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Abstract
We report theoretical calculations of the band structure of AgCd$_2$GaS$_4$ using the full-potential linear augmented plane wave method and experimental measurements of the valence band x-ray photoelectron spectroscopy. We find that the valence band maximum and the conduction band minimum are located at the Γ point of the Brillouin zone resulting in a direct energy gap of 1.0 eV compared to our measured experimental value of 2.15 eV. Our analysis of the partial density of states shows that there is a weak covalent interaction between Ag and Ga atoms and between Ag and Cd atoms, and a substantial covalent interaction between Ag and S atoms. Thus the Ga–Ag and Cd–Ag bonds are basically of ionic character, and Ag–S bonds are of covalent character. The theoretical results of the density of states are in agreement with the valence band x-ray photoelectron spectroscopy measurements with respect to spectral peak positions. We have analyzed the calculated density of states and find a strong/weak hybridization between the Ag, Cd, Ga and S states in the valence and conduction bands.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The quaternary sulfide AgCd$_2$GaS$_4$ was discovered during an investigation of the quasi-ternary system Ag$_2$S–CdS–Ga$_2$S$_3$ [1, 2]. Recently single crystal growth of AgCd$_2$GaS$_4$ has been performed by the solution-melt technique using AgGaS$_2$ excess as a solvent and single crystal blocks of $\sim$1 cm^3 scale were selected from the cylindrically grown boule [3]. An observation of the optical properties of AgCd$_2$GaS$_4$ single crystal substrates reveals that the energy band gap E_{g} is 2.15 eV and transparency over the spectral range $\lambda = 0.63$–13 μm [3, 4]. In several studies the formation of wide solid solution ranges of AgCd$_2$GaS$_4$ has been found by

substitutions in cation or anion sub-lattices. This crystal may be considered as a parent of a wide family of structure-related 'mixed' crystals where the properties can be tuned through the variation of chemical composition [5–9]. The coexistence of a noncentrosymmetric structure and a wide transmittance range suggests that AgCd$_2$GaS$_4$ is a promising material for infrared (IR) nonlinear optical applications. The knowledge of the physical properties of AgCd$_2$GaS$_4$, however, is very limited and further investigation is of interest to estimate the technological potential of this material. We believe that the understanding of the band structure will be a first step in this direction.

In this paper we propose to study the band structure of AgCd$_2$GaS$_4$ using both theoretical and experimental methods. For the theoretical study we will use the full-potential linear augmented plane wave (FP-LAPW) method which has proven

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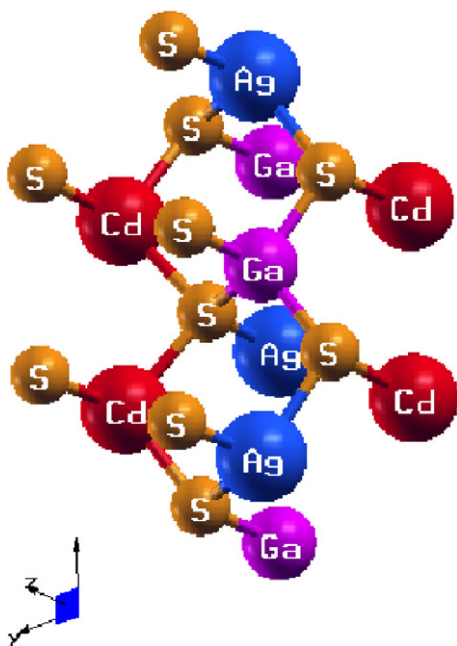
Figure 1. The crystal structure of AgCd₂GaS₄.

to be one of the most accurate methods [10, 11] for the computation of the electronic structure of solids within density-functional theory (DFT). The results of these calculations will be compared to our measurements of the valence band x-ray photoelectron spectroscopy (VB-XPS). In this way we can compare theory and experiment and thus provide a better understanding of the electronic structure of this compound.

The experimental x-ray photoelectron spectroscopy technique is described in section 2. In section 3 we present the details of our band energy calculations. Principal results of band energy calculations and comparison with the experimentally obtained results are given in section 4. Section 5 presents general conclusions.

2. Experimental details

The investigated crystals were grown using the initiated alloys AgGaS₂–CdS taken into stoichiometry ratio. The raw materials were of purity 99.99 wt%. The mixture was prepared using vacuum evaporated platinum crucibles. To eliminate pure sulfur an additional treatment in hot oxygen flow was done. After that the mixture was heated at a rate of 40 K h⁻¹ up to 1062 or 1086 °C depending on the excess of Cd-S. At these temperatures the melt was mixed by acoustic means for 10–15 min and the slow cooling process was carried out with a rate of 8.6 K h⁻¹ with a final quenching in cold water. An x-ray diffractometer was used to monitor the crystalline structure of the grown crystals.

X-ray photoelectron spectroscopy (VB-XPS) measurements were done using x-rays, of energy $E = 1486.6$ eV, which were formed using a monochromated rotating anode Al Kα x-ray source. The ejected photoelectrons were analyzed by a 300 mm mean radius spherical-sector electron energy analyzer with 0.74 mm slits with a pass energy of 160 eV. The instrumental spectral energy resolution is 0.45 eV derived from

the Gaussian convolution of the analyzer broadening and the natural line broadening of the x-ray source (0.24 eV). The binding energy scale is measured with respect to the Fermi level and was referenced using the Fermi edge of an ion-bombarded silver reference sample that is regularly used to calibrate the spectrometer. A sample-dependent shift was subsequently applied to the zero of the binding energy scale as the valence band maximum (VBM) in all cases. AgCd₂GaS₄ surface preparation was performed under ultra high vacuum, in a preparation chamber connected to the XPS analysis chamber, using atomic hydrogen cleaning without introducing electronic destroying.

The sample was annealed at 395 K under exposure to a 10 kilo-Langmuir dose of a H₂ flow propagating through a thermal gas cracker with a cracking output equal to about 30%, together with a 2 h annealing at 420 K. Before the treatment we observed a substantial contribution from the oxygen. The treatment was performed until the oxygen presence becomes less than background.

3. Theoretical calculations

AgCd₂GaS₄ crystallizes in the noncentrosymmetric orthorhombic space group $Pmn2_1$ (see figure 1). We have used the experimental lattice constants $a = 8.1395$ Å, $b = 6.9394$ Å, $c = 6.6013$ Å and atomic positions given in [1, 2, 12]. We have employed the full-potential linear augmented plane wave (FP-LAPW) method as incorporated in the WIEN2K code [13]. This is an implementation of the density-functional theory (DFT) [14] with different possible approximations for the exchange–correlation (XC) potential. Exchange and correlation were treated separately within the different approximations. We have used the local-density approximation (LDA), and different generalized gradient approximations (GGA): PBE-GGA, PW2-GGA and EV-GGA in order to establish the influence of these approximations on the value of the energy gap, the band structures and the partial density of states. Scalar relativistic equations are used to obtain self-consistency.

In order to achieve energy eigenvalues convergence, the wavefunctions in the interstitial regions ware expanded in plane waves with a cut-off $K_{max} = 9/R_{MT}$, where R_{MT} denotes the smallest atomic sphere radius and K_{max} gives the magnitude of the largest K vector in the plane wave expansion. The valence wavefunctions inside the spheres are expanded up to $l_{max} = 10$ while the charge density was Fourier expanded up to $G_{max} = 14$ au⁻¹. The muffin-tin radii were assumed to be 2.35, 2.49, 2.18 and 2.08 au for Ag, Cd, Ga and S respectively.

Self-consistency is obtained using 300 **k**-points in the irreducible Brillouin zone (IBZ). The BZ integration was carried out using the tetrahedron method [15, 16]. The band structure and density of states (DOS) are calculated using 500 **k**-points. The self-consistent calculations are considered to have converged when the total energy of the system is stable within 10⁻⁵ Ryd.
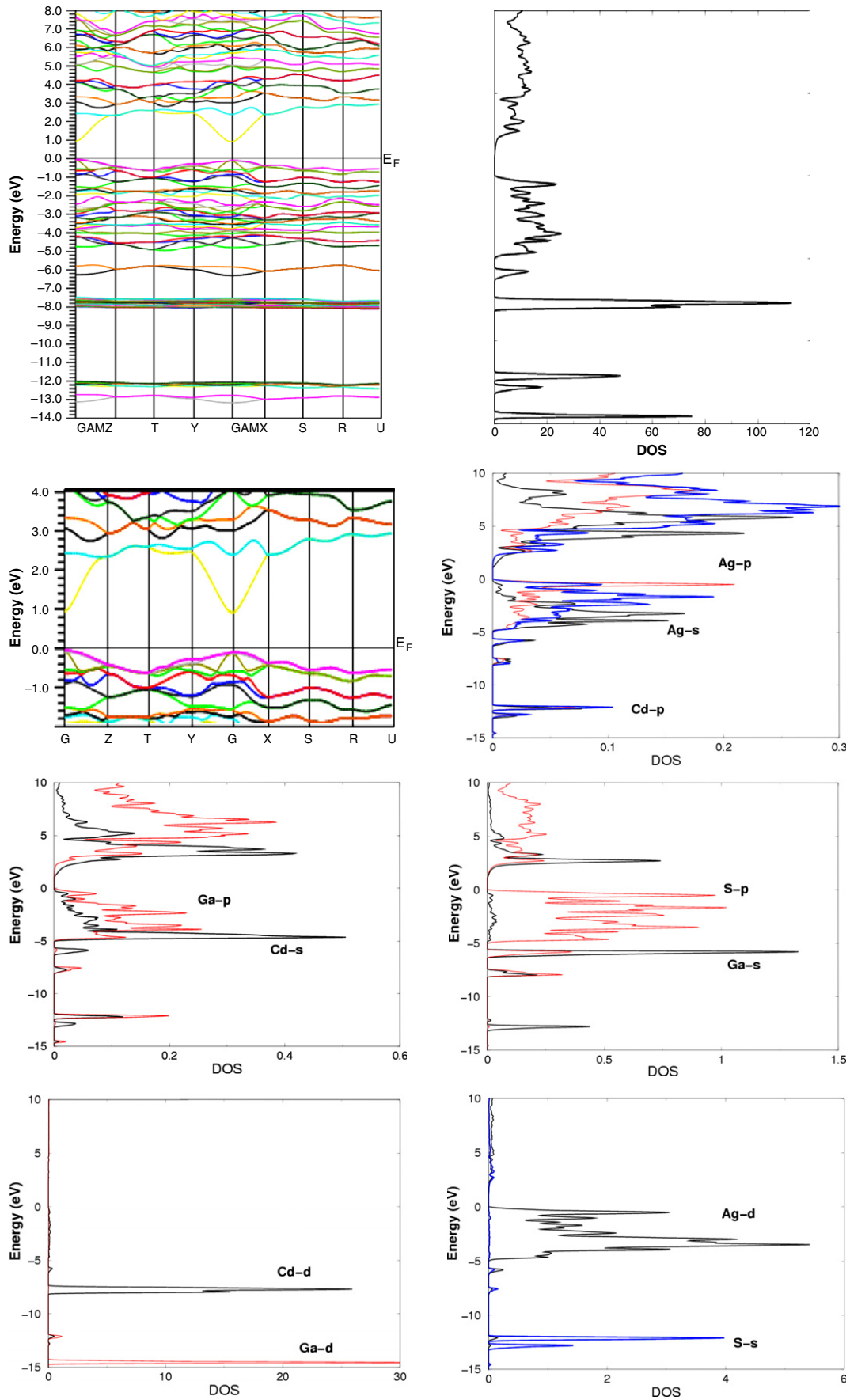
Figure 2. Band structure and total density of electronic states (states/eV unit cell), along with Ag-s/p, Cd-s/p/d, Ga-s/p/d, and S-s/p partial densities of states (PDOS) for AgCd$_2$GaS$_4$ crystal.

4. Results and discussion

4.1. Band structure and density of state

The band structure, total density of states (TDOS) along with the Ag-s/p/d, Cd-s/p/d, Ga-s/p/d and S-s/p partial (PDOS) for AgCd$_2$GaS$_4$ crystal are shown in figure 2. From the PDOS we are able to identify the angular momentum character of the various structures. It is found that the lowest energy of conduction bands (CBs) and the highest energy of valence bands (VBs) is located at the Γ point making it a direct band gap material. The gap is 1.0 eV in comparison with our measured one (2.15 eV). We found that the theoretical value of the energy gap is less than the measured one which is consistent with the general trend of the LDA and GGA approximations. It is observed that the valence bands are flat while the conduction bands show free electron behavior. The bands can be assigned according to total and partial density of states, as plotted in figure 2. The bands lying around −14.5 eV are mostly Ga-d states with a small admixture of Cd-s/p and S-s states. The VB's ranging from −13.0 to −12.0 eV mostly originate from S-s, Ga-s, and Cd-s/p states. Around −7.5 eV, there are some bands derived from Cd-s/p/d, S-s/p and Ga-s/p states. Ag-s/p/d, Ga-s/p, Cd-s/p and S-p states have contributions to VBs between −6.0 and the Fermi energy (E_F). The top of VBs largely originate from the Ag-d states with a small mixing of S-p and Ag-s/p terms, and the bottom of CBs are mainly composed of Ga-s/p states with a small mixing of S-p and Ag-p states. From the PDOS, we note a strong hybridization between Cd-p and Ag-s states around −4.5 and 3 eV. Also Cd-p is strongly hybridized with Ag-p at CBM and VBM. Cd-s strongly is mixed with Ga-p at around −14.0, −12.5, −5.0, and 5.0 eV. S-p is strongly hybridized with Ga-s at around −6.0, −7.5 eV and at the CBM. Now we elucidate the feature of chemical bonding from the nature of total DOS and angular momentum projected DOS (partial DOS). We observe that the DOS, ranging from −5.0 eV to E_F is larger for Ag-d states (5.8 electrons/eV), S-p states (1.0 electrons/eV), Cd-s (0.56 electrons/eV) and Ga-p (0.22 electrons/eV) by comparing the total DOS with the angular momentum projected DOS of Ag-d, S-p, Cd-s, and Ga-p, states as shown in figure 2. These results show that some electrons from S-p, Cd-s, and Ga-p, states transfer into VBs and take part in weak covalence interactions between Ag and Ga atoms and between Ag and Cd atoms, and the substantial covalence interactions between Ag and S atoms. All the Ga–Ag and Cd–Ag bonds are basically of ionic character, and Ag–S bonds are of covalent character. Accordingly, we can also say that the covalent strength of Ag–S bonds is stronger than that Ga–Ag or Cd–Ag bonds.

It is interesting that the obtained band structure near the G point of the Brillouin zone clearly shows the existence of two-sub-bands both for the top of valence band as well as for the bottom of conduction band. They possess substantially different energy dispersion corresponding to different effective masses. Using an approach of evaluating the effective masses developed in [20] we have found that the valence band prevailingly possesses two type of carriers with effective masses equal to about 0.63 m^* and 0.82 m^*. At the same time
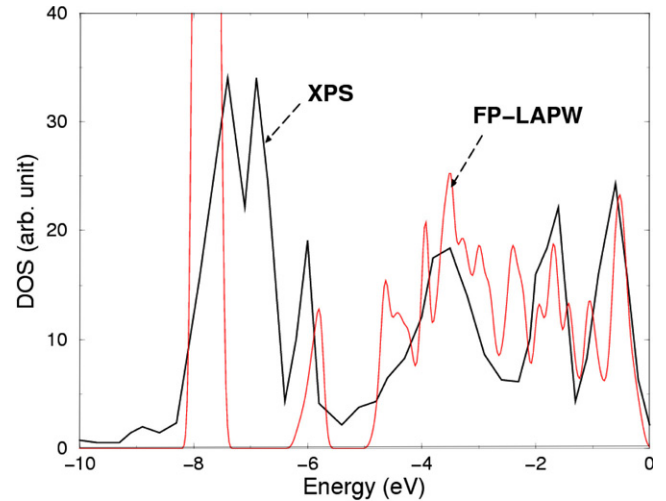
Figure 3. Calculated total density of states using the FP-LAPW method in comparison with the measured total density of states using the XPS technique for the valence band.

the conduction band shows values of corresponding effective masses equal to 0.51 m^* and 0.72 m^*.

The valence band density of states data was analyzed in the energy range in which the experiment was conducted (−10.0 to 0.0 eV). The comparison of the theoretical and experimental data (XPS) is shown in figure 3. We note a reasonable agreement in the matter of the general behavior and position of the peaks. However the magnitude of the theoretical DOS is significantly different from the experimental value. We would like to mention that the difference between the magnitudes of the experimental and the theoretical curves can be made smaller if we choose a larger broadening in our theoretical calculations. In the present calculation the broadening is around 0.003 eV. Such discrepancies in the magnitude may reflect the existence of intrinsic defect states which give additional localized states superimposed on the perfect band energy structure of the investigated single crystals. Other works have reported discrepancies in ternary silver crystals [17–19]. It is clear that the main discrepancies are observed in the spectral range between −6 and −8 eV. This could be due to the mixture of ionic and covalent bonding around −7.5 eV, derived from Cd-s/p/d, S-s/p and Ga-s/p states and Ag-s/p/d, Ga-s/p, Cd-s/p contributing to VBs between −6.0 up to the E_F level. Another possible reason for the discrepancies may be caused by existence of surface localized states, which in the case of the borate give an additional redistribution of the charge density which in connections with different charged intrinsic defects typical for the ternary compounds [17] may modify the experimental spectra.

5. Conclusions

In this work we have reported band energy calculations on optically nonlinear AgCd$_2$GaS$_4$ crystals. The density of electronic states deduced from these measurements is compared with the calculated density of states obtained from FP-LAPW method. Our calculations show that the

VBM and the CBM are located at Γ resulting in a direct energy gap. The calculated energy gap is around 1.0 eV in reasonable agreement with our measured value of 2.15 eV. We have established that the DOS, ranging from -5.0 eV to E_F is larger for Ag-d states (5.8 electrons/eV), S-p states (1.0 electrons/eV), Cd-s (0.56 electrons/eV) and Ga-p (0.22 electrons/eV) with respect to the total DOS with the angular momentum projected DOS of Ag-d, S-p, Cd-s, and Ga-p, states. Our results show that some electrons of Cd-s and Ga-p states transfer into VBs and take part in weak covalent interactions between Ag and Ga atoms and between Ag and Cd atoms, and substantial covalent interactions between Ag and S atoms. The Ga–Ag and Cd–Ag bonds are basically of ionic character, and Ag–S bonds are of covalent character. Accordingly, we can also say that the covalent strength of Ag–S bonds is stronger than that Ga–Ag or Cd–Ag bonds. The main discrepancies between theoretical and experimental DOS are observed in the spectral range -6 to -8 eV. This effect may be a consequence of a mixture of ionic and covalent bonds around -7.5 eV, derived from Cd-s/p/d, S-s/p and Ga-s/p states and Ag-s/p/d, Ga-s/p, Cd-s/p contributing to VBs between -6.0 and the E_F level forming additional intrinsic trapping levels. Our calculations are generally in good agreement with our XPS measurements. We would like to conclude by stating that the agreement between our calculated and measured DOS shows the reliability of the full-potential calculations. The existed discrepancies reflect the presence of intrinsic defect states typical of the chalcopyrite crystalline structure.

Acknowledgments

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