GENERAL INTRODUCTION

This thesis is divided into three parts: (I) the general theory of the electronic states in crystalline solids; (II) the energy band structures of some divalent metals of hexagonal close-packed structure; and (III) the energy band structure of some compound semiconductors of Wurtzite structure.

The study of the electronic energy bands of solids has been the subject of many investigations. It has been observed that when a large number of atoms come close together to form a solid, the energy levels of the new system, i.e., the solid, are no longer sharp levels, because, the Coulomb and exchange interactions between the electrons of the different atoms force the sharp electronic levels to spread into bands. Since the core electrons are relatively strongly bound, the bands arising from the valence electrons, and, at most, the outermost core electrons will be important in determining the electronic properties of the solid. Moreover, as we will be dealing with crystalline solids consisting of periodic arrays of atoms, the whole energy band system can be restricted to the first Brillouin Zone and a dispersion relation between the energy, $E$, and the wave vector, $\mathbf{k}$, throughout the Brillouin Zone determines the general nature of the solid. From this $E-\mathbf{k}$ relation one can then easily determine the densities of states, the optical absorption spectra and the Fermi Surfaces for metals, or, the energy gaps for semiconductors and insulators. However, before obtaining these properties, one is required to solve the crystal Hamiltonian which is a many-body one. Therefore, one is
compelled to take the help of the one electron approximation to reduce the many-electron Schrödinger equation to the one-electron form. Several methods for solving this one-electron Schrödinger equation exist; the most notable being the Green's function, the tight-binding, the Orthogonalised Plane Wave (O.P.W.) and the Augmented Plane Wave (A.P.W.) methods. Part I deals with a short description of the one-electron theory, the Brillouin Zone, the Fermi Surface, the different methods of energy band calculations with a special emphasis on the A.P.W. method and its Composite Wave Variational version, and the application of the group theory to the energy band problem, with the h.c.p. crystal as an example.

In an energy band problem, the accurate construction of the crystal potential is very crucial. For monovalent metals it was found that such construction could be avoided through the Quantum Defect (Q.D.) method whose importance lies in the fact that it enables one to use the experimentally determined spectroscopic term values directly in the energy band problem. Part II describes this method and its generalisation for polyvalent metals. This part then goes on to describe the calculation of the energy band structures of four divalent h.c.p. metals: Be, Mg, Zn and Cd by the Composite Wave Variational version of the A.P.W. method in conjunction with the Q.D. method. In the process we have utilised the elegant machinery of Group Theory via the Projection Operator technique to reduce the size of the secular determinant to manageable proportions and also to gain an insight into the symmetries of the various energy bands. The studies of the Fermi Surfaces, the densities of states and the absorption spectra of these metals, have been carried out
using these band structure data.

Since the electronic energy band calculations of compounds necessitate the solving of a secular determinant of a very high order at a general point inside the Brillouin Zone, it is practicable to solve the secular determinant only at the highest symmetry points, where it can be factorised with the help of group theory. In order to obtain the energy bands throughout the Brillouin Zone one then needs some interpolation scheme obeying the full crystal symmetry. The first chapter of Part III describes the development of a parametrised band interpolation for the Wurtzite structure. Utilising the first principle band structure calculations of Herman et al at only the very high symmetry points, the detailed band structures of a number of Wurtzite compounds have been constructed using this parametrised band scheme. Chapter 2 of this part describes a new first principle method for the determination of the energy band structure of complicated solids. The salient features of this method are firstly, that it combines the advantages of both the A.P.W. and the O.P.W. methods, and secondly, that the reduction of the magnitudes of the inscribed spheres considered here, leads to the O.P.W. method on the one hand, while their increase to the largest possible values approaches the A.P.W. method. The method is also very useful in partially solving the convergence difficulties faced by both the O.P.W. and the A.P.W. methods when these are applied to complicated solids. This chapter also describes the application of this method to the determination of the energy values at the highest symmetry points $\Gamma$ and $A$ inside the Brillouin Zone for Wurtzite ZnS.