CHAPTER 6

ELECTRONIC AND MAGNETIC STRUCTURE OF ZINC-BLENDE TYPE CaX (X = P, As and Sb) COMPOUNDS

6.1 INTRODUCTION

Almost the complete search for possible magnetic materials has been performed utilizing transition metal doping into III-V semiconductors or II-VI compounds (Sato and Katayama 2000, Sata and Katayama 2001). In addition to dilute magnetic semiconductors (Matsukura et al 1998), new classes of materials were discovered. In the case of Cr- or Mn-doping into GaAs or InSb, end materials are known to possess the half-metallic band structures by the first-principles calculations (Shirai et al 1998, Shirai 2001, 2003 and Ogawa et al 1999). Some of the ferromagnetic materials in zinc-blende type CrAs and CrSb were indeed successfully synthesized experimentally (Akinga et al 2000 and Zhao et al 2001). These materials are obtained as products of doping. In all these compounds, ferromagnetism arises due to the presence of transition 3d metal atom.

Apart from these compounds, several Ca based compounds such as La-doped CaB₆, Ca (O, C) and Ca (O, N) compounds were studied as possible ferromagnetic materials (Monnier and Delly 2001, Elifmov et al 2002 and Kenmochi et al 2004). In CaB₆, the ferromagnetism reported in the literature was argued as due to defect-mediated spin-polarization. Inter-orbital exchange interactions between degenerate molecular orbitals in an anion cluster could
be large enough to cause ferromagnetic behaviour. The same argument was observed for CaO compound in the NaCl-type structure. In these compounds, the ferromagnetism was favoured due to the anion p-like electrons.

Kusakabe et al (2004) has proposed half-metallicity in zinc-blende type CaX (X = P, As and Sb) compounds. In these compounds, the ferromagnetism arises due to the anion p-like electrons and partial involvement of cation d-orbitals. Sieberer et al (2006) found half-metallic ferromagnetism in many II-V ZB compounds using the full potential linearized augmented plane wave method with generalized gradient approximations. Other half-metallic alkaline earth based compounds have been already discussed in Chapter 5.

In this Chapter, the electronic band structure calculations and magnetic properties of calcium pnictide, CaX (X = P, As and Sb) compounds in the zinc-blende structure were studied using local (spin) density approximation. In these compounds, the important character of the band structure is that the top most valence band becomes almost dispersionless. This flat band, which creates a sharp peak in the density of states at the Fermi level, originates from hybridization of p-like states of pnictides and Ca 3d-like states. Ferromagnetism arises in this p-d hybridized band.

However, the occurrence of p-electron half-metallic ferromagnetism in these compounds distinguished them from the transition metal based binary compounds where the transition metals carry the magnetic moments. In these compounds, the magnetic moments appear in the anion p-like states and therefore make them an interest. To understand the physical, electronic, and magnetic properties of these compounds, a detailed description of the electronic structure of these compounds is needed.
6.2 PRESENT WORK

CaX (X = P, As and Sb) compounds in the hypothetical zinc-blende type structure were studied by using the tight-binding linear muffin-tin orbital method in order to explore the electronic and magnetic properties of these compounds at their equilibrium volume and volume compression. For the calculations, local (spin) density approximation was employed. Both spin-polarization and non-spin-polarization calculations are carried out for each compounds. The motivation was to find an analogue of half-metallic transition metal based binary compounds. The band structures and density of states were presented.

6.2.1 Crystal Structure and Method of Calculation

CaX (X = P, As and Sb) compounds are the intermetallic compounds made of a strong cation and a weak anion, which are known as the Zintl phase (Iandelli and Franceschi 1973). Thus, the valency of Ca is almost +2 while the anions have three extra electrons each. The crystal structure of these compounds known in the literature belongs to the NaO-type structure (space group: P-62m, No.: 189) (Haridon et al 1976). In this structure, these compounds do not show magnetism (Kusakabe et al 2004, Sieberer et al 2006). The calculations have been carried out for hypothetical zinc-blende structure. It (space group: I-43m, No.: 216) is an ordered diamond cubic structure. It is shown in Figure 3.1(d). The cation atom is located at (0, 0, 0) and anion atom is at (0.25, 0.25, 0.25) positions.

The calculations were performed using the self-consistent TB-LMTO method (Andersen and Jepsen 1984) based on the density functional theory (Hohenberg and Kohn 1964, Kohn and Sham 1965) within the local (spin) density approximation. The exchange-correlation potential has been calculated using von Barth and Hedin (1972) parameterization scheme. The total energies are calculated within the atomic sphere approximation. Atomic
sphere approximations divides the crystal into space filling spheres centered on each of the atomic site. The atomic sphere radii have been chosen in such a way that the difference in the potential is minimum at the sphere boundary and the charge flow is in accordance with electro negativity criteria. The total and partial density of states was calculated using the tetrahedron method (Jepsen and Anserensen 1971). All relativistic effects have been taken into account except the spin-orbit coupling. The energy eigenvalues were calculated for 245 \( k \)-points in the irreducible part of the Brillouin zone for both non-magnetic and ferromagnetic phases and energy \( E \) as well as \( k \)-convergence was also checked.

It is well known that this method gives accurate results for close packed structures (Christensen 1985). Hence, it becomes necessary to include empty spheres in zinc-blende structure. Without breaking the crystal symmetry two non-equivalent empty spheres were included at the position (0.50, 0.50, 0.50) and (0.75, 0.75, 0.75) to get close packing. With the inclusion of empty spheres and combined correction terms, the errors in this method are minimized. The basis set is chosen to have angular momentum components of s, p and d orbitals for both the atoms. All lower states were treated as core states. The following valence orbitals were used in the present calculations:

\[
\begin{align*}
\text{Ca: } & 4s^2 \ 4p^0 \ 3d^0, \\
\text{P: } & 3s^2 \ 3p^3 \ 3d^0, \\
\text{As: } & 4s^2 \ 4p^3 \ 4d^0 \ \text{and} \ \\
\text{Sb: } & 5s^2 \ 5p^3 \ 5d^0 \ 4f^0
\end{align*}
\]

6.3 TOTAL ENERGY CALCULATION AND RELATED PROPERTIES

The calculated total energy/molecule as a function of volume for the both ferromagnetic and nonmagnetic phase is given in Figure 6.1. From this figure, one can find easily that all the three compounds are more stable in the ferromagnetic phase, in agreement with earlier theoretical observations (Kusakabe et al 2004, Geshi et al 2004, Sieberer et al 2006).
Figure 6.1 Total energy per formula unit vs. Volume (Å³) of CaP, CaAs and CaSb compounds in ZB-type structure
However, on compression, these compounds are found to undergo a magnetic phase transition to the non-magnetic phase. The calculated total energies as a function of volume were fitted to the Birch equation of state (Birch 1978) to obtain the ground-state properties. The calculated lattice parameters in both ferromagnetic and nonmagnetic phases are given in Tables 6.1 and 6.2 along with the earlier FLAPW-GGA results, this shows an excellent agreement. Since Ca has a large ionic radius, the lattice constant becomes large. The calculated bulk modulus decreases from CaP to CaSb suggesting that the compressibility increases from CaP to CaSb for both phases.

In addition, the cohesive energy is calculated for these compounds using the equation (5.1). The calculated cohesive energy $E_{coh}$ is given in Tables 6.1 and 6.2. The comparison of the $B_0$ and $E_{coh}$ shows clear decrease with heavier atom (CaP, CaAs and CaSb). From the Table 6.1, one can observe easily that the total energy difference between the ferromagnetic phase and nonmagnetic phase ($\Delta E = E_{FM} - E_{NM}$) is high. These compounds are more stable in ferromagnetic phase.

6.4 ELECTRONIC BAND STRUCTURE CALCULATIONS AND DENSITY OF STATES

The self-consistent scalar relativistic band structures of CaP, CaAs and CaSb were obtained in the ferromagnetic and non-magnetic phases at their equilibrium volume along the high-symmetry directions.

The calculated spin-dependent energy band structures of the ZB-type CaP, CaAs and CaSb compounds in ferromagnetic phase at their equilibrium lattice constant are illustrated in Figures 6.2 - 6.4.
Table 6.1 Calculated ground-state properties in ZB-type ferromagnetic phase and the total energy difference, $\Delta E = E_{\text{FM}} - E_{\text{NM}}$ in (Ryd. /f.u.)

<table>
<thead>
<tr>
<th></th>
<th>CaP</th>
<th>CaAs</th>
<th>CaSb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Present</td>
<td>Others $^{a,b}$</td>
<td>Present</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>6.465</td>
<td>6.556</td>
<td>6.627</td>
</tr>
<tr>
<td></td>
<td>6.588</td>
<td></td>
<td>6.805</td>
</tr>
<tr>
<td>$B_0$ (GPa)</td>
<td>55.04</td>
<td>-</td>
<td>48.04</td>
</tr>
<tr>
<td>$E_{\text{coh}}$ (eV)</td>
<td>7.13</td>
<td>-</td>
<td>6.56</td>
</tr>
<tr>
<td>$\Delta E$</td>
<td>0.010</td>
<td>-</td>
<td>0.009</td>
</tr>
</tbody>
</table>

$^a$ Kusakabe et al 2004 and Geshi et al 2004

$^b$ Sieberer et al 2006

Table 6.2 Calculated ground-state properties in ZB-type nonmagnetic phase

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$a$ (Å)</th>
<th>$B_0$ (GPa)</th>
<th>$E_{\text{coh}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaP</td>
<td>6.456</td>
<td>53.32</td>
<td>8.40</td>
</tr>
<tr>
<td>CaAs</td>
<td>6.628</td>
<td>47.73</td>
<td>7.84</td>
</tr>
<tr>
<td>CaSb</td>
<td>7.073</td>
<td>40.37</td>
<td>7.13</td>
</tr>
</tbody>
</table>
The overall band profiles for these compounds are same and are in agreement with the earlier results (Kusakabe et al 2004, Geshi et al 2004, Sieberer et al 2006). In the energy band diagram, the lowest lying band arises from the pnictogen s-like states (around -8 eV) and is well separated from other bands. The other bands near the Fermi level mainly originate from pnictide p-like states and calcium d-like states, which can be easily deduced from the partial density of states.

Moreover, the upper valence band arises mainly due to the p-like states of pnictogen. Five electrons per formula unit of CaX (X = P, As and Sb) compounds fill the bands i.e. the valence band is completely filled except for a vacant state. Hence, the top of the valence band becomes half filled. In addition, the valence band is strongly spin polarized. The top of the valence band is found to be almost dispersionless in the whole Brillouin zone. Above the valence band is the empty conduction band, which arises from the Ca s- and d-like states.

In all these compounds, the bond formation occurs from the Ca s-like states and pnictogen p-like states. Magnetism arises mainly due to the pnictogen p-like states and partially from Ca d-like states. In this magnetic structure, the majority spin states are completely filled and are well below the Fermi level, opening a bandgap at the Fermi level and is insulating. On the other hand, for minority spin state that is half filled, the Fermi level locates exactly at the top of the valence band making it to be a metal. The system is thus half-metallic. This result is in contrast to similar half-metals like CrAs, CrSb and MnAs, where the majority spins are metallic and minority spins have a gap (Sanvito and Hill 2000, Shirai 2003). The majority-spin bandgap value for these compounds is given in Table 6.3 along with the available theoretical data (Sieberer et al 2006).
Figure 6.2 Spin-dependent electronic band structures of ZB-type CaP compound at its equilibrium volume
Figure 6.3 Spin-dependent electronic band structures of ZB-type CaAs compound at its equilibrium volume
Figure 6.4  Spin-dependent electronic band structures of ZB-type CaSb compound at its equilibrium volume
In the ZB-type structure, the cations are under the tetrahedral environment. From the total and partial density of states histogram one can find easily the anion p-likes states are hybridized with the cation d-like states. The calculated magnetic moment for all these compounds is 1.00 $\mu_B$ per formula unit as expected. The localized pnictogen p-like state is completely filled except for a vacant state. This is responsible for total magnetic moment of 1.00 $\mu_B$ per formula unit for all these compounds. The calculated magnetic moment is given in Table 6.3 along with partial magnetic moment at each atomic site. From the table, it can be seen that magnetic moment arises mainly from the pnictogen and there is small contribution from Ca and empty spheres at interstitial positions. This result is in contrast with ZB-type transition metal pnictides and chalcogenides, where the anion p-likes states are completely filled and the magnetic moment is mainly formed by the 3d electron states.

### Table 6.3 Total and partial magnetic moments ($\mu$) in $\mu_B$ and majority spin-bandgap ($E_{g\uparrow}$) in eV in the ZB-type ferromagnetic phase

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Magnetic moments</th>
<th>$E_{g\uparrow}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cation</td>
<td>Anion</td>
</tr>
<tr>
<td>CaP</td>
<td>0.1462</td>
<td>0.7736</td>
</tr>
<tr>
<td>CaAs</td>
<td>0.1631</td>
<td>0.7464</td>
</tr>
<tr>
<td>CaSb</td>
<td>0.1852</td>
<td>0.7151</td>
</tr>
</tbody>
</table>

$^a$ Sieberer et al 2006

Figure 6.5 shows the total and partial spin-dependent density of states of these compounds at their equilibrium lattice constant. The valence band is spin polarized with an exchange splitting of ~0.52 eV and is in agreement with the earlier results (Kusakabe et al 2004, Geshi et al 2004).
Figure 6.5 Spin-dependent total (upper panel) and partial (lower panel) density of states of ZB-type CaX (X = P, As and Sb) compounds at their equilibrium volume
A sharp peak appears at the top of the valence band. This peak is well below the Fermi level for the majority spin state, whereas the Fermi level is located exactly on the peak for the minority spin states. From the partial density of states histogram, it can be seen that the valence band arises mainly from the pnictogen p-like states and there is a partial mixing of Ca d-like states.

### 6.4.1 Volume Dependence of Half-Metallic Ferromagnetism

Since the lattice parameter of an epitaxially grown film depends on the lattice constant of the substrate, it is important to know the robustness of the half-metallicity with respect to the variation of the interatomic distance. The electronic structure and magnetic properties of these compounds were studied as a function of volume. Figure 6.6 shows the spin-dependent total density of states of these compounds in ferromagnetic phase at their reduced volume. From the figure, it can be seen that these materials lose their half-metallicity and magnetic properties for a volume reduction of 47% (CaP), 49% (CaAs) and 59% (CaSb), respectively. Here, the valence band is not spin polarized and the Fermi level lies within the valence band, making it to be completely metallic and non-magnetic. There is broadening of pnictogen p-like valence band on decreasing the cell volume, which makes it to lose its half-metallicity and magnetic property. This effect can also be seen in Figure 6.1, which shows the plot of total energy vs. volume, where there is a transition from magnetic to nonmagnetic phase on compressing the cell volume. Figure 6.7 shows the variation of lattice constant with magnetic moment for all the three compounds. From the figure, it can be seen that the calculated magnetic moment of 1.00 $\mu_B$ per formula unit remains constant for large volume compression. However, on still reducing the cell volumes, the magnetic moment starts decreasing monotonically and becomes nonmagnetic.
Figure 6.6 Spin-dependent total density of states of ZB-type CaP, CaAs and CaSb compounds at their reduced volume
6.5 SUMMARY

In this work, the electronic band structure calculations and magnetic properties of zinc-blende calcium pnictide compounds were studied at their equilibrium state as well as for large volume compression. Total energy calculations show that at equilibrium condition these compounds are stable in the ferromagnetic phases when compared to non-magnetic phase in agreement with earlier results. The electronic band structure shows that these compounds exhibit half-metallicity. The calculated magnetic moment is 1.00 $\mu_B$ per formula unit as expected. The magnetism arises mainly from the pnictogen p-like states and partially due to Ca d-orbitals. On compression, these compounds lose their half-metallic property. It suggests that half-metallicity exist only upto a particular cell volume. Unit cell volume plays an important role in exhibiting half-metallicity.