CHAPTER

1

Part I

ELECTRONIC BAND STRUCTURE OF $AgCd_2GaS_4$: THEORY AND EXPERIMENT

We report theoretical calculations of the band structure of $AgCd_2GaS_4$ *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 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.*

1.1 HISTORICAL REVIEW

The quaternary sulfide $AgCd_2GaS_4$ was discovered during an investigation of quasi-ternary system Ag_2S-CdS-Ga_2S_3 [1,2]. Recently, single crystal growth of $AgCd_2GaS_4$ has been performed by solution-melt technique using $AgGaS_2$ excess as a solvent and single crystal blocks of ~1 cm^3 scale were selected from the cylindrically grown boule [3]. An observation of optical properties of $AgCd_2GaS_4$ 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 $AgCd_2GaS_4$ have 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 chemical composition variation [5-9]. The coexistence of a no centrosymmetric structure and wide transmittance range suggests that, $AgCd_2GaS_4$ is a promising material for Infrared (IR) nonlinear optical applications. The knowledge of the physical properties of $AgCd_2GaS_4$, 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 chapter we propose to study the band structure of $AgCd_2GaS_4$ 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 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.