CHAPTER 4

STRUCTURAL PHASE TRANSITION AND PRESSURE-INDUCED METALLIZATION IN BARIUM CHALCOGENIDES

4.1 INTRODUCTION

The heavy alkaline-earth chalcogenides (AEX, AE = Mg, Ca, Sr, Ba, X=O, S, Se, Te) have been subjected to intense scrutiny, both experimentally and theoretically, because of the interesting physical phenomenon these compounds exhibit, as well as wide range of technological applications they find. The oxides and sulphides of these compounds are used as x-ray, photo and cathode-ray luminophors and are also used in electronic and opto-electronic devices (Asano et al 1978, Kaneko et al 1983, Yamashita et al 1984, Kaneko and Koda 1988, Pandey and Sivaraman 1991). Apart from these applications, oxides of magnesium and calcium form the important constituents of the refractory ceramics.

Except MgSe and MgTe all the other AEX crystallize in the six-fold coordinated NaCl-type (B1) structure with cubic symmetry and are insulators. The band gap in these insulators is formed between the p-like valence band of the chalcogen atom and the sd-like conduction band of the metal atom. The optical band gap in AEX is found to range from 2.5 to 6 eV. Experimental high pressure studies show that most of these chalcogenides undergo structural phase transition from the B1 structure to the eight-fold coordinated CsCl-type structure (B2) under pressure.
Among the alkaline-earth chalcogenides, barium chalcogenides (BaS, BaSe and BaTe) have been extensively studied experimentally as well theoretically. High pressure XRD studies of BaS (Yamaoka et al 1980), BaSe and BaTe (Grzybowski and Ruoff 1983, 1984, 1984a) show that these compounds undergo a structural phase transition from the B1 to the B2 phase at pressures of 65, 60 and 48 kbar respectively.

Apart from the pressure-induced B1-B2 structural phase transition, these compounds exhibit the interesting phenomenon of IMT in their B2 phase at high pressures. Within the one-electron theory, the metallization (Ross and McMahan 1981) may be described as due to the broadening of bands under pressure and subsequent overlap of the filled valence bands and the empty conduction bands. Electrical resistivity measurements (Grzybowski and Ruoff 1984) show that BaTe metallizes at 200 kbar. From the optical absorption and electrical resistivity measurements (Ruoff and Grzybowski 1985) metallization of BaSe is predicted to occur at about 400 kbar. Later Weir et al (1987) determined the metallization pressure of BaSe from the optical absorption, optical reflectivity and the electrical resistivity measurements. The metallization pressure determined from all three set of data are found to vary slightly. The value determined by resistivity is $520 \pm 20$ kbar, by optical absorption extrapolation about 460 kbar and by optical reflectivity extrapolation about 480 kbar. However, they believe that the value $520 \pm 20$ kbar determined by resistivity to be the most accurate one because the other two values were obtained by extrapolation of their respective data points. High pressure optical absorption studies on BaS (Weir et al 1987) indicate the metallization pressure to be around 800 kbar.

calculated the volume for the B1 and B2 phases at B1-B2 structural phase transition for BaS, BaSe and BaTe. Also prior to the experimental observations, they predicted the metallization volume and pressure for these compounds. Wei and Krakauer (1985) using the linear augmented plane wave (LAPW) method calculated the B1-B2 structural transition pressure and the metallization pressure, for BaSe and BaTe. In both the methods, the calculated values of B1-B2 structural transition pressure and volume are in good agreement with the experimental observations. The metallization volume and pressure are found to be underestimated. This error arises mainly because both the methods use the LDA to the exchange correlation part of the potential.

The serious problem of using LDA lies in the fact that it underestimates zero pressure band gap by 30-50%. This is because the position of the conduction bands relative to the valence bands is not calculated correctly in the LDA (Hamann 1979). Two approaches can be used to rectify this. One is by providing self-interaction correction (SIC) to the LDA (Perdew and Zunger 1981, Perdew and Levy 1983). However, this scheme is applicable to systems in which bands are narrow compared to the band gap (Norman and Perdew 1983). It is not known how to extend this scheme to problems where the bands are broad compared to the band gap. An alternative approach is, to take into account the non-local corrections to LDA (Langreth and Mehl 1983). The calculations by Norman and Perdew (1983) using Langreth Mehl (1983) non-local exchange correlation potential yield only small improvements over the fundamental band gap. However, recent work by (Levine and Louie 1982, Sham and Schlüter 1983, Wang and Pickett 1983, Rodrigues et al 1985, Satpathy et al 1985, van Camp et al 1986) indicate that LDA might be expected to improve as the system becomes more metallic or free-electron like i.e., it will be more accurate when close to the IMT than at the equilibrium volume. Thus, a fairly accurate estimate of the IMT pressure and volume might still be possible within the LDA, even though the zero pressure band gaps are incorrect.
In the present work, the electronic band structure, structural phase transition and the IMT of BaS, BaSe and BaTe have been studied. Under ambient conditions all the three compounds crystallize in the B1 structure. Using the ASA total energies, the B1-B2 structural phase transition has been studied. Also in the B2 structure the IMT has been studied.

4.2.1 Method of calculation

The electronic band structures for these compounds in the B1 and B2 structures have been obtained self-consistently by means of the TB-LMTO method (Andersen and Jepsen 1984), which is discussed in detail in section 2.6. The total energies were calculated within the ASA (Andersen 1975, Andersen et al 1979). The exchange-correlation potential within the LDA was calculated using the parameterization scheme of von-Barth and Hedin (1972). The most important relativistic corrections, namely, Darwin’s corrections and mass-velocity terms were included while the spin-orbit coupling term is neglected (MacDonald and Vosko 1979, Christensen 1984, Bachelet and Christensen 1985). The energy eigenvalues were calculated for 512 k-points in the entire Brillouin zone. Convergence of eigenvalues and k-points were checked as follows: The number of k-points were increased to 1000 at the equilibrium volume and the total energy is found to change only by 0.3 to 0.4 mRy. The band gap is essentially unchanged and the change in the energy minimum position or curvature is not significant. The energy eigenvalues were converged self-consistently to $10^{-6}$ Ry. The total and the partial density of states were calculated using the tetrahedron method (Jepsen and Andersen 1971).

It is well known that the LMTO method gives accurate results for close packed structures (Jarlborg and Freeman 1979, Glötzl et al 1980) and since NaCl-type structure is a loose packed structure, it becomes necessary
to include empty spheres. Empty spheres are simple space filling "atomic spheres" with zero nuclear charge but with definite charge density after self-consistency is reached. The inclusion of empty spheres in the LMTO calculations appears to account to a large extent for the nonsphericity of the charge distribution (Bachelet and Christensen 1985). In particular, this becomes important for total energy calculations where the structural energy difference is only hundredths of rydberg. Without breaking crystal symmetry two equivalent empty spheres (Christensen 1985) were included at the positions (0.25, 0.25, 0.25) and (0.75, 0.75, 0.75), whereas the metal and non-metal atoms occupy the positions (0,0,0) and (0.5,0.5,0.5). In the LMTO-ASA method, the crystal is divided into space-filling spheres centered on all atomic sites. To optimize the calculations equal sphere radii were chosen for both metal and non-metal atoms in the case of both B1 and B2 structures so that the potential is continuous at the sphere boundaries.

The basis set is chosen to have angular momentum components of $s$, $p$ and $d$ for both atoms. Apart from this, the so-called cc terms (Andersen 1975) which correct for the non-spherical shape of the atomic cells and the truncation of the higher partial waves ($l>2$) inside the spheres were included. This extension beyond the ASA is necessary for the calculation of total energies (Skriver 1982, 1985, McMahan and Moriarty 1983). With the inclusion of the empty spheres and cc terms, now the errors in the LMTO method are minimized.

For each of the compound the following basis orbitals were treated as valence states.

- $\text{Ba} : 6s^2, 6p^6, 5d^6$, $\text{Te} : 5s^2, 5p^4, 5d^0$
- $\text{Ba} : 6s^2, 5p^6, 5d^6$, $\text{Se} : 4s^2, 4p^3, 4d^0$
- $\text{Ba} : 6s^2, 5p^6, 5d^6$, $\text{S} : 3s^2, 3p^3, 3d^0$. 

In the high pressure region the overlap of the semicore-like Ba-5p states with states on the other atoms cannot be neglected. Hence, in the calculations for BaS and BaSe, Ba-5p bands were treated as fully relaxed valence band states. For BaTe, Ba-5p bands were kept in the core itself. This is because the volume/molecule for BaTe (85.71 Å³) is large when compared to that of BaSe (71.5 Å³) and BaS (65.14 Å³) and also among these compounds, BaTe has the lowest value of bulk modulus. Because of these reasons, the structural phase transition and metallization occur at a low pressure in the case of BaTe. Therefore, the problem of core-core overlap does not arise in the calculation for BaTe and hence it does not become necessary to treat Ba-5p bands as relaxed valence band states in the case of BaTe.

4.2.2 Total energy calculation

In order to study the structural phase stability for each of the compounds, the total energies were calculated for both B1 and B2 structures by changing the volume from about 1.1V₀ to 0.7V₀, where V₀ is the equilibrium volume. The calculated total energies were fitted to the Birch (1978) EOS to obtain the ground state properties and P-V relation. The pressure is calculated by taking the volume derivative of the energy and the bulk modulus (Kᵢ) is calculated from the P-V relations.

For predicting pressure-induced structural phase transitions, Gibb's free energy (G) for the two phases B1 and B2 have to be calculated, which is given by

\[ G = E_{\text{tot}} + PV - TS \]  (4.1)

Here \( E_{\text{tot}} \) is the total internal energy, T is the temperature and S is the entropy. Since the theoretical calculations were done in the zero
temperature limit \(T = 0\) K the Gibb's free energy becomes equal to the enthalpy \(H\), which is

\[
H = E_{\text{tot}} + PV
\]  \hspace{1cm} (4.2)

Knowing the total internal energy, pressure and volume, the enthalpy can be calculated. At a given pressure, a stable structure is one for which enthalpy has its minimum value. If there is a polymorphic transition from one structure to another at a pressure \(P_t\), then the two structures are said to be in thermodynamic equilibrium at this pressure only when the enthalpy of the B1 phase becomes equal to the enthalpy of the B2 phase i.e.,

\[
H = E_{\text{tot}}(B1) + P_t V_f(B1)
\]  \hspace{1cm} (4.3)

for the B1 structure becomes equal to

\[
H = E_{\text{tot}}(B2) + P_t V_f(B2)
\]  \hspace{1cm} (4.4)

for the B2 structure. The transition pressure is calculated using the relation,

\[
P_t = \frac{E_{\text{tot}}(B2) - E_{\text{tot}}(B1)}{V_f(B1) - V_f(B2)}
\]  \hspace{1cm} (4.5)

where \(E_{\text{tot}}(B1)\) and \(E_{\text{tot}}(B2)\) are the total internal energies for the B1 and B2 phases and \(V_f(B1)\) and \(V_f(B2)\) are the volumes for B1 and B2 phases at transition.

The total energy curves for these compounds in the B1 and B2 structures are shown in Figures 4.1 to 4.3. At ambient conditions, in agreement with the experimental observations, these compounds are stable in the B1 structure. The calculated equilibrium lattice constant and the bulk modulus (Kalpana et al 1994b) in both the B1 and B2 structures are given...
Fig. 4.1 Calculated total energy of BaS in the B1 and B2 phases
Fig. 4.2 Calculated total energy of BaSe in the B1 and B2 phases
Fig. 4.3 Calculated total energy of BaTe in the B1 and B2 phases
in Table 4.1 and compared with the experimental and earlier theoretical results. In the case of BaTe, the equilibrium lattice constant agrees well with the experimental value, whereas for BaS and BaSe, the calculated values of lattice constants are 1.4% and 1.2% lower than the experimental values. This discrepancy may be due to the treatment of the semicore-like Ba-5p band as valence band states in the calculations for BaS and BaSe.

The theoretical P-V curve for these compounds along with the experimental data are shown in Figures 4.4 to 4.6. From these figures it can be seen that, there is a good agreement with the experimental results over the entire pressure range studied. In general, it is usually found that the ground state properties are well predicted within the LDA and that the inclusion of the cc terms and the empty spheres makes the LMTO-ASA functional sufficiently accurate.

Figures 4.7 to 4.9 show the variation of enthalpy with pressure for these compounds. As described earlier, the transition pressure is calculated at which, the enthalpy for the two structures become equal. The calculated values of transition pressure, volume and the volume reduction are given in Table 4.2 and are compared with the available experimental and the other theoretical results. The calculated values of transition pressure (Kalpana et al 1994b) of 60 kbar and 52 kbar of BaS and BaSe are in good agreement with the experimental values of 65 kbar and 60 kbar respectively. For BaTe the calculated value of 39 kbar is slightly lower than the experimental value of 48 kbar. The slightly low value of transition pressure may also be due to the neglect of temperature effects and zero-point motion.

4.2.3 Band structure

The self-consistent scalar relativistic band structures were obtained for BaS, BaSe and BaTe in the B1 and B2 phases at equilibrium volume as well in the high pressure region. The simplest qualitative picture of the
Table 4.1  Equilibrium lattice constant (a) and Bulk modulus ($K_0$) for the B1 and B2 phases of BaS, BaSe and BaTe

<table>
<thead>
<tr>
<th></th>
<th>BaS</th>
<th>BaSe</th>
<th>BaTe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Expt.(^1)</td>
<td>TB-LMTO</td>
<td>ASW(^2)</td>
</tr>
<tr>
<td>$K_0$(B1) kbar</td>
<td>556</td>
<td>525</td>
<td>-</td>
</tr>
<tr>
<td>$K_0$(B2) kbar</td>
<td>340</td>
<td>608</td>
<td>-</td>
</tr>
</tbody>
</table>

5. Grzybowski and Ruoff (1984), Ruoff and Grzybowski (1985)
Fig. 4.4  Pressure - volume curve of BaS in the B1 and B2 phases. Experimental data points are from Yamaoka et al (1980)
Fig. 4.5  Pressure-volume curve of BaSe in the B1 and B2 phases. Experimental data points are from Ruoff and Grzybowski (1985)
Fig. 4.6 Pressure - volume curve of BaTe in the B1 and B2 phases. Experimental data points are from Ruoff and Grzybowski (1985)
Fig. 4.7 Variation of enthalpy with pressure of BaS in the region of phase transition
Fig. 4.8 Variation of enthalpy with pressure of BaSe in the region of phase transition
Fig. 4.9 Variation of enthalpy with pressure of BaTe in the region of phase transition
Table 4.2 Transition pressure, volumes and volume reduction for the B1-B2 structural transition in BaS, BaSe and BaTe

<table>
<thead>
<tr>
<th></th>
<th>BaS</th>
<th>BaSe</th>
<th>BaTe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Expt. 1</td>
<td>TB-LMTO</td>
<td>Expt. 2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( P_1 ) (kbar)</td>
<td>65</td>
<td>60.3</td>
<td>60</td>
</tr>
<tr>
<td>( V_1(B1)/V_0(B1) )</td>
<td>0.896</td>
<td>0.873</td>
<td>-</td>
</tr>
<tr>
<td>( V_2(B2)/V_0(B1) )</td>
<td>0.773</td>
<td>0.753</td>
<td>-</td>
</tr>
<tr>
<td>( V_2(B2) - V_1(B1) )</td>
<td>13.7</td>
<td>13.8</td>
<td>13.9</td>
</tr>
<tr>
<td>( % )</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2. Grzybowski and Ruoff (1983)  
3. Wei and Krakauer (1985)  
electronic structure of these ionic insulators can be obtained by considering the valence states of each atom. In the simplest picture, the two valence 6s electrons of the metal atom, namely, Ba will be transferred to the chalcogen atom p states, namely, S-3p, Se-4p or Te-5p states which are in deficit of two electrons. With this type of charge transfer between the metal and the non-metal atoms, the compound formed will be an ionic insulator with the chalcogen atom p states forming the upper valence band and the metal atom 6s states as the conduction states. Since the top most filled valence p bands have their maxima at Γ-point and the bottom most empty conduction s bands have their minimum at Γ-point, the compound is expected to be a direct band gap semiconductor or insulator with the gap occurring between Γ-points.

Figures 4.10 to 4.15 show the band structures of BaS, BaSe and BaTe plotted along the high symmetry directions Γ-X-W-L and their corresponding DOS plots in the B1 structure at equilibrium volume.

The overall band profiles are found to be the same for all the three chalcogenides and are in agreement with the LAPW calculations (Stepanyuk et al. 1989a). In BaS and BaSe the low lying bands are the Ba-5p bands which were relaxed from the core. These bands are missing in BaTe in which they were treated as core states. The next single band which is very narrow is the chalcogen atom s band. As said earlier the upper valence bands are formed from the chalcogen atom p states which have their maximum energy at Γ-point. Above the gap, the low lying conduction states are not pure Ba-6s states, instead they are the hybrids from the Ba-6s and 5d band states. In the free Ba atom, the unoccupied Ba-5d states are only slightly above the occupied 6s states, therefore in the compound the low lying 5d states mix with the 6s states causing the conduction bands to be of combined 6s and 5d nature. The presence of Ba-5d states lowers the conduction band in particular, at the X-point making the compound an indirect band gap semiconductor with band gap occurring between Γ and X-
Fig. 4.10 Band structure of BaS in the B1 phase at equilibrium volume
Fig. 4.11  Density of states of BaS in the B1 phase at equilibrium volume
Fig. 4.12 Band structure of BaSe in the B1 phase at equilibrium volume
Fig. 4.13 Density of states of BaSe in the B1 phase at equilibrium volume
Fig. 4.14 Band structure of BaTe in the B1 phase at equilibrium volume
Fig. 4.15 Density of states of BaTe in the B1 phase at equilibrium volume
points. Moreover, the shape of the conduction bands is similar to that of the fcc noble or transition metals, which is due to the fact that the Ba atoms constitute a fcc sublattice.

The calculated values of band gap at ambient conditions (Kalpana et al 1994b) are given in Table 4.3 along with the experimental and other theoretical results. When compared to the experimental values, the band gap values are underestimated by 30-50%. As said earlier this order of error is expected while working with LDA, which underestimates the band gap values. It is seen that, the valence bands are correctly described by these calculations, while the conduction band levels are found to be lower than those determined by optical experiments. However, there is a good agreement with other theoretical results, namely, LAPW (Wei and Krakauer 1985) and ASW (Carlsson and Wilkins 1984) methods which use the same type of approximation, namely, LDA.

Figures 4.16 and 4.17 show the band structures for these compounds in the B1 and B2 phases at the structural transition pressures. From the figures, it can be seen that the structural transition induces a large reduction in the band gap value. This is in agreement with the optical absorption studies on BaTe (Syassen 1986) which show that at the B1-B2 transition, the band gap of the lowest energy structure drops discontinuously from about 2.6 eV (B1) to 1.6 eV (B2) and then shifts further to lower energy with increasing pressure. In the B2 structure, the band structures are the same as those of the B1 structure except that now the valence p bands of the chalcogen atom occur at M and the bottom of the Ba-5d bands at Γ. The gaps are still positive even after the structural transition, indicating that the metallization occurs only after structural transition. Upon further compression, the band gap value decreases and becomes zero.
Table 4.3  Fundamental band gap $E_g$ (eV) of BaS, BaSe and BaTe in the B1 structure

<table>
<thead>
<tr>
<th></th>
<th>Expt.$^1$</th>
<th>TB-LMTO</th>
<th>LAPW$^2$</th>
<th>ASW$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaS</td>
<td>3.9</td>
<td>2.3</td>
<td>-</td>
<td>2.1</td>
</tr>
<tr>
<td>BaSe</td>
<td>3.6</td>
<td>2.0</td>
<td>1.8</td>
<td>1.8</td>
</tr>
<tr>
<td>BaTe</td>
<td>3.1</td>
<td>1.6</td>
<td>1.5</td>
<td>1.4</td>
</tr>
</tbody>
</table>

1. Saum and Hensley (1959)  
2. Wei and Krakauer (1985)  
Fig. 4.16 Band structure of BaS, BaSe and BaTe in the B1 phase at structural transition
Fig. 4.17 Band structure of BaS, BaSe and BaTe in the B2 phase at structural transition
Figure 4.18 shows the band structure in the B2 phase at metallization volume. Figures 4.19 to 4.21 show the corresponding DOS plots. From the band structures it can be seen that in BaS and BaSe before metallization, the direction of the fundamental band gap changes from indirect (\( \Gamma - M \)) to direct at \( \Gamma \). In BaTe the indirect gap remains the same until band-overlap metallization occurs. This observation is in agreement with the earlier LAPW (Wei and Krakauer 1985) and ASW (Carlsson and Wilkins 1984) results. Here, metallization phenomenon arises due to the broadening of the bands under pressure and subsequent overlap of the empty conduction and the filled valence bands. From Figure 4.18, it can also be noted that the Ba-5p bands which are lower in energy than the chalcogen atom s band at normal conditions have moved up now with the application of pressure and at metallization it is higher in energy than the chalcogen s band. In the B2 phase, the volume dependence of the band gap is shown in Figure 4.22. The fundamental band gaps for all the three compounds decrease monotonically with volume.

The metallization volume and pressure are given in Table 4.4 along with the experimental and other theoretical results. From the table it can be seen that the metallization volume and pressure are lower than the experimental values. The metallization volume and pressure were expected to be well predicted within LDA, however the calculations show that the error arising due to the underestimation of the band gap value is reflected in the metallization volume and pressure. It should be noted that the error in the metallization pressure is large when compared to the metallization volume. This is because even for a small change in volume, there is a large change in the pressure. However, these results are in good agreement with the earlier LAPW (Wei and Krakauer 1985) results.
Fig. 4.18  Band structure of BaS, BaSe and BaTe in the B2 phase at metallization volume
Fig. 4.19  Density of states of BaS in the B2 phase at metallization volume
Fig. 4.20  Density of states of BaSe in the B2 phase at metallization volume
Fig. 4.21 Density of states of BaTe in the B2 phase at metallization volume
Fig. 4.22 Volume dependence of band gap of BaS, BaSe and BaTe in the B2 phase
Table 4.4  Metallization volume and pressure of BaS, BaSe and BaTe

<table>
<thead>
<tr>
<th></th>
<th>BaS</th>
<th>BaSe</th>
<th>BaTe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Expt.</td>
<td>TB-LMTO</td>
<td>ASW²</td>
</tr>
<tr>
<td>Vₘ/V₀</td>
<td>-</td>
<td>0.574</td>
<td>0.62</td>
</tr>
<tr>
<td>Pₘ(kbar)</td>
<td>800</td>
<td>491</td>
<td>320</td>
</tr>
</tbody>
</table>

3. Wei and Krakauer (1985)  
To summarize, the electronic and structural properties of alkaline-earth chalcogenides BaS, BaSe and BaTe have been calculated by means of the TB-LMTO method. From the ASA total energies, the structural phase transition in these compounds has been studied. At ambient conditions all the three compounds are stable in the B1 structure and under pressure they undergo a structural transition to the B2 structure, which are in agreement with the experimental observations. The calculated equilibrium lattice constant and the bulk modulus are in agreement with the experimental observations. For BaTe, the lattice constant is in good agreement with the experimental result whereas for BaS and BaSe they are 1.4% and 1.2% less than the experimental results. Even though this order of error is negligible, the reason for this discrepancy may be due to the treatment of the semicore-like Ba-5p bands as relaxed band states.

The structural transition pressures are calculated from the enthalpy calculations. The transition volumes and volume reduction at transition are in very good agreement with the experimental values. The transition pressures are only slightly lower than the experimental values. It may also be noted that the transition pressures are more difficult to determine than the transition volumes. The slightly low values of transition pressures may be due to the neglect of the temperature effects and the zero-point motion. The inclusion of zero-point motion may increase the transition pressure by about 5 kbar. However, the experimental trend of decreasing transition pressure with increasing atomic number is reproduced in the calculations.

The band structures at ambient as well in the high pressure regions were calculated. The overall band profiles for these compounds are the same and are in agreement with the earlier results. The calculated band gaps at ambient conditions underestimate the measured ones by about 30-
50%. In the B2 structure, the band gap values have been calculated as a function of volume. At high pressures these compounds go to the metallic phase which occurs due to the overlap of the filled valence bands and the empty conduction bands. The calculated metallization volume and hence pressures are lower than the measured values. The main reason for these discrepancies is due to the errors introduced by the LDA to the exchange-correlation part of the potential. It is usually found that the position of the conduction bands relative to the valence bands are not calculated correctly in LDA, which underestimates the band gaps in semiconductors and insulators by 30-50%. As mentioned earlier, this may be corrected by introducing either SIC or by considering non-local corrections to LDA. SIC is found to be applicable to systems in which the bands are narrow compared to the band gap i.e., for systems such as \(3d\) transition-metal oxides. Recently, Svane and Gunnarsson (1990) have implemented the SIC formalism within the TB-LMTO method and have applied it to the \(3d\) monoxides. Their results greatly improve the description of the physics of these systems proving them to be wide-gap charge transfer insulators in agreement with the experiment. Moreover, Svane (1992) has showed that SIC-LSDA also leads to a correct antiferromagnetic and semiconducting ground state for \(La_{2}CuO_{4}\), with the gap and magnetic moment in good agreement with the experiment. But this SIC is appreciable only to strongly correlated systems and not to ionic insulators.

An alternative approach is to take into account the full non-local exchange-correlation potential. However, it is found from the calculations for Ne and NaCl by Norman and Perdew (1983) that non-local corrections yield only small improvements over LDA in the fundamental gaps.

In the recent calculations (Cardona et al 1988, Gorczyca and Christensen 1991, Brudevoll et al 1993, Christensen and Gorczyca 1994), the band gaps that are in agreement with the experimental values are reproduced by adjusting the conduction bands at the high symmetry points.
The so-called "adjusted band gaps" are produced by adding effective external potentials sharply peaked at each atomic site. These potentials are added both on real atoms and empty sphere sites. The valence state and the ground state properties are found to be only slightly affected by these extra potentials. The optical spectra obtained from such adjusted bands agree well with experiment.

Finally, the calculations show that the LDA yields good results for the ground state for which it was designed but poorer ones for the excited states. Even though many approaches are being tried to modify the DFT in order to obtain a good description of the excited states, still the problem remains unsolved.