

STRUCTURE OF INORGANIC COMPOUNDS

Dedicated to the memory of G.A. Kiosse

Crystal Structure of α''' -(Zn_{1-x}Cd_x)₃As₂ ($x = 0.26$)

G. F. Volodina^a, V. S. Zakhvalinskii^b, and V. Kh. Kravtsov^a

^a Institute of Applied Physics, Academy of Sciences of Moldova, Academiei st. 5, MD2028 Chisinau, Moldova

^b Belgorod State University, ul. Pobedy 85, Belgorod, 308015 Russia

e-mail: volodinagal@rambler.ru

Received June 28, 2012

“...the arrangement of large anions is rather uniform: it obeys the law of close packing of uniform layers. This law yields generally one of two packing types: cubic or hexagonal. At the same time, the variety of the mineral crystal world, the so-called “mineralogy game,” is reduced to different ways of occupying voids in uniform close packing and to various corresponding patterns.”

(N.V. Belov [1])

Abstract—Single crystals of the α''' -phase of (Zn_{1-x}Cd_x)₃As₂ solid solution ($x = 0.26$) have been prepared and investigated by X-ray diffraction analysis. The tetragonal unit-cell parameters are found to be $a = b = 8.5377(2)$ Å, $c = 24.0666(9)$ Å, sp. gr. $I4_1/amd$, $Z = 16$. Zn and Cd atoms in the crystal statistically occupy three symmetrically independent positions in the mirror planes and are tetrahedrally coordinated by arsenic atoms. (Zn,Cd) tetrahedra share edges to form a three-dimensional structure framework. The α''' -phase is geometrically related to the fluorite structure. The character of arrangement of tetrahedral vacancies in fluorite-like unit cells is revealed. Chains of tetrahedral vacancies form microchannels oriented parallel the a and b axes, which pierce the three-dimensional structure framework at different levels along the c axis. The structure of α''' -Cd₃As₂ crystals is found to be similar to that of α''' -(Zn_{0.74}Cd_{0.26})₃As₂.

DOI: 10.1134/S1063774513040226

INTRODUCTION

The number of physicochemical, electric, and optical properties of semiconductor compounds $A_3^{\text{II}}B_2^{\text{V}}$ ($A - \text{Zn, Cd}; B - \text{P, As}$) and their solid solutions have made for their wide use in micro- and optoelectronics applications. These compounds, being of great interest, are investigated in different aspects [2–6]. The unlimited mutual solubility of $A_3^{\text{II}}B_2^{\text{V}}$ compounds allows one to prepare materials with tailored properties by varying the composition of solid solutions. In this paper we report the results of determining the structure of a single crystal of three-component solid solution (Zn_{0.74}Cd_{0.26})₃As₂ (**I**).

EXPERIMENTAL

Sample Preparation

Binary compounds were previously synthesized from pure (99.999%) Zn, Cd, and As materials in

graphitized and evacuated quartz ampoules. The thus obtained Zn₃As₂ and Cd₃As₂ compounds were subjected to distillation in the vapor phase under a temperature gradient in evacuated quartz ampoules and then used to prepare (Zn_{1-x}Cd_x)₃As₂ solid solutions.

The crystals under study were grown by the modified Bridgman method. A stoichiometric mixture of the initial Zn₃As₂ and Cd₃As₂ compounds (in a ratio of 3 : 1), placed in an evacuated graphitized quartz ampoule surrounded by an additional vacuum jacket, was heated to 900°C, kept at this temperature for 4 h, and then slowly cooled with a temperature gradient (1.5 K/cm) at a rate of 5 K/h to 720°C. Further cooling to room temperature was carried out with the furnace switched off. We obtained ingots with a volume of single-crystal blocks of about 1 cm³. Their compositions and structural states were monitored by X-ray spectroscopy (on a QUANTA 600 3D electron microscope) and X-ray diffraction analysis (on a DRON-UM1 diffractometer). Microprobe elemental analysis revealed a correspondence between the charge composition and the single crystal grown. The X-ray pow-

Table 1. Crystallographic characteristics, experimental details, and the results of structure refinement for $\alpha''\text{-(Zn}_{0.74}\text{Cd}_{0.26})_3\text{As}_2$

| | |
|--|---|
| <i>M</i> | 383.19 |
| Crystal system, space group, <i>Z</i> | Tetragonal, <i>I4₁/amd</i> , 16 |
| <i>a</i> , <i>c</i> , Å | 8.5377(2), 24.0666(9) |
| <i>V</i> , Å ³ | 1754.25(8) |
| <i>D_x</i> , g/cm ³ | 5.804 |
| Radiation; λ, Å | MoK _α , 0.71073 |
| μ, mm ⁻¹ | 30.540 |
| <i>T</i> , K | 293 |
| Crystal size, mm | 0.20 × 0.10 × 0.10 |
| Diffractometer | Xcalibur E |
| Scan mode | ω |
| Absorption correction | Semiempirical (from equivalents) |
| <i>T_{min}</i> , <i>T_{max}</i> | 0.1502, 0.0640 |
| θ _{max} , deg | 29.97 |
| Ranges of indices <i>h</i> , <i>k</i> , <i>l</i> | −10 ≤ <i>h</i> ≤ 12, −6 ≤ <i>k</i> ≤ 11, −24 ≤ <i>l</i> ≤ 33 |
| Number of reflections: measured/unique (<i>N₁</i>), <i>R_{int}</i> /with <i>I</i> > 2σ(<i>I</i>) (<i>N₂</i>) | 2421/717, 0.0275/521 |
| Refinement technique | Full-matrix least squares based on <i>F</i> ² |
| Number of parameters refined | 36 |
| <i>S</i> for <i>F</i> ² | 1.000 |
| <i>R₁</i> / <i>wR₂</i> for <i>N₁</i> | 0.0379/0.0410 |
| <i>R₁</i> / <i>wR₂</i> for <i>N₂</i> | 0.0242/0.0401 |
| Extinction ratio | 0.000580(16) |
| Δρ _{min} /Δρ _{max} , e/Å ³ | −0.977/0.865 |
| Programs | SHELX97 [7] |

der diffraction pattern of the ingot sample coincides with that calculated from the single-crystal data, which confirms the homogeneous composition of the blocks.

X-Ray Experiment and Structure Refinement

The X-ray diffraction data were obtained for a fragment of single-crystal ingot 0.2 × 0.1 × 0.1 mm in size at room temperature on an Xcalibur E diffractometer equipped with a two-dimensional EOS CCD detector and a graphite monochromator (MoK_α radiation). The data were collected and processed using the CrysAlis^{Pro} program (Oxford Diffraction Ltd., Version 1.171.33.66). The measured reflection intensities were refined taking into account the Lorentz factors and polarization and absorption corrections. The structure was resolved by the direct method and refined within the anisotropic approximation of thermal atomic displacements using the SHELX97 software [7]. The crystallographic data and experimental details are listed in Table 1. $\alpha''\text{-(Zn}_{0.74}\text{Cd}_{0.26})_3\text{As}_2$ crystals are interpreted within the sp. gr. *I4₁/amd*. Zn and Cd atoms are statistically distributed in the structure over three symmetrically independent positions. The individual occupancy of each position was refined along with other structural parameters under the assumption that the total occupancy of Cd and Zn atoms in each position is equal to that of the corresponding Wyckoff position of the space group. The atomic coordinates, the corresponding Wyckoff position, its occupancy by each metal atom, and the atomic displacements are given in Table 2. The structural data were deposited with the Inorganic Crystal Structure Database (ICSD no. CSD 424703).

Table 2. Coordinates of basis atoms, position occupancies, and equivalent atomic displacements in the $\alpha''\text{-(Zn}_{0.74}\text{Cd}_{0.26})_3\text{As}_2$ structure

| Atom, occupancy | Wyckoff position | <i>x</i> | <i>y</i> | <i>z</i> | <i>U_{eq}</i> , Å ² × 10 ³ |
|------------------------------|------------------|-----------|------------|-----------|--|
| Zn1/Cd1 0.364(7)/0.636(7) | 16 <i>h</i> | 0 | −0.0354(1) | 0.0709(1) | 22(1) |
| Zn2/Cd2 0.942(6)/0.058(6) | 16 <i>h</i> | 0.2544(1) | 0.2500 | 0.0512(1) | 25(1) |
| Zn3/Cd3 0.902(6)/0.098(6) | 16 <i>h</i> | 0.5 | −0.0316(1) | 0.0680(1) | 24(1) |
| As1 1.0 | 8 <i>e</i> | 0.5 | −0.25 | 0.0006(1) | 17(1) |
| As2 1.0 | 8 <i>e</i> | 0 | 0.25 | 0.0038(1) | 20(1) |
| As3 1.0 | 16 <i>g</i> | 0.2592(1) | 0.0092(1) | 0.125 | 19(1) |

RESULTS AND DISCUSSION

In all $A_3^{\text{II}}B_2^{\text{V}}$ compounds (A is Zn or Cd and B is P or As) and solid solutions based on them, nonmetal atoms form a somewhat distorted cubic close packing, while metal atoms occupy tetrahedral voids in it. When describing the structures of these compounds, one can generally select a common fragment: a “cell” of defect antifluorite, in which Ca atoms of the CaF₂ structure are replaced with B anions, while A cations occupy positions of F atoms. Two tetrahedral voids in each cell are vacant. $A_3^{\text{II}}B_2^{\text{V}}$ compounds and their solid solutions form a number of polymorphic modifications upon heating: α -, α' -, α'' -, and α''' -phases, which are stable at room temperature, and high-temperature β -phases. In the cubic structures of β -modifications with a fluorite-type cell, metal atoms statistically occupy tetrahedral voids; in tetragonal structures of α -phases, metal atoms are ordered: two tetrahedral voids located on the solid diagonal of the fluorite cell remain unoccupied. The mutual arrangement of these cells determines the structural features of all α -phases of $A_3^{\text{II}}B_2^{\text{V}}$ compounds [5, 8–13].

We determined the atomic structure of the (Zn_{0.74}Cd_{0.26})₃As₂ single crystal. Due to the concentration composition, this compound can be assigned, according to the classification of [3, 5], to the α''' -modification in the polymorphic series of (Zn_{1-x}Cd_x)₃As₂ solid solutions ($0.17 < x < 0.56$) at a temperature of 298 K. The tetragonal unit-cell parameters of crystal I are as follows: $a = b = 8.5377(2)$ Å, $c = 24.0666(9)$ Å, sp. gr. $D_{4h}^{19} - I4_1/amd$, and $Z = 16$. The structure of the α''' -phase I is also geometrically related to the fluorite structure. Here, As atoms occupy sites of a slightly distorted fcc cell with a side a' equal to half of the [110] diagonal of the tetragonal cell of I ($a' = 6.037$ Å), which is very close to a quarter of the parameter c ($c' = 6.017$ Å). The tetragonal unit cell of the α''' -phase contains eight such “fluorite cells”. The a' and b' axes make an angle of 45° with the a and b axes of the tetragonal cell. The coordinates of the atoms forming a pseudocubic “fluorite cell” (1) (Fig. 1) are listed in Table 3. The (x, y, z) atomic coordinates for the tetragonal cell are translated to the (x', y', z') coordinates for the “fluorite cell” using the inverse transposed transition matrix $(M^{-1})' = 1 \ -1 \ 0/1 \ 1 \ 0/0 \ 0 \ 4$ with allowance for the displacement of the coordinate origin to the point O (0.75, -0.25, -0.5): $x' = x - y + 0.75$; $y' = x + y - 0.25$, and $z' = 4z - 0.5$. The atomic coordinates for the ideal CaF₂ structure are given in the parentheses. The (0.25, 0.25, 0.25) and (0.75, 0.75, 0.75) cation positions remain vacant. As in the α -Cd₃As₂ (II) structure [9], the maximum deviation ($\Delta x', \Delta y' = \pm 0.11$ Å) of the fcc cell from the ideal position was observed for the As3 atom located near the

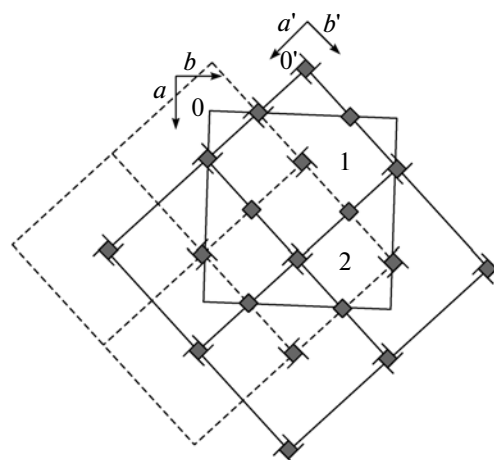


Fig. 1. Geometric relationship between the tetragonal cell of α''' -(Zn_{0.74}Cd_{0.26})₃As₂ with selected “fluorite cells” (versions 1 and 2) in the projection along the [001] direction. The vertical symmetry axes of the sp. gr. $I4_1/amd$ are indicated.

fourfold screw axis; metal atoms are displaced to the nearest tetrahedral void by 0.27–0.35 Å.

To describe the structure of the α''' -phase I, we use the schemes applied to an analysis of the Cd₃As₂ struc-

Table 3. Coordinates of atoms forming a fluorite-like cell in the α''' -(Zn_{0.74}Cd_{0.26})₃As₂ structure (version 1 in Fig. 1)

| Atom | x' | y' | z' |
|---------|---------------|---------------|---------------|
| As3 | 1.00 (1.0) | 0.0184 (0.0) | 0.0 (0.0) |
| | 0.0 (0.0) | -0.0184 (0.0) | 0.0 (0.0) |
| | 0.0 (0.0) | 1.0184 (1.0) | 0.0 (0.0) |
| | 1.0 (1.0) | 0.9816 (1.0) | 0.0 (0.0) |
| | 0.0184 (0.0) | 0.0 (0.0) | 1.0 (1.0) |
| | 0.9816 (1.0) | 0.0 (0.0) | 1.0 (1.0) |
| | -0.0184 (0.0) | 1.0 (1.0) | 1.0 (1.0) |
| | 1.0184 (1.0) | 1.0 (1.0) | 1.0 (1.0) |
| As1 | 0.50 (0.5) | 0.0 (0.0) | 0.4976 (0.5) |
| | 1.00 (1.0) | 0.50 (0.5) | 0.5024 (0.5) |
| As2 | 0.00 (0.0) | 0.50 (0.5) | 0.5152 (0.5) |
| | 0.50 (0.5) | 1.00 (1.0) | 0.4848 (0.5) |
| Zn1/Cd1 | 0.2854 (0.25) | 0.7854 (0.75) | 0.780 (0.75) |
| | 0.2146 (0.25) | 0.7146 (0.75) | 0.22 (0.25) |
| Zn2/Cd2 | 0.2544 (0.25) | 0.2456 (0.25) | 0.7048 (0.75) |
| | 0.7544 (0.75) | 0.7456 (0.75) | 0.2952 (0.25) |
| Zn3/Cd3 | 0.7816 (0.75) | 0.2816 (0.25) | 0.772 (0.75) |
| | 0.7184 (0.75) | 0.2184 (0.25) | 0.228 (0.25) |
| | (0.25) | (0.25) | (0.25) |
| | (0.75) | (0.75) | (0.75) |

Note: the atomic positions of ideal fluorite structure are given in the parentheses.

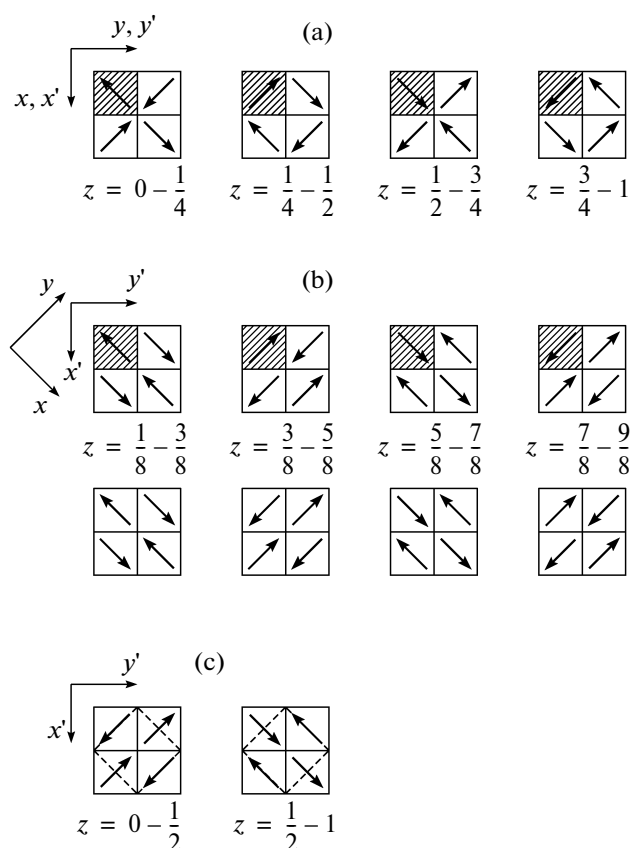


Fig. 2. Layer-by-layer projections of “fluorite cells” on the x' , y' plane in the crystal structures of (a) α - Cd_3As_2 , (b) α''' - $(\text{Zn}_{0.74}\text{Cd}_{0.26})_3\text{As}_2$ (the upper and lower rows correspond to versions 1 and 2 of the cell choice (see Fig. 1)), and (c) α'' - Cd_3As_2 . Dotted lines indicate the tetragonal-cell axes. Arrows indicate the positions of tetrahedral vacancies in the solid diagonal of the cube and are directed from top to bottom.

tures in [8, 9]. Let us consider the “fluorite cell” layers in the projection on the $a'b'$ plane and the arrangement of tetrahedral vacancies therein. As in α -phase **II**, there are four such layers along the z axis. A tetragonal cell of compound **II** contains 16 fluorite-like cells. The axis directions of tetragonal and fluorite-like cells coincide. The relationship between these two structures, according to [9], is shown in Fig. 2a.

The cell volume of α''' -phase **I** corresponds to eight “fluorite cells”; however, for convenience of comparison with α -phase **II**, we selected 16 cells (four per layer) (Fig. 1). Their occupation scheme is shown in Fig. 2b. A comparison of the figures shows that both structures contain a column of four “fluorite cells” located along the z axis, where metal atoms and, correspondingly, unoccupied tetrahedral voids are arranged in the same way (hatched squares in the schemes). This column is schematically shown in Fig. 3.

Different sets of symmetry elements for the spatial groups $I4_1/cd$ in α -phase **II** and $I4_1/amd$ in α''' -phase **I**

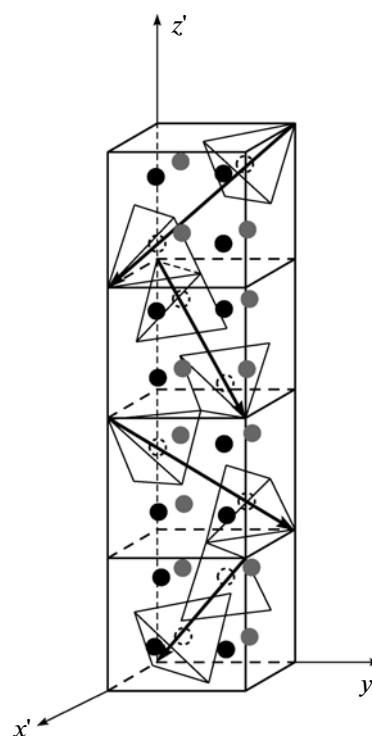


Fig. 3. Schematic diagram of occupation of a “fluorite-cell” column of the common structural fragment of α - Cd_3As_2 and α''' - $(\text{Zn}_{0.74}\text{Cd}_{0.26})_3\text{As}_2$ crystals: dark circles—metal atoms in the foreground, bright circles—metal atoms in the background, and open circles—tetrahedral vacancies. The centers of As atoms are located at the vertices of cubes and tetrahedra.

orient this column in different ways in the crystal space. These columns in the structure of α -phase **II** have symmetries of the right- and left-handed fourfold screw axes in checkerboard order. All columns in α''' -phase **I** have identical symmetry of either left- or right-handed fourfold screw axes, depending on the choice of “fluorite cells” (1 or 2, respectively) (Fig. 1).

The results of the first structural interpretation of Cd_3As_2 (**III**) crystals ($a = b = 8.95 \text{ \AA}$, $c = 12.65 \text{ \AA}$, sp. gr. $P4_2/nmc$) were reported in [8, 9]. The scheme of structure **III** shown in Fig. 2c differs from that for structure **II** but coincides with the structural fragments of the α''' -phase of the crystal under study; here, the axes of fluorite-like and tetragonal cells also make an angle of 45° . It was shown in [10, 11] that crystals **III** are isomorphic in the high-temperature (stable in the temperature range of $405\text{--}940^\circ\text{C}$) α''' -phase, which can also exist at room temperature if there is a low concentration of impurities or lattice defects. An interpretation of the crystal structure of α''' -phase **I** confirms the assumptions [3, 5] of the structural relationship between α'' - and α''' -phases of $A_3^{\text{II}}B_2^{\text{V}}$ compounds and the increase in the parameter c by a factor of 2 at the $\alpha'' \rightarrow \alpha'''$ transition.

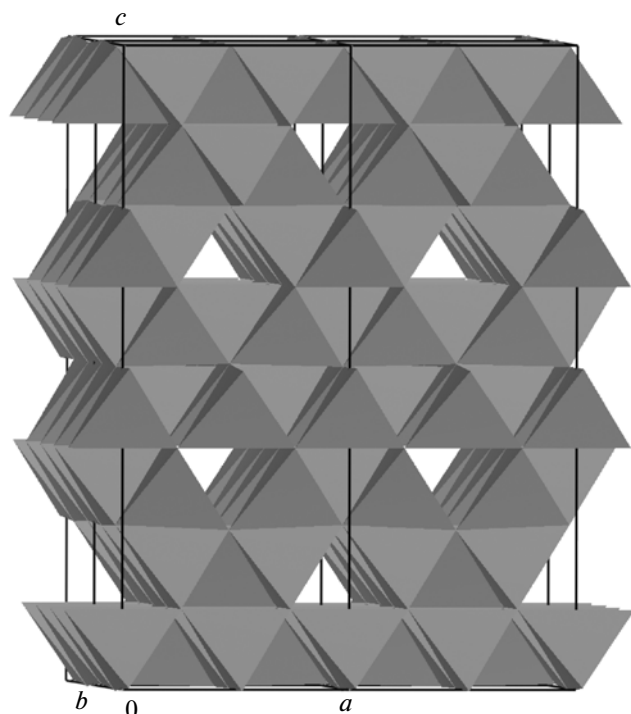


Fig. 4. General view of the $\alpha'''-(\text{Zn}_{0.74}\text{Cd}_{0.26})_3\text{As}_2$ structure. Metal atoms coordinated by As atoms are shown as tetrahedra.

Metal atoms in crystal structure **I** are located in tetrahedra with the intrinsic symmetry of the m mirror plane. They share edges to form a three-dimensional structural framework, which is pierced by microchannels formed by chains of tetrahedral vacancies; these microchannels are oriented parallel to the a and b axes and located at different levels along the c axis (Fig. 4). The metal–As and As–As interatomic distances in

Table 4. Interatomic distances in (Zn, Cd)-tetrahedra of the $\alpha'''-(\text{Zn}_{0.74}\text{Cd}_{0.26})_3\text{As}_2$ structure

| Atoms | Distance, Å | Atoms | Distance, Å |
|--------------------------|---------------|----------------------|---------------|
| Zn1/Cd1–As2 | 2.9228(7) | As2–As3 | 4.1983(6) × 2 |
| As2 ^{a*} | 2.5679(8) | As2–As2 ^a | 4.2728(1) |
| As3 | 2.5950(5) × 2 | As3–As2 ^a | 4.4052(7) × 2 |
| | | As3–As3 ^b | 4.4250(9) |
| Zn2/Cd2–As1 ^c | 2.4391(8) | As2–As3 | 4.1983(6) × 2 |
| As2 | 2.4529(8) | As3–As3 ^d | 4.1126(9) |
| As3 | 2.7178(5) × 2 | As3–As1 ^c | 4.1947(7) × 2 |
| | | As2–As1 ^c | 4.2702(1) |
| Zn3/Cd3–As1 | 2.4709(9) | As1–As3 | 4.2527(6) × 2 |
| As1 ^c | 2.9164(8) | As1–As1 ^c | 4.2689(1) |
| As3 | 2.4966(5) × 2 | As3–As1 ^c | 4.1947(7) × 2 |
| | | As3–As3 ^e | 4.1126(9) |

* Symmetry code a: $-x, -y, -z$; b: $-y - 1/4, x - 1/4, -z + 1/4$; c: $-x + 1, -y, -z$; d: $y + 1/4, -x + 3/4, -z + 1/4$; e: $-y + 3/4, x - 1/4, -z + 1/4$.

tetrahedra (see Table 4) are close to those in the α -, α'' - Cd_3As_2 [9, 10] and α -, α' - Zn_3As_2 [13] structures.

With allowance for the isostructurality of polymorphic modifications of $A_3^{\text{II}}B_2^{\text{V}}$ compounds (A is Zn or Cd and B is P or As) and their solid solutions it can be assumed that similar to $\alpha'''-(\text{Zn}_{0.74}\text{Cd}_{0.26})_3\text{As}_2$ structure have three component $\alpha'''-(\text{Zn}_{1-x}\text{Cd}_x)_3\text{P}_2$ solid solutions found in the Cd–Zn–As–P systems [3].

Yakimovich et al. [2] noted that the α''' -phase is formed only upon the mutual replacement of metal atoms in $A_3^{\text{II}}B_2^{\text{V}}$ structures (the mutual replacement of P and As does not lead to its formation). The reason is that the structural transformations in $A_3^{\text{II}}B_2^{\text{V}}$ compounds are accompanied by a change in the arrangement of cation vacancies due to the transition of metal atoms to the nearest tetrahedral void [12]. The presence of metal atoms of two types in a certain ratio leads to the formation of the α''' -phase, which should be considered a superstructure with respect to the α'' -phase.

ACKNOWLEDGMENTS

This study was supported by the Project CSSDT 11.817.05.03a (Republic of Moldova) and state contract no. P895 (Russian Federation).

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Translated by A. Sin'kov