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Description of concentration polytypism in $Cd_{1-x}Cu_xIn_2Se_4$ by commensurately modulated structures

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The description of polytypes as commensurately modulated structures with different modulation vectors is presented for the concentration polytypism appearing in the solid solution of the $CdIn_2Se_4$ compound in the multinary system Cd-Cu-In-Se. The crystal structure of the 4Q-$Cd_{1-x}Cu_xIn_2Se_4$ polytype was determined.

Chalcogenide / Polytype / Commensurate modulated structure

Introduction

The compound $CdIn_2Se_4$ is characterized by a pseudo-cubic lattice (tetragonal space group $P\bar{4}2m$, $a \approx b \approx c \approx$ 5.82 Å, Z = 1) [1,2]. The Cd atoms occupy Wyckoff position 1*a* (0 0 0), the In atoms position 2*f* (½ 0 ½), and the Se atoms position 4*n* (*x x z*) with $x \approx$ ¼. The coordination polyhedra of the Cd and In atoms are Se_4 tetrahedra. Position 1*d* (½ ½ 0), which is vacant in the ideal structure, has tetrahedral surrounding too and may be partly occupied by Cd cations. Consequently, position 1*a* will be defective as required by the charge balance and the structure will be partly disordered (Fig. 1). In the case of complete statistical occupation of positions 1*a* and 1*d* and an ideal value of the parameter x = ¼ for position 4*n*, the structure contains the Bravais translation ½ ½ 0 and can be transformed into a smaller tetragonal cell with $a = a_0/\sqrt{2}$, corresponding to space group $P\bar{4}m2$.

However, the vacancies may alternate regularly. For instance, in the $ZnIn_2Se_4$ structure (space group $I\bar{4}2m$, $a \approx b \approx$ 5.71, $c \approx$ 11.45 Å, Z = 2) Zn and In atoms occupy randomly positions 2*a* (0 0 0) and 4*d* (0 ½ ¼), and Se atoms occupy position 8*i* (*x x z*) with $x \approx$ ¼ [3,4]. This structure can also be described in space group $I\bar{4}$, with the Se atoms occupying Wyckoff position 8*g* (*x y z*) with $x \approx y \approx$ ¼ [5]. The main difference between the two descriptions of this structure consists in the displacements of the Se atoms, which are in the case of space group $I\bar{4}2m$ related by the symmetry plane and the 2-fold axis (Fig. 2). Literature data also contain information about the existence of a tetragonal structure for $CdIn_2Se_4$ with unit-cell parameter ratio $c/a \approx 4$ [6,7].

The subject of this paper was to study the crystal structure of phases formed by partial substitution of Cd and In atoms by Cu atoms in the system Cu_2Se-CdSe-In_2Se_3.

Experimental

Samples of the system Cu_2Se-CdSe-In_2Se_3 were synthesized by the direct single-temperature method. The maximal temperature of synthesis for samples in the range 90-100 mol.% $CdIn_2Se_4$ was 1223 K. The synthesis was followed by annealing at 823 K for 300 hours. The phase analysis was based on X-ray powder diffraction patterns obtained in the step-scan mode using a DRON-4-13 diffractometer (Cu *K*α radiation, Ni filter). Structure refinements were performed by the Rietveld method [8]. Single crystals were investigated using Laue and rotation techniques at the first stage. Intensities for the structure refinement were recorded on an automatic diffractometer CAD-4 (graphite monochromator, Mo $K\alpha_1$ radiation). An absorption correction was applied based on azimuth scans. All calculations for the determination and refinement of the structure were performed using the WinCSD program package [8].

Results and discussion

During the investigation of the phase equlibria in the system Cu_2Se-CdSe-In_2Se_3 a compound with composition close to the ternary phase $CdIn_2Se_4$, but with different lattice parameters, was discovered. For

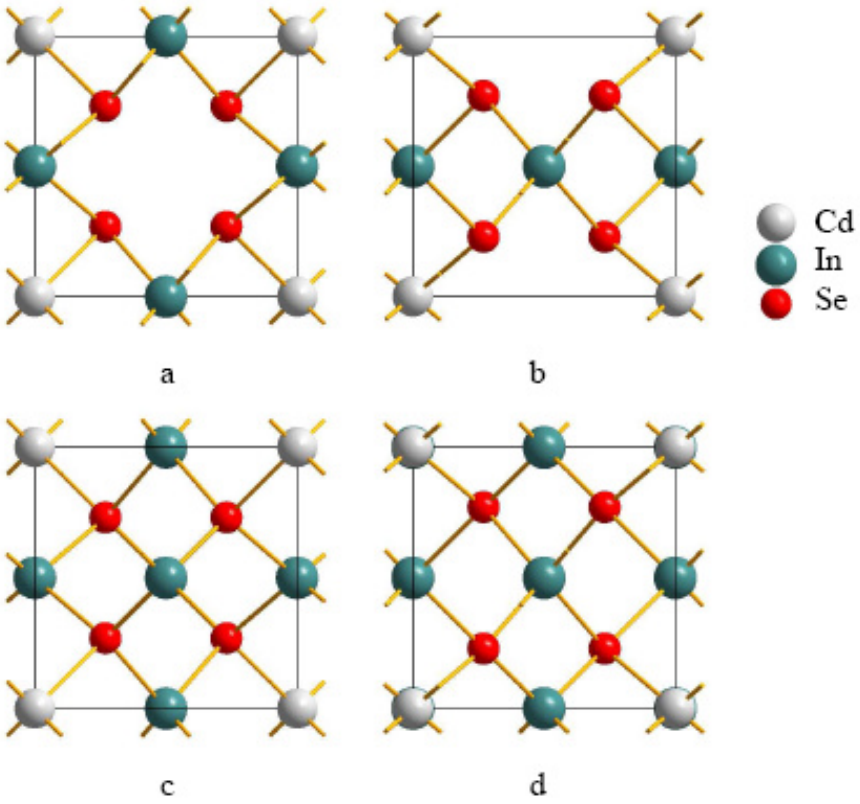

Fig. 1 Projections of the structure of $CdIn_2Se_4$ (space group $P\bar{4}2m$): ideal structure onto the (a) *XY* and (b) *YZ* plane, disordered structure onto the (c) *XY* and (d) *YZ* plane.

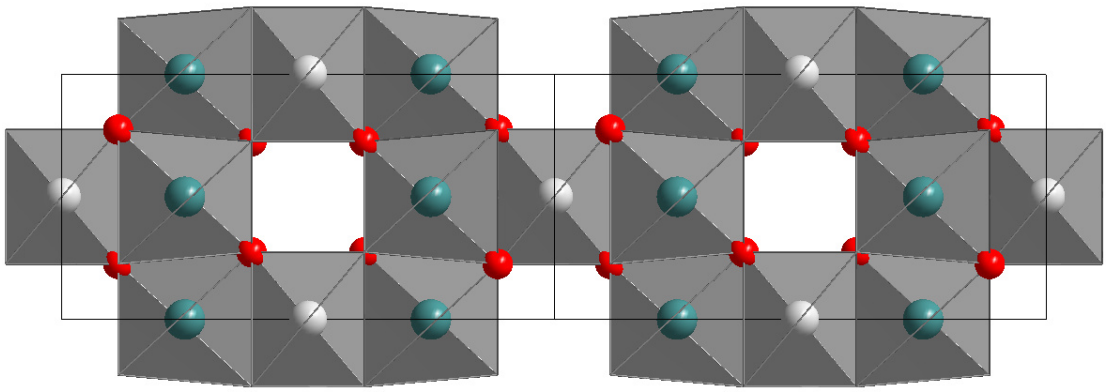

Fig. 2 Projection of the structure of $ZnIn_2Se_4$ (space group $I\bar{4}2m$) onto the *YZ* plane.

a body-centered tetragonal cell (a = 5.806(2), c = 23.252(6) Å), the non-centrosymmetric space groups $I422$, $I\bar{4}2m$, $I\bar{4}m2$, and $I4mm$ and are allowed in Laue class $4/mmm$. The experimental set of hkl reflections was characterized by non-standard extinctions. Only reflections with $l = 4n$ and $l = 4n\pm1$ were present, which was the evidence for a special pseudo-symmetry of the structure. For instance, lines $hk2$ and $hk6$ were not observed. The structure was solved by the analysis of a 3D distribution of interatomic functions in space group $I\bar{4}2m$ and refined by the least-squares method (Table 1). The refinement showed strong correlations between the variations of the displacement parameters due to the

Table 1 Parameters from the refinements of three models for the structure of $Cd_{0.95}Cu_{0.05}In_2Se_4$.

Model	3D superstructure	modulated model (1)	modulated model (2)
Space group	$I\bar{4}2m$	$P\bar{4}m2$ (½ ½ γ)	$P\bar{4}m2$ (½ ½ γ)
a (Å)	5.806(2)	5.806(2)	5.806(2)
c (Å)	23.252(6)	11.626(3)	5.813(2)
Modulation vector	–	0 0 ½	0 0 ¼
Z	4	2	1
t-section (t_0)	–	¼	0
No. of collected reflections	418	418	418
No. of independent reflections	249	249	249
$2\theta_{max}$ (°)	65.0	65.0	65.0
Weighting scheme	$1/\sigma^2(F)+0.008F^2$	$1/\sigma^2(F)+0.002F^2$	$1/\sigma^2(F)+0.0015F^2$
R, *wR* (all reflections)	0.0530, 0.0549	0.0431, 0.0442	0.0443, 0.0461
R, *wR* (main reflections *HKL*0)	–	0.0406, 0.0415	0.0424, 0.0426
R, *wR* (satellite reflections *HKLM*)	–	0.0477, 0.0485	0.0478, 0.0486
Goodness of fit	1.00	1.00	1.05
No. of refined parameters	12 (isotropic approximation)	25	13
Atomic coordinates, equivalent isotropic displacement parameters (Å^2), population and modulation parameters	Cd 4*e* (0 0 *z*) *z*=0.1250(1), *B*=1.38(5) In1 4*d* (0 ½ ¼), *B*=1.2(2) In2 4*c* (0 ½ 0), *B*=1.2(2) Se1 8*i* (*x x z*) *x*=0.2262(3) *z*=0.3181(1), *B*=1.27(7) Se2 8*i* (*x x z*) *x*=0.2725(3) *z*=0.0686(2), *B*=1.37(7)	Cd 4*e* (0 0 *z*) *z*=0.2556(2), *p* = 0.5, *B*=0.93(2) U1=[cosx_4]$_z$×0.0035(3) U2=[sinx_4]$_z$×0.0123(4) U3=-[sinx_4]$_p$×0.275(3) U4=[cosx_4]$_p$×0.389(3) In1 2*d* (0 ½ ½), *B*=0.94(2) In2 2*c* (0 ½ 0), *B*=0.94(2) Se1 4*g* (¼ ¼ *z*) *z*=0.6370(2), *B*=1.08(3) U1={[cosx_4]$_x$-[cosx_4]$_y$}× 0.0082(3) U2={[sinx_4]$_x$-[sinx_4]$_y$}× 0.0710(7) Se2 4*g* (¼ ¼ *z*) *z*=0.1364(2), *B*=0.88(2) U1={[cosx_4]$_x$+[cosx_4]$_y$} × 0.0404(6) U2=- {[sinx_4]$_x$+[sinx_4]$_y$}× 0.0067(3)	Cd 2*d* (0 ½ ½), *p* = 0.5, *B*=1.18(1) U1=-[cosx_4]$_z$×0.0012(4) U2=[sinx_4]$_p$×0.667(5) In 2*a* (0 0 0), *B*=1.15(2) Se 4*g* (¼ ¼ *z*) *z*=0.7267(2), *B*=1.10(1) U1=-{[cosx_4]$_x$+[cosx_4]$_y$}× 0.0289(6) U2=-{[sinx_4]$_x$+[sinx_4]$_y$}× 0.0120(3)

pseudo-symmetry of the structure. A projection of the structure of $Cd_{0.95}Cu_{0.05}In_2Se_4$ onto the *YZ* plane is shown in Fig. 3.

The structure of $Cd_{0.95}Cu_{0.05}In_2Se_4$ contains the double number of structural slabs in the translation periodicity along the 4-fold axis compared to the $ZnIn_2Se_4$ structure, and four times more than the simplest prototype, $CdIn_2Se_4$. Following the generally accepted nomenclature of heteropolytypical structures, one should use the following designations: 1Q for the $CdIn_2Se_4$ structure (Q – tetragonal symmetry), 2Q for the $ZnIn_2Se_4$ structure, and 4Q for the $Cd_{0.95}Cu_{0.05}In_2Se_4$ structure.

The special symmetry revealed by the peculiar extinctions in the diffraction pattern indicated an alternative way to describe the symmetry of the structure. It was possible to introduce a fourth index, *M*, in two models: (1) $M = \mathrm{mod}(L,2)$, (2) $M = \mathrm{mod}(L,4)$. For both models the reflection set was transformed to *HKLM* with regular extinctions $H+K+M \neq 2n$. This gave a possibility to describe the structure of the 4Q-$Cd_{0.95}Cu_{0.05}In_2Se_4$ compound as a

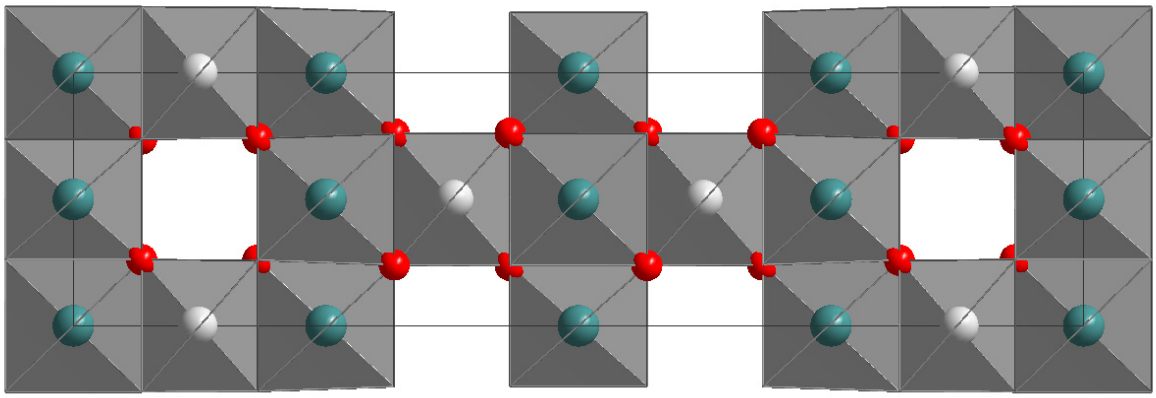

Fig. 3 Projection of the structure of $Cd_{0.95}Cu_{0.05}In_2Se_4$ (space group $I\bar{4}2m$) onto the *YZ* plane.

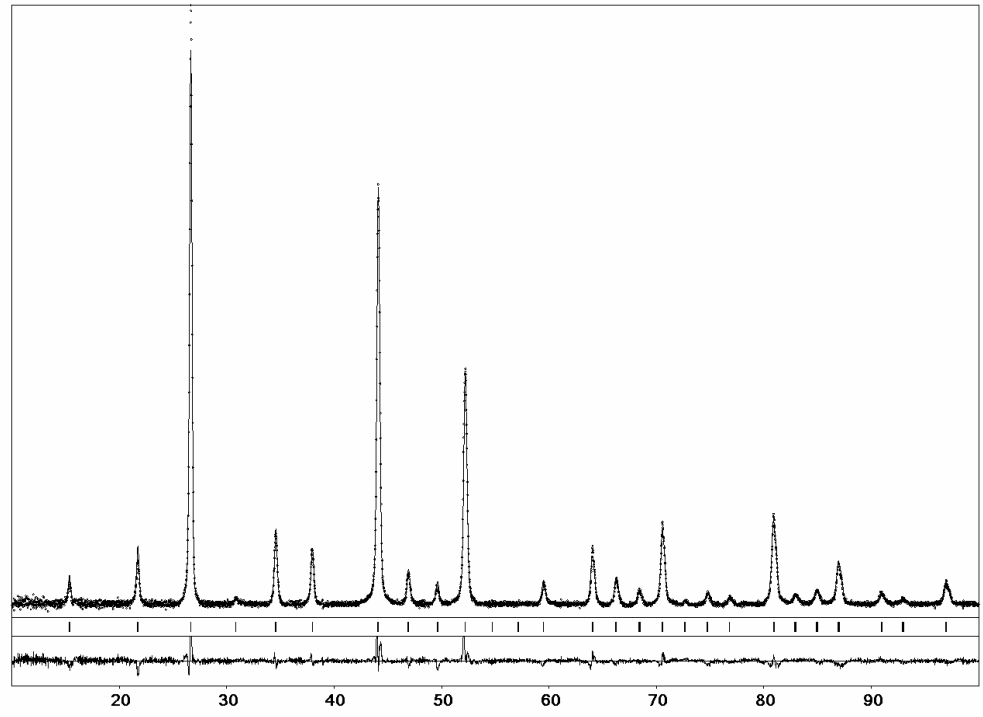

Fig. 4 Experimental (dotted line), calculated (solid line), and difference diffraction patterns of $CdIn_2Se_4$ (Cu *K*α radiation).

Table 2 Parameters from the refinements of two models for the structure of $Cd_{0.982}Cu_{0.018}In_2Se_4$.

Model	3D superstructure	modulated model
Space group	$I\bar{4}2m$	$P\bar{4}m2$ (½ ½ γ)
a (Å)	5.8043(2)	5.8043(2)
c (Å)	11.6380(5)	5.8190(3)
Modulation vector	–	0 0 ½
Z	2	1
t-section (t_0)	–	¼
No. of collected reflections	1599	1599
No. of independent reflections	276	276
$2\theta_{max}$ (º)	58.2	58.2
Weighting scheme	$1/\sigma^2(F)+0.004F^2$	$1/\sigma^2(F)+0.002F^2$
R, *wR* (all reflections)	0.0456, 0.0572	0.0466, 0.0506
R, *wR* (main reflections *HKL*0)	-	0.0402, 0.0435
R, *wR* (satellite reflections *HKLM*)	-	0.0612, 0.0648
Goodness of fit	1.02	1.00
No. of refined parameters	11	8
Atomic coordinates, equivalent isotropic displacement parameters (Å^2) and modulation parameters	Cd 2*a* (0 0 0), *B*=1.09(5) In 4*d* (0 ½ ¼), *B*=1.08(4) Se 8*i* (*x x z*) *x*=0.2719(3) *z*=0.1142(1), *B*=0.72(3)	Cd 2*a* (0 0 0), *p* = 0.5, *B*=0.92(4) U1=$[\cos x_4]_p$×0.490(5) In 2*d* (0 ½ ½), *B*=1.01(2) Se 4*g* (¼ ¼ *z*) *z*=0.7710(2), *B*=0.58(2) U1={$[\cos x_4]_x$+$[\cos x_4]_y$}×0.0159(6) U2=-{$[\sin x_4]_x$+$[\sin x_4]_y$}×0.0148(7)

Table 3 Parameters from the refinements of two models for the structure of $CdIn_2Se_4$.

Model	3D superstructure	modulated model
Space group	$P\bar{4}2m$	$P\bar{4}m2$ (½ ½ γ)
a (Å)	5.8289(4)	5.8281(3)
c (Å)	5.8186(8)	5.8202(5)
Modulation vector	–	0 0 0
Z	1	1
t-section (t_0)	-	0.125
No. of independent reflections	82	46
$2\theta_{max}$ (º)	100.0	100.0
R_B	0.0686	0.0699
R_p	0.0803	0.0812
No. of refined parameters	6	8
Atomic coordinates, equivalent isotropic displacement parameters (Å^2) and modulation parameters	Cd 1*a* (0 0 0), *B*=0.7(2) In 2*f* (½ 0 ½), *B*=0.79(9) Se 4*n* (*x x z*) *x*=0.2690(5) *z*=0.2285(9), *B*=0.55(4)	Cd 2*a* (0 0 0), *p* = 0.5, *B*=0.92(4) U1=-$[\sin x_4]_z$×0.0091(1) U2=-$[\cos x_4]_p$×0.2217(9) In 2*d* (0 ½ ½), *B*=0.75(6) Se 4*g* (¼ ¼ *z*) *z*=0.7845(1), *B*=0.43(5) U1={$[\cos x_4]_x$+$[\cos x_4]_y$}×0.0115(1) U2={$[\sin x_4]_x$+$[\sin x_4]_y$}×0.0114(1)

4D modulated structure, with a fourth Bravais vector [½ ½ 0 ½] and the following commensurate modulation vectors: **q** = {0 0 ½} for (1) and **q** = {0 0 ¼} for (2) [9-11]. The unit-cell parameters are consequently a = 5.806(2) Å and c = 23.252/2 = 11.626 Å for (1), c = 23.252/4 = 5.813 Å for (2) . Model (2) corresponds to the 1Q structure with average symmetry described in the 3D-space group $P\bar{4}m2$. Systematic extinctions of the satellite reflections corresponding to centering indicated the superspace group $P\bar{4}m2$ (½ ½ γ) (or $W_{P\bar{4}m2}$(-1 1 -1) in agreement with [11]), which was confirmed by least-squares refinements for both models. Calculations of the structure factors led to values of the fourth coordinate $t_i = t_i + t_0$, where t_i is equal to 0 and ½ with the initial value t_0 = ¼ for the model (1), and 0, ¼, ½, and ¾ with the initial value t_0 = 0 for the model (2), determined in the process of the structure refinement. A special feature of these structure models is the modulation of the occupancy of the position of the Cd(Cu) atoms, which has both sine and cosine components of the modulation wave with different amplitudes, resulting in both different substitution and defects with respect to the fourth coordinate (coinciding with the Z axis). The application of a least-squares refinement to the commensurately modulated structure made it possible to avoid correlations in the refinement of the anisotropic displacement parameters and to decrease the number of variables. Results of the refinements of the different models are presented in Table 1.

For the single crystal of composition $Cd_{0.982}Cu_{0.018}In_2Se_4$, a body-centered tetragonal cell was determined, a = 5.783(1), c = 11.580(2) Å, which suggested a $ZnIn_2Se_4$-type structure (space group $I\bar{4}2m$). A least-squares refinement in the anisotropic approximation led to a value of R = 0.043, which supported the high probability of this structure model. However, this diffraction pattern also showed evidence for supersymmetry. For instance, the reflections with $l \neq 2n$ are generally significantly weaker than the reflections with even l indexes. The introduction of a fourth index M = mod(L,2) transforms the reflection set to $HKLM$ with regular extinctions $H+K+M \neq 2n$. It is thus possible to describe the structure of the 2Q-$Cd_{0.982}Cu_{0.018}In_2Se_4$ compound as a 4D modulated structure with the commensurate modulation vector **q** = {0 0 ½}. The unit-cell parameters become a = 5.783(1), c = 11.580/2 = 5.790 Å, corresponding also here to the 1Q-structure with average symmetry described in the 3D space group $P\bar{4}m2$. The superspace group, as in the first case, is $P\bar{4}m2$ (½ ½ γ). The calculations of the structure factors resulted in values of the fourth coordinate $t_i = t_i + t_0$, where t_i is equal to 0 and ½ with the initial value t_0 = 0, determined in the process of the structure refinement. The modulation of the occupancy of the position of the Cd(Cu) atoms defines the location of defects and occupation by Cd and Cu atoms. The results of the refinement of the basic and supersymmetry models are listed in Table 2.

X-ray powder diffraction data (it was not possible to obtain single crystals suitable for structure analysis) allowed us to reexamine literature data on the structure of the phase $CdIn_2Se_4$ (space group $P\bar{4}2m$) and an alternative model in superspace group $P\bar{4}m2$ (½ ½ γ), similar to those used in the previous cases, with a modulation vector **q** = {0 0 0}, was introduced. A zero modulation vector corresponding to the statistical displacement of atoms from the ideal positions was first discussed in [9] and applied in a structure determination in [12]. Calculations of structure factors were performed for the value of the fourth coordinate t_0 = 1/8. The results of the least-squares refinement of the basic and modulated structure models are given in Table 3. A comparison of experimental and calculated diffraction patterns is shown in Fig. 4.

As one can see from Tables 1-3, the cation positions Cd(Cu) and In are not always the same, *i.e.* the Wyckoff positions 0 0 0 and ½ 0 ½ are sometimes interchanged. But the structural motif remains the same. For instance, a refinement in the superspace group $P\bar{4}m2$ (½ ½ γ) 0s0 instead of $P\bar{4}m2$ (½ ½ γ) leads to a shift of the Wyckoff positions and to a change of the modulation amplitudes (for this case of commensurate modulation; if only the satellites of the first order are present these groups are indistinguishable).

We conclude that it is possible to describe the polytypes of $CdIn_2Se_4$ in a single structure type, as the packing of structure fragments with different commensurate modulation vectors. The application of this approach is not limited to the $Cd_{1-x}Cu_xIn_2Se_4$ system. Partial isomorphous substitution by other cations may lead to the formation of more complex polytypes. The application of modulated structures to the description of polytypes was first demonstrated on SiC by Yamamoto and Inoue [13]. The symmetry of polytype structures within a model with commensurate modulation and the advantages of the description of physical properties caused by the change of wave vector will be discussed in a separate paper.

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