10. Davis E. A. Optical absorption, transport and photoconductivity in amorphous selenium / F. Mott., E. A. Davis // Journal of Non-Crystalline Solids. – V. 4. – P. 107. – 1970.

11. Hahn H. Uber ternere chalkogenide des Thallium mit gallium und indium/ H. Hahn. B. Wellman // Naturwissenshaften. – 1967. – B. 54. – № 2. – S. 42.

12. Langon H. P. D. Electrical and Optical Properties of Vitreous Selenium / H. P. D. Langon // Phys. Rev. – 1963. – V. 130. – № 1. – S. 134–143.

13. High-Pressure Raman Study of the Ternary Chalcogenides *TlGaS₂, TlGaSe₂, TlInS₂* and *TlInSe₂* / W. Henkel, H. D. Hochheimer, C. Carlone [et al.] // Phys. Rev. B. – 1982. – V. 26. – P. 3211–3221.

14. Hochdrucksynthese und kristal-istructuren von *TlInS₂-II* und *TlInS₂-III* / J. Range, G. Engert, W. Muller [et al.] // Z. Naturforsch. – 1974. – B. 29. – S.181.

15. Pankove J. I. Optical Processes in Semiconductors / J. I. Pankove. – New Jersey : Prentice-Hall, 1971. – 422 p.

16. J. Tauc Optical Properties of Solids / J. Tauc. – Amsterdam : F. Abeles, 1970. – 277 p.

17. El-Nahass M. M. Optical and Photoelectric Properties of *TlInS2* Layered Single Crystals / M. M. Sallam, M. M. El-Nahass // Egypt. J. Solids. – 2008. – Vol. 31. – No 1.

18. Gasanly N. M. Coexistence of Indirect and Direct Optical Transitions, Refractive Indices, and Oscillator Parameters in *TlGaS2, TlGaSe2,* and *TlInS2* Layered Single Crystals / N. M. Gasanly // Journal of the Korean Physical Society. – Vol. 57. – No 1. – July 2010. – P. 164–168.

19. Urbach F. The Long-Wavelength Edge of Photographic Sensitivity and of the Electronic Absorption of Solids / F. Urbach // Physical Review. – 1953. – V. 92. – P. 1324–1325.

Китик Иван, Мирончук Галина, Парасюк Олег, Данильчук Сергей, Божко Владимир, Замуруева Оксана. Оптические свойства кристаллов системы *Tl₁₋ₓIn₁₋ₓSnₓS₂* (x=0; 0,1; 0,20; 0,3; 0,4; 0,5). В данной работе изучалась кристаллическая система *Tl₁₋ₓIn₁₋ₓSnₓS₂* (x = 0,1; 0,20; 0,3; 0,4; 0,5), а именно влияние частичного катионного замещения ионов *In* ионами *Sn* на оптические характеристики исследуемых соединений. Рассмотрены закономерности изменения оптических спектров поглощения в кристаллах твёрдых растворов от температуры и состава. Оценена ширина запрещённой зоны соединений для различных температур, прямых и непрямых переходов. Определены по экспериментальной зависимости *lnα (hv)* при различных температурах $E_g(0)$ и α_0. Рассчитана концентрация заряженных дефектов, ответственных за экспериментально установленное значение Δ_0.

Ключевые слова: коэффициент поглощения, ширина запрещённой зоны, слоистые структуры.

Kituk Ivan, Myronchuk Galina, Parasyuk Oleg, Danylchuk Sergej, Bojko Volodimyr, Zamuruyeva Oksana. Optical properties of crystals of *Tl₁₋ₓIn₁₋ₓSnₓS₂* (x=0; 0,1; 0,20; 0,3; 0,4; 0,5). The influence of partial cationic substitution of In ions by Sn ions on the optical characteristics of the solid solutions *Tl₁₋ₓIn₁₋ₓSnₓS₂* (x = 0,1; 0,20; 0,3; 0,4; 0,5) has been studied. A comparative analysis of temperature behavior of optical absorption edge over the temperature range from 77 to 300 K is performed for alloys with (x = 0,1; 0,20; 0,3; 0,4; 0,5).

The band gap of compounds at different temperatures, for direct and indirect transitions have been estimated. From the experimental dependences *lnα (hv)* at different temperatures the constants $E_g(0)$ and α_0 in the Urbach rule have been determined. The concentration of charged defects responsible for the experimentally determined value of characteristic energy has been calculated.

Key words: absorption, band gap, layered structure.

UDC 004.942 Volodymyr Bozhko,

Alina Tretyak,
Lesya Bulatetska,
Valeriy Bekenev,
Oleg Parasyuk,
Oleg Khyzhun,

Electronic structure of $AgCd_2GaS_4$

In the present work we report on measurements of *X-ray* photoelectron (*XP*) valence-band spectrum including the comparatively wide energy region corresponding to location of upper core-levels (up *to ~80 eV* with respect to the bottom of the valence band) of the atoms constituting a quaternary *AgCd₂GaS₄* single crystal grown by the Bridgman

method. Electronic structure of $AgCd_2GaS_4$ are also theoretically studied by using the first-principles full potential linearized augmented plane wave (*FP-LAPW*) method. The *FP-LAPW* method has been employed in the present work to calculate binding energies of upper core-levels for the $AgCd_2GaS_4$ compound. With respect to values of binding energies of the *Cd 4p*, *Ag 4p* and *Ga 3d core-levels*, the theoretical and experimental data for the $AgCd_2GaS_4$ compound were found to be in agreement to each other. Curves of dominant partial densities of states of $AgCd_2GaS_4$ have been compared on a common energy scale with the *XP* valence-band spectrum of the compound under consideration.

Key words: $AgCd_2GaS_4$; Electronic structure; First-principles band-structure calculations; *X-ray* photoelectron spectroscopy; densities of states.

Introduction. A quaternary $AgCd_2GaS_4$ compound crystallizes in the orthorhombic structure (space group $Pmn2_1$; lattice parameters: *a = 8.1395(9) Å, b = 6.9394(8) Å*, and *c = 6.6014 (7) Å* [11]). It is formed in accordance with a peritectic reaction $L+\beta(CdS)\Leftrightarrow AgCd_2GaS_4$ and exists in the *67–78 mol % CdS* homogeneity region [12]. Tetrahedral coordination of the constituent atoms is characteristic of the unit cell of $AgCd_2GaS_4$ [15]. In the structure of $AgCd_2GaS_4$, there are three non-equivalent types of sulfur atoms (Fig. 1), which occupy 4b and two different 2a sites. The non-central space group of the crystal structure of the $AgCd_2GaS_4$ compound makes it a very prospective material for optoelectronics and non-linear optics. The $AgCd_2GaS_4$ compound reveals intense luminescence, high photosensitivity, and wide transparency range [13,14]. The compound is n-type semiconductor with the width of energy gap, E_g, of 2.15 eV at about 300 K.
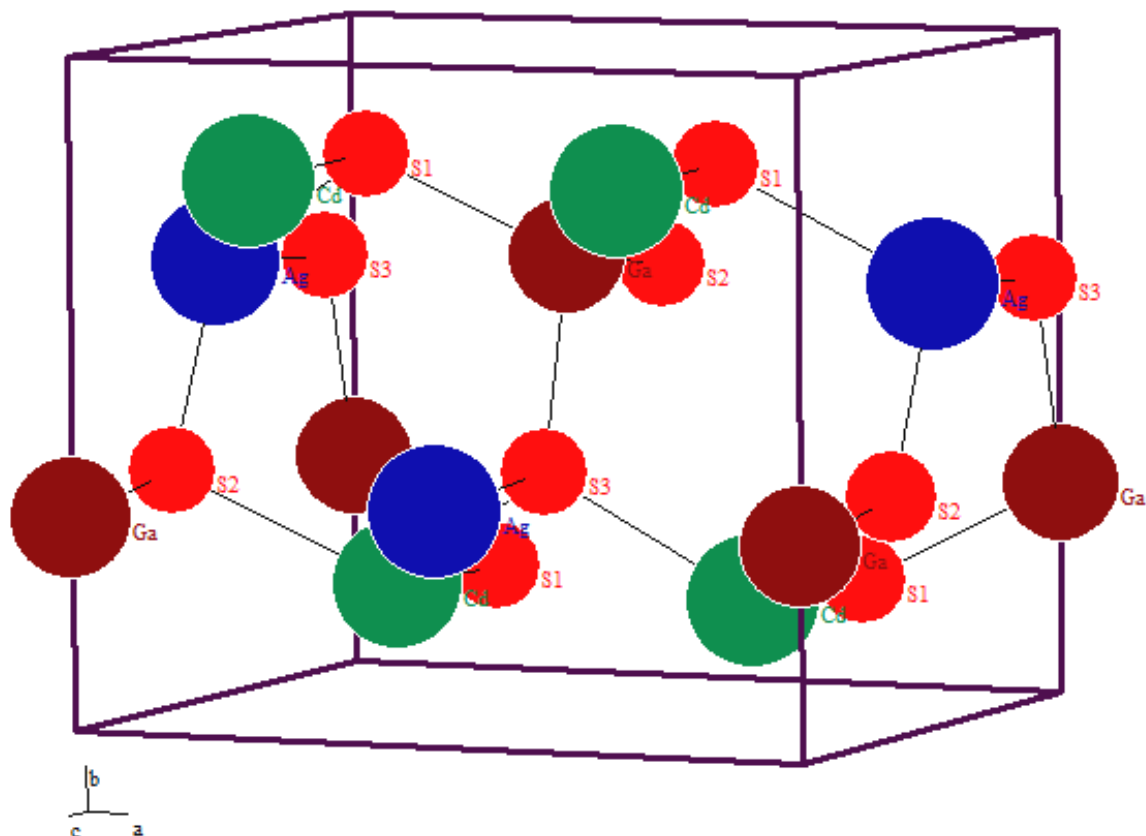

Fig. 1. *Crystal structure of $AgCd_2GaS_4$ (unit cell is outlined)*

The valence-band occupations and optical susceptibilities of $AgCd_2GaS_4$ have been calculated comparatively recently by Reshak et al. [4; 8]. It has been established that the valence band maximum and conduction band minimum are located at the Γ point of the Brillouin zone. This means that $AgCd_2GaS_4$ is a direct-gap semiconductor. In addition, Reshak et al. [4,8] have established a strong negative uniaxial anisotropy for optical properties of $AgCd_2GaS_4$. Recently in Ref. [7], X-ray photoelectron (XP) core-level and valence-band spectra for pristine and Ar$^+$-ion irradiated (001) surface of $AgCd_2GaS_4$ single crystal have been measured and those measurements have revealed high chemical stability of (001) $AgCd_2GaS_4$ surface.

Further, electronic structure of *AgCd₂GaS₄* has been calculated employing the full potential linearized augmented plane wave (FP-LAPW) method [7]. Additionally, in Ref. [7]. X-ray emission bands representing the energy distribution of the valence *Ag d, Cd d, Ga p* and *S p* states have been recorded and compared on a common energy scale with the *XP* valence-band spectrum of the *AgCd₂GaS₄* compound. The *FP-LAPW* calculations of the electronic structure of the *AgCd₂GaS₄* compound have revealed that its upper valence band is composed mainly from contributions of the *Ag* d states, with also significant contributions of the p states associated with *S* and Ga atoms, whilst the bottom of the conduction band of *AgCd₂GaS₄* is dominated by contributions of the unoccupied *Ga* s states [7].

In the present paper we aim at a study of XP valence-band spectrum including the comparatively wide energy region corresponding to location of upper core-levels of the atoms constituting a quaternary *AgCd₂GaS₄* compound (up *to ~80 eV* with respect to the bottom of the valence band). Additionally, we aim at first-principles calculations of the electronic structure of *AgCd₂GaS₄*. Therefore, ab initio *FP-LAPW* method has been employed in the present work to calculate binding energies of upper core-levels of the *AgCd₂GaS₄* compound. Curves of dominant partial densities of states of *AgCd₂GaS₄* have been also compared in the present work on a common energy scale with the XP valence-band spectrum of the compound under consideration.

Basic results and its discussions

1. Experimental. In the present study, we have used the AgCd₂GaS₄ single crystal grown by the Bridgman method. Its synthesis was described in detail in [7]. Briefly, for the growth, a 20 g batch of appropriately weighed amounts of high-purity elementary substances (purity of Ag, Cd, Ga and S better than 99,999 wt.%) was placed into an ampoule, following by its evacuating and soldering. We have used the preliminary synthesis of the batch by the direct bonding of the elementary sulfur by heating the ampoule in the flame of the oxygen-gas burner and further homogenization in the rotating furnace. The actual growth process was performed in a vertical two-zone furnace by the gradual growth of the crystal onto the formed seed. A high-quality *AgCd₂GaS₄* single crystal was derived using the following growth conditions: growth zone/annealing zone temperature of the furnace ~1100/650°C; temperature gradient at the solid-melt interface ~2,0°/mm; growth rate 0.15 mm/h; annealing duration 100 h. The diffraction pattern of the compound was indexed in the space group *Pmn*2₁, and the refined unit cell periods being in agreement with the data originally reported for this compound in Refs [11,14].

The *AgCd₂GaS₄* single crystal for the present XPS measurements was prepared in the shape of a thin plate with the following dimensions: length ~7 mm, width ~5 mm, and height ~1 mm. The plate was cut from the boule to obtain (001) surface. The plate was polished in castor oil containing additions of beryllium abrasive No. 28 to gain a high-quality optical surface following the technique reported in Ref [5]. Fig. 2 presents a photo image of the *AgCd₂GaS₄* plate used in the present experimental studies.
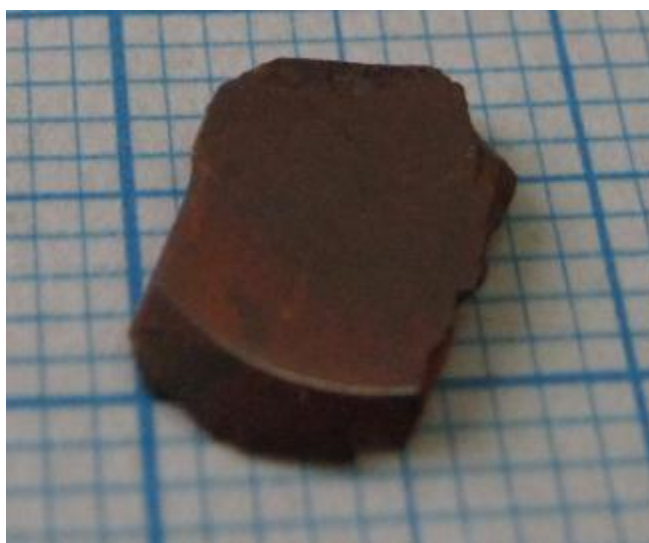

Fig. 2. *Panoramic view of the polished AgCd₂GaS₄ plate*

Fig. 4. *Partial densities of the Cd 4p states of AgCd$_2$GaS$_4$*

Fig. 5. *Partial densities of the Ag 4p states of AgCd$_2$GaS$_4$*
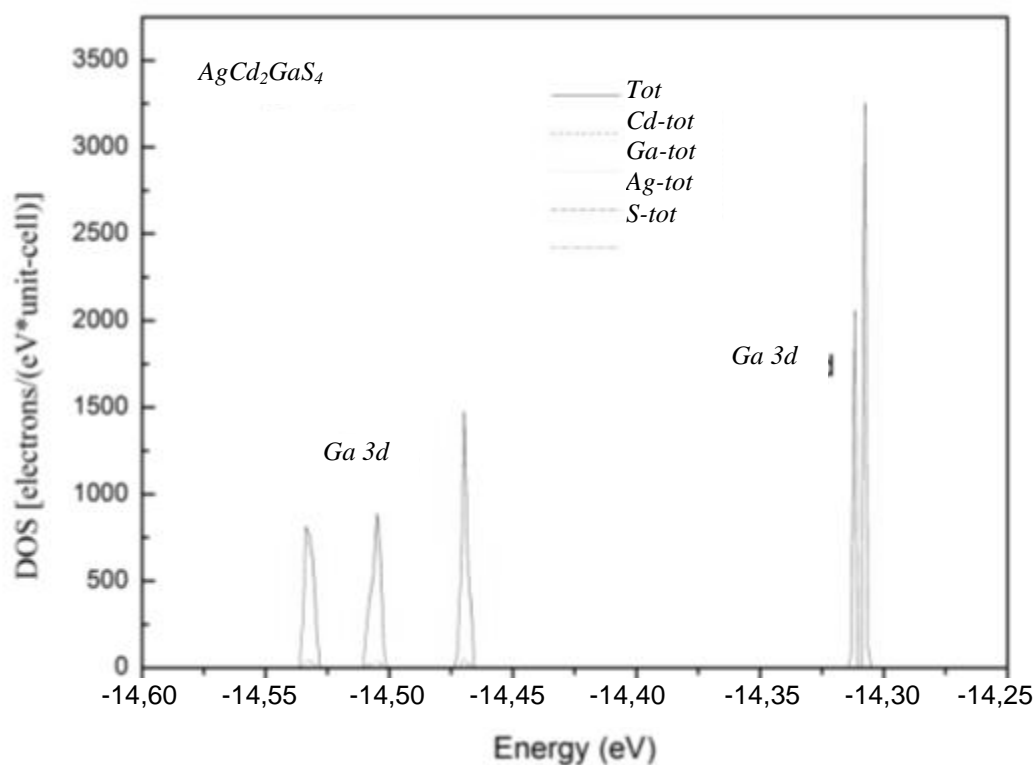
Fig. 6. *Partial de nsities of the Ga 3d states of AgCd₂GaS₄*

Fig. 7 shows comparison of the XP valence-band spectrum (shifted by 0,5 eV towards the Fermi energy) and the total DOS of the *AgCd₂GaS₄* compound provided that a common energy scale is used. In addition, total DOS and the most important partial densities of states, mainly the *Ag d, Cd d, Ga p* and S p states, in the valence-band region of AgCd₂GaS₄ as established in Ref. [7] are also shown in Fig. 7, for comparison. The lowest band D ranging from –7,6 to –8,2 on the curve of total DOS of *AgCd₂GaS₄* presented in Fig. 7 is formed almost exclusively due to contributions of the *Cd d* states. Some small contributions of the *Ga* s and *S p* states in the band *D* was also detected by the *FP-LAPW* calculations in Ref. [7]. As can be seen from Fig. 7, the curve of total DOS of *AgCd₂GaS₄* contains the band C ranging from –5,7 to –6,3 eV, which is separated by a 1,3 eV gap from the band D. The band C is composed mainly due to contributions of the Ga s states. Minor contributions of the S p s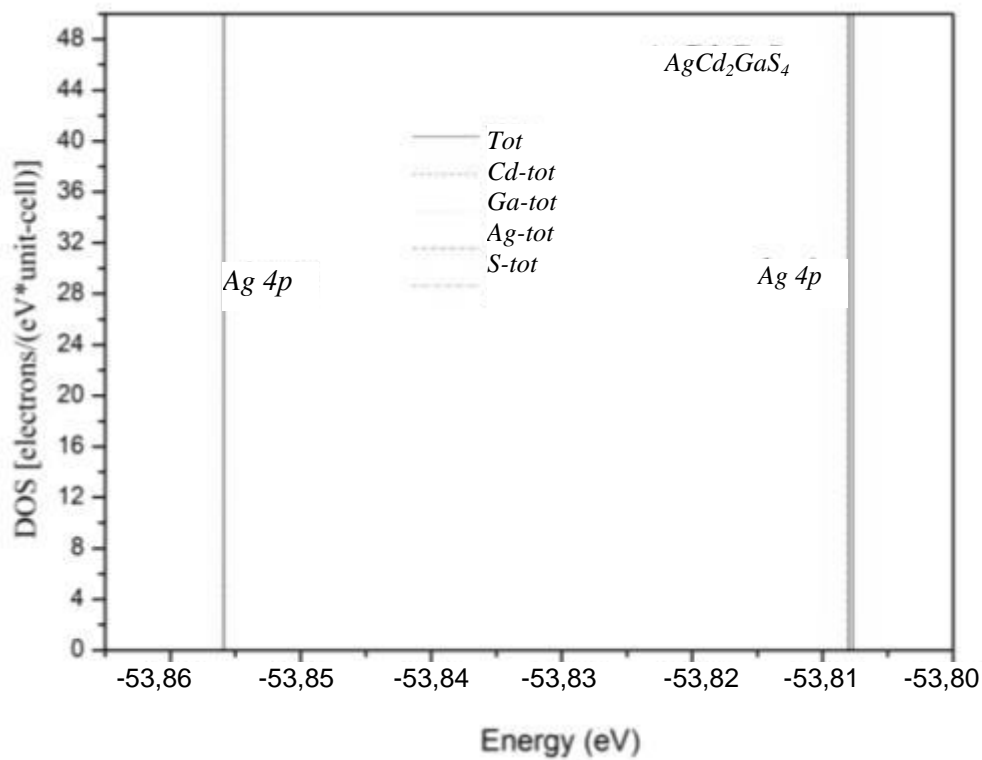tates in the band C were found to be characteristic of the electronic structure of the *AgCd₂GaS₄* compound [7]. Furthermore, the sub-band B of the valence band of *AgCd₂GaS₄* is composed mainly of the contributions of Ag d states. As one can see from Fig. 7, there exist a 0,8 eV gap between the band C and the sub-band B on the curve of total DOS of *AgCd₂GaS₄*. The upper sub-band A of the valence band of *AgCd₂GaS₄* is composed mainly of contributions of the Ag d and S p states in almost equal proportions. Those states are strongly hybridized within the energy region corresponding to the position of the sub-band A of the curve of total *DOS* of *AgCd₂GaS₄*. As Fig. 7 demonstrates, energy positions of the sub-bands *A* and *B* of the theoretical curve of total *DOS* and the experimental *XP* valence-band spectrum of *AgCd₂GaS₄* are close to each other. The binding energy position of the theoretical band *D* of *AgCd₂GaS₄* is somewhat underestimated compared with the experimental XP measurements made for this compound.
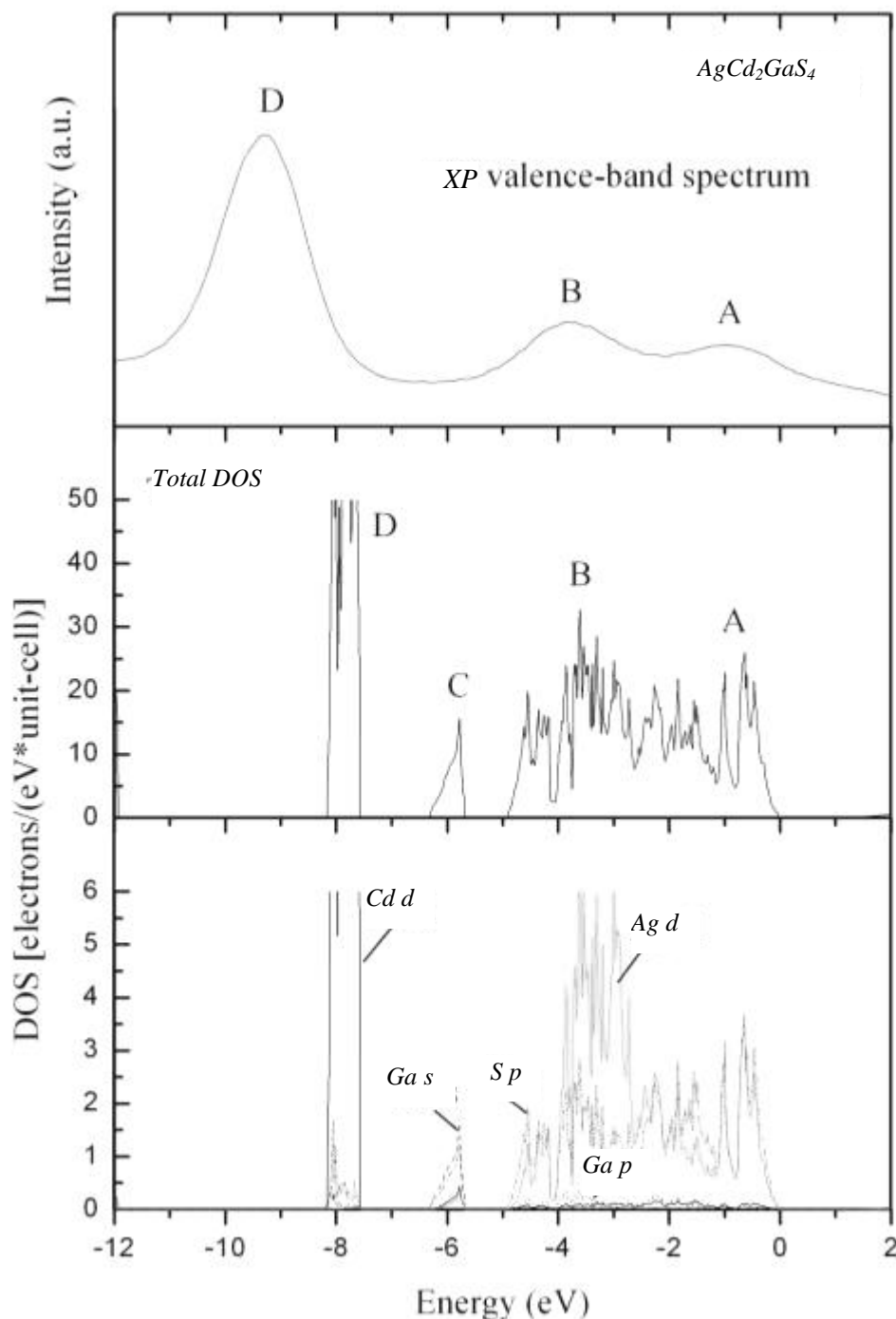
Fig. 7. *Comparison on a common energy scale of curves of partial Ag d, Cd d, Ga s, and S p densities of states (bottom panel), curve of total DOS (middle panel) and XP valence-band spectrum (upper panel) of AgCd₂GaS₄*

It is worth mentioning that the band C presente d on the on the curve of total *DOS of AgCd₂GaS₄* is not visible on the *XP* valence-band spectrum of the compound as Fig. 7 reveals. This band is formed by contributions of the *Ga s* states as it has been mentioned above. This fact can be explained by minor photoionization cross-section value of *Ga 4s* electrons that is more than 25 times smaller compared to those of *Ag 4d* and *Cd 4d* electrons, the principal contributors to the sub-band B and the band D, respectively, on the curve of total *DOS* of *AgCd₂GaS₄* (see Fig. 7) when exciting the *XP* spectra with a Mg Kα source [16].

In addition, photoionization cross-section value for *Ga 4s* electrons is smaller more than one order of magnitude in comparison with that of *S 3p* electrons, other significant contributors to the sub-band A on the curve of total *DOS* of *AgCd$_2$GaS$_4$*.

Conclusions. The *XP* valence-band spectrum including the comparatively wide energy region corresponding to location of upper core-levels of the atoms constituting a quaternary *AgCd$_2$GaS$_4$* compound (up *to ~80 eV* with respect to the bottom of the valence band) has been measured. For such a purpose, *AgCd$_2$GaS$_4$* single crystal grown by the Bridgman method has been used. To verify the experimental data, electronic structure of *AgCd$_2$GaS$_4$* has been also theoretically studied employing the first-principles *FP-LAPW* method. With this aim, partial densities of states of upper core-levels for the *AgCd$_2$GaS$_4$* compound have been calculated. The theoretical and experimental data regarding energy positions of the *Cd 4p*, *Ag 4p* and *Ga 3d* core-level spectra of the *AgCd$_2$GaS$_4$* compound were found to be in agreement to each other.

References

1. Blaha P. WIEN97 [Elektronik resourse] : A Full Potential Linearized Augmented Plane Wave Package for Calculating Crystal Properties / P. Blaha, K. Schwarz, J. Luitz. – Vienna : Technical University, 1999. – 1 електрон. опт. диск (CD-ROM) ; 12 см.
2. Blöchl P. E. Improved tetrahedron method for Brillouin-zone integrations / P. E. Blöchl, O. Jepsen, O. K. Andersen // Physical Review B. – 1994. – Vol. 49, № 23. – P. 16223–16233.
3. Electron energy structure of defect chalcopyrite CdGa$_2$Se$_4$ / A. A. Lavrentyev, B. V. Gabrelian, B. B. Kulagin [et al.] // Bulletin of the Russian Academy of Sciences : Physics. – 2009. – Vol. 73, № 8. – P. 1140–1142.
4. Electronic band structure of AgCd$_2$GaS$_4$: theory and experiment / A. H. Reshak, S. Auluck, I. V. Kityk [et al.] // Journal of Physics : Condensed Matter. – 2008. – Vol. 20, № 32. – P. 325213.
5. Electronic structure and fundamental absorption edges of *KPb$_2$Br$_5$, K$_{0.5}$Rb$_{0.5}$Pb$_2$Br$_5$,* and *RbPb$_2$Br$_5$* single crystals / A. Y. Tarasova, L. I. Isaenko, V. G. Kesler [et al.] // Journal of Physics and Chemistry of Solids. – 2012.– Vol. 73, № 5. – P. 674–682.
6. Electronic structure of cadmium selenogallate *CdGa$_2$Se$_4$* as studied using ab initio calculations and X-ray photoelectron spectroscopy / A. A. Lavrentyev, B. V. Gabrelian, I. Ya. Nikiforov [et al.] // Journal of Alloys and Compounds. – 2009. – Vol. 481, № 1–2. – P. 28–34.
7. Electronic structure of non-centrosymmetric *AgCd$_2$GaS$_4$* and *AgCd$_2$GaSe$_4$* single Crystals / V. L. Bekenev, V. V. Bozhko, O. V. Parasyuk [et al.] // Journal of Electron Spectroscopy and Related Phenomena. – 2012. – Vol.185. – P. 559–566.
8. First and second harmonic generation of the optical susceptibilities for the non-centro-symmetric orthorhombic AgCd$_2$GaS$_4$ / A. H. Reshak, V. V. Atuchin, S. Auluck, I. V. Kityk // Journal of Physics : Condensed Matter. – 2008. –Vol. 20, № 32. – P. 325234.
9. Ma S. H. Structural, elastic, electronic, and optical properties of defect-chalcopyrite structure *CdGa$_2$X$_4$ (X = S, Se)* compounds / S. H. Ma, Z. Y. Jiao, X. Z. Zhang // Journal of Materials Science. – 2012. – Vol. 47, № 8. – P. 3849–3854.
10. Perdew J. P. Generalized Gradient Approximation Made Simple / J. P. Perdew, S. Burke, M. Ernzerhof // Physical Review Letters. – 1996. – Vol. 77. № 18. — P. 3865–3868.
11. Pervukhina N.V. Re-determination of the crystal structure of the quaternary phases silver dicadmium(II) gallium tetrasulfide, *AgCg$_2$GaS$_4$* / N. V. Pervukhina, V. V. Atuchin, O. V. Parasyuk // Acta Crystallographica Section E. – 2005, Vol. 61, № 5. – P. i91–i93.
12. Phase equilibria in the quasi-ternary system Ag$_2$S-CdS-Ga$_2$S$_3$ / I. D. Olekseyuk, O. V. Parasyuk, V. O. Halka [et al.] // Journal of Alloys and Compounds. – 2001. – Vol. 325, № 1–2. – P. 167–179.
13. Single-crystal growth and properties of *AgCd$_2$GaS$_4$* / I. D. Olekseyuk, O. V. Parasyuk, O. M. Yurchenko [et al.] // Journal of Crystal Growth. – 2005. – Vol. 279, № 1–2. – P. 140–145.
14. Structural and optical properties of noncentrosymmetric quaternary crystal *AgCd$_2$GaS$_4$* / V. V. Atuchin, V. Z. Pankevich, O. V. Parasyuk [et al.] // Journal of Crystal Growth. – 2006. – Vol. 292, № 2. – P. 494–499.
15. X-ray powder diffraction study of semiconducting alloys *Ag$_{1-x}$Cu$_x$Cd$_2$GaS$_4$* and *AgCd$_2$Ga$_{1-x}$In$_x$S$_4$* / I. D. Olekseyuk, O. V. Parasyuk, O. A. Husak [et al.] // Journal of Alloys and Compounds. – 2005. – Vol. 402, № 1–2. – P. 186–193.
16. Yeh J. J. Atomic subshell photoionization cross ections and asymmetry parameters: 1<= Z<= 103 / J. J. Yeh, I. Lindau // Atomic Data and Nuclear Data Tables. — (1985). — Vol. 32, №1. — P. 1–155.

Божко Володимир, Третяк Аліна, Булатецька Леся, Бекеньов Валерій, Парасюк Олег, Хижун Олег. Електронна структура *AgCd$_2$GaS$_4$*. Рентгенівський фотоелектронний (РФ) спектр валентних електронів монокристалу *AgCd$_2$GaS$_4$*, вирощеного методом Бріджмена, досліджено в широкому енергетичному інтервалі, котрий уключав спектри внутрішніх електронів, розміщені на відстані аж до ~80 eB від нижнього краю

валентної зони. Електронна структура сполуки $AgCd_2GaS_4$ також розрахована «з перших принципів» методом приєднаних плоских хвиль – повного потенціалу (*ППХ-ПП*). Величини енергій зв'язку (*E_{зв}*) внутрішніх *Cd4p-*, *Ag4p-* і *Ga3d*-електронів, що отримані теоретично для $AgCd_2GaS_4$ за допомогою *ППХ-ПП* методу, добре збігаються з експериментальними значеннями *E_{зв}*, котрі виміряні для досліджуваного кристала за допомогою РФ-спектроскопії. Виконано суміщення кривих парціальних щільностей станів складових атомів сполуки $AgCd_2GaS_4$ у єдиній енергетичній шкалі з РФ-спектром валентних електронів.

Ключові слова: $AgCd_2GaS_4$, електронна структура, розрахунок електронної структури з перших принципів, рентгенівська фотоелектронна спектроскопія, щільність станів.

Божко Володимир, Третяк Алина, Булатецкая Леся, Бекеньов Валерий, Парасюк Олег, Хижун Олег. Электронная структура $AgCd_2GaS_4$. Рентгеновский фотоэлектронный (*РФ*) спектр валентных электронов монокристалла $AgCd_2GaS_4$, выращенного методом Бриджмена, исследован в широком энергетическом интервале, который включал спектры внутренних электронов, расположенных на расстоянии до ~80 эВ от нижнего края валентной зоны. Электронная структура соединения $AgCd_2GaS_4$ также рассчитана «из первых принципов» методом присоединенных плоских волн – полного потенциала (*ППВ-ПП*). Величины энергий связи (*E_{св}*) внутренних *Cd4p-*, *Ag4p-* и *Ga3d*-электронов, полученные теоретически для $AgCd_2GaS_4$ посредством *ППВ-ПП* метода, хорошо совпадают с экспериментальными значениями *E_{св}*, которые измерены для исследуемого кристалла с помощью *РФ*-спектроскопии. Выполнены совмещения кривых парциальных плотностей состояний составляющих атомов соединения $AgCd_2GaS_4$ в единой энергетической шкале с *РФ*-спектром валентных электронов.

Ключевые слова: $AgCd_2GaS_4$, электронная структур, расчет электронной структуры из первых принципов, рентгеновская фотоэлектронная спектроскопия, плотность состояний.

УДК 621.315.592

Оксана Замуруєва,
Галина Мирончук,
Олег Парасюк

Оптичні, електричні та фотоелектричні властивості кристалів Ag₂In₂Si(Ge)Se₆

У роботі досліджено оптичні, електричні та фотоелектричні властивості маловивчених халькогенідних напівпровідників $Ag_2In_2Si(Ge)Se_6$. Показано, що досліджувані матеріали проявляють властивості невпорядкованих систем, обумовлених технологічними дефектами й структурними особливостями сполуки. Вивчено спектри оптичного поглинання напівпровідників $Ag_2In_2Si(Ge)Se_6$, розраховано коефіцієнт поглинання α, оцінено ширину забороненої зони. Інтерпретацію експерементальних результатів здійснено в межах моделі Мотта для невпорядкованих систем.

Ключові слова: напівпровідники, оптичне поглинання, дефекти, ширина забороненої зони.

Постановка наукової проблеми та її значення. Аналіз досліджень цієї проблеми. Кристали $AgInSe_2$, $AgInTe_2$ належать до великого класу з'єднань зі структурою халькопіриту $A^IB^{III}C_2^{VI}$, які мають технологічно привабливі властивості для створення різноманітних оптоелектронних приладів. Низка кристалів із цієї групи, такі як $CuInSe_2$, $CuGaSe_2$, $CuInS_2$, $AgGaS_2$, $AgGaSe_2$, є комерційно доступними й знайшли застосування у виробництві приладів нелінійної оптики та сонячних елементів. Останнім часом практичний інтерес мають й інші з'єднання цієї групи, у тому числі й $AgInSe_2$ та $AgInTe_2$, які є електронно-хімічними аналогами бінарних з'єднань $A^{II}B^{VI}$ [11].

Оптичні спектри вирощених у вигляді тонких плівок $AgInSe_2$ і $AgInTe_2$ вивчено в роботі [6]. Згідно з цими даними, кристали $AgInSe_2$ і $AgInTe_2$ є прямозонними й ширина забороненої зони становить 1,21 та 1,16еВ, відповідно, що робить їх перспективними матеріалами для перетворювачів сонячної енергії. Результати досліджень фотопровідності $AgInSe_2$ [8] засвідчили наявність хороших