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Review of the doctoral thesis of M.Sc. Eng. Myron Rudysh,
entitled: *Theoretical study of I-II-VI$_2$ group chalcopyrite crystals for photovoltaic application*

This research work was accomplished at the Jan Długosz University in Częstochowa,
Faculty of Science and Technology, Department of Theoretical Physics, Poland
under supervision of **dr hab. Michał Piasecki, prof. UJD**.

The doctoral dissertation M.Sc. Eng. Myron Rudysh is written on **264** pages and consists of: 8 numbered chapters, including introduction and conclusions and lists of abbreviations, symbols, figures (**96**) and tables (**44**). The total number of references, **291** items, is a very extensive bibliography. Moreover, the author included the list of his academic achievements: papers from *JCR* list (**27**), other publications from Scopus/Web of Science data bases (**6**), other publications (**8**), the list of his conference presentations: oral presentations (**71**) and poster presentations (**10**), the list of patents (**3**) and list of scientific projects (**2**). There is also an abstract in Polish and English and the prospects of future study.

In recent years high dynamics in modification of conventional solar cells technology, in order to improve the efficiency in conversion of the solar energy in the electric energy by the photovoltaic effect, has been observed. The study presented in the dissertation concerns the search for attractive semiconductor materials that can be used in photovoltaics. The aim of the dissertation is an investigation of structural, electronic, optical, elastic and other physical properties of the selected I-III-VI$_2$ (I = Cu, Ag, III = Al, Ga, In, VI = S, Se, and Te) crystals using theoretical methods.

The main part of the presented for review doctoral dissertation was preceded by the introduction/**Chapter 1**, in which the author presents some general information about the chalcopyrite semiconductors with chemical formula I-III-VI$_2$ (I = Cu, Ag, III = In, Ga, Al, VI = S, Se, Te) or II-IV-V$_2$ (II = Be, Mg, Zn, Cd, IV = C, Si, Ge, Sn, V = N, P, As, Sb) and their potential applications. In this work the results of the theoretical investigation of I-III-VI$_2$ crystals using an *ab initio* method based on the density functional theory (DFT) were presented. The goal of the work is the systematic study of the structure, electronic, optic and other physical properties of I-III-VI$_2$ crystals using the DFT methods. Finally, in this chapter the author described the aim and tasks of the dissertation, thesis, hypothesis of the work, and scientific novelty. Additionally, it is also attached the list of publications on the subject of the thesis of dissertation (**4** / M.Sc. Eng. Myron Rudysh is the first author), conferences activities: oral presentations (**17**), poster presentations (**4**) and list of scientific projects (**1**).

Wpłynęło 17.10.2022r.

In **Chapter 2** the literature review of structure and selected physical properties of I-III-VI_2 crystals was presented. In particular, it was described:

- the structure and origin of I-III-VI_2 crystals (I = Cu, Ag, III = Al, Ga, In, VI = S, Se, and Te), which crystalizes in tetragonal structure of D_{2d}^{12} space group and have four formula units (Z = 4) in the unit cell; two types of crystal lattice deformation in these crystals (tetragonal deformation $\eta = c/2a$ and displacement of the anion atoms described by the parameter u),
- the growing technology of the selected chalcopyrites,
- the electronic structure modeled by theoretical methods of the selected chalcopyrites,
- the electronic structure studied experimentally using X-ray photoelectron spectroscopy (XPS) of the selected materials: In_2Se_3, $CuIn_5Se_8$, $CuIn_3Se_5$, $CuInSe_2$, $ZnGeP_2$, $ZnGeAs_2$, $CuGaS_2$, $CuAlS_2$, $CuInSe_2$, $AgInSe_2$, $CuGaS_2$, $CuInSe_2$, $AgInSe_2$ and $CuAlS_2$.

Moreover, in the subsection 2.2.2. the phenomenon of birefringence in crystals was described and some examples of chalcopyrite semiconductors, which show birefringence were presented. This subsection contains also the classical description of the NLO phenomenon in crystals and the response of the material medium to the applied strong electric field, expressed by the linear polarization characterized by the $\chi^{(1)}$ linear electric susceptibility and nonlinear polarization of higher orders characterized by the $\chi^{(2)}$ second- and $\chi^{(3)}$ third-order nonlinear electrical susceptibilities. In particular, the author described the conditions of the Second Harmonic Generation (SHG) characterized by the three-rank $\chi^{(2)}$ tensor, which is finally represented by the second-order d_{ij} tensor (NLO coefficients) after reduction of the number of components according to Kleinman symmetry and followed by the used notation. Additionally, some parameters such as: transparency window, energy band gap E_g, NLO coefficients and damage threshold were listed for the mentioned above I-III-VI_2 crystals (Table 2.5). The subsection 2.4. *Photovoltaic application of chalcopyrite crystals of I-III-VI_2 group* contains review of literature of solar cells based on I-III-VI_2 materials as absorbing layers (2.4.1.) as well as simulation of the photovoltaic characteristics of I-III-VI_2-based solar cells (2.4.2).

Chapter 3 contains description of the methods of the electronic structure calculations. Moreover, in this chapter the general concept of quantum mechanics, mathematical description of the wave functions and Schrödinger equation for a system consisting of N interacting particles with potential energy U and mass m_k in the Cartesian coordinate system, which is the fundamental issue of quantum mechanics for description of electronic levels in solids, were presented. The solution of this equation with the help of numerical methods and with the use of various approximations that simplify this problem, which are divided into *ab initio* and *semi-empirical* was also commented. The important part of this chapter refers to the history and basic concept of the most effective and popular method for calculations the quantum systems based on the DFT. In particular, the author described the exchange-correlation functionals (for the description of the quantum interaction of electrons/exchange and correlation interaction), pseudopotentials (for simplification of the description of electron-ion interaction of complex systems with many particles), norm-conserving pseudopotential and ultrasoft pseudopotential used in quantum mechanics and solid state physics to perform a precise calculation of electronic structure and physical properties of analyzed systems. In the subsection 3.8 and 3.9 the author consider the problem of electron in crystal field (for ideal periodic crystal lattice) and introduced the main concept of the reciprocal lattice used in physics to solve some problems. The subsection 3.10. contains a short description of the CASTEP code (CAmbridge Serial Total Energy Package) used in this work to calculate some physical properties of the selected I-III-VI_2 crystals from the first principles. In particular, the CASTEP code software was used for: solving Kohn-Sham equations, optimization of geometric structure of selected I-III-VI_2 crystals and calculating the energy spectra, electron density distribution, total and partial density of states, optical spectra, atomic charges and Milliken population, effective Born charges, dielectric constants and phonon frequencies, Raman and infrared spectra, elastic parameters for the selected I-III-VI_2 crystals.

In **Chapter 4** the structure, electronic and some optical properties of the selected I-III-VI_2 crystals (I = Ag Cu, III = Al, Ga, In, VI = S, Se, Te) carried out using DFT method were described. The following parameters of calculations and crystal structure optimization were used: the local density approximation (LDA) with the Ceperley-Alder-Perdew-Zunger (CAPZ) parameterization and the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof parameterization (PBE) used to take into account the exchange and correlation effects, the geometric optimization of the crystal unit cell performed in order to calculate the parameters of the crystals for the electron density in the ground state, the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm used for geometry optimization of the crystal before calculation of the electronic characteristics (total electronic energy, band energy dispersion, total and partial density of states, dielectric functions and vibrational properties).

In particular, the structure, electronic and some optical properties were carried out for the following 18 I-III-VI_2 crystals: $AgAlS_2$, $AgAlSe_2$, $AgAlTe_2$, $AgGaS_2$, $AgGaSe_2$, $AgGaTe_2$, $AgInS_2$, $AgInSe_2$, $AgInTe_2$, $CuAlS_2$, $CuAlSe_2$, $CuAlTe_2$, $CuGaS_2$, $CuGaSe_2$, $CuGaTe_2$, $CuInS_2$, $CuInSe_2$ and $CuInTe_2$. The considered, mentioned above crystals crystalizes in tetragonal structure of D_{2d}^{12} space group. There are 4 primitive cells in structure and each unit cell contains 8 atoms. To calculate the band-energy structure of the studied crystals a primitive cell was taken into consideration. For the studied 18 I-III-VI_2 crystals the unit cell parameters a, c and the unit cell volume V were determined using the GGA and LDA functionals and compared to that obtained by other authors using experimental methods (Tables 4.1). Moreover, to compare the optimized crystals structure with the experimental ones, the parameter of relative deviation of the unit cell volume d_r and relative mean root squared deviation D_r of the distance matrix d_{ij} were determined and analyzed. Additionally, the crystal lattice deformation parameters: the tetragonal deformation parameter η and the anion displacement parameter u were determined, analyzed and compared to that obtained from experimental data (Tables 4.1).

In the **subsection 4.2.1.** the results of electronic band structure calculations using GGA functional of the selected18 I-III-VI_2 crystals were presented (Figures 4.6 and 4.7). Moreover, the band gap E_g values of the selected 18 I-III-VI_2 crystals calculated using the LDA and GGA functionals were presented in Figure 4.8. In general, the band gap E_g of the selected 18 I-III-VI_2 crystals increases with increasing electronegativity of the III and VI ions: from In to Ga to Al and from Te to Se to S, while there is no general trend observed considering the I cations. In Figure 4.9. the DFT calculated band gaps E_g of the selected 18 I-III-VI_2 crystals were compare to experimental ones. Figure 4.9 shows that the values of the band gap E_g calculated using both exchange-correlation LDA and GGA functionals are smaller than the experimental values for the whole group of the selected 18 I-III-VI_2 crystals. Moreover, the dependence of the band gap E_g on the molar mass μ for calculation with the LDA and GGA functionals together with the experimental values of the band gap E_g of the selected 18 I-III-

VI_2 crystals were shown in Figure 4.10. It was observed that the values of band gap E_g decreases with increasing molar mass μ. From the obtained Pearson's coefficients it follows that the calculated values of the band gap E_g are less correlated with the molar mass μ than the experimental ones. Such an underestimation of the band gap E_g values is typical for calculations with the LDA and GGA functionals. In order to overcome it, the scissor operator Δ_g was used, which shifts the conduction band to the higher energies without any modification of the calculated eigenfunctions. The scissor operator Δ_g values applied for correction of the band gap E_g values underestimation of the selected 18 I-III-VI_2 crystals for LDA and GGA functionals were collected in Table 4.3.

For studied I-III-VI_2 crystals the degenerate Γ_{15} energy level, which corresponds to the states at the top of the valence band, splits into the nondegenerate Γ_4 level and the twice degenerate Γ_5 state (Figure 4.11), due to the influence of a crystal field. The magnitude of the crystal field energy Δ_{CF} was determined by the energies of these levels $E(\Gamma_5)$ and $E(\Gamma_4)$. Crystal field energies Δ_{CF} obtained for the selected 18 I-III-VI_2 crystals using the GGA functional and the corresponding literature data were collected in Table 4.4. The values of the crystal field energies Δ_{CF} obtained from the band-energy structure calculations agree well with the literature data. Additionally, in the subsection 4.2.1 the theoretical description of the effective mass of charge carriers m^* in crystals and the procedure of determination the effective mass of charge carriers m^* of the selected I-III-VI_2 crystals from the electronic band structure were presented (Figs. 4.6 and 4.7). The calculated effective mass m^* of charge carriers for electron m_e^* and hole m_h^* in the selected 18 I-III-VI_2 crystals for Z – Γ – X directions were collected in Table 4.5, while the corresponding values of m_e^* and m_h^* of selected I-III-VI_2 crystals reported in the literature were presented in Table 4.6. Moreover, it was found that m_h^* is greater than m_e^* and the anionic substitution S → Se → Te reduces the effective mass in the Γ – Z direction, while the cationic substitution Ag → Cu leads to decrease in the effective mass both, holes and electrons.

In the **subsection 4.2.2.** the author presented the results of calculations of the total and partial density of electronic states (DOS) for individual atoms and the orbital moments of electrons of the selected 18 I-III-VI_2 crystals (Figure 4.13 calculated using GGA functional). Moreover, the atomic populations of the constituent atoms, lengths and overlap populations of the shortest atomic bonds and bond ionicity of the selected 18 I-III-VI_2 crystals, determined using GGA and LDA functionals, were presented in Table 4.7 and 4.8.

In the **subsection 4.3.** the optical properties of investigated I-III-VI_2 crystals were presented. In the first part of this subsection some theoretical analysis concerning the dielectric function $\varepsilon(\omega)$ and its real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts in crystalline materials was presented. In particular, for crystals the dielectric constant 2nd rank ε_{ii} tensor was considered. In case of I-III-VI_2 crystals the ε_{ii} tensor has two independent components $\varepsilon_{11} = \varepsilon_{22} \neq \varepsilon_{33}$. In Figure 4.14. the relation of the real $\varepsilon_1(E)$ and imaginary $\varepsilon_2(E)$ part of dielectric function on energy E of the selected 18 I-III-VI_2 crystals calculated for photon energies from 0 up to 20 eV for polarization vector [100] and [001] using GGA functionals were shown. Moreover, the degree of anisotropy of dielectric constant ε calculated for the investigated crystals were determined using the $\delta\varepsilon$ parameter expressed by the static and total dielectric constants. The uniaxial anisotropy parameter $\delta\varepsilon$ of selected 18 I-III-VI_2 crystals calculated using LDA and GGA functionals were collected in Table 4.9. The comparison of the obtained in this work theoretical values of the dielectric constant as a function of energy E with the experimental ones for the selected $AgGaTe_2$ crystal were shown in Figure 4.15. Moreover, in this subsection the following optical parameters of the selected 18 I-III-VI_2 crystals were calculated, presented and discussed: refractive index n, reflection coefficient R, absorption coefficient α and extinction coefficient k. Figure 4.16. shows the reflection $R(E)$, absorption coefficient $\alpha(E)$, refractive indices $n(E)$ and extinction coefficients $k(E)$ as a function of the photon energy E in the spectral range from 0 to 30 eV of the selected 18 I-III-VI_2 crystals calculated using the GGA functional. In Table 4.10 the optical parameters: $\varepsilon_{1,x}(0)$, $\varepsilon_{1,z}(0)$, $n_x(0)$, $n_z(0)$ and $\Delta n(0)$) of the selected I-III-VI_2 crystals calculated with LDA and GGA functionals were collected. Additionally, the DES model of calculations based on classical polarizability theory of optical activity was applied to determine the parameters of electrogyration, electro-optic and second-harmonic generation effects (the subsection 4.3.2). Moreover, the dielectric constants tensor ε_{ij}, polarization tensor a_{ij}, linear electro-optic tensor r_{ijk}, electrogyration tensor g_{ijk}, second-order nonlinear susceptibility tensor d_{ijk} were considered. The following values were calculated and compared to the experimental data taken from the literature: electronic polarizability α'_{Ag}, α'_{Ga}, α'_{S}, refractive indices n_o, n_e, optical rotation constants ρ_{11}, ρ_{22}, ρ_{33}, linear electro-optic coefficients r_{41}, r_{52}, r_{63}, electrogyration coefficient g_{41} and nonlinear coefficient d_{36}.

In the **subsection 4.4** the calculated total density of electronic states for $AgGaS_2$, $AgInSe_2$, $CuGaS_2$, and $CuInSe_2$ crystals using the GGA functional were compared to the obtained experimentally XPS spectra (data taken from literature) in the energy range from 0 to –20 eV (Figure 4.18). It was revealed that the bands with the lowest energy corresponding to the Ga-3d and In-4d states show a significant difference in location compared to the corresponding band positions obtained on the basis of experimental data. In Table 4.11 the values of the energy shifting of the d-levels of Ga or In for $AgGaS_2$, $AgInSe_2$, $CuGaS_2$ and $CuInSe_2$ crystals relative to the energy of experimental position of d-level obtained from XPS spectra were summarized and discussed. It was shown that the calculations using LDA and GGA functionals lead to a shift in the levels position of the localized d-orbitals to higher energy for mentioned above I-III-VI_2 crystals. It was concluded, considering this shift in levels positions, that DFT does not describe well the d-levels for Ga and In atoms in the studied materials. Therefore, it was necessary to use the corrections that allow to obtain the proper results of calculations, better consistent with the experiment. The Hubbard correction method (DFT + U) was used in order to correct the shift of electronic levels. Finally, in Figure 4.20. the calculated density of state for $AgGaS_2$, $AgInSe_2$, $CuGaS_2$ and $CuInSe_2$ crystals with using different values of Hubbard parameter U, together with the experimental XPS spectra taken from literature were presented. In Table 4.12. position of d-levels of cations Ga and In in the selected I-III-VI_2 crystals ($AgGaS_2$, $AgInSe_2$, $CuGaS_2$, $CuInSe_2$) and corresponding U parameter values were collected.

In **Chapter 5** the elastic properties of I-III-VI_2 crystals, acoustic waves propagation and Debye temperature determination in I-III-VI_2 crystals were investigated using the *ab initio* calculations performed by the LDA and GGA functionals. In the introduction of this chapter the selected issues concerning the elastic properties in crystals were described. In particular, the Hooke's law for the anisotropic crystals at low stresses, was written in the tensor form and expressed by the second rank σ_{ij} mechanical stress tensor, four-rank C_{ijkl} elastic constants tensor, four-rank S_{ijkl} elastic compliance tensor and second rank ε_{kl} deformation tensor. Finally, considering the symmetry conditions and using the Voigt's notation the Hooke's law was expressed by the elastic stiffness tensor C_{ij} written in the form of a matrix containing 36 components. For each symmetry of the crystal, matrices of elastic constants C_{ij} were derived and the independent coefficients of the elastic constants matrix C_{ij} for all types of symmetry were given (Table 5.1). For I-III-VI_2 of the tetragonal structure, there are following equalities of the coefficients $C_{22} = C_{11}$, $C_{23} = C_{13}$, $C_{44} = C_{55}$, and in consequence there are 6 independent components of the C_{ij} elastic stiffness tensor: C_{11}, C_{12}, C_{13}, C_{33}, C_{44} and C_{66} (Table 5.1). The calculated components of the C_{ij} tensor for the selected 18 I-III-VI_2 crystals using LDA and GGA functionals were collected in Table 5.3. Moreover, using the C_{ij} values, the following parameters selected 18 I-III-VI_2 crystals were calculated: linear compressibilities k_a and k_c along the a and c axis, respectively (Figure 5.2), elastic compliance coefficients S_{ij} (Table 5.4.), anisotropic Young's modulus E_i and Poisson's ratio v_{ij} (Table 5.5) using LDA and GGA functionals. Additionally, the elastic properties of I-III-VI_2 polycrystals were studied and the polycrystalline elastic modules such as: the bulk modulus B, shear modulus G, Young's modulus E and Poisson's ratio v were calculated using LDA and GGA functionals. They were obtained by calculating the average of anisotropic elastic constants for single crystals. For tetragonal crystals, the bulk modulus B_{VHR} and shear modulus G_{VHR} were determined using the Voigt-Reuss-Hill average schemes. The estimated values of the bulk modulus B, shear modulus G, Young's modulus E and Poisson's ratio v of the selected 18 I-III-VI_2 polycrystals calculated using LDA and GGA functionals were collected in Table 5.6. The results were discussed in relation to the experimental data (Figure 5.3). Moreover, the following dependences for the selected 18 I-III-VI_2 crystals calculated using LDA and GGA functionals were presented and analyzed: the dependence of the modulus B of elasticity on the molar mass M (Figure 5.4), dependence of the modulus B on the volume V (Figure 5.5.), dependence of bulk modulus B on the density (Figure 5.5) and dependence of the modulus B as function of band gap E_g (Figure 5.7.).

To study the anisotropy of elastic properties, a set of coefficients that describe the degree of anisotropy of the crystal were calculated. In particular, the following three parameters/shear anisotropic factors: A_1, A_2, and A_3 (for three directions (100) (010) and (001) of the shear planes) expressed by the elastic constants C_{ij} were calculated and used to determine the shear anisotropy of I-III-VI_2 crystals. The formulas for A_1, A_2, and A_3 parameters for tetragonal structure were determined and the calculated shear anisotropy factors A_1 and A_2 for the selected 18 I-III-VI_2 crystals using LDA and GGA functionals were presented (Figures 5.8 and 5.9). Additionally, the universal anisotropy index A^U, which shows the general measured anisotropy and includes the contribution of both the shear anisotropy G and the bulk anisotropy B was determined. The A^U parameter can be calculated using bulk modulus B_V, B_R, and shear modulus G_V, G_R in Voigt and Reuss approximation. The anisotropy of elastic properties were also determined by other parameters: the factors of anisotropy of the bulk modulus A_B and the factor of anisotropy of the shear modulus A_G. Calculated bulk anisotropy index A_B, shear anisotropy index A_G and universal anisotropy index A^U determined for the selected 18 I-III-VI_2 crystals using LDA and GGA functionals were presented in Figures 5.10, 5.11 and 5.12 respectively. Moreover, to show the anisotropy of investigated crystals the three-dimensional (3D) surfaces for the values of the studied anisotropic parameters were constructed. The 3D surface representation of Young's modulus E, bulk modulus B and shear modulus G as well as their (100) and (001) planar projections of the selected 18 I-III-VI_2 crystals plotted for the GGA-calculated elastic coefficients were presented in Figures 5.14, 5.15 and 5.16, respectively.

In the **5.2.3 subsection** some basic issues considering the acoustic waves propagation in crystals were described and the velocities of the sound propagation in I-III-VI_2 crystals were determined from the DFT calculations. In particular, the equation for the plane monochromatic wave propagation with velocity v in the crystal, expressed by the elastic tensor C_{ijkl} and density of the crystal ρ was presented. For considered I-III-VI$_2$ crystals (of tetragonal structure), there are 6 equation for the Γ_{ik} components expressed by the elastic constants C_{ij} (Eq. 5.37). Finally, the formulas for the velocities of longitudinal L and transverse T$_1$ and T$_2$ waves were determined for the following acoustic waves propagation directions: [100], [110] and [001] (Equation 5.38). As a result, the elastic constants C_{ij} of the selected 18 I-III-VI$_2$ crystals were used to calculate the velocities of longitudinal L and transverse T$_1$ and T$_2$ acoustic waves in the [100], [110] and [001] crystallographic directions. Additionally, the average sound velocities (v_m) were calculated for the selected 18 I-III-VI$_2$ crystals using LDA and GGA functionals (Figure 5.17). To estimate the anisotropy of the speed of acoustic waves in the investigated crystals the percentage anisotropy index A expressed by the maximal v_{max} and minimal v_{min} values of the sound speed in the crystal, was defined (Eq. 5.23). The sound velocities v and anisotropy of sound velocity indices A of the selected 18 I-III-VI$_2$ crystals, calculated using LDA and GGA functionals were collected in the Table 5.7. Additionally, from the calculated propagation velocities of longitudinal L and transverse T$_1$ and T$_2$ acoustic modes the Debye temperature Θ_D for the investigated crystals was determined. The longitudinal v_l, transverse v_t, average sound velocities v_m, crystal density ρ and Debye temperatures Θ_D calculated using LDA and GGA functionals as well as the experimental values of Θ_D taken from the literature for the selected 18 I-III-VI$_2$ crystals were collected in Table 5.8.

In the introduction of **Chapter 6** some elements of the group theory necessary to determine representation all fundamental vibrations in I-III-VI$_2$ crystals were described. In particular, the phonon spectra for I-III-VI$_2$ crystals limited to excitations of vibrational modes close to the center of the Brillouin zone (in the Γ-point for $\mathbf{k} = 0$) were considered. The elements of symmetry operations of I-III-VI$_2$ crystals were presented in the Table 6.1. The primitive cell of I-III-VI$_2$ crystals contains 8 atoms, so the phonon spectrum has 24 branches (3 are acoustic (at $\mathbf{k} \to 0$ the frequency is $\omega \to 0$) and remaining branches are optical. Finally, the total irreducible representation, which describe all fundamental vibrations for I-III-VI$_2$ crystals was determined (Eqs. 6.4, 6.5 and 6.6). In the subsections 6.1.2. and 6.1.3. the selection rules for the infrared absorption and the tensor of Raman scattering for I-III-VI$_2$ crystals were described. In the subsections 6.2, 6.3 and 6.4 the results of DFT calculations of vibrational properties of AgGaS$_2$, AgGaSe$_2$ and AgGaTe$_2$ crystals were presented. The phonon spectra of AgGaX$_2$ crystals (X = S, Se, and Te) presented in this work were carried out using the plane-waves pseudopotential method based on the DFT method. In the subsections 6.1.2. and 6.1.3. the selection rules for phonon spectra, which determined the types of symmetry of vibrations active in IR and Raman spectra of I-III-VI$_2$ crystals were described. The conditions of Raman scattering were described by a symmetric 2nd rank Raman polarizability tensor. The scattering geometries in Raman spectra were described using Porto notation. Moreover, the following relations were calculated: the dispersion curves $\omega(q)$, phonon density of states $N(\omega)$ (Figures 6.1, 6.6 and 6.11), partial phonon density of states $N(\omega)$ for Ag, Ga and S atoms (Figures 6.2, 6.7 and 6.12) using the LDA functional. The vibrations of A_1, A_2, E, B_1 and B_2 symmetry in AgGaS$_2$, AgGaSe$_2$ and AgGaTe$_2$ crystals were visualized in Figures 6.3, 6.8 and 6.13. The calculated using the LDA functional Raman and IR spectra were presented in Figures 6.4/6.9/6.14 and 6.5/6.10/6.16 for AgGaS$_2$, AgGaSe$_2$ and AgGaTe$_2$ crystals, respectively. The calculated Raman spectra were given for the incident light $\lambda = 514.5$ nm in the spectral range from 0 to 400 cm^{-1} for the sample at temperature T = 300 K. In Tables 6.6, 6.9 and 6.12 the calculated and experimental phonons wavenumbers determined from Raman and IR spectra for $AgGaS_2$, $AgGaSe_2$ and $AgGaTe_2$ crystals were given.

To calculate the effective Born charges for $AgGaX_2$ (X = S, Se and Te) crystals, the independent displacements of Ag, Ga and S/Se/Te atoms were considered. In Tables 6.7./6.10/6.13 the Born effective charges Z^*, eigenvalues of the symmetric part $Z^*(\lambda)$ and dynamic charges Q_d calculated for the $AgGaX_2$ (X = S, Se and Te) crystals were collected. Tables 6.8/6.11/6.14 show the values of static ε_0 and electronic ε_∞ dielectric constants calculated for $AgGaX_2$ (X = S, Se and Te) crystals using the LDA functional. Position of the intensive A_1 mode in Raman spectra of $AgGaX_2$ (X = S, Se and Te) crystals calculated using LDA functional were presented in Figure 6.15. In Figures 6.17 and 6.18 the dependences of dynamic charges of atoms on the type of anion in $AgGaX_2$ (X = S, Se and Te) crystals and dependence of static ε_0 and electronic ε_∞ dielectric constants for $AgGaX_2$ (X = S, Se and Te) crystals were presented.

In **Chapter 7** the structure parameters, electronic structure, optical spectra, elastic and thermodynamic properties of $CuGa(S_{1-x}Se_x)_2$ solid solutions investigated using DFT method were described. The effect of the anion substitution in $CuGa(S_{1-x}Se_x)_2$ was studied by a partial substitution of sulfur S with selenium Se (with x = 0, 0.25, 0.5, 0.75 and 1.0). The structure/ coordination environment of chalcogen atoms in $CuGaS_2$ and CuGaSe structures and the interatomic distances of the cation-anion described on the basis of literature data were presented in Figure 7.1. For $CuGaSe_{0.5}S_{1.5}$, CuGaSeS and $CuGaSe_{1.5}S_{0.5}$ samples the average atomic volume slightly decreases depending on the selenium content (Figure. 7.2). Moreover, the following parameters of $CuGa(S_{1-x}Se_x)_2$ solid solutions were calculated using GGA and/or LDA functionals and compared with the experimental values determined on the basis of literature data:

- the lattice cell parameters a and c (Table 7.1) and their dependences on Se content in $CuGa(S_{1-x}Se_x)_2$ (Figure 7.3), tetrahedral deformation parameter η as a function of Se concentration in $CuGa(S_{1-x}Se_x)$ (Figure 7.4),
- the band gap values E_g and corresponding scissor operator values Δ_g for $CuGaS_2$ and $CuGaSe_2$ crystals (Table 7.2), band structures of $CuGaSe_2$ and $CuGaS_2$ crystals (Figure 7.5), derivative of the band gap E_g vs. Se ions concentration for $CuGa(S_{1-x}Se_x)$ and $CuAl(S_{1-x}Se_x)_2$ solid solutions (Table 7.3), band gaps of E_g of $CuGa(S_{1-x}Se_x)$ compounds as a function of Se ions concentration (Figure 7.6), partial density of states of $CuGa(S_{1-x}Se_x)$ solid solutions (Figure 7.7),
- the dielectric ε constants as a function of energy E and refractive indices n_a and n_c of $CuGa(S_{1-x}Se_x)$ determined for the incident light of 500 nm wavelength (Figure 7.8 and 7.9),
- the elastic constants (Table 7.4), bulk moduli and their dependences on the Se content in $CuGa(S_{1-x}Se_x)$ (Figure 7.10), densities ρ, sound velocities v_l, v_t, v_m and Debye temperatures Θ_D of $CuGa(S_{1-x}Se_x)$ (Table 7.5) and Debye temperatures Θ_D dependences on the Se content in $CuGa(S_{1-x}Se_x)$ (Figure 7.11).

The presented doctoral dissertation ends with conclusions (**Chapter 8**) and analysis of the obtained theoretical results. Additionally, in the part entitled *Prospects of future study* the author present future research plans related with I-III-VI_2 semiconductors and other related groups of materials with the structure of chalcopyrite for applications in solar cells technology.

The structure and composition of the doctoral dissertation is well thought out. There are some issues in the dissertation such as: *nonlinear optical effects in I-III-VI$_2$ crystals* (Chapter 2/subsection 2.2.2), *methods of the electronic structure calculation* (Chapter 3), *elastic and acoustic properties of I-III-VI$_2$ group crystals* (Chapter 5/ subsections 5.1, 5.2), which are very well written and in my opinion can be useful as didactic materials/script for students. Moreover, I have noticed in the dissertation some editorial imperfections like: incorrect numbering of oral presentations (page 295), in the subsection 7.2.2. *Optical properties of* $CuAl(S_{1-x}Se_x)_2$ *solid solution* the results for $CuGa(S_{1-x}Se_x)_2$ solid solutions were described, there are some words in Ukrainian language (page 152). Moreover, there are some terminological inaccuracies such as: *dispersion of the real* $\varepsilon_1(\omega)$ *and imaginary* $\varepsilon_2(\omega)$ *part of dielectric function*, while all figures show dependences on energy $\varepsilon_1(E)$ and $\varepsilon_2(E)$ (Figure 4.14, page 137) or *Fig. 4.16 shows the spectral dependence of the reflection spectrum* $R(\omega)$ *and the absorption coefficient* $\alpha(\omega)$ *of the refractive indices* $n(\omega)$ *and the extinction coefficient* $k(\omega)$ *as a function of the photon energy in the spectral range from 0 to 30 eV* (page 146), while all parameters R, α, n *and* k are presented as a functions of energy E; in the subsections 6.3, 6,4 and 6.5 the values of phonons vibrations are given in cm^{-1}, which are the units of wavenumbers typically used for description of Raman active bands, while the author used the terminology *phonon frequencies (in cm^{-1})*; instead of *the sound velocities propagation* should be the sound propagation with velocities (page 196); instead of *acoustic vibrations* should be acoustic waves (page198). The above comments do not dimmish the substantive value of the submitted doctoral dissertation.

Moreover, the points that need some explanation are the following:

- The accuracy of the theoretical results presented in Tables 4.1, 4.10, 5.3, 5.4, 5.8, 6.6 and 6.9 require some comments as to their relation to the corresponding experimental results taken from the literature.
- What was the intension of the author to undertake theoretical research of vibrational properties (Raman and IR spectra) in view the thesis of doctoral dissertation *Modification of the cationic-anionic composition of I-III-VI$_2$ crystals is an effective way of tuning the properties of the materials useful for photovoltaic applications*?

Summary

Analyzing the above-described content of the doctoral dissertation M.Sc. Eng. Myron Rudysh, it should be noted that in terms of characterization of the selected physical properties of a huge group of I-III-VI$_2$ crystals, using an *ab initio* calculations based on the DFT, the dissertation covers a very extensive research material. Presented in the dissertation results of theoretical calculations allow determination of the optimum material from the studied group I-III-VI$_2$ with the best parameters for application as absorbers in photovoltaic solar cells. Moreover, an important aspect of the research was a comprehensive approach to the subject of the study, investigation with the use of many advanced computational techniques leading to theoretical results, corresponding to the experimental ones obtained with many experimental methods, with the aim to characterize a huge group of I-III-VI$_2$ semiconductors for photovoltaics. The application of the above-mentioned advanced computational techniques as well as analysis of physical phenomena for study structure, electronic, optical, elastic, some spectroscopic and other physical properties, requires knowledge of selected issues from the theory of solid state physics, quantum mechanics, linear and nonlinear optics, optical spectroscopy as well as the ability to analyze the calculated data, and finally to interpret the results of complex issues. It was a considerable challenge met excellently by M.Sc. Eng. Myron Rudysh. Results of investigations of the mentioned above I-III-VI_2 crystals contribute to the search for the advanced materials for photovoltaics and in my opinion also bring a significant contribution to the materials science.

The most important achievements of the doctoral dissertation include:

- Determination of the structure, electronic, some optical and elastic properties of the following 18 chalcopyrite I-III-VI_2 crystals: $AgAlS_2$, $AgAlSe_2$, $AgAlTe_2$, $AgGaS_2$, $AgGaSe_2$, $AgGaTe_2$, $AgInS_2$, $AgInSe_2$, $AgInTe_2$, $CuAlS_2$, $CuAlSe_2$, $CuAlTe_2$, $CuGaS_2$, $CuGaSe_2$, $CuGaTe_2$, $CuInS_2$, $CuInSe_2$ and $CuInTe_2$ using the GGA and/or LDA functionals. In particular, the values of the following crystal structure parameters were calculated: the unit cell parameters a and c, unit cell volume V, tetragonal deformation parameter η and anion displacement parameter u. For the mentioned above I-III-VI_2 crystals the following electronic parameters were calculated: electronic band structure, energy band gap E_g values, crystal field energies Δ_{CF}, effective mass m^* of charge carriers for electrons m_e^* and holes m_h^*, atomic populations of the constituent atoms, lengths and overlap populations of the shortest atomic bonds and bond ionicity. Moreover, the following optical parameters were investigated: the dispersion of the real ε_1 and imaginary ε_2 part of dielectric function calculated for photon energies from 0 up to 20 eV for polarization vector [100] and [001], uniaxial anisotropy parameter $\delta\varepsilon$ of the dielectric function ε, the reflection R, absorption coefficient α, refractive indices n and extinction coefficient k as a function of the photon energy in the spectral range from 0 to 30 eV and the optical constants ($\varepsilon_{1,x}(0)$, $\varepsilon_{1,z}(0)$, $n_x(0)$, $n_z(0)$ and $\Delta n(0)$). Considering the elastic properties the following parameters were calculated for the mentioned above I-III-VI_2 crystals: the components of the elastic stiffness tensor C_{ij} (C_{11}, C_{12}, C_{13}, C_{33}, C_{44} and C_{66}), linear compressibilities k_a and k_c along the a and c axis, respectively, elastic compliance coefficients S_{ij}, anisotropic Young's modulus E_i and Poisson's ratio v_{ij}, shear anisotropy factors A_1 and A_2, anisotropy indices (bulk A_B, shear A_G and universal A^U) for single crystals and modulus (bulk B, shear G, Young's E) and Poisson's ratio v for polycrystals. Additionally construction of the 3D surfaces and (100) and (001) planar projections of modulus: Young's E, bulk B and shear G and elastic compliance coefficients were presented. Moreover, the analysis of the sound propagation in I-III-VI_2 crystals and calculations of longitudinal v_l, transverse v_t and average sound velocities v_m, crystal density ρ and the Debye temperature Θ_D was presented.
- Calculations of the dispersion curves $\omega(q)$, phonon density of states $N(\omega)$, partial phonon density of states $N(\omega)$ for Ag, Ga and S/Se/Te atoms, Raman and IR spectra, phonons wavenumbers of A_1, A_2, E, B_1 and B_2 modes (determined from Raman and IR spectra) for $AgGaS_2$, $AgGaSe_2$ and $AgGaTe_2$ crystals.
- Calculations of the structure, electronic, some optical and elastic properties of $CuGa(S_{1-x}Se_x)_2$ solid solutions (for x = 0, 0.25, 0.5, 0.75 and 1.0). In particular, the following parameters were determined: the lattice cell parameters a and c and their dependences on Se content in $CuGa(S_{1-x}Se_x)_2$, tetrahedral deformation parameter η as a function of Se concentration in $CuGa(S_{1-x}Se_x)$, the band gap values E_g and corresponding scissor operator values Δ_g for $CuGaS_2$ and $CuGaSe_2$ crystals, band structures of $CuGaSe_2$ and $CuGaS_2$ crystals, band gaps of E_g and partial density of states of $CuGa(S_{1-x}Se_x)$ as a function of Se concentration, the dielectric ε constants as a function of energy E and

refractive indices n_a and n_c of $CuGa(S_{1-x}Se_x)$ for the incident light of 500 nm wavelength, the elastic constants, bulk moduli B and their dependences on the Se content in $CuGa(S_{1-x}Se_x)$, densities ρ, sound velocities v_l, v_t, v_m and Debye temperatures Θ_D of $CuGa(S_{1-x}Se_x)$ and Debye temperatures Θ_D dependences on the Se content in $CuGa(S_{1-x}Se_x)$.

In summary, I would like to emphasize that the doctoral dissertation presented for review contains very extensive research material resulting from the theoretical study of a huge group of I-III-VI_2 (I = Cu, Ag, III = Al, Ga, In, VI = S, Se, and Te) crystals using an *ab initio* methods based on the density functional theory (DFT). In summary of the work, the doctoral student presents conclusions that prove that the thesis of the work have been achieved. I rate the thesis very positively and I consider the undertaken subject very important.

In full consistence with the above, I can say with conviction that the doctoral dissertation of M.Sc Eng. Myron Rudysh fully meets the requirements for doctoral dissertation in accordance with the valid Acts of Law in Poland: the Act of March 14, 2003 on academic degrees and scientific title, as well as degrees and title in the field of art (Dz. U. z 2016 r. poz. 882) and the Act of July 20, 2018 Law on Higher Education and Science (Dz. U. z 2018 r. poz. 1669) and I apply to the Rada ds. Nadawania Stopni Naukowych i Stopni w Zakresie Sztuki Uniwersytetu Humanistyczno-Przyrodniczego im. Jana Długosza w Częstochowie for the admission of M.Sc. Eng. Myron Rudysh to the next stages of the procedure of conferment of doctor in physical sciences.

Reasumując pragnę podkreślić, że przedstawiona do recenzji rozprawa doktorska zawiera bardzo obszerny materiał badawczy będący wynikiem pracochłonnych obliczeń metodami DFT dużej grupy półprzewodnikowych kryształów I-III-VI_2 (I = Cu, Ag, III = Al, Ga, In, VI = S, Se, and Te). W podsumowaniu pracy Doktorant przedstawia wnioski, które dowodzą, że założone cele pracy zostały osiągnięte. Pracę oceniam bardzo pozytywnie a podjętą tematyką uważam za bardzo istotną.

W związku z powyższym, z przekonaniem mogę stwierdzić, że rozprawa doktorska mgr. inż. Myron Rudysh, w pełni spełnia wymogi stawiane pracom doktorskim zgodnie z ustawą z dnia 14 marca 2003 r. o stopniach naukowych i tytule naukowym oraz o stopniach i tytule w zakresie sztuki (Dz. U. z 2016 r. poz. 882, wraz z późniejszymi zmianami) oraz ustawą z dnia 20 lipca 2018 r. Prawo o szkolnictwie wyższym i nauce (Dz. U. z 2018 r. poz. 1669) i wnioskuje do Rady ds. Nadawania Stopni Naukowych i Stopni w Zakresie Sztuki Uniwersytetu Humanistyczno-Przyrodniczego im. Jana Długosza w Częstochowie o dopuszczenie mgr. inż. Myron Rudysh do dalszych etapów przewodu doktorskiego.

Dobrosława Kasprowicz