# PRESSURE EFFECT ON ELECTRON SPECTRA OF INDIUM AND THALLIUM HALOGENIDES

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The structural and electronic properties of indium and thallium halogenides have been studied theoretically in a wide pressure range using self-consistent calculations within the pseudopotential method. The crucial role of a cation $ns^2$ electron pair in the structure formation and the stabilization of compounds with low-valence cations has been confirmed. The limiting values of pressure that induce phase transitions into a high-symmetry structure of the CsCl type and into a metallic state have been determined. The sequence of structural phase transitions in InCl crystals has been found.

## 1. Introduction

The formation of compounds of the $\mathrm{A^{III}B^{VII}}$ type is often associated with the cation's ability to exist in the +1 valence state. These compounds differ from ordinary ones of the $\mathrm{A}^N\mathrm{B}^{8-N}$ type in that the most remote $s$-orbital of cation $A$ has a configuration of completed shell. In the so-called "ten-electron" compounds, this inertial pair of cation $s$-electrons forms a valence band together with anion $p$-states, whereas the lowest – by the energy – conduction bands are formed by cation $p$-states. As a result, the electronic properties of such semiconductors differ from those of other ionic or covalent compounds. In particular, a forbidden zone is located at boundaries of the Brillouin zone with a prevailingly intracation exciton, and the $s$-electron pair of a cation brings about the strong static screening and the strong electron–phonon interaction.

The presence of a cation $ns^2$-electron pair gives rise to the emergence of a nonstandard anionic environment and such structural ordering, where cations are located very close to one another. Such structures often demonstrate the temperature and baric polymorphisms, which testifies to the existence of competing, energetically close solutions for the ground-state equation. From this point of view, the study of structural properties and the dynamics of electron spectra of layered crystals such as indium and thallium halogenides – in particular, under the action of external pressure – is of fundamental interest for researching the process of stabilization in compounds with a reduced valence and for elucidating the role of the "sole" inert $s$-electron pair of a metal ion.

Another aspect of the problem that draws attention of researchers is the study of structural phase transitions insulator–metal or semiconductor–metal induced by various exterior factors: by variations of the temperature, pressure, and chemical composition. Experimental data testify that the transition origins are different for different types of substances. As a result, a number of mechanisms has been suggested for such transitions. For instance, these are (i) a transition with the energy band overlapping induced by the disappearance of the forbidden band between the valence and conduction bands; (ii) a transition in an antiferromagnet of the "order–disorder" type; (iii) a modification of the crystal spatial symmetry, which results in a change of its band structure; (iv) the Mott transition, when the metallic state disappears owing to the loss of a correlation between electrons; (v) transitions that involve the strong electron–phonon interaction (polaron effects).

Of the mechanisms described above, the simplest one is a transition with the energy band overlapping. The disappearance of the forbidden band occurs gradually, so that the crystal volume, the number of free charge carriers, the conductivity, and other parameters change continuously. In practice, the most demonstrative examples of transitions with the energy band overlapping were obtained in high-pressure experiments. Here, the energy gap disappearance takes place owing to the broadening and the complete overlapping of electron energy bands, which results from a reduction of interatomic distances.

This work aimed at the theoretical study of the structural and electronic properties of orthorhombic indium and thallium monohalogenides in a wide range of the external pressure. The research included the determination of equilibrium lattice parameters, the bulk elastic modulus, the limiting pressures of phase transitions into a highly symmetric structural type. The calculations of the electron spectrum dispersion induced by a pressure change allowed us to determine the conditions for

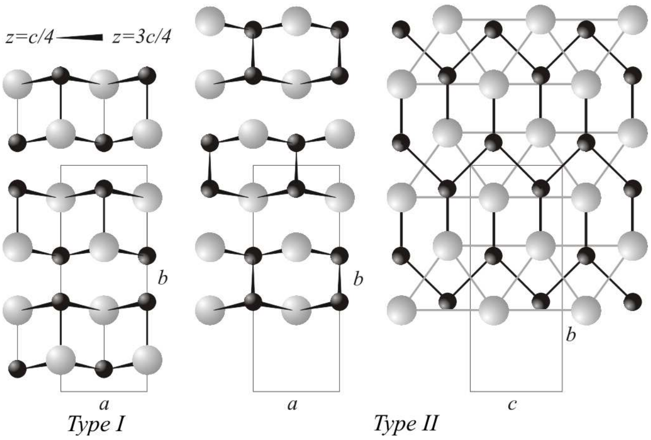

Fig. 1. Projections of a crystal structure of the TlI type onto planes $(a, b)$ and $(b, c)$ for the layer arrangement according to type I (NaCl) and II (CsCl) [6]. Metal and halogen are denoted by dark and light balls, respectively

the compounds under consideration to transit into the metallic state.

## 2. Crystal Structure

Under normal conditions, InCl crystallizes into a cubic lattice with the spatial symmetry $P2_13$ and with the unit cell containing 32 formula units [1, 2].

The structure of InCl crystals is a deformed version of the NaCl structure, in which the edge of a cubic unit cell is twice as long as that in nondeformed NaCl. In sodium chloride, $Na^+$ and $Cl^-$ layers are parallel to cross-section (111). A $Na^+$ ion in such a layer is octahedrally surrounded by three $Cl^-$ ones from each of the neighbor layers. In the second sphere, it is surrounded by 12 $Na^+$ ions which form a cuboctahedron; six of them lie in its own layer, and three more ions do in each neighbor $Na^+$ layer. All the Na–Na distances are identical.

Under normal pressure, indium halogenides (InI, InBr) and thallium iodide crystallize in a layered orthorhombic structure of the TlI type with the spatial nonsymmorphous symmetry group $D_{2h}^{17}$ $(Cmcm)$ [2–5].

At a temperature of 120 °C, InCl crystals transform into the orthorhombic phase.

A unit cell of those crystals contains four formula units, and a primitive one does two formula units.

The structure under consideration (the coordination number (c.n.) $= 7$) can be regarded as an intermediate one between structures of the NaCl (c.n. $= 6$) and CsCl (c.n. $= 8$) types. Figure 1 illustrates two cases where the structure of TlI-type crystals is considered to be formed from either NaCl-type (type I) or CsCl-type (type II) layers.

A layer of type I (NaCl) consists of two sublayers of indium and halogen atoms, with the nearest anions and cations being bound. Every ion has four neighbors in its second coordination sphere (Fig. 1). In this case, the crystal looks like that composed of layers of deformed cubes, whose vertices are alternatively occupied by In and halogen ions. From this point of view, the structure is composed of rock salt layers shifted by $(\frac{1}{4}a, \frac{1}{4}a, 0)$ with respect to a hypothetical parent structure ($a$ being the lattice constant).

An internal link in the type-II (CsCl) layer is a cation-cation bond, where every metal atom is connected with two similar atoms (the angle between bonds equals 80°). Metal atoms form cation chains in the plane $(b, c)$ of the crystal which are believed to be responsible for a strongly pronounced anisotropy of optical properties.

## 3. Theoretical Calculations

The calculations of the total electron energy of crystals were carried out self-consistently in the local density functional approximation. The electron energies and densities were determined by solving the Kohn–Sham equations [7].

The method of generalized gradient approximation (GGA) was used to describe the exchange-correlation potential. In this work, we used the Perdew–Burke–Ernzerhof (PBE) representation [8] for this potential. Ultrasoft Vanderbilt pseudopotentials [9] were used for the description of ionic potentials. The representation of those pseudopotentials requires the basis of plane waves to be smaller than that in the case of norm-conserving pseudopotentials, which reduces the time of computer calculations. The inequality $\Delta E < 2 \times 10^{-6}$ eV for the electron energy difference between consequent iterations was selected as a criterion of self-consistent procedure convergence.

Before the calculation of basic properties of the electron spectrum such as the total energy, the dispersion of electron states in **k**-space, and the distribution of the density of states, the optimization of ion positions in the unit cell and the lattice parameters of crystals under investigation was carried out. The relaxation procedure was considered to converge, when the magnitudes of forces acting upon the atoms became less than 0.05 eV/Å and the bulk stress was less than 0.1 GPa.

The equilibrium volume $V_0$ (the unit cell volume, at which the total energy is minimal), the bulk modulus of compression $B_0$, and its derivative with respect to the

**Experimental and theoretical equilibrium structural parameters of crystals in the orthorhombic phase**

| Crystal | InI | | InBr | | InCl | | TlI | |
|---|---|---|---|---|---|---|---|---|
| | Exper. | Theor. | Exper. | Theor. | Exper. | Theor. | Exper. | Theor. |
| a | 4.75 | 4.815 | 4.46 | 4.45 | 4.242 | 4.242 | 4.57 | 4.66 |
| b | 12.76 | 12.811 | 12.39 | 12.09 | 12.32 | 12.320 | 12.92 | 12.99 |
| c | 4.91 | 4.921 | 4.73 | 4.63 | 4.689 | 4.689 | 5.24 | 5.31 |
| y/b (In,Tl) | 0.40 | 0.407 | 0.38 | 0.401 | 0.388 | 0.112 | 0.37 | 0.375 |
| y/b (I,Cl) | 0.14 | 0.147 | 0.16 | 0.153 | 0.155 | 0.155 | 0.11 | 0.121 |
| $V_0$, Å$^3$ | 148.80 | 151.77 | 130.69 | 124.57 | 122.53 | 245.05 | 154.7 | 160.7 |
| $E_0$, eV | – | −3765.0 | – | −3862.2 | – | −3952,1 | – | −3400.1 |
| $B_0$, GPa | – | 21.2 | – | 22.8 | – | 26.30 | – | 20.9 |
| $B_0'$, GPa | – | 6.7 | – | 4.1 | – | 9.6 | – | 7.6 |

pressure $B_0'$ were found by fitting the Birch–Murnaghan equation of state of the third order [10, 11] using the least square method until the obtained dependences of the total energy on the unit cell volume were attained.

In the Table, the experimental and theoretical values for equilibrium lattice parameters and ion positions in the crystal unit cell, as well as the ground state parameters $E_0$, $V_0$, $B_0$, and $B_0'$, are tabulated.

The calculated values of crystal lattice parameters differ from experimental ones to within 3.1%, whereas the ion positions differ from the corresponding experimental data by no more than 4.2%. A certain excess in theoretically obtained values for lattice parameters $a$, $b$, and $c$ was induced by neglecting the zero vibrations and overestimating the binding energy value in the local density approximation formalism.

All orthorhombic compounds of the TlI type are neatly distinguished in the structural diagram (Fig. 2), where the dependences of the structure packing density on the lattice parameter ratio $c/a$ are depicted. The lattice parameter $a$ affects cation–anion bonds, whereas the parameter $c$ is determinative for interactions along cation chains. This means that smaller values of $c/a$ correspond to shorter cation–cation distances in comparison with those reckoned from cations to the nearest anion environment. At a normal pressure, the value of $c/a$ in a TlI crystal is considerably higher than that in indium monohalogenides. The ratio $c/a$ in InI decreases as the pressure grows, whereas it increases in InBr (at pressures above 4 GPa) and TlI. This evidences that the InI crystal is characterized by an exclusively high compressibility along the $c$-axis. When the pressure grows, intercation distances in the monohalogenides concerned diminish much quicker than the lengths of cation–anion bonds. However, the shape of a coordination polyhedron around a cation changes slightly.

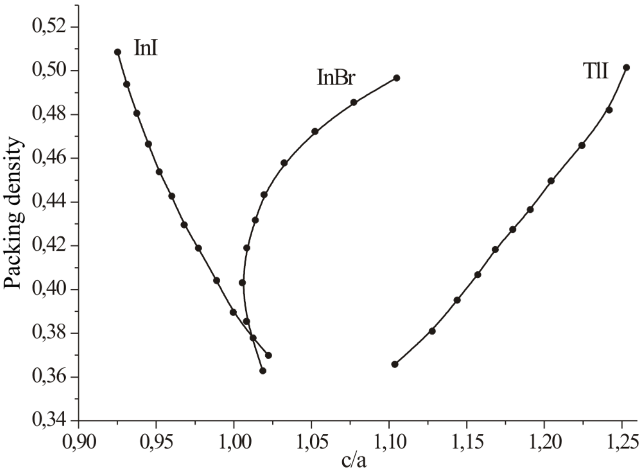

Fig. 2. Dependences of the crystal structure packing densities on the ratio $c/a$

In Fig. 3, the dependences of theoretical lattice parameters in InI, InBr, and TlI crystals on the applied external hydrostatic pressure are exhibited. It is worth noting a good agreement between the theoretically calculated values of structural parameters and experimental data [5]. The lattice parameters change anisotropically, as the pressure increases. The crystalline structure is more compressible in the $(b, c)$-plane which contains cation chains In–In (Tl–Tl).

To study whether the structural transitions are possible, we also calculated the dependences of the total energies of examined compounds on the unit cell volume in a cubic structure of the CsCl type. For an InI crystal, the TlI-type structure becomes less stable than the CsCl-type one at $V/V_0 = 0.65$, i.e. at a pressure of 19 GPa.

A similar scenario takes place in an InBr crystal as well. However, the pressure of a structural transition is much lower here (3.2 GPa, i.e. $V/V_0 = 0.73$). These values agree well with experimental data on the pressure of the transition into a highly symmetric phase (3.5 GPa) [12]. For orthorhombic TlI, the transition into

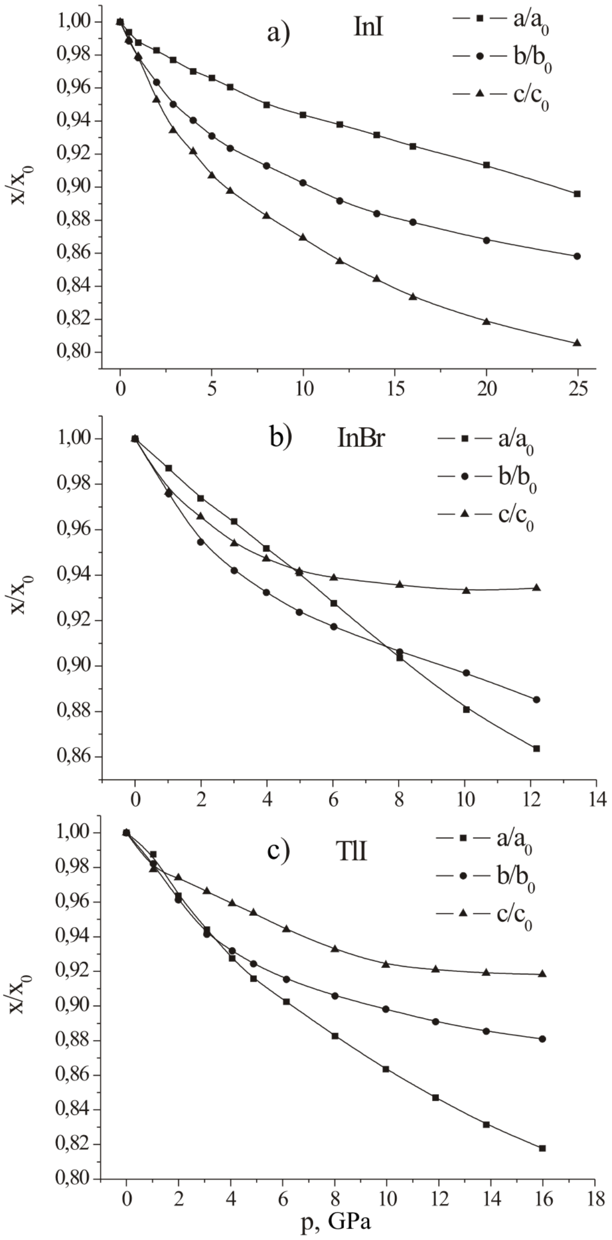

Fig. 3. Dependence of relative lattice parameters in InI ($a$), InBr ($b$), and TlI ($c$) on the pressure

the structural type CsCl occurs at a pressure of 0.5 GPa ($V/V_0 = 0.91$), which agrees with experimental data [13].

Figure 4 demonstrates that two structural transitions are characteristic of InCl crystals. The first transition occurs from a deformed cubic phase (the symmetry group $P\ 2_13$) into a structure of the TlI type (the symmetry group $Cmcm$) at $V/V_0 = 0.94$, i.e. at a pressure of 0.7 GPa. It is followed by the second transition into

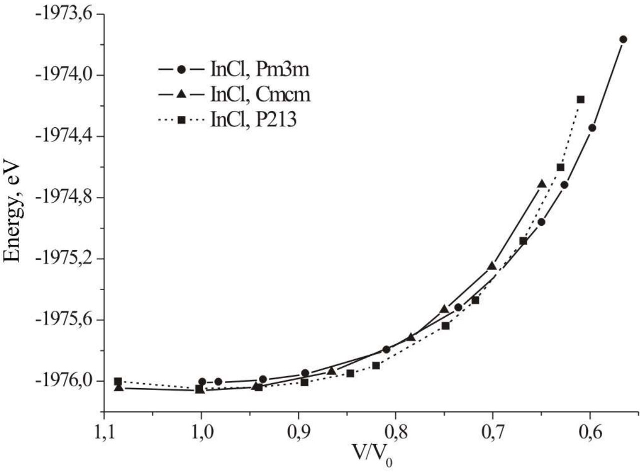

Fig. 4. Total energy per one formula unit for InCl crystals in three structural types

a highly symmetric CsCl phase (the symmetry group $Pm3m$) at a pressure of 14.5 GPa ($V/V_0 = 0.7$).

On the basis of structural lattice parameters obtained at various pressures, we studied pressure-induced variations in the band-energy spectrum of InI, InCl, InBr, and TlI crystals. The calculations were executed in the basis of 4136 plane waves (the cut-off kinetic energy $E_{\text{cut}} = \frac{1}{2}G_{\max}^2 = 300$ eV). The choice of such a large basis of plane waves in the case of ultrasoft pseudopotentials was predetermined by the inclusion of indium $4d$-orbitals and thallium $5d$-orbitals into the band structure calculation scheme. To obtain the band-energy diagram, after the self-consistent potential had been determined (it required to execute 8 iterations), the energy values were tabulated at 126 points which were localized on the edges and highly symmetric lines of 1/8 of the irreducible part of the Brillouin zone.

A comparison of band-energy parameters obtained for indium and thallium iodide crystals making use of ultrasoft pseudopotentials with the data of previous calculations made on the basis of norm-conserving pseudopotentials demonstrated their good agreement.

The analysis of band diagrams showed that those bands which form a forbidden gap demonstrate a rather weak dispersion, except for directions toward the Brillouin zone center. The narrowest energy intervals in the forbidden band are localized far from point Γ. It is inherent to all compounds of the $A^{III}B^{VII}$ family both cubic and orthorhombic, and it mainly stems from the electron configuration of those "ten-electron" compounds possessing an excess metallic $s$-electron pair.

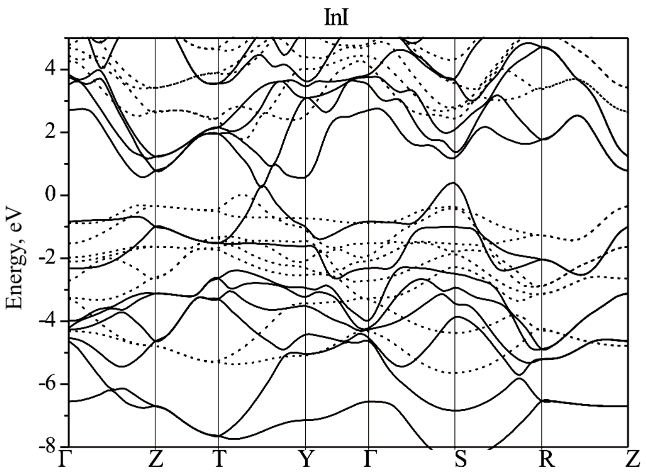

Fig. 5. Band-energy diagrams for InI under a pressure of 0 (dotted curves) and 16 GPa (solid curves)

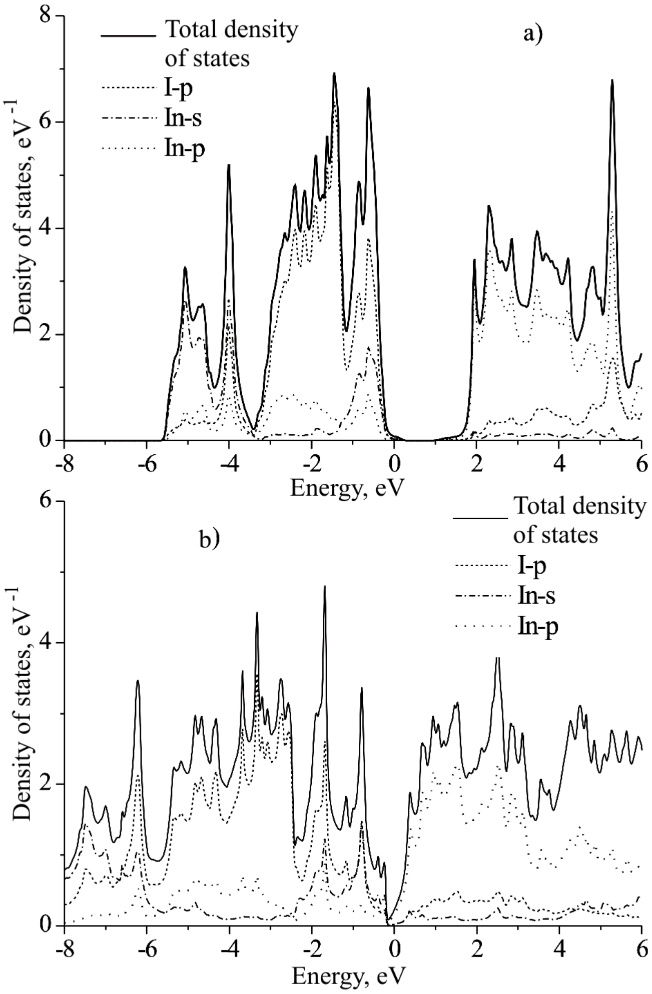

Fig. 6. Distributions of the total density of states and partial contributions of separate orbitals to the band structure of InI under normal conditions (*a*) and under a pressure of 16 GPa (*b*)

While comparing the obtained theoretical results and experimental data, one should bear in mind that the energy gap width was underestimated, provided that calculations were carried out in the local density approximation.

A decrease in the distance between ions at a deformation of the lattice was found to result in an increase of the electron energy band dispersion in the **k**-space and a reduction of the forbidden gap. At a pressure of 16 GPa (Fig. 5) along highly symmetric lines $T \rightarrow Y$ and $\Gamma \rightarrow Z$ in the Brillouin zone (they characterize interactions along the $c$-axis), unfilled $p_z$-states from the In conduction band mix with the states from the highest valence band which originate from In $s$-orbitals. Such an interaction results in the disappearance of the direct forbidden gap along the $T \rightarrow Y$ line, i.e. the metallization of In–In bonds along the crystal $c$-axis takes place. The direct forbidden gap width decreases simultaneously with a reduction of the cation–cation distance, which evidences the crucial role that the $5s^2$-orbital of In plays in the phase transition of the crystal into the metallic state.

Those considerations are confirmed by the results of calculations of the energy parameters of one-dimensional zigzag chains generated by InI molecules. The translation vector in such a model structure corresponds to the parameter $c$ of the three-dimensional crystal lattice. Our researches showed that an enhancement of the $sp$-hybridization between indium orbitals gives rise to strong coupling interactions, so that the valence and conduction bands intersect at a pressure of 15 GPa. However, in a real crystal structure, there are also additional interactions between the cation and the anions which form a trigonal prism. Owing to the influence of $I^-$ electron orbitals, no overlapping between the conduction and valence band states takes place along the $\Gamma \rightarrow Z$ line.

An enhancement of the cation $s-p$ mixing which leads to the coupling interaction and to a reduction of the energy gap width is also confirmed, when considering the dependences of the electron density of states (Fig. 6).

As a rule, cations are more weakly polarized in an electric field than anions. However, cations with the $ns^2$-configuration are characterized by a higher polarizability in comparison with that of cations of the same radius with the inert gas configuration. Perhaps, this can be related to a smaller energy difference between $^1S$

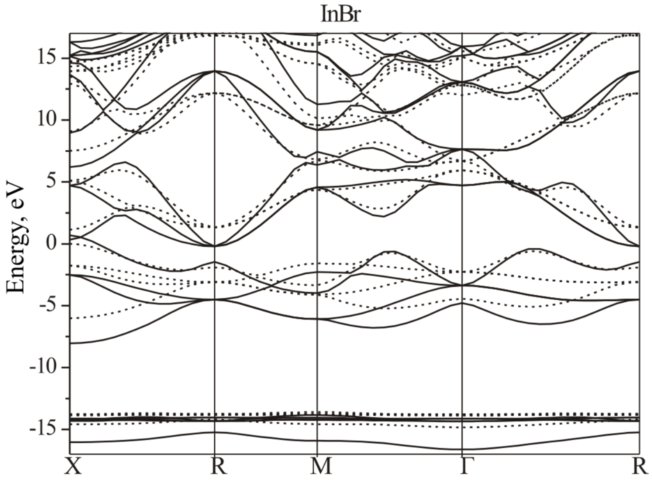

Fig. 7. Band-energy diagrams for InBr with the CsCl-type structure under a pressure of 3.2 (dotted curves) and 6.5 GPa (solid curves)

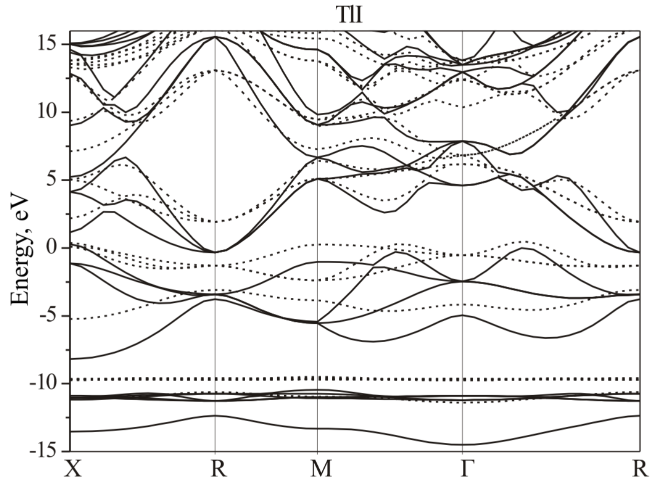

Fig. 8. Band-energy diagrams for TlI with the cubic structure of the CsCl type under a pressure of 0.5 (dotted curves) and 14 GPa (solid curves)

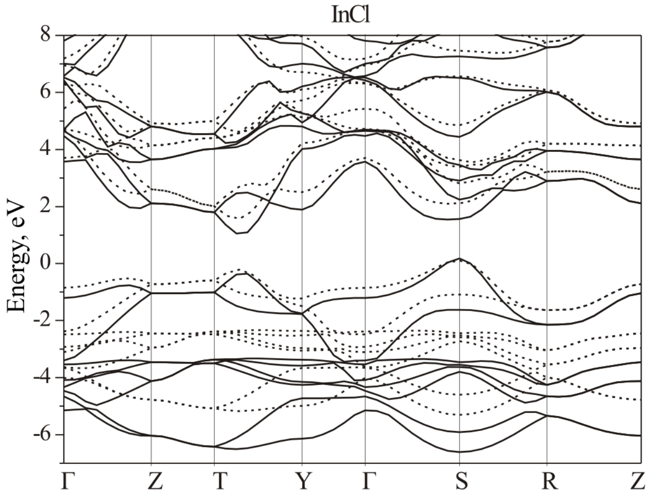

Fig. 9. Band-energy diagrams for InCl in the orthorhombic phase under a pressure of 0.7 (dotted curves) and 6.5 GPa (solid curves)

and $^1P$ states. An opportunity of $s-p$ hybridizations of a sole $5s^2$ pair owing to a deformation of its coordination octahedron is supposed. As a result, the dipole-dipole interaction emerges between the ions. A decrease in the energy induced by this interaction compensates the energy growth stimulated by a lattice deformation.

The results of calculations of the polarization energy of indium halogenides [14] confirm the thesis that $5s^2$-ions are prone to the distortion of their original centrosymmetric ordering with the passage to a noncentrosymmetric one.

The reduction of cation-cation distances makes the interaction between In($5s$)/In($5p$) and I($5p$) states stronger and results, therefore, in a subsequent growth of the coupling interaction between cations. This effect is strong enough to compensate an electrostatically and structurally disadvantageous situation which arises with the growth of an external pressure. Therefore, the phase transition of the InI crystal from a low-symmetry phase of the TlI type into a highly symmetric one of the CsCl structural type occurs only at a very high pressure. On the basis of calculations of the total energy of the InI crystal in the cubic CsCl phase, the limiting pressure for the structural phase transition was estimated to be 19 GPa. Hence, the transition of InI into the metallic state precedes the phase transition into the CsCl-type structure. After this structural transition, the compound remains metallic; however, the cation–anion interaction comes to the foreground, whereas the In–In one does not play a crucial role any more.

The calculations of the dependences of the total energies of InBr and TlI single crystals on the unit cell volume in the cubic CsCl structural type (the spatial symmetry group $Pm3m$) showed that this phase becomes energetically more beneficial at a pressure of 3.2 GPa in InBr and at 0.5 GPa in TlI.

In Figs. 7 and 8, the calculated band-energy diagrams of indium bromide and thallium iodide, respectively, in the cubic structure after the phase transition are exhibited. From the diagram analysis, it follows that the transition into the metallic state in InBr and TlI crystals takes place after the phase transition into the CsCl structural type, in contrast to InI ones. The limiting pressure of the transition into the metallic state amounts to 6.5 GPa for InBr and 14 GPa for TlI.

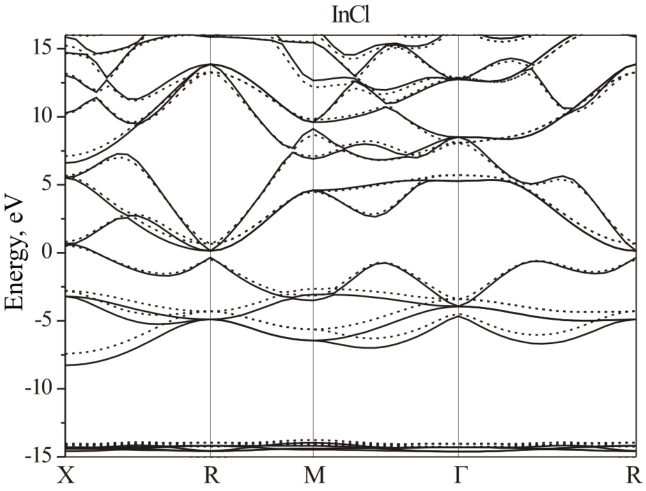

Fig. 10. Band-energy diagrams for InCl in a cubic phase of the CsCl type under a pressure of 14.5 (dotted curves) and 17.5 GPa (solid curves)

In Fig. 9, the pressure-induced modification of the band diagram for an InCl crystal in an orthorhombic phase of the TlI type is illustrated. The direct and indirect gaps decrease as the pressure grows.

For InCl crystals, their transition into the metallic state occurs already in a highly symmetric phase of the CsCl type (InCl transforms into this phase at a pressure of 14.5 GPa). The pressure of the corresponding transition is equal to 17.5 GPa (Fig. 10).

## 4. Conclusions

Theoretical researches of structural and electronic properties of indium and thallium monohalogenides under the influence of external pressure have been carried out in the framework of the electron density functional theory, by using ultrasoft pseudopotentials. It is found that, in the case of the external pressure growth and owing to the electron energy band broadening, a delocalization of valence states in the low-symmetry structure takes place, which causes an enhancement of the coupling interaction between cations and to a reduction of the distance between them. The role of the excess $ns^2$-electron pair of a metal ion changes from the non-coupling to coupling one. The distribution of electron states together with the coupling interaction between cations lead to a high pressure needed for an InI crystal to transit into an electrostatically and structurally more advantageous, highly symmetric phase of the CsCl type. The structural phase transition is also preceded by the transition into a quasi-one-dimensional metallic state in InI crystals, whereas in InBr and TLI crystals, the transition into the metallic state takes place after the transition into the highly symmetric phase. Two structural transitions were revealed in InCl crystals: from a phase of the NaCl type into an orthorhombic phase of the TlI type and then into a phase of the CsCl type.

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### ВПЛИВ ТИСКУ НА ЕЛЕКТРОННИЙ СПЕКТР ГАЛОГЕНІДІВ ІНДІЮ І ТАЛІЮ

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Резюме

На основі самоузгоджених розрахунків методом псевдопотенціалу проведено теоретичне вивчення структурних і електронних властивостей кристалів галогенідів індію і талію у широкому діапазоні зміни зовнішнього тиску. Підтверджено визначальну роль надлишкової $ns^2$-електронної пари катіона у формуванні структури та стабілізації сполук, що містять катіони зі зниженою валентністю. Визначено значення граничних тисків фазових переходів у високосиметричний структурний тип CsCl і переходів напівпровідник–метал. Встановлено послідовність структурних фазових переходів у кристалах InCl.