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# Structure similarity and lattice dynamics of InSe and $In_4Se_3$ crystals

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In the work it was shown that the $In_4Se_3$ crystal is similar by its dynamical properties to the InSe modulated crystal. The transformation of the $D_{6h}^4$ symmetry group of $\beta$-InSe crystal to $D_{2h}^9$ group of the $In_4Se_4$ structure and the $D_{2h}^{12}$ group of $In_4Se_3$ structure has been investigated. In spite of structure corrugation of $In_4Se_3$ layer, it is shown that the region of the weak bond in this crystal by the dynamical characteristics is similar to the weak bond region in InSe crystal.

**Key words:** *heterojunction, InSe, $In_4Se_3$, stability, phonon spectra*

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## 1. Introduction

Recently, semiconductors with a layered structure have been applied to manufacture heterojunctions because the peculiarities of their composition produce an ideal heterocontact. Due to the distinct asymmetry of chemical bonds in these compounds and the presence of boundaries of the neighbouring layers with saturated bonds, practically perfect surfaces without defects and undesired electric fields can be created.

For traditional non-layered materials, in order to construct a heterostructure, their symmetry and crystalline parameters should be conformed. This cannot be always done with the desired accuracy and the choice of the component materials of the heterostructure is in this way severely restricted. The presence of strong chemical bonds only between atoms in a single layer permits to grow heterojunctions and superlattices in the direction of the weak bond by means of the so-called van der Waals epitaxy [1]. The method of manufacturing the heterojunctions from layered compounds results in structures with physical characteristics corresponding to perfect heterojunctions. It is also possible to create a heterocontact from two materials with different physical properties, different crystalline parameters and with various types of crystal symmetry.

From this point of view the layered semiconducting crystals belonging to the $A^{III}B^{V}$ group are particularly interesting in applications because some of them exhibit a wide range of non-linear optical, electrical and mechanical effects. At present, some experimental and theoretical results concerning superlattices grown by the van der Waals epitaxy from the well investigated semiconductors such as InSe and $GaSe$ have already been published [2,3].

If the basis structures are layered, there exists a simple and an effective method to construct heterojunctions: it is the so-called "deposition on the optical contact" method. Weak bonds result in perfect boundaries when the crystal is naturally cleaved. Freshly cleaved boundaries of layered crystals made to contact together interact by the van der Waals forces, which is similar to the interaction between layers of a bulk semiconductor. This type of heterocontacts contains a small amount of surface defects, therefore, the charge transport is conditioned by the tunnelling or by the diffusion phenomena. These junctions are well described by the perfect diode model.

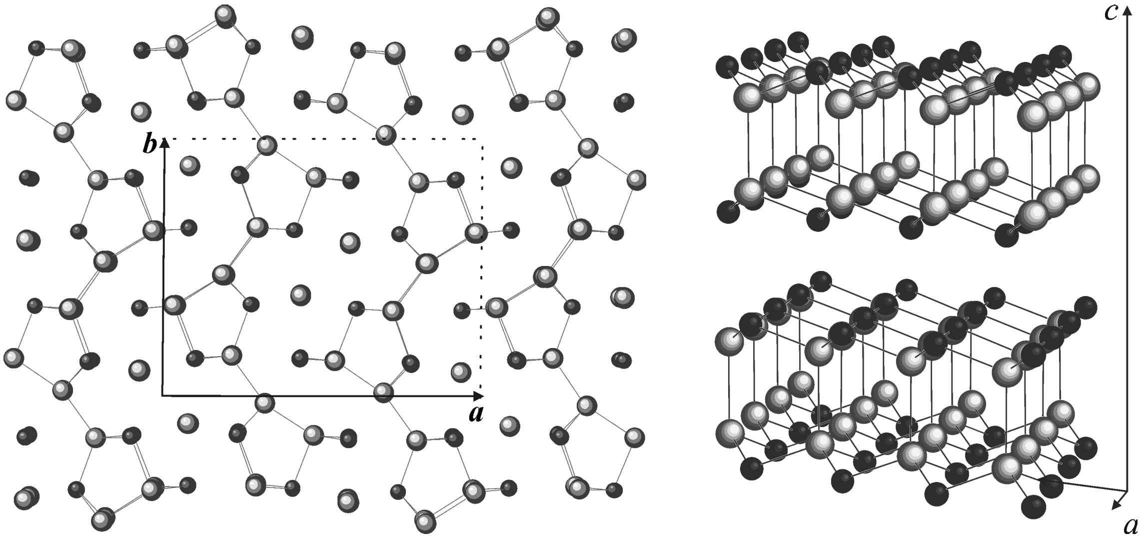
In this paper we will consider another type of heterojunctions: the InSe/$In_4Se_3$ layered crystals with different symmetry and structure, composed of atoms of one type. We will discuss the process of formation, their physical properties and we will analyse the perfect quality of heterocontact of these heterojunctions.

## 2. Forming the $In_4Se_3$ structure from InSe

Let us consider a possible way of forming the $In_4Se_3$ structure from that of InSe.

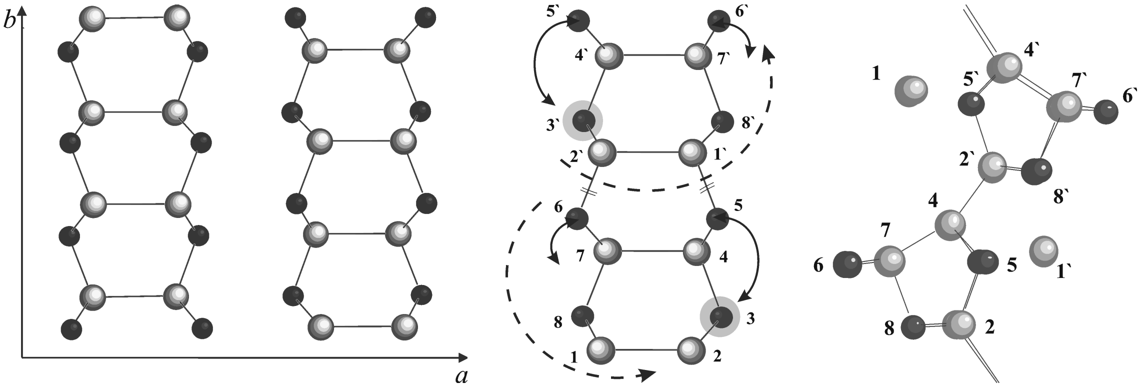
The $In_4Se_3$ crystal belongs to the orthorhombic system described by the $D_{2h}^{12}$ space group with the basic vectors of the elementary cell: $a_1 = 1.5296$ nm, $a_2$ =1.2308 nm, $a_3$ = 0.40806 nm. The crystal structure of the $In_4Se_3$ crystal is presented in figure 1a. The InSe crystal exists in three allotropic phases: $\beta$-InSe (the structure is presented in figure 1b, hexagonal system, space group $D_{6h}^{4}$, parameters of the crystalline lattice: $a'$=0.4048 nm, $c'$=1.693 nm, $\epsilon$-InSe (hexagonal system, space group $D_{3h}^{1}$) and $\gamma$-InSe (rhombohedric system, space group $C_{3v}^{5}$, parameters of the crystalline lattice: $a'$=0.4 nm, $c'$=2.495 nm). The symmetry group of the $\beta$-phase of InSe is the closest to the $D_{2h}^{12}$ group. It differs from the $\epsilon$-InSe phase by the presence of the centre of symmetry. There is one atom of selenium less in the structural unit of $In_4Se_3$ in comparison with four structural units of InSe. Because there are four structural units present in the elementary cell of the $In_4Se_3$ crystal, the enlarged cell should be composed of $4 \times 4$ structural units of InSe, i.e. 32 atoms. The structure with such an enlarged cell will be further denoted as $In_4Se_4$.

To introduce the enlarged cell of $In_4Se_4$ one should remember, that the values of parameters $a_3$ and $a'$, as well as $a_1$ and $c'$ are close together. Moreover, the positions of In (or Se) atoms divide the distances Se–Se (or In–In) in the $\vec{a}'$ direction in the same ratio which is characteristic of the $z$-components of the respective positions of




(a) (b)

**Figure 1.** (a) The projection of the $In_4Se_3$ crystal structure on the plane perpendicular to the strong-bond direction. Light circles denote In atoms, dark circles denote Se atoms. (b) The structure of the $\beta$-InSe.




(a) (b)

**Figure 2.** (a) The elementary cell of $In_4Se_4$; (b) A single layer belonging to the $In_4Se_3$ cell structure. Numbers denote atoms. No. 3 denotes the positions of Se atoms which will become vacancies during the formation of the $In_4Se_3$ structural unit. Solid arrows denote translations of atoms, two dashes denote broken bonds, dashed arrows denote rotations of structural units (see the text). Near by, the actual structure of the $In_4Se_3$ monolayer is presented, atoms are labelled by numbers.

atoms in $In_4Se_3$. Therefore, as the elementary cell we can choose the parallelepiped in the volume of InSe which contains two layers of InSe composed of 16 structural units. This cell is described by the following basic vectors: $\vec{a}_1$ - which is equal to the $\vec{c}'$ vector of the hexagonal system, $\vec{a}_3$ - which is equal to the one of the $\vec{a}'$ basic vectors of the hexagonal system (e.g. it can be $\vec{a}'_1$), and $\vec{a}_2$ - which is the linear combination of basic vectors of the hexagonal system: $\vec{a}_2 = 2\vec{a}'_1 + 4\vec{a}'_2$. The structure of the enlarged cell of $In_4Se_4$ is presented in figure 2a. The lengths of the basic vectors of this cell are: $a_1$ =1.693 nm, $a_2$ =1.402 nm, $a_3$ =0.4048 nm. Their values are close to those of the basic vectors of the elementary cell of the $In_4Se_3$ crystal.

The crystalline lattice of the $In_4Se_4$ structure is described by the $D_{2h}^9$ space group with the following symmetry elements (in the notation of Kovalev [4]):

$$\begin{aligned}
&(\{h_1|0\}, \{h_2|\tfrac{1}{2}\tfrac{1}{2}0\}, \{h_3|\tfrac{1}{2}\tfrac{1}{2}0\}, \{h_4|0\}, \{h_{25}|0\},\\
&\{h_{26}|\tfrac{1}{2}\tfrac{1}{2}0\}, \{h_{27}|\tfrac{1}{2}\tfrac{1}{2}0\}, \{h_{28}|0\}) \times T_{\mathrm{n_1}\vec{a}_1+\mathrm{n_2}\vec{a}_2+\mathrm{n_3}\vec{a}_3}\\
&\mathrm{n_1}, \mathrm{n_2}, \mathrm{n_3} = \pm 0, \pm 1, \pm 2, ...
\end{aligned}$$

The $D_{2h}^{12}$ symmetry group of the $In_4Se_3$ crystal differs from the $D_{2h}^9$ group by the presence of additional non-primitive translations in the (001) direction, connected with the $h_2$, $h_3$, $h_{26}$ and $h_{27}$ elements of the point group.

If the vacancies of selenium were formed in the $In_4Se_4$ structure, then this structure would consist of the structural units of $In_4Se_3\Box$, and it would be described by the $D_{2h}^9$ symmetry group. The layer of this structure would be changed in the following way (see figure 2b): the 5-1′ and 6-2′ bonds would be broken, the 2-5-4 (2′-5′-4′) bonds would be formed, and the 6-7 (6′-7′) bonds would be shifted. After these changes, the layer presented in figure 3a is formed, with deformed structural units of $In_4Se_3\Box$, which is perpendicular to the $\vec{a}_1$ direction. As follows from figure 3a, this layer has the structure of a pseudochain, with identical conformation of structural units in different chains. However, such an arrangement of chains is not convenient, because it does not correspond to the dense packing in the layer. The parallel translation of each consecutive chain along the $\vec{a}_3$ direction by the distance $a_3/2$ changes the conformations of two nearest structural units which belong to different pseudochains (figure 3b). This translation of each second pseudochain is connected with additional non-primitive translations $\vec{a}_3/2$, added to the elements of the space group $D_{2h}^9$, which contains the following point group elements: $h_2$, $h_3$, $h_{26}$, $h_{27}$. Moreover, this translation moves the indium atoms, which belong to structural units of the neighbouring chains, closer. Accordingly, clusters of the $(In_3)^{5+}$ cations are formed, which bound the chains into a layer similar to the layer of the $In_4Se_3$ crystal.

The strong covalent bond in the above mentioned cluster of indium atoms leads further to the rotation of the structural units of $In_4Se_3\Box$ by a certain angle around the $\vec{a}_3$ axis. As a result, the actual structure of the $In_4Se_3$ crystal layer is formed. It should be noted here that the strong covalent bond in the In–In–In cluster causes the smaller length of the basic vector $\vec{a}_2$ in the $In_4Se_3$ crystal, in comparison with the same vector in the $In_4Se_4$ structure.

The exchange of bonds during the formation of $(In_3)^{5+}$ clusters leaves a weak bounded indium atom which places itself in the interlayer space. The arrangement of

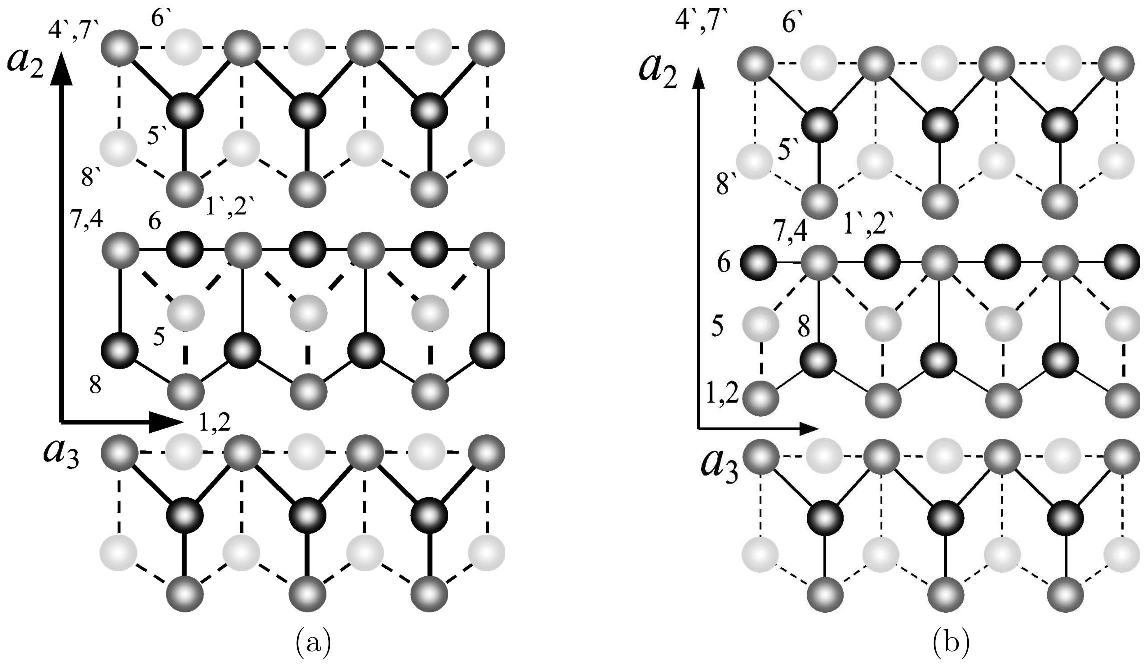



**Figure 3.** (a) The model of a layer of the $In_4Se_3\square$ structure with deformed structural units (numbering of atoms is the same as in figure 2b); (b) The model of a layer of the $In_4Se_3\square$ structure with pseudochains translated along the $a_3$ direction.

atoms and the rotation of the structural units of $In_4Se_3$ in opposite directions around the $\vec{a}_3$ axis cause new interlayer bonds in comparison with the layered structure of $In_4Se_4$. Thus, the weak interlayer bond is strengthened, and the length of the $\vec{a}_1$ basic vector for the $In_4Se_3$ crystal is smaller in comparison with the basic vector of $In_4Se_4$. These are the reasons for the layered character of the $In_4Se_3$ crystal being not so distinct, as in the case of the InSe crystal. Therefore, we see that the $In_4Se_3$ crystal cannot be described as a layered crystal in the usual way, i.e. as consisting of flat layers held together by van der Waals forces.

## 3. The dynamics of the $In_4Se_4$ structure

The interesting peculiarity of the InSe/$In_4Se_3$ heterojunctions is the one-dimensional modulation of the boundary surface of the InSe crystal induced by the $In_4Se_3$ crystal. In the model of the InSe/$In_4Se_3$ superlattice composed of the layers arranged in the weak-bond direction, except the one-dimensional periodicity in this direction, there also appears the one-dimensional modulation of the InSe layer at the interlayer surface in the $\vec{a}_2$ direction induced by the crystalline structure of $In_4Se_3$. Therefore, quantum wires should be formed in such a superlattice.

We will show hereinafter that the dynamical properties of the $In_4Se_4$ structure are similar to those of the $In_4Se_3$ crystal. For this reason we will calculate the phonon spectrum of the $\beta$-phase of InSe. We will apply the six-parameter model of the central exchange interaction proposed in [5] to describe the lattice dynamics of GaSe. The

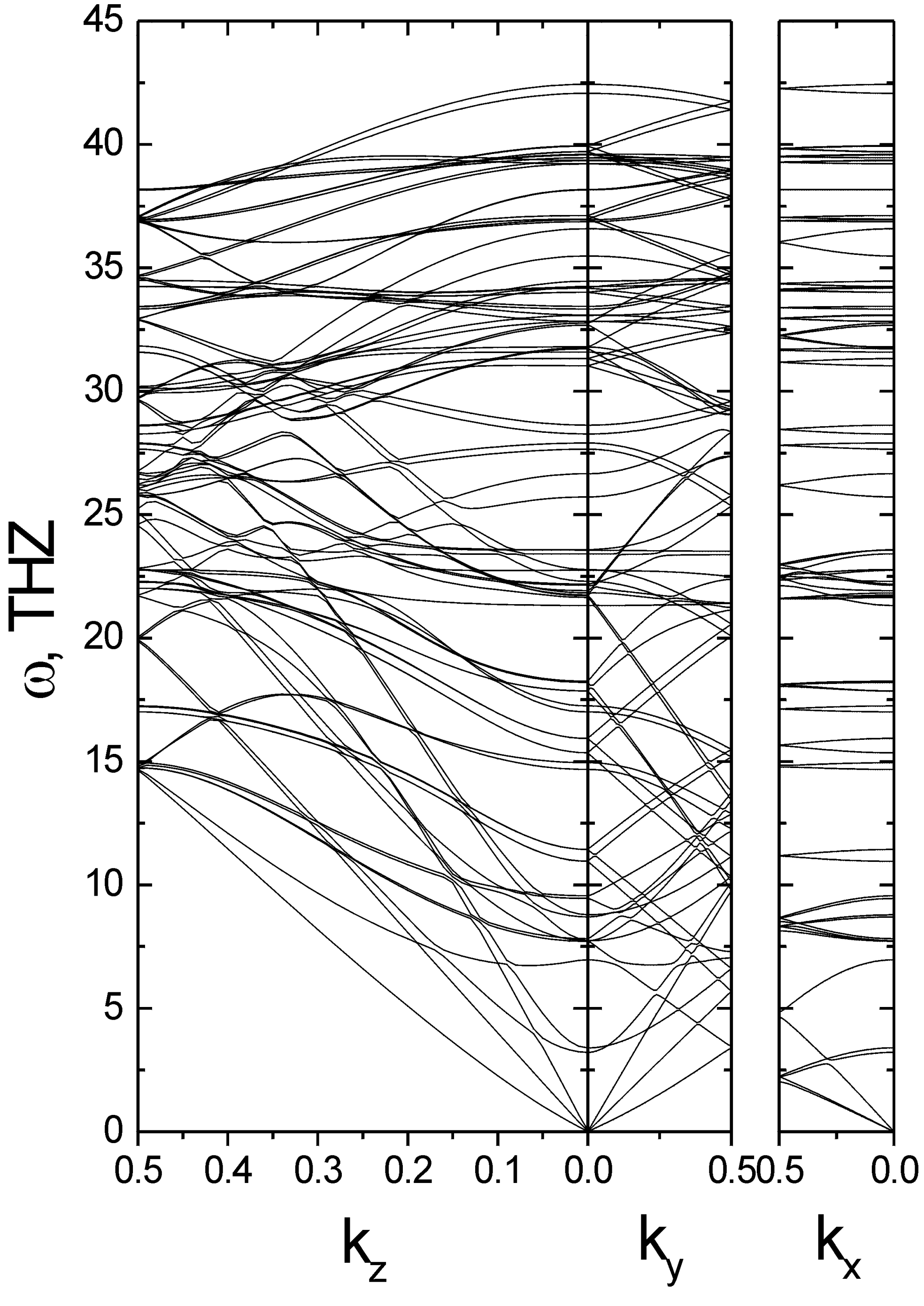



**Figure 4.** The phonon spectrum of the $In_4Se_4$ structure along the principal directions in the Brillouin zone.

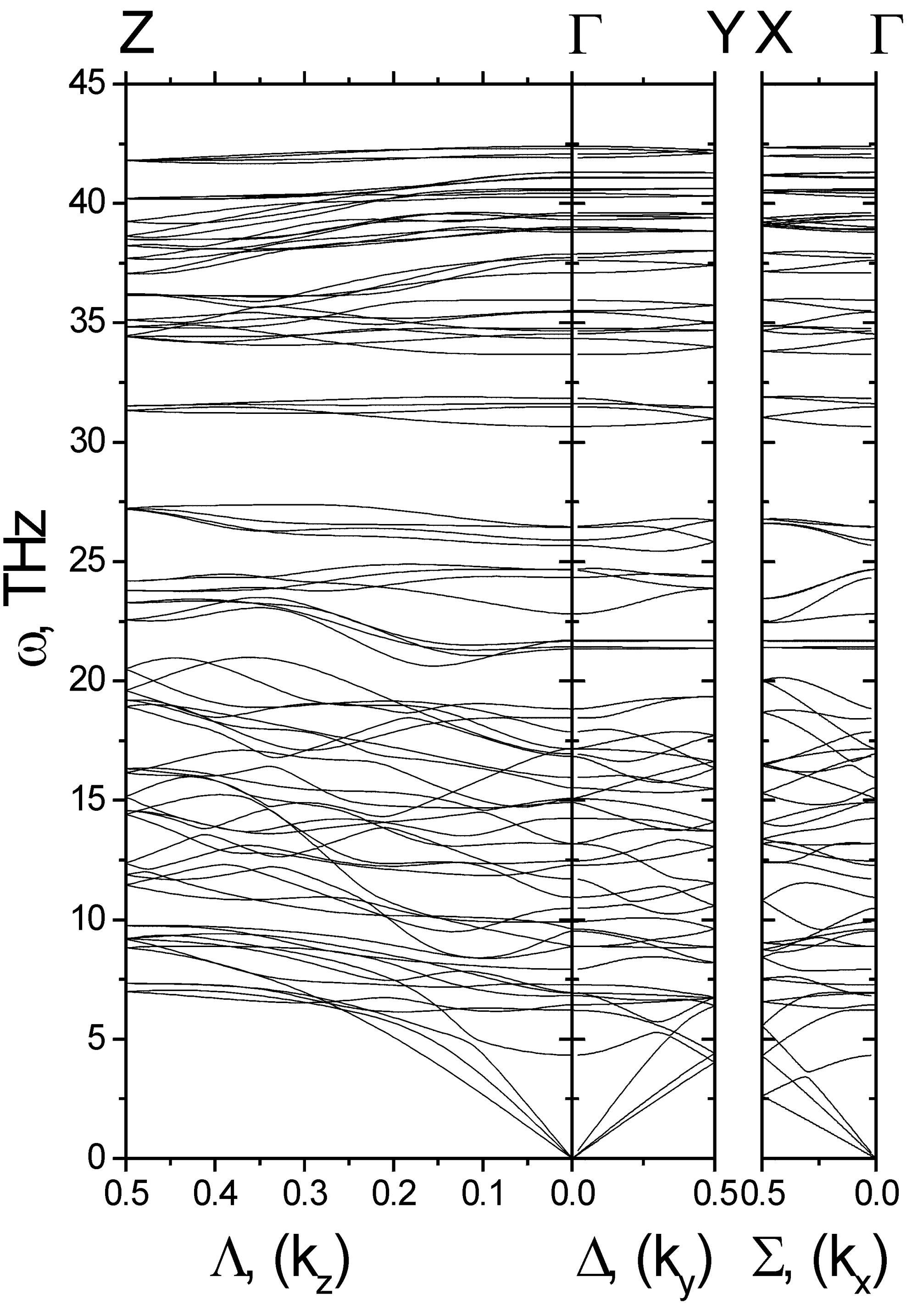



**Figure 5.** The phonon spectrum of the $In_4Se_3$ crystal along the principal directions in the Brillouin zone.

unknown parameters of this model were determined from the data concerning the Raman scattering of light in $\beta$-InSe [6] and from its elastic properties [7]. The long-range Coulomb interaction was not taken into account in the calculations of the phonon spectrum.

The phonon spectrum of the $In_4Se_4$ structure with the enlarged elementary cell is presented in figure 4. This spectrum was obtained by the well known procedure of folding the phonon spectrum of the InSe crystal which has a smaller elementary cell. In figure 4 we see a large number of branches with a small dispersion, which appear in the forbidden range of frequencies in the phonon spectrum of InSe, in the weak-bond direction. From the point of view of lattice dynamics, which depends only on the masses of atoms, on their mutual configuration and on the interatomic distances, the structure of $In_4Se_4$ is fully equivalent to the hexagonal crystal of the $\beta$-InSe. Only the geometry of the elementary cell is the subject of change, and the symmetry is lowered from $D_{6h}^4$ to $D_{2h}^9$. We can model the structural unit of $In_4Se_3$ by introducing vacancies in place of atoms. This leads to the change of arrangement of atoms, and consequently their positions became non-equivalent. During this process the symmetry ($D_{6h}^4$) of the InSe crystal is really lowered, and there appear some changes in the phonon spectrum. However, the low-frequency parts of the phonon spectrum of the $In_4Se_3$ crystal and of the $In_4Se_4$ crystal are similar.

The phonon spectrum of the $In_4Se_3$ crystal calculated by us [8] is presented in figure 5. One should notice similar frequency values of the lowest optical branches in the $\Gamma$ point of the Brillouin zone and their dispersion which is described by the saddle point topology in the phonon spectra of both crystals. Moreover, the experimental and the calculated elastic moduli for both crystals in the weak-bond direction are in full agreement (38.2 GPa, [7,9]). These two factors and the homology of the considered structure is the basis for a high quality of the InSe/$In_4Se_3$ heterocontact. Although the structure of crystal layers is warped, the weak-bond region in this crystal is similar to the respective region in the InSe crystal according to dynamical properties.

## 4. Conclusion

Our results show that high-quality diode structures with reproducible properties can be prepared from indium selenides by simple, low-cost methods such as thermal oxidation of crystalline substrates or joining semiconductor elements to form optical contacts.

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## СПОРІДНЕНІСТЬ СТРУКТУР І ДИНАМІКА ГРАТКИ КРИСТАЛІВ InSe ТА $In_4Se_3$

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У роботі показано, що кристал $In_4Se_3$ за своїми динамічними властивостями близький до модульованого кристалу InSe. Досліджено перетворення групи симетрії $D_{6h}^4$ кристалу $\beta$-InSe до групи $D_{2h}^9$ структури $In_4Se_4$ і до групи $D_{2h}^{12}$ $In_4Se_3$. Показано, що незважаючи на гофрованість структури шару $In_4Se_3$, область слабкого зв'язку у ньому за динамічними властивостями є подібною до області слабкого зв'язку у кристалі InSe.

**Ключові слова:** *гетероструктури, InSe, $In_4Se_3$, стабільність, фононні спектри*

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