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X-ray Diffraction Study of the Cu_2Se–In_2Se_3–Cr_2Se_3 System near $CuInCr_2Se_5$

A. S. Antsyshkina, G. G. Sadikov, T. I. Koneshova, and V. S. Sergienko
Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,
Leninskii pr. 31, Moscow, 119991 Russia
e-mail: antas@igic.ras.ru

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Abstract—The structure of three compounds in the Cu_2Se–In_2Se_3–Cr_2Se_3 system near $CuInCr_2Se_5$ is determined by single-crystal x-ray diffraction: $CuInCr_4Se_8$ (**I**), $Cu_2In_2Se_4$ (**II**), and $Cu_{0.5}In_{0.5}Se$ (**III**). **I** has a cubic (spinel type) structure: $a = 10.606(4)$ Å, $Z = 4$, sp. gr. $F\bar{4}3m$. **II** has a pseudotetragonal (sphalerite type) structure: $a = 5.774(2)$ Å, $c = 11.617(6)$ Å. The structure of **II** was solved in a reduced unit cell with $a = 5.774(2)$ Å, $b = 5.774(2)$ Å, $c = 7.095(6)$ Å, $\alpha = 113.95(5)°$, $\beta = 113.95(5)°$, $\gamma = 90.00(4)°$, $Z = 1$, sp. gr. $P1$. **III** has a triclinic cell (disordered structure of **II**): $a = 4.088(1)$ Å, $b = 4.091(2)$ Å, $c = 4.101(1)$ Å, $\alpha = 60.05(1)°$, $\beta = 60.08(1)°$, $\gamma = 89.98(4)°$, $Z = 1$, sp. gr. $P1$. The Cu and In atoms in **I** sit in inequivalent tetrahedral sites, and the Cr atoms reside in octahedral interstices of the close packing of Se atoms. The bond lengths are In–Se = 2.538(6), Cr(1)–Se(1) = 2.514(7), Cr(1)–Se(2) = 2.576(8), and Cu–Se = 2.437(5) Å. In **II**, all of the atoms sit in tetrahedral sites; the mean bond lengths are In–Se = 2.578(6) and Cu–Se = 2.44(1) Å. In **III**, the Cu and In atoms are fully disordered in the same tetrahedral site; the mean Cu(In)–Se bond length is 2.508(6) Å.

INTRODUCTION

The compounds existing in the Cu_2Se–In_2Se_3–Cr_2Se_3 system have not yet been studied in sufficient detail. In particular, crystal-chemical data (bond lengths, coordination and valence states of atoms) for these compounds are missing. At the same time, these compounds are known to be high-temperature magnetic semiconductors [1–4] and may, therefore, be of practical interest.

In this work, we report results of an x-ray diffraction (XRD) study of single crystals with the nominal composition $CuInCr_2Se_5$. XRD examination of crystal fragments showed that the crystals consisted of two phases, $CuInCr_4Se_8$ (**I**) and $Cu_2In_2Se_4$ (**II**), which were reported earlier to result from $CuInCr_2Se_5$ decomposition [3].

EXPERIMENTAL

The samples we used in XRD studies were dark brown with metallic luster, irregularly shaped, no greater than 0.02–0.05 mm in size.

Intensity data for structural analysis of **I** (four samples; here, we present data for one of them) and **II** were collected on an Enraf-Nonius CAD-4 diffractometer at 20°C (MoK_α radiation, graphite monochromator, $\theta/2\theta$ scan mode, $\theta_{max} = 28°$–$30°$).

The structures of **I** and **II** were solved by the direct method. In structure refinement, we used a full-matrix least squares technique, with anisotropic thermal parameters (for **I**, the structures of the four samples were refined independently).

Compound **I** has a cubic structure: $a = 10.606(4)$ Å, $V = 1193.0(2)$ Å^3, $M = 1018$, $F(000) = 1784$, $\rho_{calc} = 5.67$ g/cm^3, $\mu_{Mo} = 31.5$ mm^{-1}, $Z = 4$, sp. gr. $F\bar{4}3m$ (no. 217).

The final refinement statistics for **I**: $R_1 = 0.0431$, $wR_2 = 0.1181$ for 148 reflections considered observed on the criterion $F_0 \geq 4\sigma(F_0)$; $R_1 = 0.1145$, $wR_2 = 0.1809$ for 248 measured reflections; GOF = 0.866, 13 adjustable parameters, $\Delta\rho_{max} = 4.92$, $\Delta\rho_{min} = -2.84$ e/Å^3. In addition, the structure was refined in sp. gr. $Fd3m$ (no. 227) (**IV**) (see below for details).

Crystalline phases similar to **II** were described earlier in [5–8]. The tetragonal cell parameters reported in those works agree with our results: $a = 5.774(4)$ Å, $c = 11.617(6)$ Å. However, refinement in the space group $I\bar{4}2d$ (no. 122), proposed in [5–8], showed a displacement of the Se atom from the one-parameter position 8*d* by 0.15 Å along the *b* axis.

The structure of **II** can be solved in the lower symmetry space group $P\bar{4}2c$ (no. 112). The Cu and In atoms then reside each in two twofold positions, one position occupied by one type of atom (2*b* and 2*d*, respectively), and the other occupied by a random mixture of atoms (2*e* and 2*f*). The corresponding bond distances are In(1)–Se = 2.600 Å, Cu(1)–Se = 2.409 Å, In(2)–Se = 2.517 Å, and Cu(2)–Se = 2.502 Å.

Table 1. Atomic position coordinates and isotropic thermal parameters (U_{eq}) in the structures of **I**, **II**, and **III**

Atom	*x*	*y*	*z*	U_{eq}, Å^2
		I		
In(1)	0	0	0	0.015(2)
Se(1)	0.1169(3)	0.3832(3)	0.1169(3)	0.013(2)
Se(2)	0.1380(4)	–0.1380(4)	0.1380(4)	0.014(1)
Cr(1)	0.1201(6)	0.6201(6)	0.1201(6)	0.008(1)
Cu(1)	0.25	0.25	0.25	0.012(4)
		II		
In(1)	0.5335(5)	0.9343(4)	0.5773(5)	0.0145(8)
In(2)	0.2827(5)	1.1842(4)	0.0768(5)	0.0137(7)
Se(1)	0.909(1)	0.7878(9)	0.8263(8)	0.014(1)
Se(2)	0.1368(7)	0.557(1)	0.3278(7)	0.0115(9)
Se(3)	0.6794(8)	1.058(1)	0.3285(7)	0.014(1)
Se(4)	0.408(1)	1.3329(8)	0.8269(8)	0.013(1)
Cu(1)	0.782(1)	0.683(2)	0.077(2)	0.022(1)
Cu(2)	1.032(2)	1.434(2)	0.577(2)	0.024(2)
		III		
Se	0.1515(9)	0.402(1)	0.448(1)	0.017(1)
Cu(In)	–0.1006(9)	0.651(1)	0.948(1)	0.016(1)

Table 2. Bond lengths (Å), R_1 factors, and Flack parameters (*F*) for samples **I**–**I'''**

Sample	**I**	**I'**	**I''**	**I'''**
In(1)–Se(2)	2.534(4)	2.543(7)	2.532(7)	2.545(6)
Cr(1)–Se(1)	2.513(7)	2.523(9)	2.514(7)	2.514(6)
Cr(1)–Se(2)	2.580(8)	2.567(9)	2.576(8)	2.572(7)
Cu(1)–Se(1)	2.446(3)	2.428(5)	2.439(5)	2.435(5)
R_1	0.0431	0.0518	0.0512	0.0664
F	0.09	–0.09	0.58	0.62
R_1^*	0.0469	0.0560	0.0490	0.0646
*F**	0.91	1.08	0.38	0.32

* Inverted model.

Table 3. Bond lengths in **II**

Atoms	*l*, Å	Atoms	*l*, Å
In(1)–Se(1)	2.579(6)	In(1)–Se(2)	2.586(6)
In(1)–Se(3)	2.561(6)	In(1)–Se(4)	2.589(6)
In(2)–Se(1)	2.573(6)	In(2)–Se(2)	2.576(6)
In(2)–Se(3)	2.590(6)	In(2)–Se(4)	2.585(6)
Se(1)–Cu(1)	2.45(1)	Se(1)–Cu(2)	2.42(1)
Se(2)–Cu(1)	2.45(1)	Se(2)–Cu(2)	2.43(1)
Se(3)–Cu(1)	2.44(1)	Se(3)–Cu(2)	2.44(1)
Se(4)–Cu(1)	2.42(1)	Se(4)–Cu(2)	2.43(1)

To rule out "forced" site occupation in the high-symmetry space group, the structure of **II** was solved in a reduced unit cell, containing no symmetry elements: $a = 5.774(2)$ Å, $b = 5.774(2)$ Å, $c = 7.095(6)$ Å, $\alpha = 113.94(5)°$, $\beta = 113.95(5)°$, $\gamma = 90.06(4)°$, $V = 193.6(3)$ Å^3, $M = 672.6$, $F(000) = 292$, $\rho_{calc} = 5.767$ g/cm^3, $\mu_{Mo} = 29.98$ mm^{-1}, $Z = 1$, sp. gr. $P1$.

The final refinement statistics for **II**: $R_1 = 0.0778$, $wR_2 = 0.2134$ for 662 reflections considered observed on the criterion $F_0 \geq 4\sigma(F_0)$; $R_1 = 0.1189$, $wR_2 = 0.2647$ for 1062 measured reflections; GOF = 1.047, 74 adjustable parameters, $\Delta\rho_{max} = 4.49$, $\Delta\rho_{min} = -5.45$ e/Å^3.

Compound **II** seems to undergo a solid-state transformation during annealing. The resulting phase, of composition $Cu_{0.5}In_{0.5}Se$ (**III**), has a triclinic structure with $a = 4.088(1)$ Å, $b = 4.091(2)$ Å, $c = 4.101(1)$ Å, $\alpha = 60.05(1)°$, $\beta = 60.08(1)°$, $\gamma = 89.98(4)°$, $V = 48.60(2)$ Å^3, $M = 168.1$, $F(000) = 73$, $\rho_{calc} = 5.75$ g/cm^3, $\mu_{Mo} = 29.97$ mm^{-1}, $Z = 1$, sp. gr. $P1$.

The final refinement statistics for **III**: $R_1 = 0.1055$, $wR_2 = 0.2602$ for 357 reflections considered observed on the criterion $F_0 \geq 4\sigma(F_0)$; $R_1 = 0.1175$, $wR_2 = 0.2766$ for 449 measured reflections; GOF = 0.977, 19 adjustable parameters, $\Delta\rho_{max} = 4.63$, $\Delta\rho_{min} = -6.40$ e/Å^3.

The atomic positional and thermal parameters in the structures of **I**, **II**, and **III** are presented in Table 1; the bond lengths in the four samples of **I** are listed in Table 2; and those in **II** are listed in Table 3.

All crystallographic computations were performed with SHELXS-86 [9] and SHELXL-93 [10].

RESULTS AND DISCUSSION

The Cu and In atoms in **I** reside in tetrahedral sites of the spinel structure, and the Cr atoms sit in octahedral interstices of the close packing of Se atoms.

The bond lengths inferred from the four intensity data sets for **I** are in reasonable agreement (Table 2). The mean bond lengths are In–Se(2) = 2.538(6) Å, Cr(1)–Se(1) = 2.514(7) Å, Cr(1)–Se(2) = 2.576(8) Å, and Cu–Se = 2.437(5) Å.

The degree of structural similarity between **I** (Fig. 1b) and classical spinel **IV** (Fig. 1a) can be inferred from the fact that refinement in the $Fd3m$ space group led to reasonable *R* factors for the four samples, $R_1 = 0.0486$, 0.0524, 0.0575, and 0.0698, with average In–Se and Cu–Se bond lengths of 2.490, 2.486(3), 2.487(3), and 2.486(3) Å.

The In and Cu atoms sit in two different tetrahedral sites in the $F\bar{4}3m$ model and in one, mixed occupancy site in the $Fd3m$ model.

There are grounds to believe that all the single-crystal samples of **I** consist of mosaic blocks corresponding to one of the two possible forms (phases), which may interconvert in response to temperature changes. It is

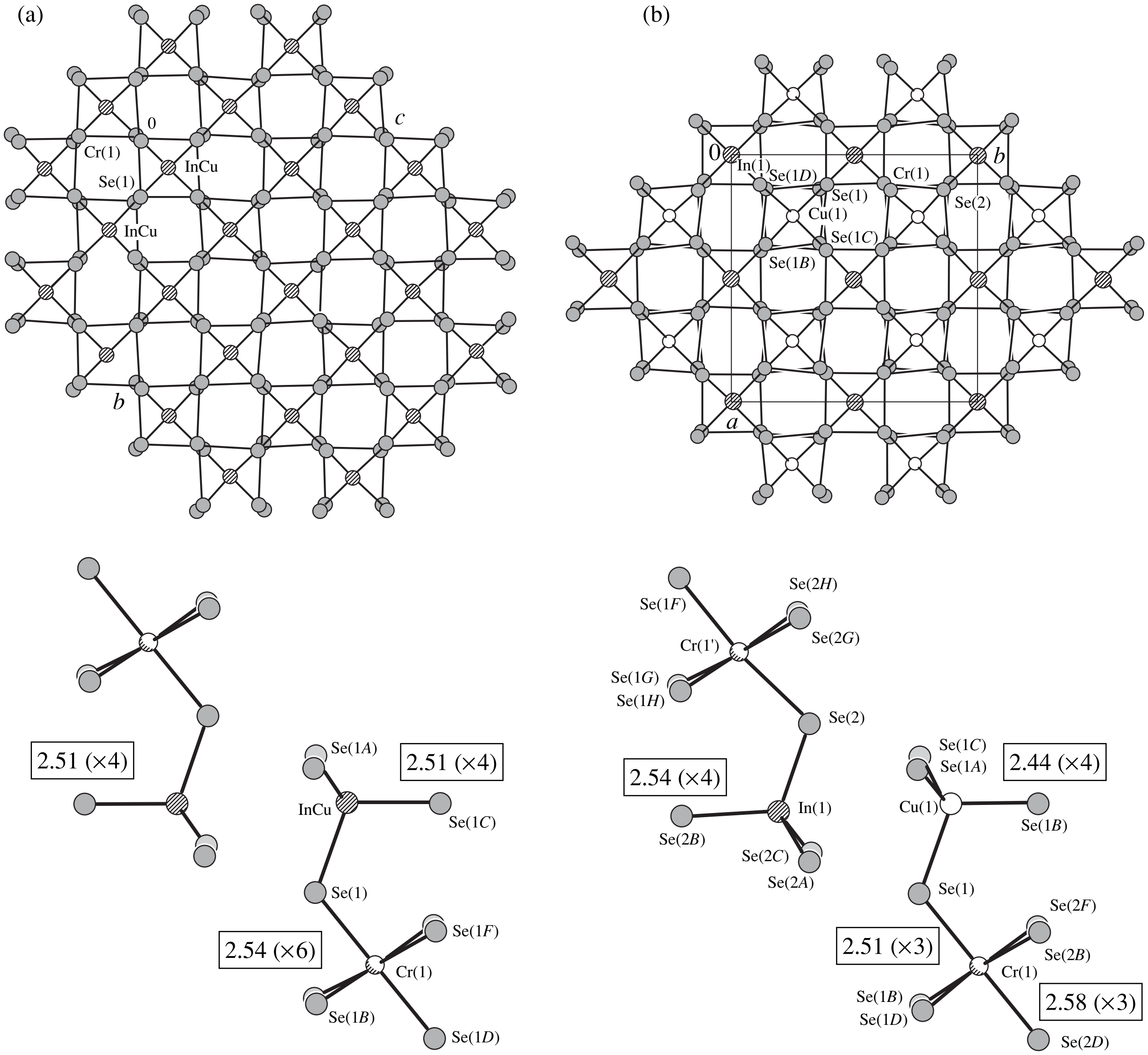

Fig. 1. Structural models of $CuInCr_4Se_8$: (a) sp. gr. *Fd*3*m* (**IV**), (b) sp. gr. $F\bar{4}3m$ (**I**). Top: entire unit cell; bottom: equivalent structural fragments.

the crystal temperature which determines the relationship between the number of blocks of each phase. Comparison of models **IV** (high-temperature, disordered phase) and **I** (ordered phase) attests to the possibility of a second-order phase transition, often encountered in analogous compounds and involving ordering of the metal atoms in tetrahedral sites (Fig. 1). An important point is that these models have the same unit cell and that the parameter-free positions of Cu and In are equivalent. In going from **I** to **IV**, the displacements of equivalent Se atoms are 0.059–0.069 Å (against the 0.12-Å vibrational amplitude), and those of the Cr atoms are 0.092 Å (which is close to the vibrational amplitude). The Cu and In positions in the two structures formally coincide. One should, however, keep in mind that the In and Cu atoms sit in two different tetrahedral positions in the $F\bar{4}3m$ model and in the same position in the *Fd*3*m* model. Therefore, in the course of ordering some of the Cu and In atoms must be displaced by at least 4.58 Å (Fig. 1). Actually, since direct exchange between neighboring sites is unlikely, the displacements are substantially larger.

This process, involving displacements of a large number of rather heavy atoms, is only possible owing to some favorable features of the structures involved. In the spinel structure, only half of the octahedral sites are occupied. The occupancy of the tetrahedral sites is even lower: 7/8 of the tetrahedra are empty. Thus, there is enough space for diffusion of atoms. Moreover, the Cr

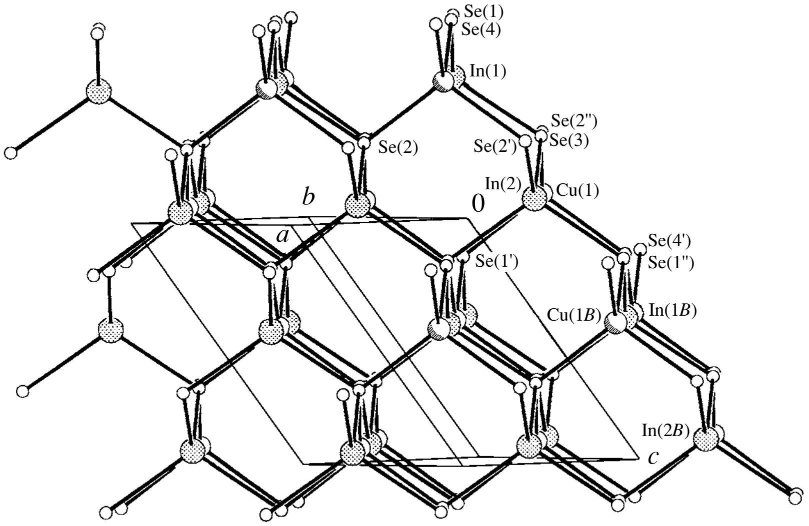

Fig. 2. Structure of **II**.

sublattice, which has the smallest vibrational amplitude (Table 1), remains virtually unchanged. The tetrahedral sublattice of the In and Cu atoms also persists. The close packing of Se atoms, reinforced by the Cr sublattice and quasi-invariable In/Cu sublattice is a good matrix for the migration of heavy atoms. Moreover, each occupied tetrahedron share faces with four empty octahedra. These octahedra, in turn, are surrounded by occupied tetrahedra (Fig. 1). In the course of ordering, the In and Cu atoms migrate through empty octahedra, leading to the formation of an ordered (or disordered) phase energetically more favorable at a given temperature.

At the same time, the three-layer close packing of the Se atoms undergoes certain changes and readily adapts itself to the size of metal atoms, e.g., by changing the size of the tetrahedral interstices occupied by Cu and In atoms. the flexibility of the anion sublattice is also favorable for diffusion of atoms through triangular faces. The processes in question may also be favored by point defects and dislocations.

In the $F\bar{4}3m$ space group, **I** may crystallize in two enantiomorphs. Comparison of the Flack parameters and the corresponding R_1 factors (Table 2) indicates that samples **I** and **I'** consist of only one absolute configuration, whereas samples **I''** and **I'''** are dominated by the other configuration, which constitutes ≈50–60% of the twinned crystal. The polarity of the ordered structure is determined by the initial (accidental) distribution of defects and dislocations contributing to the formation of fluctuons and phasons.

The $F\bar{4}3m$ model is also supported by its R_1 factor (0.0431) being smaller than that for of $Fd3m$ model (0.0492).

The unit cell of **II** (sphalerite type) contains two inequivalent Cu atoms, two In atoms, and four Se atoms (Fig. 2). The Cu and In atoms are in tetrahedral coordination with four inequivalent Se atoms. The mean bond lengths, Cu–Se = 2.43(1) Å and In–Se = 2.578(6) Å) (Table 3) are close to those in the $I\bar{4}2d$ model of **II** (2.439 and 2.592 Å, respectively) [7]. The Cu(In) tetrahedra share corners. The Cu and In atoms in the structure of **II** are arranged in the form of layers, which alternate with Se layers.

The ordered structure of **II**, containing one $Cu_2In_2Se_4$ formula unit per cell, all the atoms in a unit cell being inequivalent, transforms into the disordered structure of $Cu_{0.5}In_{0.5}Se$ (**III**). This transition is accompanied by a slight reduction in density, whereas the unit-cell volume (more precisely, the minimum identity volume) decreases by a factor of 4. The disorder develops in four positions occupied in **II** by the Cu(1), Cu(2), In(1), and In(2) atoms and four positions occupied by Se.

The Cu(In)–Se bond length ranges from 2.501(6) to 2.514(6) Å, with an average of 2.508 Å.

Note that the Cu–Se bond lengths in **I** and **II** differ very little (about 2.44 Å), whereas the In–Se bond length in **I** (2.54 Å) is shorter than that in **II** (2.58 Å). No matter what the origin of this distinction (different structure types, the presence of Cr in **I**, etc.), the Cu–Se and In–Se bond lengths are liable to vary because Cu and In atoms may substitute for each other owing to thermally activated migration processes.

The Cu_{In} and In_{Cu} antisite defects reduce the volume of the tetrahedra and the In–Se bond length and increase the Cu–Se bond length. The magnitude of this effect depends on the Cr content. The process culminates in a fully disordered structure with a mean Cu(In)–Se bond length close to 2.50 Å.

A similar situation holds when the structure of **II** transforms to the fully disordered structure of **III**

(In–Se = 2.580 Å and Cu–Se = 2.44 Å in **II** and Cu(In)–Se = 2.508 Å in **III**) and also in **I**: in the $F\bar{4}3m$ phase (differentiated tetrahedral sites), In–Se = 2.538 Å and Cu–Se = 2.437 Å; in the $Fd3m$ phase (equivalent tetrahedral sites), Cu(In)–Se = 2.508 Å.

CONCLUSIONS

Using single-crystal XRD, we determined the In–Se, Cr–Se, and Cu–Se bond lengths in the structure of $CuInCr_4Se_8$. All of the phases obtained in the synthesis of $CuInCr_2Se_5$ are unstable.

$CuInCr_2Se_5$ is a nonstoichiometric spinel phase ($CuInCr_2Se_5 = Cu_{1.6}In_{1.6}Cr_{3.2}Se_8$) deficient in Cr and enriched in Cu and In. As a result of second-order phase transitions, associated primarily with different disordering processes, this compound decomposes to form a spinel phase of composition $CuInCr_4Se_8$ (**I**) and a sphalerite phase of composition $Cu_2In_2Se_4$ (**II**).

According to XRD results, **I** undergoes a structural transformation from a high-temperature (sp. gr. $Fd3m$) to a low-temperature ($F\bar{4}3m$) phase as a result of Cu and In ordering into tetrahedral sites, without changes in the arrangement of the Cr atoms in octahedral interstices of the close packing of Se atoms.

A different process (displacement of Cr atoms from octahedral interstices) leads to the formation of the polar sphalerite phase $Cu_2In_2Se_4$, which also undergoes structural changes (even at room temperature): the ordered arrangement of the Cu and In atoms in tetrahedral sites (along certain directions in the structure of **II**) is unstable and gradually changes to the disordered arrangement of Cu and In in **III**, which reduces the unit-cell volume by a factor of 4.

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