The compound semiconductors like GaP, GaAs, GaSb, ZnS and ZnSe have zinc blende structures. GaP, GaAs and GaSb are III-V compound semiconductors having valence atomic structures as $s^2p^1$ for Group III and $s^2p^3$ for Group V atoms. Similarly for II-VI compound semiconductors the atomic valence configuration for Group II and Group VI atoms are $s^2p^0$ and $s^2p^4$ respectively. In the process of bonding not only these electrons form the $sp^3$ hybridisation but also there is a net charge transfer from cation to anion. With increasing core, the band gap decreases, as a result of this the metallicity increases as in elemental semiconductors. With this the core-orthogonalisation contribution in the valence wavefunctions increases and the spin-orbit splitting also increases [6.1].

Most of the differences between the zincblende semiconductors can be ascribed to variations in the competing bonding mechanisms, i.e. covalency versus ionicity. The ionicity in P is higher than that of As and the ionicity in As is higher than in Sb. Hence the band gap is large in GaP and it is decreases from GaP to GaAs to GaSb.

Although there is a net charge transfer from cation to anion, it is very difficult to quantify it and separate it from the covalent bonding charge. Nevertheless, it should be apparent that the compound semiconductors are partly ionic, for example, from the fact that the charge density maximum along the bonding direction is closer to the anion than cation [6.2].

The effect of ionicity on the charge density was studied by Chelikowsky and Cohen [6.3]. The lowest band is purely ionic, the second band is purely covalent and the other two bands are admixture of covalent and ionic bonds. All the III-V semiconductors are 70% covalent and 30% ionic and II-VI semiconductors are 40%
covalent and 60% ionic [6.2]. Recently an accurate charge density measurement using electron diffraction technique fully supported the theoretical calculation of the ionicity of GaAs [6.4].

Nara et al calculated the anisotropies of CPs in a series of semiconductors with diamond and zinc blende structures [6.5]. His calculations showed that the nature of the anisotropies remained same in all samples, but the effect of ionicity was to reduce the magnitudes of the anisotropies. Since the Group IV semiconductors were covalent, the anisotropies were quite large in these materials and due to ionicity the anisotropies reduced in III-V compound semiconductors and in II-VI semiconductors the anisotropies were further reduced. The nature of the anisotropies varied from sample to sample in the low momentum regions only. This had established that the anisotropies were governed by Jones zone area in the high momentum region and in the low momentum regions they were dependent on the detailed nature of the band structures.

The present measurements on the directional CPs of GaP and GaAs were done with a view to check the pseudopotential calculations of Nara et al and see whether the predicted decrease in the anisotropy as one goes from elemental to compound semiconductors is justified or not. We have also taken the ACPAR measurements to compare them with CP data for understanding the effects of positron and also see how ionicity affects the ACPAR results. The CP measurements in ZnS and ZnSe were carried out to see the effect of bonding differences in them.

6 1. Gallium Phosphide

Gallium phosphide has the lattice constant is 5.431\( \text{Å} \) which is same as in Si and the band gap is 2.2 eV. The atomic configurations of Ga is 3s\(^2\)3p\(^1\) and for P it is 2s\(^2\)2p\(^3\).
(a) Compton Profile

(i) Experimental Method

The first measurement on compound semiconductor was carried on GaP to see the effect of ionicity on the Compton profiles \([6.6]\). Measurements were carried out along (100) and (111) directions using 59.54 keV \(\gamma\)-rays from a 200 mCi of \(^{241}\text{Am}\) point source \([6.7]\). The samples used were single crystals of size 25 mm diameter \(\times\) 3 mm thick obtained from MCP Electronic Materials Ltd., England. The gain of the system was fixed at 60 eV/channel. The instrumental function of the detector was 370 eV at the incident energy. For each sample about 55,000 counts were collected at the peak of the profile. The data were processed in the same manner as described earlier. The fraction of photons multiply scattered was estimated to be 0.105. Finally the profiles were normalised in the range 0.0 to 6.0 a.u. to the free electron Hartree-Fock value of 19.589.

(ii) The Profile Anisotropy

The peak of the profile along (100) direction was found to be more than that in Si and Ge. This is due to the effect of the ionic bond. The profile at \(q = 1.4\text{a.}u\.) had a secondary peak in all directions. The reason for this will be discussed later. The anisotropy between (100) and (111) is plotted in Fig. 6.1. In comparing the same anisotropy with Si (see Fig. 5.7), we find that the result is drastically different at the low momentum region. The phase of the anisotropy is just opposite to that of Si in the low momentum region. The same behaviour was also seen by comparing the present data with Ge data. In order to explain the results we carried out an empirical pseudopotential calculation to get the directional CPs. The method of calculations with the parameters have been described earlier \([6.8]\). Because of lack of core-orthogonalisation term in the pseudowavefunctions, the profiles were
Fig. 6.1: Anisotropy in CP of GaP; both experimental and theoretical data
short ranged in the momentum space and seen to be peaked in the low momentum region. Although the pseudopotential calculation does not predict the absolute profiles correctly, it is expected to provide the anisotropies correctly because of the cancellation of the core-orthogonalisation effects in different directions. Hence, we compared experimental CP anisotropy (Fig. 6.1) with the calculated CP anisotropy from local and local+nonlocal pseudopotentials given in Tables 4.1, 4.2 and 4.3. It is apparent that the theoretical calculations have reasonable agreement with the experimental data. The non-local calculation is found to have more anisotropy than the local one. The extrema in the q dependence of anisotropy are found to be somewhat shifted towards higher q values compared to theory. It is worth seeing if this shift can be accounted by the core-orthogonalisation correction which may be different for different directions [6.9]. The same kind of shift was seen earlier by Nara et al in case of Si and Ge.

(iii) The B(r) Functions

As discussed already, the autocorrelation functions for a filled band case go to zero at the lattice constants. The autocorrelation functions calculated along (100) and (111) directions seemed to go to zero exactly at the lattice constants.

(b) Doppler Broadening of Positron Line Shape Studies

(i) Experimental Method

The positron studies in compound semiconductors were done to compare them with CP data to see the effect of positron distributions in it and the effect of ionicity on the positron distributions [6.10]. The same samples were taken for DBPA lineshape studies. A $7\mu$Ci of $^{22}$Na positron source in the form of aqueous NaCl was deposited on a thin Ni foil by evaporation method and was sandwiched between two slices of the samples. The detector and electronics used for the experiment
Fig. 6.2: Doppler broadening of positron annihilation (DBPA) line shape spectrum along (100) direction of GaP.

Fig. 6.3: DBPA line shape anisotropy of GaP; (-•-), samples as obtained, (○- ○-), samples after heat treatment.
have been described before. The detector had a resolution of 1020 eV at 514 keV of $^{85}$Sr line. The 511 keV positron annihilation radiations were measured at a source detector distance of 5 cm. The gain of the system was fixed at about 87 eV/channel. About 70,000 counts were collected at the peak of each sample. The raw data were tail stripped and then deconvoluted as discussed already in Chapter 3.

(ii) The Profiles and Anisotropy

The profile for (100) direction is plotted in Fig 6.2. Like in CP data a secondary peak is also observed at q = 1.4 a.u.. The directional profile is plotted in Fig. 6.3. As can be seen from the figure, the sign of anisotropy in this case is opposite to that of CP anisotropy. This suggests that the positron wave function is anisotropic in the interstitial positions.

In order to improve the resolutions of the experiment we carried out the long-slit angular correlation experiments.

(c) The Long-Slit ACPAR Studies

(i) Experimental Method

The samples were first annealed at 800°C to remove the as-grown defects and then chemically etched prior to the measurement. The samples were checked for the presence of defects by lifetime measurements which showed a very small long-lifetime component. The first component $\tau_f$ was 221 psec which agreed with the reported value. The angular correlation set-up with the electronics was described previously. The resolving time of the fast-slow coincidence set-up was fixed at 100 nsec. The slit length was 30 cm and the geometry was set at a momentum resolution of 1 mrad. About 20,000 counts were collected at the peak of the profile and the total counts under the profile were about 1,16000. Background coincidences were measured by removing the sample from its position. The data were analysed following the
Fig. 6.4: Momentum distribution of GaP; (o, Δ), CP data and (- - -), ACPAR data. Both are normalised to unit area after subtracting the core profile from CP data.
procedure outlined in Chapter 3. Finally the momentum distribution was obtained by folding the profile around \( p_z = 0 \) which was determined by equalising the area of approximately 0.5 a.u. strip on either side.

(ii) The Nature of Profiles

The results for the (100) and (111) directions without subtracting core are presented in Fig. 6.4 [6.11]. The profiles are quite symmetric within statistical error limits. It is seen from this figure that the profile is flat at the low momentum region along (100) direction, whereas the profile along (111) direction has a peaking in the same momentum region. This agrees fairly well with the data of Erskine and McGervey [6.12]. The dip seen in (100) profile of Shulman et al [6.13] is not reproduced here. It is because the resolution of our set-up was 1 mrad and the data were measured at room temperature. The poor resolution of the set-up has made the profile flat at the low momentum region of (100) direction. The \((3p, 2p)\sigma\) bonding along (111) direction makes the profile peaked along that direction.

Like in CP and DBPA data a hump is observed around \( q = 1.4a.u. \) in (111) direction. Shulman et al [6.13] could not find the hump in other directions than (110) direction which they attributed to the Umklapp origin. Our present findings of the humps is substantiated by the angular correlation data of Columbino et al for (111) direction of Si and Ge [6.14]. Their experimental as well as theoretical data both supported the existance of hump around \( p_z = 1.4a.u. \). They attributed the hump to arise from the \( sp^3 \) hybridised orbitals. We also believe the humps to arise from the same reason. As described in the earlier Chapter the pseudopotential band structure calculation of Stroud and Ehrenreich did not show any hump in the high-momentum region because the core orthogonalisation term was neglected in their calculations.
Fig. 6.5: Percentage anisotropy in the momentum distribution of GaP; (—○—), CP data and (−−−), ACPAR data.

Fig. 6.6: Theoretical CP anisotropy of GaP before RIF convolution.
Comparison of CP and ACPAR Data

(i) The Profile Anisotropy

In Fig. 6.5 we compare the CP and ACPAR anisotropies to obtain more informations and better understanding of the positron wavefunction distributions in semiconductors. We find that the percentage anisotropy of ACPAR data is more than that of Doppler broadening data. It is mainly due to the poor resolution of the Doppler broadening set-up. The percentage anisotropy of ACPAR data is also more than that of CP anisotropy and its sign is opposite to that of CP. But In Si and Ge the percentage anisotropy of CP data is in the same phase of ACPAR data. But the theoretical calculation for CP anisotropy without RIF convolution shows a rising trend in the anisotropy near q=0, but still the magnitude is positive whereas the ACPAR data also shows a rising trend, but the anisotropy is negative (Fig. 6.6). The opposite nature of the CP and ACPAR anisotropic data is mainly due to the resolution of the Compton scattering set-up. However, the magnitude difference between CP and ACPAR anisotropic data at the low momentum region is quite large compared to that seen in Si and Ge. The difference between the CP and ACPAR anisotropies is due to the anisotropic positron wavefunction in the interstitial positions in different crystallographic directions. The magnitude difference between Si or Ge and GaP is due to more anisotropic positron wavefunction coming from the annihilations of the positrons with the ionic charge distributions.

(ii) The B(r) Functions and Anisotropy

For a further interpretation of the present ACPAR data and to compare with our CP data, we have determined the autocorrelation functions, $B(r)$ and $B^{2\gamma}(r)$ for CP and ACPAR data, respectively. Before comparing the two sets of data, they were corrected for their resolutions in the manner described earlier. The resolution
Fig. 6.7: Resolution corrected Autocorrelation functions for (100) direction of GaP; (-•-), CP data, (-○-), ACPAR data. At the origin both are normalised to unity.

Fig. 6.8: Resolution corrected Autocorrelation functions for (111) direction of GaP; (-•-), CP data, (-○-), ACPAR data. At the origin both are normalised to unity.
corrected $B(r)$ and $B^{2\gamma}(r)$ functions for different directions are plotted in Fig. 6.7 for (100) direction and in Fig. 6.8 for (111) direction for a comparison. The $B^{2\gamma}(r)$ function extends to higher $r$ values whereas $B(r)$ function falls very rapidly. This suggests that the positron wavefunction is confined in the interstitial region than in the nuclear region. Due to nuclear repulsion the positron stays in the interstitial region and it is mainly reflected in the valence profile only. The $B^{2\gamma}(r)$ function for (111) direction not only extends to the higher $r$ values, but also has a larger first zero shift at the lattice point. It is mainly due to the presence of P at that point.

The autocorrelation anisotropy between (111) and (100) directions in CP as well as ACPAR data are plotted in Fig. 6.9. As expected the CP data show a marked dip at the bond length whereas the ACPAR data do not show such a dip. It is because the (100) direction in ACPAR measurement is not isotropic because of the localisation of positrons in the large interstitial region available in that direction. The small dip occurring in the Compton autocorrelation anisotropy near $z=1$. a.u. might be due to the statistical errors present in the data analysis [6.15].

6.2. Gallium Arsenide

The lattice constant of GaAs is 5.65 $\text{Å}$ which is same as in Ge with band gap 1.4 eV. The atomic configurations of Ga is $3s^23p^1$ and for As it is $3s^23p^5$. The bonding is $(3p, 3p)\sigma$ and $(3p, 3p)\pi$ for covalency.

(a) Compton Profile

(i) Experimental Procedure

The samples used were single crystals of 25 mm diameter and 3 mm thickness obtained from MCP Electronic Materials Ltd. England. Measurements were carried out along (100) and (111) directions, using 59.54 keV $\gamma$-rays scattered at an angle of about 175° from a 3 Ci $^{241}$Am annular source. Details of the spectrometer have
Fig. 6.9a: Resolution corrected autocorrelation function anisotropy for CP data of GaP. \( R_b \) is the bond distance.

Fig. 6.9b: Resolution corrected autocorrelation function anisotropy for ACPAR data of GaP (\( \bullet \)) and Ge (\( -o- \))
been given in Chapter 3 [6.16]. We took one set of data for (111) direction and two sets of data for (100) direction to check the reproducibility. For each measurement about 60,000 counts were collected at the peak of the profile at 30 eV per channel setting. The method of data processing was done in the same method as discussed in Chapter 3. The fraction of double scattering and double scattering distribution were estimated by employing a two-dimensional numerical calculation. Finally the profiles were normalised in the range of 0 to 6. at. units to the free atom profile value of 26.065 [6.17].

(ii) The Profiles and Anisotropy

The theoretical profiles were calculated using local and non-local pseudopotentials given in Tables 4.1, 4.2 and 4.3. Since the theoretical profiles were higher than the experimental profiles in the low momentum regions because the pseudowavefunctions used for our calculations did not have necessary oscillatory behaviour at the atomic centre due to lack of core orthogonalisation, we compared the experimental profile anisotropy between (100) and (111) directions with the theoretical anisotropies shown in Fig. 6.10. The CP anisotropy calculated from non-local pseudopotential theory has a better agreement with the experimental anisotropy. The calculated profile anisotropy has oscillations shorter than the experimental anisotropy. This might be due to the core orthogonalisation term which is not isotropic in all directions. Discrepancy between theory and experiment is more pronounced in the higher $q$ region.

(iii) The $B(r)$ Functions and Anisotropy

The autocorrelation functions had exact zero passages in both the theoretical and experimental data. The autocorrelation anisotropy between (111) and (100) directions have negative extrema at the bond length in the theoretical data. But
Fig. 6.10: Compton profile anisotropy in GaAs

Fig. 6.11: Autocorrelation anisotropy in GaAs
the negative dip in the experimental anisotropy occurs somewhat below the bond length distance (Fig. 6.11). The cause of this shift is not clear to us at present which was not observed in case of GaP data. The small peak observed at \( z = 1 \) a.u. might be due to the systematic errors in the data analysis as discussed already in connection with GaP data.

(b) The Long-Slit ACPAR Studies

(i) Experimental Method

For long-slit angular correlation studies along (100), (110), (111), (211) and (221) directions of GaAs were taken to compare with the long-slit angular correlation studies of Ge for isolating ionic effects. The samples were first annealed at 700\(^{8}\) C to remove the as-grown defects and then chemically etched and diamond polished prior to the measurement. The angular correlation set-up with the electronics was described previously. The resolving time of the fast-slow coincidence set-up was fixed at 100 nsec. The resolution of the set up was 1 mrad. About 30,000 counts were collected at the peak of the profile. The raw data were processed in the similar manner as done for GaP. Finally the profiles were normalised to unity from 0 to 2.5 a.u. [6.18].

(ii) The Nature of Profiles

The angular correlation profiles for (100), (1\(\overline{1}0\)), (111), (211) and (221) directions without subtracting the core contribution are presented in Fig. 6.12 and 6.13. The profiles along (100) and (110) are flat at the low momentum region and the profiles along (111), (211) and (221) are sharply peaked at the same region. The dips along (100) and (110) directions vanish because the data were measured at room temperature and with 1 mrad resolution. As explained already the dips are due to the \((3p, 3p)\pi^*\) bonds. The sharp peak along (111) is due to \((3p, 3p)\sigma\) bond
Fig. 6.12: ACPAR data for (100), (110) and (111) directions

Fig. 6.13: ACPAR data for (211) and (221) directions
at the first bond length. The effect of this is also seen for (211) and (221) directions shown in Fig. 6.13. In order to see the differences in the enhancement effects in elemental and compound semiconductors we have plotted a GaAs (110) profile along with Shulman et al.'s Ge (110) profile in Fig. 6.14 for comparison. It can be seen from the figure that Ge has a steeper fall at the Zone face as compared to GaAs. This fall is attributed to the many-body enhancement. Since we have corrected the effects of the resolution function, this behaviour may be arising because of weaker prominent many-body enhancement effects in compound semiconductors. But to get a clearer picture on this aspect, one needs to do the GaAs experiment at higher resolution and at low temperature as in the case of Ge. The dehancement effect at the high momentum region can not be intrepreted here due to the same region. Nevertheless, we will try to circumvent this problem in the reconstruction method.

(iii) The Profile Anisotropies

The percentage anisotropies were obtained with repect to (100) direction in all four crystallographic directions and are plotted in Fig. 6.15 and 6.16. The anisotropies are reduced in all directions in comparison to Ge data. This is also observed in CP anisotropies in GaP and GaAs. This is due to the effect of the ionicity on the anisotropies. The anisotropy between (100) and (110) is most prominent. The anisotropy of other directions are similar because of the cubic symmetry in those directions. We could see oscillations at the higher momentum regions of the anisotropies. This comes because our data had only 30,000 counts at the peak.

(iv) The $B(r)$ Functions and Anisotropies

The autocorrelation functions in GaAs behave in the same way as in GaP. There were deviations in zero passages in all directions. Since we are interested to see the effect of ionicity in GaAs, we took $B^{2\gamma}(r)$ along (110) direction for both GaAs and
Fig. 6.14: ACPAR data for (110) direction; (→), GaAs and (→) Ge.
Fig. 6.15: Percentage ACPAR anisotropy of momentum distribution of GaAs; (-) refers to (100)-(110) and (—) to (100)-(111)

Fig. 6.16: Percentage ACPAR anisotropy of momentum distribution of GaAs; (-•-) refer to (100)-(211) and (—) to (100)-(221)
Ge [6.19]. The effect of resolution function was taken equally in both sets of data. It is observed that the magnitude of oscillations are reduced for GaAS in comparison with Ge. This is once again the effect of ionicity on the autocorrelation functions. As can be seen from the Fig. 6.17, zero crossings in both GaAs and Ge are same within statistical error, but deviate considerably from the actual values. However the difference between first and second zero crossings match exactly with the lattice spacing ($a_{110} = 7.55a.u.$). This shows the periodicity of the positron wavefunctions in the system, but the deviations are due to the positron wavefunction effects as discussed already.

The autocorrelation anisotropy between (111) and (100) is similar to our earlier finding in GaP. The interpretations also remain same.

6.3. Gallium Antimonide

(a) The Long-Slit ACPAR Studies

We have no CP measurements in GaSb. We took the ACPAR measurements along (100) and (111) directions to compare with the measurements taken in GaP and GaAs.

(i) The Profiles and the Anisotropy

The experimental long-slit angular correlation data were taken along (100) and (111) directions of GaSb with 1mrad resolution. The method for data taking and data processing is as mentioned earlier. The experimental profiles along (100) and (111) directions behave in the same way as in GaP and GaAs. The profiles had more values at the zero momentum than GaP and GaAs because of the large core contributions. The percentage anisotropy is shown in Fig. 6.18. The shape of this anisotropy is also in the same phase as in GaP and GaAs. Since the shapes are same, the interpretation are also same as in GaP and GaAs. The autocorrelation
Fig. 6.17: ACPAR autocorrelation function along (110) direction; (-•-), GaAs, (o), Ge (Shulman et al)
Fig. 6.18: Percentage anisotropy of profiles in GaSb

Fig. 6.19: Difference of the scaled profiles for ZnS and ZnSe: experiment, • • • and theory, -x-
anisotropy remained similar to that of GaP and GaAS.

6.4. Zinc Sulphide and Zinc Selenide

   The CP data were measured in the polycrystalline Zinc Sulphide and Zinc Selenide samples. The samples were in powder form. The pellets were 25 mm in diameter. For ZnS and ZnSe there were two separate measurements. For ZnS the thicknesses of the samples were 2.5 mm and 3.2 mm and for ZnSe the thicknesses were 3.0 and 3.6 mm. The double scattering parameters were 0.0329 and 0.0222 for 3.2 mm of ZnS. For 2.5 mm sample of ZnS the parameters were 0.0292 and 0.0201. Both the data were identical within the statistical error limits. For ZnSe, the double scattering parameters were 0.0328 and 0.0236 for 3 mm sample and the same for 3.6 mm sample were 0.0400 and 0.0240. Here also the data were identical. The isotropic CPs for ZnS and ZnSe were calculated taking the local pseudopotentials from Table. 4.1. Since the theoretical profiles could not be compared with measure data directly, we took the difference between scaled profiles of ZnS and ZnSe of the experimental and theoretical profiles for a comparison (Fig. 6.19). The lattice constants of ZnS and ZnSe are 5.41 and 5.65 Å. The theoretical data showed that the two profiles are same. But the experimental data are different. This change can be attributed to the contribution of the core-orthogonalisation effect which is more in ZnSe than in ZnS. The theoretical calculation does not show it due to lack of this term.

6.5. The Reconstruction of Momentum Density in GaAs

   We have measured long-slit ACPAR data in GaAs along five different crystallographic directions. It is then possible to reconstruct the three dimensional momentum density $\rho^{2\gamma}(p)$ from these data easily. We have seen in the last chapter
Fig. 6.20: Reconstructed $\rho(p)$ and $\rho^{2\gamma}(p)$ for (110) direction.
that for reconstructing $\rho(p)$ from Si CP data, Pattison et al used six directions [6.20]. We follow the same method here. We have generated (210) direction in the same way as done by Mueller et al [6.21],

$$J_{210}(q) = \frac{1}{4} [J_{100}(q) + J_{110}(q) - 2J_{111}(q) + 2J_{211}(q) + 2J_{221}(q)]$$

We have used an expansion of four cubic harmonics for simultaneous equation solution. The data $\rho_{110}^{2\gamma}(p)$ is generated following (5.17). The CP data were calculated along the same six directions using non-local empirical pseudopotential theory and then reconstructed using the same methods. The reconstructed $\rho_{110}^{2\gamma}(p)$ and $\rho_{110}(p)$ are plotted in Fig. 6.20. $\rho^{2\gamma}(p)$ shows oscillations in the low momentum region. This is expected because for the reason of geometry, the long-slit apparatus does not yield accurate information about the behavior of $\rho_{110}^{2\gamma}(p)$ at that region [6.22]. It is seen that the $\rho_{110}^{2\gamma}(p)$ shows a clear enhancement effect at the zone boundary whereas $\rho(p)$ is a smooth data. The fall around the Jones zone is sharper for $\rho^{2\gamma}(p)$ than $\rho(p)$. The reduction of high momentum region of $\rho_{110}^{2\gamma}(p)$ in comparison to $\rho_{110}(p)$ is due to the dehancement effects. The Umklapp component in $\rho_{110}^{2\gamma}(p)$ is also clearly observed. The $\rho_{110}(p)$ does not show the Umklapp component because the core-orthogonalisation term is neglected.
References


