:

$$V_{cr} + H_{cr} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \delta / 3 & 0 & 0 \\ 0 & 0 & \delta / 3 & 0 \\ 0 & 0 & 0 & -2\delta / 3 \end{pmatrix} \quad (8)$$

Further, let us consider the 4mm phase without center of symmetry. In this case the potential $V_{cr}$ can be written as $V_{cr} = V'_{cr} + V''_{cr}$, where the potentials $V'_{cr}$ and $V''_{cr}$ have 4/mmm and 4mm symmetry respectively. The representation of the group $m3m$, which is induced by the identical representation of its subgroup 4mm, is the direct sum of three irreducible representations : $\Gamma_1 \oplus \Gamma_{12} \oplus \Gamma_{15}$ of $m3m$. It means that perturbation $V''_{cr}$ can be decomposed into linear combination of basis functions of $\Gamma_{12}$ irreducible representations, which are transformed like the three components of a polar vector $(x, y, z)$:

$$V''_{cr} = j_1 x + j_2 y + j_3 z \quad (9)$$
The invariance of $V''_{cr}$ with respect to matrices $D^{\Gamma_1}_{\Gamma_2}(g)$, which belong to the $\Gamma_{15}$ irreducible representations of $m3m$, leads to the conditions: $j_1 = j_2 = 0$, $j_3 \neq 0$. If we denote the only one non-zero matrix element of the operator $V''_{cr}$ as

$$d = j_3 \langle S|Z\rangle,$$  \hspace{1cm} (10)

then the matrix $V''_{cr}$ on the basis of $S, X, Y, Z$ functions with the identical spin quantum numbers will be:

$$V''_{cr} = \begin{pmatrix} 0 & 0 & 0 & d \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ d & 0 & 0 & 0 \end{pmatrix}$$  \hspace{1cm} (11)

The selection rules for matrix elements of $k\cdot p$ and spin-orbit interaction operators (3) show that there are only two independent matrix elements of these operators, one for each of two matrices. They are the well-known Kane’s parameters with $P$ the interband matrix element of the momentum operator and $\Delta$ the spin-orbit splitting of the valence band [11].

Taking into account (8, 11) and fixing the zero on the energy scale as it was done in [8], we can write the 8x8 Hamiltonian $H = H_0 + H'$ matrix for 4mm phase like this:

$$H = \begin{pmatrix} \varepsilon_g & iP_k & iP_y & i\eta^2 P_k + d & 0 & 0 & 0 & 0 \\ -iP_k & -\Delta/3 & -i\Delta/3 & 0 & 0 & 0 & \eta\Delta/3 \\ -iP_y & i\Delta/3 & -\Delta/3 & 0 & 0 & 0 & -i\eta\Delta/3 \\ -i\eta^2 P_k + d & 0 & 0 & -\delta - \Delta/3 & 0 & -\eta\Delta/3 & i\eta\Delta/3 & 0 \\ 0 & 0 & 0 & 0 & \varepsilon_g & iP_k & iP_y & i\eta^2 P_k + d \\ 0 & 0 & 0 & -\eta\Delta/3 & -iP_k & -\Delta/3 & i\Delta/3 & 0 \\ 0 & 0 & 0 & -i\eta\Delta/3 & -iP_y & -i\Delta/3 & -\Delta/3 & 0 \\ 0 & \eta\Delta/3 & i\eta\Delta/3 & 0 & -i\eta^2 P_k + d & 0 & 0 & -\delta - \Delta/3 \end{pmatrix}$$  \hspace{1cm} (12)

here $\varepsilon_g$ is the band gap energy.

The exact dispersion law may be obtained out of the Hamilton matrix (12), using the method described in detail in [4]. This equation can be expressed in the following compact form:

$$\gamma(\epsilon) = f_1(k_x^2 + k_y^2) + f_2 k_z^2 \pm 2 f_3 \sqrt{k_x^2 + k_y^2},$$  \hspace{1cm} (13)

here

$$f_1 = P^2 \left((\epsilon + \Delta/3)(\epsilon + \delta + \Delta/3) - \eta^2 \Delta^2 / 9\right)$$ \hspace{1cm} (14)

$$f_2 = \eta^4 P^2 \delta(\epsilon + 2\Delta/3)$$ \hspace{1cm} (15)

$$f_3 = (1/3)\eta ePd\Delta$$ \hspace{1cm} (16)

$$\gamma = \epsilon \left[\epsilon - \varepsilon_g \left(\epsilon + 2\Delta/3)(\epsilon + \delta + \Delta/3) - 2\eta^2 \Delta^2 / 9\right) - d^2(\epsilon + 2\Delta/3)\right]$$ \hspace{1cm} (17)

and $\epsilon$ - is the energy of carriers. The two signs ("+" and "-"), in equation (13) correspond to two branches of energy spectrum. Such a lifting of two-fold spin degeneracy at $k_z = \sqrt{k_x^2 + k_y^2} \neq 0$ is caused by simultaneous existence of non-zero spin-orbit interaction and tetragonal field with no symmetry center as it is seen from Fig.1. It may be pointed out, that a dispersion law similar to (13) was found in wurtzite-type bulk crystals and in some two-dimensional systems (e.g. heterojunctions and inversion layers) [5].

Equation (13) can be rewritten in the spherical coordinate system as:
where
\[ \lambda(\varepsilon, \theta) = \frac{\sqrt{f_1 \sin^2 \theta + f_2 \cos^2 \theta} + 2 f_3 \sin \theta \cos \theta}{f_1 \sin^2 \theta + f_2 \cos^2 \theta} \]
\[ \mu(\varepsilon, \theta) = \frac{\gamma^2}{f_1 \sin^2 \theta + f_2 \cos^2 \theta} \]

Assume \( d = 0, \eta = 1 \) in (13-20), we turn to the Kildal equations [8]. If \( \delta = 0 \) too, then we deal with the classical equations of Kane [11] model.

3. DISCUSSION
The parameter \( d \) introduced in equation (10) is equal to zero in the 4/mmm phase, but not in 4mm. It ought to be \( d = 0; \delta = 0; \eta = 1 \) in the cubic m\( \overline{3} \)m phase too. Thus equations (13, 20) turn to the well-known Kane’s expression, which is correct for describing of Cd\(_3\)As\(_2\) disordered cubic modification.

The most suitable numerical values of the parameters \( \varepsilon_g, P, \Delta, \delta \) for Cd\(_3\)As\(_2\) [12] are \( \varepsilon_g = -0.13 \text{ eV}, \ P = 7.0 \cdot 10^{-10} \text{ eV} \cdot m, \ \Delta = 0.3 \text{ eV}, \ \delta = 0.085 \text{ eV} \). Naturally, the value of the parameter \( d \) is unknown. However, this parameter permits to describe energy band spin splitting as well as wide range of other physical phenomena mentioned above, caused by absence of a symmetry center. That is why we are going below to attempt for the first time to estimate the value of this parameter.

According to [13] the actual arrangement of the four energy levels for Cd\(_3\)As\(_2\) at \( k=0 \) is: \( 0 > \varepsilon_1 > \varepsilon_s > \varepsilon_2 \). In our model, these levels are determined by the equation: \( \gamma(\varepsilon) = 0 \). Here \( \gamma(\varepsilon) \) is a polynomial of fourth degree with respect to the carriers’ energy, as it is seen from expression (17). The root equal to zero corresponds to the top of the heavy-hole valence band. The location of other
three roots \((\varepsilon_1, \varepsilon_s, \varepsilon_2)\) depends on the parameters of the model, and can be found from the cubic equation. The formal expression for \(d^2\) from (17) is the following:

\[
d^2 = \frac{(\varepsilon - \varepsilon_g)((\varepsilon + 2\Delta/3)(\varepsilon + \delta + \Delta/3) - 2\eta^2\Delta^2/9)}{\varepsilon + 2\Delta/3}
\]  

(21)

Let \(\varepsilon_1 \to 0\), then the energy level arrangement transforms to: \(0 \approx \varepsilon_1 > \varepsilon_s > \varepsilon_2\). Hence, the condition \(d^2(0) = d^2(\varepsilon_1)_{\varepsilon_1=0}\) corresponds to this limit. One can obtain under the conditions \(\varepsilon = \varepsilon_1 \approx 0\) from (21) the next expression:

\[
d_{\text{max}}^2 \approx -\varepsilon_g \left[\delta + \frac{(1 - \eta^2)\Delta}{3}\right]
\]  

(22)

Thus, expression (22) presents the upper estimation for the parameter \(d\), which is still compatible with experimentally observed [13] energy level arrangement. Therefore, it follows \(d_{\text{max}} \approx 0.072 \text{ eV}\).

The lower estimation for \(d\) may be obtained from experimental data [14]. At low temperature the optical interband absorption coefficient shows clearly two steps due to direct transitions from holes sub-bands to the conduction band (see Fig.1). Such peculiarities of the absorption coefficient were observed only for ordered sample (40 hours of heat treatment at 150\(^\circ\)C in vacuum), i.e. for sample with 4mm-symmetry (with no symmetry center). Note, that the parameters of the sample investigated in [14] are very close to ours: \(\varepsilon_g = -0.12 \text{ eV}, \Delta = 0.3 \text{ eV}, \ P = 7 \cdot 10^{-10} \text{ eV} \cdot \text{m}, \ \varepsilon_1 = -0.03 \text{ eV}\).

The energy gap between two absorption edges from [14] is approximately equal to \((0.06 \pm 0.012) \text{ eV}\) for the sample with \(n \approx 2 \cdot 10^{18} \text{ cm}^{-3}\) (\(\varepsilon_F \approx 0.18 \text{ eV}\)).

Unfortunately, the authors of [14] wrote nothing about the sample orientation. Since spin splitting of the bands is essentially dependent on \(\theta\) (where \(\theta\) is an angle between \(k_z\)-direction and given
direction in reciprocal space) we could find only the lower estimation for \( d_{\text{min}} \) supposing, that \( \theta = \pi / 2 \). We found that \( d_{\text{min}} \approx 0.028 \, eV \). Therefore, our estimation for this parameter for the low temperature 4\( mm \) phase of cadmium arsenide is now the following: \( (0.028 < d < 0.072) \, eV \).

It is worth to note that the spin splitting of sub-bands is larger for the light hole valence band (s-like), than for conduction band (p-like). The Fig.2 shows the distribution of the allowed and forbidden states on the \( (\varepsilon, \theta) \) plane. The finite width and anisotropy of the light hole band as well as so-called “heavy hole band” are clearly visible. The so-called “heavy hole band” is rather some narrow band of heavy electron states, which are adjacent to the bottom of the conductivity band. The calculation was executed assuming \( d = 0.05 \, eV \).

The minimum of the conduction band is located at \( k=0 \), whereas the other bands reach their maximums on the so-called circles of extremes [5] within the limits of our model. We hope that further experimental investigations enable to verify the value of band structure parameter \( d \), hence the band structure of this material, more exactly.

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