# ELECTRON AND PHONON SPECTRA OF $In_x Tl_{1-x}I$ SUBSTITUTIONAL SOLID SOLUTIONS

A. FRANIV, O. BOVGYRA, O. SAVCHYN

UDC 537.226; 538.936; 621.315 ©2006 Ivan Franko Lviv National University, Faculty of Physics (8a, Kyrylo and Mefodii Str., Lviv 79005, Ukraine; e-mail: bovgyra@physics.wups.lviv.ua)

The dynamics of the parameters of the electron subsystem in substitutional solid solutions (SSSs)  $\ln_x Tl_{1-x}I$  has been studied theoretically making use of the pseudopotential method. The non-linear behavior of the dependence of the band gap width on the solution composition has been described taking internal local deformations into consideration. The theoretical results are in a good agreement with experimental data.

#### 1. Introduction

Searching for new functional materials and ways to control their properties belongs to the primary tasks of physics of semiconductors and insulators. For a rather long time, the attention of scientists has been attracted to studying the properties of semiconductors and insulators with a layered crystalline structure. This work is a continuation of the earlier ones [1– 3] devoted to studying the structure and the optical properties of layered semiconductors, which are based on monoiodide compounds of In and Tl, namely, an  $In_x Tl_{1-x}I$  SSS. Provided that the ionic bond component in such materials is preserved at a relatively high level, the anisotropy of their structure was supposed to manifest itself more clearly. It is obvious that, among other primary tasks, the production of new single crystals demands to carry out the research of their basic characteristics. In particular, these include the determination of the band gap width; the evaluation of key parameters of electron, exciton, and phonon excitations; the investigation of the structure of electron energy bands and how this structure manifests itself in optical spectra; and searching for the regularities in the variations of those parameters and characteristics, if the SSS composition changes.

## 2. Crystalline Structure of $In_x Tl_{1-x}I$

The  $In_x Tl_{1-x}I$  SSS crystallizes in a layered orthorhombic structure with the spatial group of symmetry  $D_{2h}^{17}$  (*Cmcm*). The elementary cell of those crystals contains four formula units and a primitive one two units. The character of bonds in  $In_x Tl_{1-x}I$  crystals is exposed in Fig. 1.

Every halogen ion forms five bonds with ions possessing an opposite sign, and every metal ion forms bonds with seven anions I<sup>-</sup>. Owing to such peculiarities of the layer formation, In and Tl ions are located outside the layers, while iodine ions are inside them. The crystallographic axes a and c are oriented in parallel and the axis b perpendicularly to the layers. An important feature of the  $In_xTl_{1-x}I$  crystalline structure is a relatively short distance between metal ions from adjacent layers. This predetermines a high anisotropy of physical properties of the investigated compounds  $In_xTl_{1-x}I$  in the directions not only parallel or perpendicular to the layers, but also in the layer plane itself.

### 3. Dynamics of Optical Spectra

The experimental studies of the reflection, absorption, and luminescence spectra of  $\ln_x Tl_{1-x}I$  crystals were described in works [3–6]. In particular, the absorption spectra of those SSSs demonstrate the absorption band of the ground (1s) state of an exciton within the whole range of variation of the content x. Moreover, the growth of the TII component in the SSS is accompanied by a shift of the spectrum towards the short-wave side, while the exciton bond energy increases from 4.5 meV to the value  $R_y = 6$  meV in In<sub>0.3</sub>Tl<sub>0.7</sub>I.

The results of studies of absorption spectra allow the shape of the basic SSS characteristics — the concentration dependence of the band gap width  $E_g$  to be determined (Fig. 2). We note that the absolute value of  $E_g$  was obtained on the basis of experimental data on the quantity  $E_{\rm exp}$ , taking into account the bond energy of excitons. The following typical features of the dependence  $E_g(x)$  should be emphasized: 1) an increase of the amplitude of  $E_g$  if In atoms in the cation sublattice are substituted by Tl ones and 2) nonlinearity of the  $E_g(x)$  dependence with a deflection directed downwards (in the quadratic approximation, the bowing  $\delta = 0.87$ .

ISSN 0503-1265. Ukr. J. Phys. 2006. V. 51, N 3



Fig. 1. Arrangement of atoms in an elementary cell of  $In_x Tl_{1-x}I$ . Dark spheres stand for metal ions, light spheres for halogen ones

In the linear approximation of the dependence  $E_{\rm exp}(x)$ , the concentrational shift coefficient of the exciton band (Fig. 2, dashed line) is  $\alpha = dE_{\rm exp}/dx = 0.63/x$  eV, if the composition parameter x is expressed in fractional units, or 0.0063/x eV, if in percents. According to the luminescence spectra,  $\alpha = dE_{\rm exp}/dx = 0.45/x$  eV (x is in fractional units) or 0.0045/x eV (x is in percents).

Comparing the obtained values of the coefficient  $dE_{\exp}/dx$  with the corresponding values for iodides of other metals which crystallize by forming layered structures, e.g.,  $Pb_{1-x}Mn_xI_2$  and  $Pb_{1-x}Cd_xI_2$  [7], a note should be made of their almost half as large values in the  $In_xTI_{1-x}I$  case. The reason is that the difference between the atomic pseudopotentials of In and Tl atoms is smaller than that between Pb and Cd or Pb and Mn atoms, which can be recognized while comparing the energy gap widths in InI (2.01 eV) and TlI (2.95 eV) on the one hand, and PbI<sub>2</sub> (2.6 eV) and MnI<sub>2</sub> (4.6 eV) on the other hand.

## 4. Theoretical Calculations of the Band Structure Parameters

Theoretical approaches, which attempt to describe the electronic structure of SSSs and, in particular, the nonlinear dependence of the band gap width on the solution composition, can be classified into two groups: isomorphic and polymorphic models. In the isomorphic models, the local atomic environment is replaced by a certain averaged effective one. For example, it may be a virtual crystal approximation (VCA) or a coherent potential one (CPA), which, nevertheless, cannot provide a correct theoretical description of the electronic properties of SSSs [8]. The "band anticrossing"



Fig. 2. Concentration dependence of the band gap width in  $In_x Tl_{1-x}I$  according to absorption spectra (the dashed line is its linear approximation)

(BAC) model [9] is another isomorphic approximation applicable  $\mathrm{to}$ SSSs, where a small number of highly electronegative atoms replace more electroneutral anions in the crystal lattice. The polymorphic models concentrate their attention on the basic property that distinguishes solid solutions from ordered compounds, namely, on the existence of a number of different local atomic configurations in the crystal lattice of SSSs. One of the most promising approaches to study the properties of the electron subsystem of polymorphic compounds involves calculations in the framework of the localdensity functional theory. In order to model the SSSs, this method uses superlattices, where arbitrarily given atomic configurations can be studied [10].

The conduction band, which is formed mainly by the cationic *p*-states of a metal, is the most sensitive to a variation of the composition in the system  $In_x Tl_{1-x}I$ under consideration. A "drift" of the conduction band minimum, which accompanies the variation of the  $In_x Tl_{1-x}I$  solution content, from  $k = k_{min}$  for InI (x = 1)to k = 0 for TII (x = 0), reconstructs the topology of isoenergetic surfaces in such a way that the break of the solid solubility scenario, which follows the scheme of substitution inside the sandwich-like layers In–I–In, occurs at  $x = x_{cr}$ . If  $x < x_{cr}$ , thallium can penetrate into the interlayer spaces (autointercalation), so that both simple and aggregated centers-clusters can be formed stochastically as well; the latter leads to the occurrence of large-scale fluctuations in the crystal composition. A statistical distribution of clusters and the probable interactions between them strongly complicate the whole picture. A possible way to identify those clusters has to be based on the analysis of features of the corresponding quantum-mechanical states and the structure details of optical — in particular, excitonic — spectra. The aggregation of cluster formations and, especially, the autointercalation result in the generation of holes.

Taking into account the essential role of band current carriers, the emergence of the intermediate rearrangement state can be classified as a phase transition induced by the configuration interactions and the hybridization of states. From this point of view, it is interesting to analyze the variation of the distribution of the charge density  $\rho$  between cations in the pairs In—In, In—Tl, and Tl—Tl in the framework of a statistically formulated problem. The matter is that, as the results of calculations of the function  $\rho(\mathbf{r})$ show, an enhancement of the electron charge density is observed in the intercation space in the formed rhombic structure. This evidences for the essential roles played by the configuration interactions and hybridization of cation orbitals.

In order to determine the band structure of the  $In_x Tl_{1-x}I$  substitutional solid solution *ab initio*, the norm-conserving method of nonlocal pseudopotential was used. The calculation procedure is described in detail in works [11, 12]. The features of the theory and the main approximations applied in the course of calculations can be summarized as follows:

— The total electron energy of the crystals was estimated self-consistently in the local-density-functional approximation. The calculations were carried on for  $1 \times 1 \times 1$  superlattices involving 8 atoms, with the concentration contribution of In being equal to 0, 0.25, 0.5, 0.75, and 1.

— The electron energy and the electron concentration were determined making use of the Kohn-Sham equations.

— The ionic potentials were modeled making use of the Vanderbilt ultrasoft pseudopotentials [13]. The correlation potential was approximated by the Ceperley– Alder formula at  $r_s > 1$ , where  $r_s = \sqrt[3]{3/(4\pi\rho)}$ , and by the Gell-Mann–Brueckner expression in the highdensity limit. The distribution of charge density was calculated by the method of special points [14], and the procedure of charge damping was engaged.

— The relaxation of ion positions was carried out for every crystalline structure on the basis of the calculated interatomic forces, and the integrated stress within a cell was determined. The relaxation iteration procedure was considered completed if the amplitudes of forces acting



Fig. 3. Fragments of energy band diagrams of InI and TII

on the atoms became smaller than 0.05 eV/Å and the bulk stress was less than 0.1 GPa.

According to the known approximation of a virtual crystal and to Vegard's rule [15], the crystal lattice constants in the  $In_x Tl_{1-x}I$  substitutional solid solutions are determined as linear combinations of the corresponding values for the initial components InI and TII:

$$a(x) = a_{\mathrm{InI}}x + a_{\mathrm{TII}}(1-x)$$

The calculations were carried out along the basic symmetry directions of the Brillouin zone in the basis of 4899 plane waves.

Fig. 3 exhibits the corresponding band structures of InI and TII. In the limit cases x = 0 (TII) and x = 1(InI), the calculated energy distances between electron states agree well with the known experimental data and the results of previous pseudopotential calculations [11,16]. The narrowest energy gaps are located far from  $\Gamma$  point. This feature is inherent to all compounds of class A<sub>3</sub>B<sub>7</sub>, both cubic and orthorhombic ones, and is a result, mainly, of the electron configuration of those "ten-electron" compounds with their excess s-electron pair of the metal. The maximum of the valence band for an InI crystal is observed at point  $\Sigma^*$ , as well as at the equivalent point  $C^*$ , and, in a TII crystal, on line H  $(T \rightarrow Y)$ . The bottom of the conduction band is located at point Y in the case of InI, and on line H in the case of TlI.

The direct band gap width is 1.86 eV (line H) in InI and 2.82 eV (line H) in TII. The indirect band gap width is 1.82 eV ( $\Sigma^* \to Y$ ) in InI and 3.09 eV ( $H \to Y$ ) in TII. While comparing the obtained theoretical results with experimental data, one should bear in mind that the value of the energy gap width is underestimated,

ISSN 0503-1265. Ukr. J. Phys. 2006. V. 51, N 3



Fig. 4. Energy band diagram of a crystal  $\mathrm{In}_{0.5}\mathrm{Tl}_{0.5}\mathrm{I}$ 

provided the calculations were carried out in the local-density approximation. Therefore, InI crystals are indirect-band-gap ones, while TII crystals, on the contrary, are characterized by a direct band gap.

In Fig. 4, the energy band diagram of the  $In_{0.5}Tl_{0.5}I$  substitutional solid solution is depicted.

The analysis of the partial contributions of individual orbitals to the function of the total density of states (Fig. 5) and of the partial contributions of individual bands to the electron density allowed the genesis of the valence bands of  $In_x Tl_{1-x}I$  substitutional solid solutions to be determined.

The lowest bands are formed by 4d-states of In, the bands induced by 5s-states of iodine are located above, and higher, in the range from -10 to -11 eV, the bands resulted from 5d-orbitals of thallium are dispersed.

The contribution to the formation of two following bands, which are dispersed between -6 and -4 eV, is made by both ions. The character of these bands is defined by coupling intramolecular interaction. Within the whole **k**-space, these bands are connected to the  $p_y$ -electrons of iodine with the admixture of metallic *s*electron states. Characteristic of these two bands is also the interaction between cations in the *z*-direction, which forms the interlayer bonds.

The next bands are connected with 5p-orbitals of iodine. The top of the valence complex is practically cationic with the admixture of 5p-states of the halogen.

The growth of the In content in the  $In_x Tl_{1-x}I$  substitutional solid solutions results in the narrowing of both the direct and indirect band gaps. At x = 0.75, the indirect gap becomes equal to the direct one. If the In content continues to grow, the crystal becomes the indirect-band-gap one. In Fig. 6, the results of



Fig. 5. Distributions of the total density of states and the partial contributions of individual orbitals to the energy band structure in  $In_x Tl_{1-x}I$ 

calculations of the dependence of the energy gap width on the composition of semiconducting solid solutions are displayed.

The nonlinearity of the experimental composition dependence  $E_g(x)$  for SSSs is a phenomenon that happens rather often. The expressions are known which

ISSN 0503-1265. Ukr. J. Phys. 2006. V. 51, N 3

describe such dependences in  $A_x B_{1-x} C$  substitutional solid solutions quite satisfactorily. In our case, the dependence of the energy gap width may be written down in the form

$$E_g(x) = x E_{g,\text{In}} + (1-x) E_{g,\text{Tl}} - \delta x (1-x), \qquad (1)$$

where  $\delta$  is the bowing parameter of the curve  $E_g(x)$ .

The integral value of the bowing  $\delta$  can be decomposed into the components [17]

 $\delta = \delta_{\rm VD} + \delta_{\rm CE} + \delta_{\rm SR},$ 

where  $\delta_{\rm VD}$  is the contribution made owing to the volume deformation effect which is responsible for the variation of the band gap width in the individual components, InI and TII, of the solid solution;  $\delta_{\rm CE}$  is the deflection connected with the charge redistribution among various bonds in a disordered solid solution; and  $\delta_{\rm SR}$  is the deflection coefficient that describes the variation of the band gap width when ion positions in the SSS lattice relax.

The first component  $\delta_{\rm VD}$  is connected with the volume deformation of the SSS caused by a mismatch of the lattice constants of the SSS components and reflects the response of InI and TII to hydrostatic pressure. This deflection component can be taken into account in the virtual crystal approximation.

While calculating the second component  $\delta_{\rm CE}$  of the bowing parameter, the relaxation of the interatomic bond lengths in the superlattice was not carried out. In this case, there occurs a charge redistribution between the In–I and Tl–I bonds, which results in changing the arrangement of the electron energy bands.

When the solid solution finds itself in an equilibrium configuration, i.e. after the relaxation of the interionic bond lengths, the next variation of the band structure takes place, which is accompanied by the modification of the band gap width; this modification is described by the bowing coefficient  $\delta_{SR}$ . The relaxation of ionic positions leads to a reduction of non-uniformity in the charge distribution and diminishes the volume deformation effect. In the solid solutions with cation substitution, such as InTII, the basic relaxation takes place in the anion sublattice and leads to a shift of the valence bands of the anionic nature towards higher energies.

Theoretical and experimental values of the bowing parameters of the dependence  $E_g(x)$ 

	$\delta_{ m VD}$	$\delta_{ ext{CE}}$	$\delta_{ m SR}$	$\delta_{ m theor}$	$\delta_{\mathrm{exp}}$
Direct	0.59	0.38	-0.14	0.83	0.87
Indirect band gap	0.73	0.51	-0.25	0.99	

ISSN 0503-1265. Ukr. J. Phys. 2006. V. 51, N 3



Fig. 6. Calculated dependences of the energy gap width on the composition content of the  $In_x Tl_{1-x}I$  substitutional solid solution

The obtained theoretical parameters describing the deflection of the dependences  $E_g(x)$  (see Table) agree well with the experimentally measured value  $\delta_{\exp} = 0.87 \text{ eV}$ .

We also emphasize the influence of the compositional disorder and the structural relaxation in an SSS on the band structure as a whole. Taking these effects into account results in a broadening of the valence bandwidth in an SSS, as compared with that in the virtual crystal approximation.

#### 5. Conclusions

The theoretical study of features of the band structure of the  $\ln_x Tl_{1-x}I$  substitutional solid solutions has been fulfilled in the framework of the pseudopotential method. It has been shown that the account of internal local deformations in the solid solutions, i.e. the stochastic component of the intra-crystalline potential, as well as the compositional and positional disorders, makes it possible to describe the nonlinear behavior of the experimental dependence  $E_g(x)$  quite satisfactorily.

A satisfactory agreement between the experimental data and the results of calculations serves a reason to admit that the chosen model correctly describes the structure of electron energy bands in  $\text{In}_x \text{Tl}_{1-x}$ I substitutional solid solutions. This circumstance can become a basis for the further analysis and the forecast of optical properties of those compounds, as well as for the choice of a proper approach to tackle the

problem of producing a material with a given band gap width.

- Brodyn M.S., Blonskyi I.V., Bigun M.I. et al. // Ukr. Fiz. Zh. - 1992. - 37, N 8. - P. 971 - 975.
- Blonskyi I.V., Bigun M.I., Lun Yu.O., Franiv A.V. // Ibid. - N 4. - P. 547 - 551.
- 3. Franiv A. // Ibid. 1999. 44, N 12. P. 1473 1475.
- 4. Franiv A.V. // Zh. Fiz. Dosl. 1999. **3**, N 2. P. 209 212.
- 5. Frani<br/>vA.V.// Ukr. Fiz. Zh. 2001. 46, N4. <br/>— P. 461 465.
- Blonskii I.V., Krochuk A.S., Stetsishin T.L., Franiv A.V. // Fiz. Tverd. Tela. - 1986. - 28, N 10. - P. 3136 - 3139.
- 7. Brodin M.S., Blonskii I.V. Excitonic Processes in Layered Crystals. Kyiv: Naukova Dumka, 1986 (in Russian).
- Bellaiche L., Wei S.-H., Zunger A. // Phys. Rev. B. 1997. – 56. – P. 10 233.
- 9. Shan W. et al. // Phys. Rev. Lett. 1999. 82. P. 1221.
- Kent P.R.C., Zunger A. // Phys. Rev. B. 2001. 64. -P. 115208.
- Kolinko M.I. // J. Phys.: Condens. Matter. 1994. 6, N1. - P. 167 - 172.
- Kolinko M.I., Bovgyra O.V. // Ukr. Fiz. Zh. 2001. 46, N 7. - P. 707 - 719.

- Vanderbilt D. // Phys. Rev. B. 1990. 41, N 11. P. 7892 - 7895.
- Chadi D.J., Cohen M.L. // Ibid. 1973. 8, N 5. P. 5747 - 5753.
- Huang T.F., Harris J.S. // Appl. Phys. Lett. 1998. 72.
   P. 1158.
- Kolinko M.I., Kityk I.V., Krochuk A.S. // J. Phys. Chem. Solids. - 1992. - 53, N 10. - P. 1315-1320.
- Bernard J., Zunger A. // Phys. Rev. B. 1987. 36. P. 3199.

Received 25.03.05. Translated from Ukrainian by O.I. Voitenko

# ЕЛЕКТРОННІ-ФОНОННІ СПЕКТРИ ТВЕРДИХ РОЗЧИНІВ ЗАМІЩЕННЯ $In_x Tl_{1-x}I$

А.В. Франів, О.В. Бовгира, О.В. Савчин

Резюме

У рамках методу псевдопотенціалу проведено теоретичне вивчення динаміки зміни параметрів електронної підсистеми у твердих розчинах заміщення  $In_x Tl_{1-x}I$ . Описано нелінійний характер концентраційної залежності ширини забороненої зони із врахуванням внутрішніх локальних деформацій у твердих розчинах. Результати розрахунків добре узгоджуються із експериментальними даними.