ORIGIN OF ELECTRONIC PROPERTIES OF α-Hg$_3$S$_2$Cl$_2$ POLYMORPH

O. V. Bokotey[a]*, V. V. Vakulchak[a] and O. O. Bokotey[b]

To investigate the energy bands structure of α-Hg$_3$S$_2$Cl$_2$, first-principles calculations were performed within the density functional theory (DFT) formalism using the SIESTA software package. Using the local density approximation the atomic positions are relaxed so as to minimize the forces acting on the atoms. The analysis of band energy dispersion shows that the VBM and CBM are located at Γ symmetry point, resulting in a direct energy band gap of 3.198 eV. It is established that the nature of interatomic interactions has complex character and includes covalent and ionic parts. The inclusion of spin-orbit coupling does not strongly modifies the structure of energy bands.

* Corresponding Authors
    E-Mail: bokotey_ov@ukr.net
[a]   Faculty of Physics, Uzhhorod National University, 46 Pidgirna Str., Uzhhorod, 88000, Ukraine.
[b]   Uzhhorod Specialized Boarding School, 28 Zagorska Str., Uzhhorod, 88000, Ukraine

Introduction

Hg$_3$X$_2$Y$_2$ (X = S, Se, Te; Y = F, Cl, Br, I) compounds present a class of perspective materials for nonlinear optics. Physical and chemical properties of these crystals are very useful for the creation of functional elements for optical devices. The corderoite family compounds are characterized by such optical properties as high refractive index and photoconductivity[1-3] and are materials showing presence of optical activity and electro-optic effect.[4-10] The main structural feature of mentioned crystals is the tendency to formation of various polymorphic modifications. At the same time due to the wide transparency in the visible and IR-range (from 0.3 to 40 μm) their optoelectronic features are very useful for possible applications.

Regarding α-Hg$_3$S$_2$Cl$_2$, no reports concerning electronic structure can be found in literature. Therefore, we thought it would be worthwhile to perform the band structure calculations of α-Hg$_3$S$_2$Cl$_2$. In this paper, the band structure and optical transitions of α-Hg$_3$S$_2$Cl$_2$ have been investigated using DFT. The study on the origin of electronic properties provides an important information and prediction of physical properties of title crystal.

Structure of α-Hg$_3$S$_2$Cl$_2$

The α-Hg$_3$S$_2$Cl$_2$ is cubic (a= 0.89 nm) and belongs to the space symmetry group T^5-I2$_1$3. Figure 1 displays the crystal structure of the title compound. Observe that the basic structural unit in α-Hg$_3$S$_2$Cl$_2$ is a [SHg$_3$] pyramid. Crystal structure of gyrotropic α-Hg$_3$S$_2$Cl$_2$ was determined independently by different authors.[11-19] A characteristic structural feature is the presence of two sets of octahedral spirals with different radii and twisting directions. They are located side by side, oriented in the same direction and consistently alternated.[4]

There are three crystalline phases of Hg$_3$S$_2$Cl$_2$. These are corderoite minerals α-Hg$_3$S$_2$Cl$_2$ (I2$_1$3), β-Hg$_3$S$_2$Cl$_2$ (Pm3n) and γ-Hg$_3$S$_2$Cl$_2$ (Pbmm),[20,21] which have variable structure depending on number of halogens entered into their structure. The first crystalline polymorph is metastable at normal conditions. The structure of the α-Hg$_3$S$_2$Cl$_2$ type is realized in the cases, when the chalcogen anion size is more than the halogen anion size: S^{2-}(0.182 nm), Se^{2-}(0.193 nm), Te^{2-}(0.211 nm) > Cl$^-$(0.181 nm); Te^{2-}(0.211 nm) > Br$^-$ (0.196 nm). The main feature of this structural type is existence of (Hg$_3$X$_2$)$_{2n}^{2+}$ infinite chains from [XHg$_3$] trigonal pyramids connected by the mercury atoms which are joined for two pyramids. These chains unite in three-dimensional framework in which octahedral emptiness the halogen ions are localized.[3] The mercury atoms are two-coordinated with a linear geometry. The chalcogen atoms are three-coordinated, [SHg$_3$], forming trigonal pyramids. In title crystal, the interior bond angles Hg-S-Hg are 92° and the interior bond distances Hg-S and Hg-Cl are 0.245 and 0.292 nm. In this compound the lead atoms located at the 12b and 8a Wyckoff positions in the body-cantered unit cell. Due to specific atomic structure of corderoite-type compounds one can expect a possible applications of them as a non-linear optical materials.
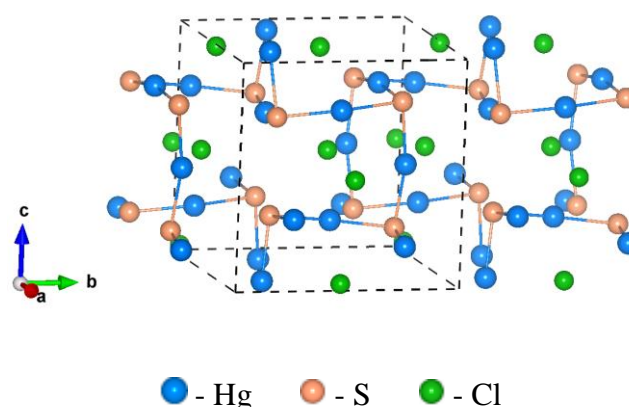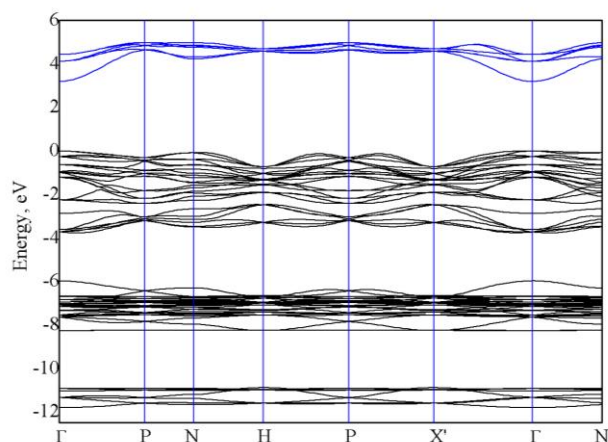

Figure 1. Crystal structure of α-Hg$_3$S$_2$Cl$_2$.

Calculation procedure

To calculate the energy bands structure of α-Hg₃S₂Cl₂, the DFT[22,23] with the local density approximation is used. The total and partial densities of electron states were determined by the tetrahedral method. We used the experimental lattice constants and atomic structure for these calculations. The DFT calculations are carried out on the minimized structure of α-Hg₃S₂Cl₂. Integration over the irreducible part of the Brillouin zone was conducted using the method of special k-points.[24,25] We determined that 4x4x4 k-point grid and a cut-off energy of 1200 Ry are sufficiently converged. We first relaxed the crystal structure with respect to the lattice constants and internal parameters. A Hubbard correction was used to obtain a better band gap value[26-28] that is mostly underestimated by LDA.
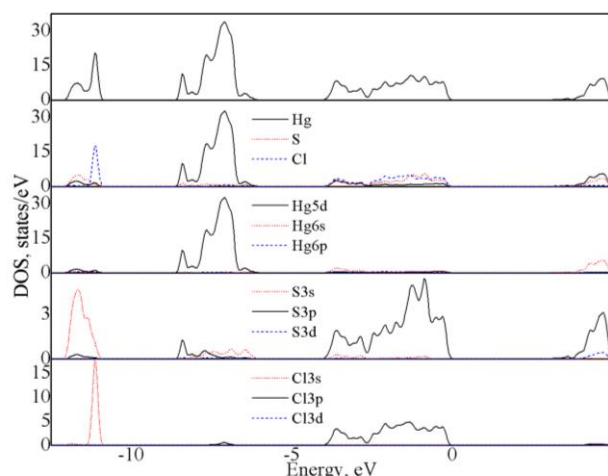

Figure 3. DOS/PDOS diagrams calculated for α-Hg₃S₂Cl₂.

Results and Discussion

The calculated band structure of α-Hg₃S₂Cl₂ using LDA+U is presented in Figure 2. The energy structure of crystal under investigation defines by short-range order in the location of atoms (pyramids [SHg₃] and octahedras [HgS₂Cl₄]). Moreover, the indirect band gap indicated in the LDA calculation is changed to a direct band gap of 3.198 eV between the valence band maximum and conductive band minimum at Γ in the LDA+U calculation. It is in satisfactory agreement with experimental data from studies of diffuse reflectance spectra.[17] α-Hg₃S₂Cl₂ is a direct band gap semiconductor.
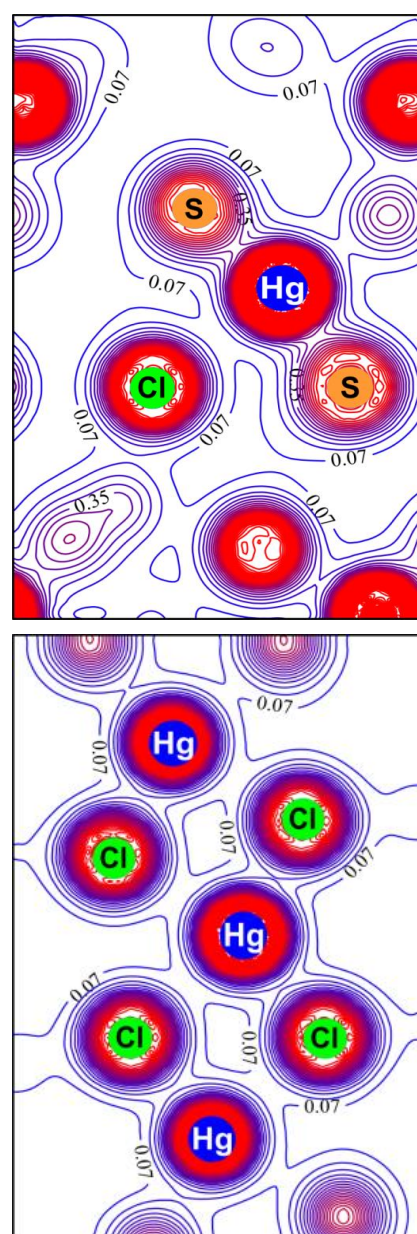

Figure 2. Band structure of α-Hg₃S₂Cl₂ polymorph

The partial DOS helps to identify the origin of electronic properties of α-Hg₃S₂Cl₂. The calculated partial density of states is illustrated in figure 3. The Fermi level is taken to be 0.0 eV. We have found that the conductive band is formed prevailingly from S-p/d states and Hg-s states. The valence band maximum consists of the S-p/Cl-p orbitals and a relatively small contribution of the Hg-s orbitals. Considering the DOS/PDOS, one can conclude that in α-Hg₃S₂Cl₂ the sulphur and chlorine atoms play more prominent role in the valence band than the mercury atoms, which is attributed to the higher electron negativity of sulphur and chlorine atoms than the mercury.

Figure 4. Spartial distribution maps of the charge density in α-Hg₃S₂Cl₂.

The bonding wave functions are localized around of chalcogen and halogen atoms.

The calculated DOS/PDOS of α-$Hg_3S_2Cl_2$ are compared with our previous DFT calculations for $Hg_3Se_2Cl_2$ and $Hg_3Te_2Cl_2$.[7,8] In general, the whole region of valence states has a complex hybrid character caused by the interaction of all atoms species inherent to the crystals of the $Hg_3X_2Y_2$ type. The analysis of rotation dispersion[16] of α-$Hg_3S_2Cl_2$ and our DFT calculations indicates that the rotation of polarization plane in this crystal is connected with direct optical transitions. Atomic transitions of [$Hg_3S_2Cl_4$] octahedra in excited electronic states makes contributions to gyrotropy caused by C_1 local symmetry group.[4] It should be noted that the direct optical transitions in the α-$Hg_3S_2Cl_2$ are localized on [$Hg_3S_2Cl_4$] octahedras.

The investigation of the band structure of solids including rather heavy atoms requires including the effect of spin-orbit coupling. The spin-orbit splitting in mercury orbitals are slight at the conductive band minimum. Thus, it not significantly affects the band gap size. In addition, the results from the calculation using spin-orbit coupling shows that the band topology near the conductive band minimum is insignificantly changed due to a larger spin-orbit splitting in the S-p orbitals at the Γ point.

To understand the bond nature of Hg-S and Hg-Cl in α-$Hg_3S_2Cl_2$, the two-dimensional charge distribution in (100) plane is plotted in figure 4. Furthermore, by consideration of the electronic charge distribution plot, one can claim the covalence origin for the Hg-S bonds and ionic nature for the Hg-Cl bonds. The presence of covalent bonding between mercury and strongly polarized sulphur atoms leads to the high magnitude of refractive index in the title compound.[3] The covalent bond arises due to the significant degree of the hybridization and the electro-negativity differences between atoms.

Conclusions

The band structure of gyrotropic α-$Hg_3S_2Cl_2$ is investigated by means of the first-principles calculations in the framework of the DFT. Using local density approximation within Hubbard correction, the atomic positions are relaxed so as minimize the forces acting on each atom. The analysis of DOS/PDOS indicates the origin of electronic properties in α-$Hg_3S_2Cl_2$ that connected with rare space symmetry group of mentioned crystal. The calculated electronic charge density distribution confirms the covalence and ionic nature for the Hg-S and Hg-Cl bonds respectively. The title compound combine important features needed for good X-ray and γ-ray detection applications, namely high atomic numbers and specific densities, wide band gap of 3.198 eV. It is in good agreement with experimental results. This may open a new area in applications of corderoite family compounds as multifunctional materials.

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