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Valence and conduction band-edges-charge densities in $Ga_{1-x}Al_xP$ mixed crystals

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Abstract

The empirical pseudopotential method (EPM) combined with the virtual crystal approximation "VCA" are used to compute electronic charge densities at Γ and X k-points of the valence and conduction band edges in the ternary GaAlP semiconductor alloy. These charge densities are used to study the modifications of the bonding and electronic properties of the alloy with respect to the molar fraction of Al in GaP.

Introduction

Ternary $A^{III}B^{III}C^{V}$ semiconductor alloys have been recognized as very useful for fabricating new electronic and optical devices. This is because of the possibility of tuning the width of the forbidden energy gap by varying the composition of the alloys. GaAlP alloys present an interest for optoelectronic devices in the visible region because the band gap increases by increasing the Al content in the alloy [1, 2].

The two zinc blende semiconductors GaP and AlP form a continuous series of alloys denoted by $Ga_{1-x}Al_xP$, where x is the mole fraction of AlP in the alloy. Both GaP and AlP crystallize in the zinc blende, their lattice constants are quite equal. Owing to the close matching of the lattice constants, $Ga_{1-x}Al_xP$ compound exhibits a small difference between GaP and AlP bond lengths. This suggests that at least in a first order approach, one can neglect lattice distortion effects and assume that the atomic position of the anion and the cation sublattices remains unchanged on going from pure compound systems. When cations are randomly distributed, the resulting system is the homogeneous alloy $Ga_{1-x}Al_xP$ which can be treated, in a first order approximation within the so-called virtual crystal approximation "VCA". In this approximation the disordered alloy is replaced by a monoatomic lattice with averaged atomic potential for the compound elements.

The EPM scheme within the VCA are used to analyze both the total valence and electron charge density at the selected k points of the Brillouin zone. Computation of the conduction-band-edge charge densities at high symmetry points can provide information about the response of specific band states to perturbations in compound semiconductors.

In an attempt to give more systematic understanding of these effects in semiconductors, this work presents some results of our calculations on the conduction-band-edge charge densities at Γ^c and X^c points for $Ga_{1-x}Al_xP$ alloys.

Calculations

The pseudopotential method used here starts with that used by Bergstresser and Cohen in their well-known treatments of cubic binary compounds [3, 4]. The pseudopotential hamiltonian

$$H = -(\hbar^2/2m)\nabla^2 + V(r) \tag{1}$$

contains an effective potential which is expanded as Fourier series in a reciprocal lattice space. For a binary compound the expansion is written in two

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parts which are symmetric and antisymmetric with respect to an interchange of two atoms about their midpoint:

$$V(r)=\sum_{G\leq G_O}[S^S(G)V_G^S+S^A(G)V_G^A]\exp(iG.r) \tag{2}$$

The limited summation reflects the fact that the effective pseudopotential is sufficiently weak, because of cancellation between the kinetic and potential energies in the vicinity of atomic cores, only few Fourier terms suffice.

The structure and form factors are given by [5]:

$$S^S(G)=\mathrm{Cos}\,G.\tau \quad ; \quad S^A(G)=\mathrm{Sin}\,G.\tau \tag{3}$$

$$V_G^{S,A}(1,2)=\frac{1}{\Omega_{1,2}}\int \frac{1}{2}[V_1(r)\mp V_2(r)]_{1,2}\exp(-iG.r)d^3r \tag{4}$$

This can be simplified through the use of the transferability approximation for atomic pseudopotentials as discussed by Phillips [6]. By writting.

$$V_G(J)=\frac{1}{\Omega_j}\int V_j(r)\exp-iG.r\,d^3\vec{r} \tag{5}$$

Where Ω_j is the volume per-atom of the monoatomic solid consisting of atoms of type J, and by assuming that the pseudopotential $V_G(j)$ is essentially independent of the particular crystalline environment of the atoms, (i.e., neglecting the dielectric screening at small G-values), we replace equation <4> by $V_G^{S,A}(1,2)$

$$V_G^{S,A}(1,2)=[\Omega_1 V_G(1)\mp\Omega_2 V_G(2)]/2\Omega_{1,2} \tag{6}$$

The form factors of GaP and AlP are listed in table 1, those of AlP, are synthesized by Y.F.Tsay [7] from the published ones of Si and GaP in reference (3).

In our calculations, the pseudopotential of the alloy has been computed by mixing the transfer's integrals "in spirit of VCA", hence for ternary $A^{III}B^{III}C^{V}$ ($Ga_{1-x}Al_xP$) semiconductor alloys, the averaged pseudopotential form factors, $V^{III}(G)$, is written by [8]

$$V^{III}(G)=(1-x)V_A(G)+xV_B(G) \tag{7}$$

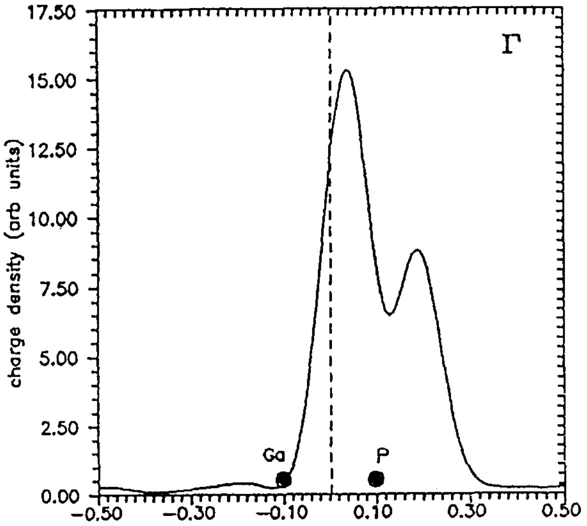
Where x is the arbitrary component element concentration for groupe III site (Ga and Al).

This pseudopotential method is employed to solve the one-electron Hamiltonian for the eigenvalues and wave functions. The method used to compute the charge densities at selected k point has been reviewed elsewhere, hence we shall only outline it briefly here [9-11]. The charge density is computed in the Brillouin zone by using appropriate wave function $\Psi_{n,K}$ for the band n at the k-point in the Brillouin zone.

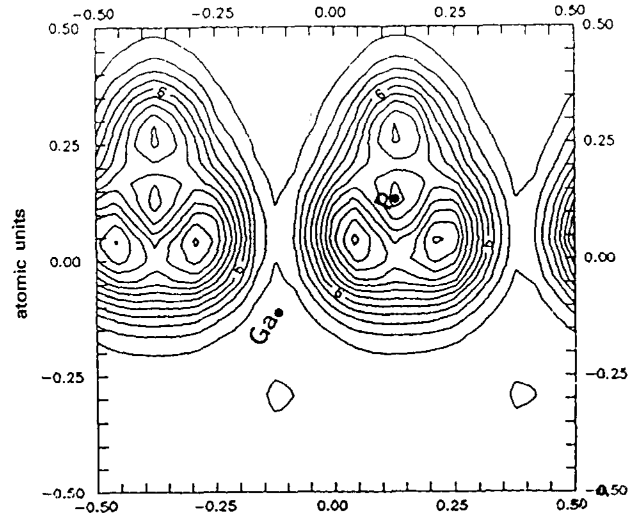
$$\rho_{n,K}(r)=2e|\Psi_{n,K}(\vec{r})|^2 \tag{8}$$

Results of Calculations

Figures 1 to 3 display the charge densities, for the sum of the four valence bands at the Γ point for GaP, AlP and for the alloy $Ga_{0.5}Al_{0.5}P$ respectively. Their corresponding charge densities present nearly the same characteristics since the bond center is displaced towards the P anion. This concentration of charge between anion and average cation (Covalent bond) is

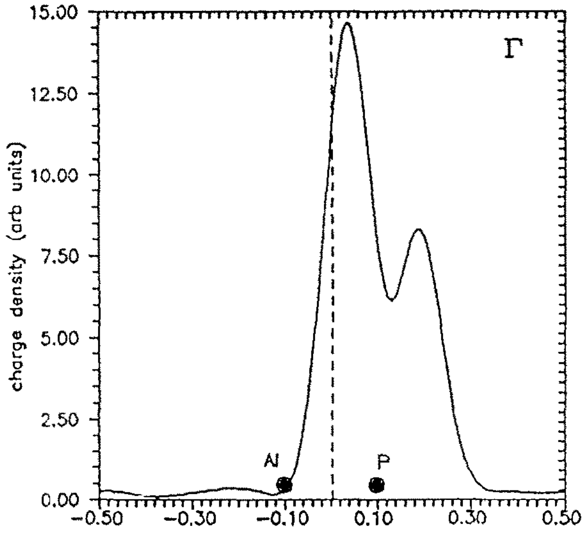


a) position (atomic units)



b) atomic units

Fig. 1. The total charge densities of the four valence bands at Γ point for GaP a) along <111> direction and b) in the (1$\bar{1}$0) plane.



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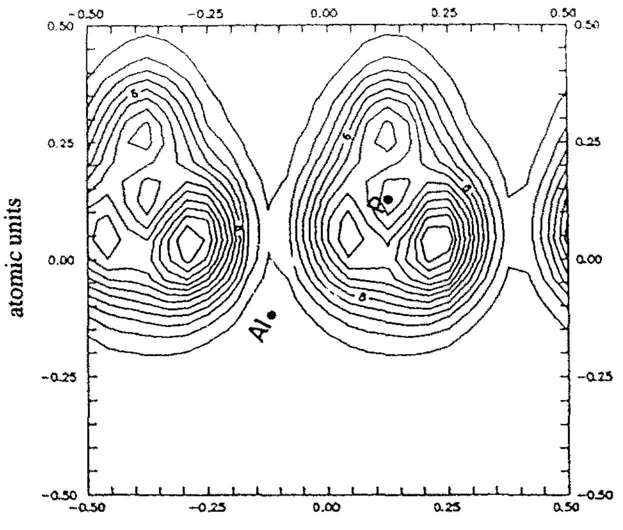
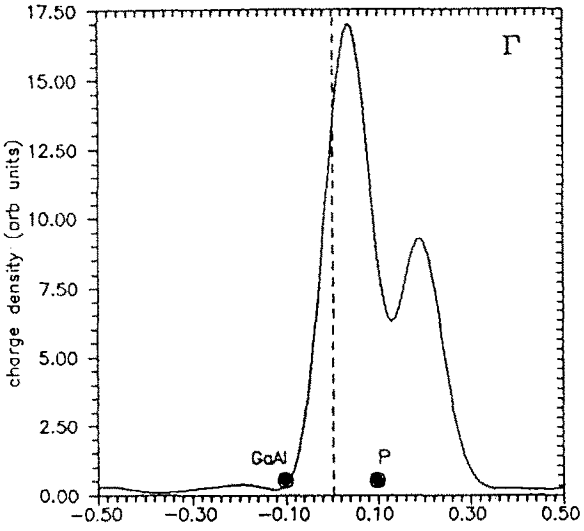


b) atomic units

Fig. 2. The total charge densities of the four valence bands at Γ point for AlP a) along <111> direction and b) in the $(1\bar{1}0)$ plane.



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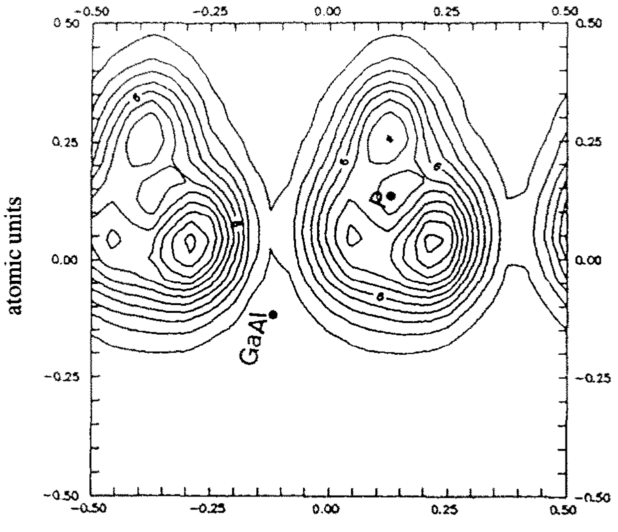


b) atomic units

Fig. 3. The total charge densities of the four valence bands at Γ point for $Ga_{0.5}Al_{0.5}P$. a) along <111> direction and b) in the $(1\bar{1}0)$ plane.

the sharing of electrons caused by quantum mechanical effects. The reason that the density of covalent semiconductors is so low is that nearest neighbors are bound together through overlapping hybridized orbitals making the charge distribution p-like. The slight difference between valence charge distribution in $Ga_{1-x}Al_xP$ ($0<x<1$), is simply explained by considering size and chemical electronegativity of the compounds.

We have then computed the valence electron charge density for the two special k points, ($2\pi/a$) (3/4, 1/4, 1/4) and ($2\pi/a$) (1/4, 1/4, 1/4), using the Chadi-Cohen scheme [12]. The total valence charge density is obtained by summing over the four occupied valence bands. The result is shown in Fig. 4 where the valence charge distribution is approximatively similar to that at the higher point Γ.

When making transition from the valence bands to the conduction bands, we can directly observe the consequences of the lack of inversion upon the charge densities at Γ^c and X^c. For $Ga_{1-x}Al_xP$, the computed charge distributions are still antibonding and s-like at Γ^c, but there is more electronic charge density surrounding the anion than the cation (Fig. 5). This is consistent with previous studies of charge distribution in III-V compound semiconductors. [9, 10, 13]

We notice in contours plots (Figs. 6-7) that the charge distribution at the cation site increases by decreasing the content of Al in the alloy for $x > 0.5$.

TABLE 1. Symmetric and antisymmetric form factors of GaP and AlP with their lattice constants.

Compounds	Form factors (in Ry)					
GaP	V_S^3	V_S^8	V_S^{11}	V_A^3	V_A^4	V_A^{11}
a = 5.45Å	-0.22	0.03	0.07	0.12	0.07	0.02
AlP a = 5.42Å	-0.21	0.04	0.08	0.13	0.08	0.03

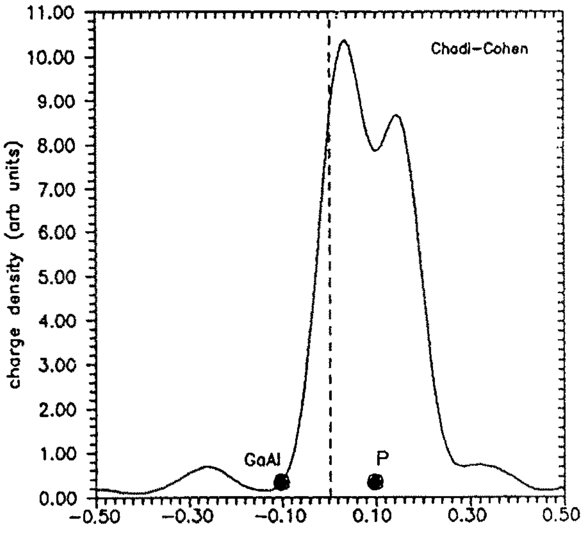


Fig. 4. The valence charge density using the Chadi-Cohen scheme along <111> direction.

The situation at X^C is quite interesting, since the charge distributions are more delocalized throughout the unit cell. The charge distribution for the first conduction band at X^C point is antibonding in both GaP, AlP and $Ga_{1-x}Al_xP$. The electron charge density topology at the X^C point consists of P_Z and d_{xy} orbitals of the cation and S and d_{3z^2-1} orbitals of the anion, to form an antibonding state, where the s-like distribution about the anion is evident in (Fig. 8). However, for the second conduction band at X, the situation is reversed; since the s-character is now evident around the cation (Fig. 9). Hence the symmetry of the $Ga_{1-x}Al_xP$ for the first and the second conduction band is X_1^C

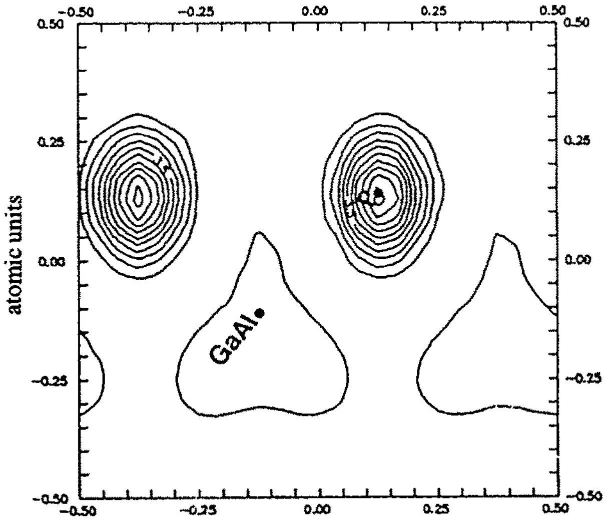
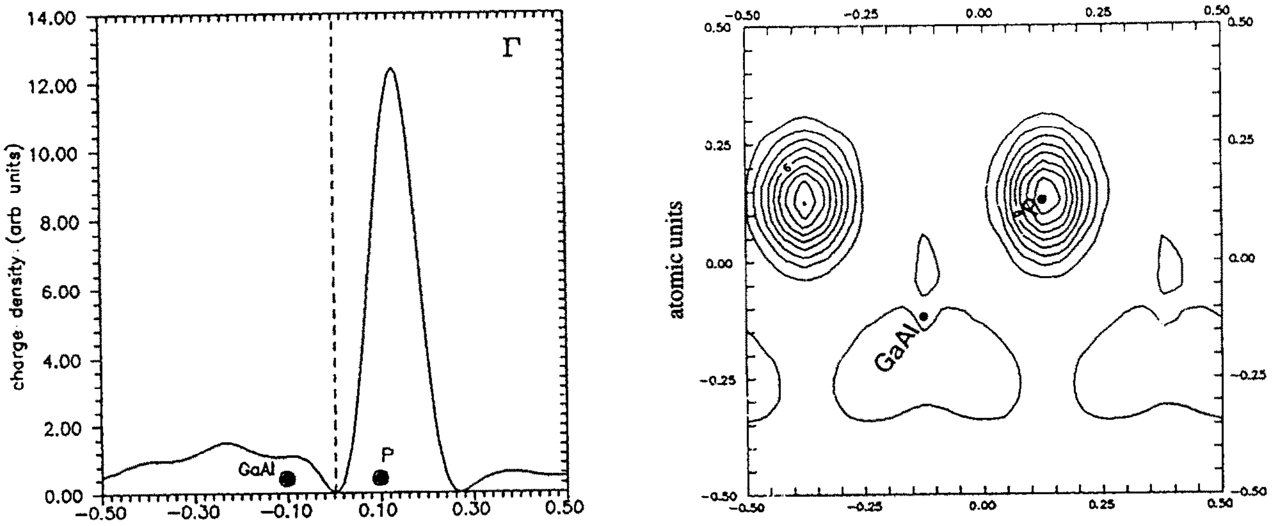


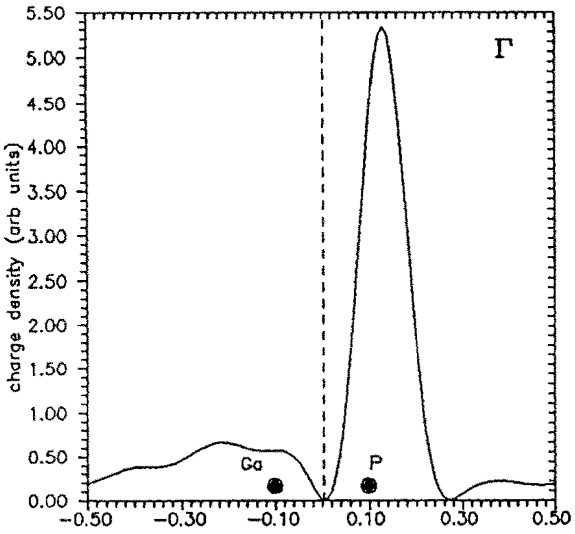
Fig. 6. Electronic charge density for $Ga_{0.9}Al_{0.1}P$ at Γ^C of the first conduction band in the (1$\bar{1}$0) plane.



a) position (atomic units)

b) atomic units

Fig. 5. Electronic charge density for $Ga_{0.5}Al_{0.5}P$ at Γ^C of the first conduction band a) along <111> direction and b) in the (1$\bar{1}$0) plane.



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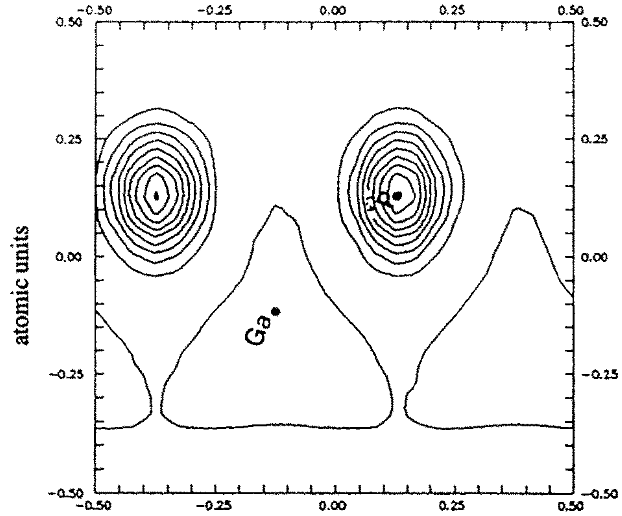
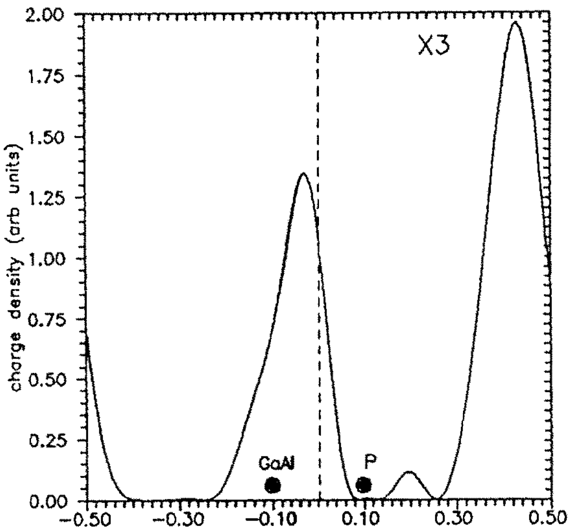


b) atomic units

Fig. 7. Electronic charge density for GaP at Γ^C of the first conduction band a) along <111> direction and b) in the $(1\bar{1}0)$ plane.



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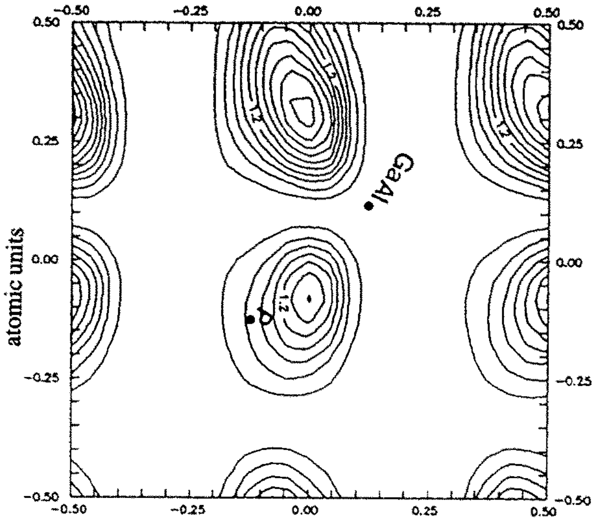
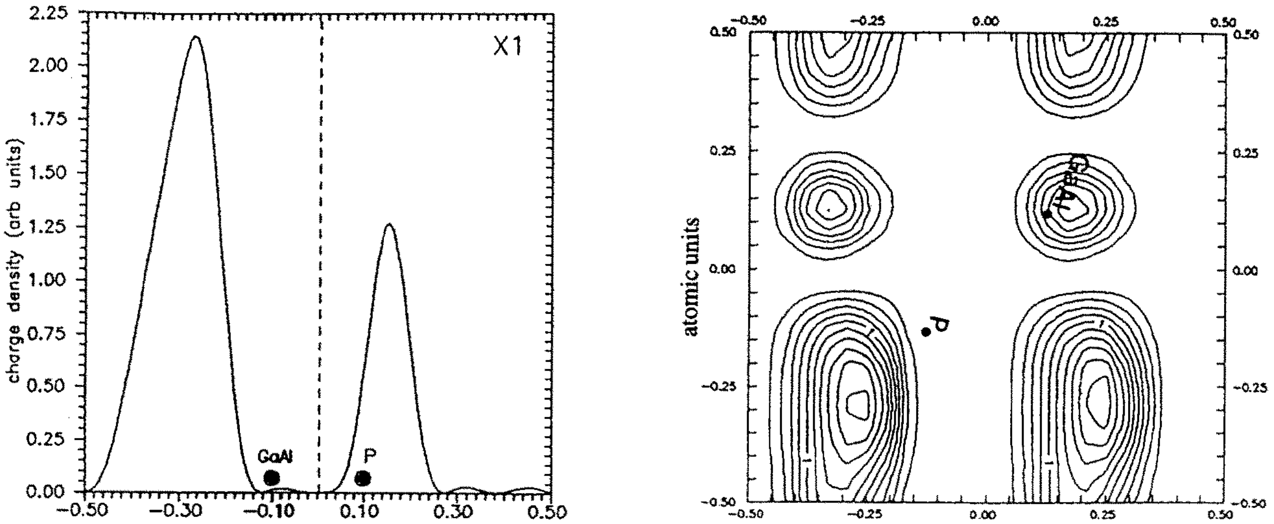


b) atomic units

Fig. 9. The second conduction band charge densities at the X point $Ga_{0.5}Al_{0.5}P$ a) along <111> direction and b) in the $(1\bar{1}0)$ plane.



a) position (atomic units)

b) atomic units

Fig. 8. The first conduction band charge densities at the X point for $Ga_{0.5}Al_{0.5}P$ a) along <111> direction and b) in the $(1\bar{1}0)$ plane.

and X_3^C respectively.

In III-V zincblende semiconductors, there is one peculiarity which still provokes confusion in their characterization: the ambiguous classification of two symmetry related states at the X point in the Brillouin zone (BZ), X_1 and X_3, in particular those of the conduction bands.

In table 2 we indicate the symmetry of the first conduction states at X for GaP and AlP by giving the angular momentum decomposition of the electronic states around each constituent ion inside spheres of Wigner-Seitz radii r_S. In all cases the radii are taken to be the same for the cation and the anion.

This table also gives the energy separation $E(X_3)$ - $E(X_1)$ obtained by four different methods: 1) ab initio relativistic pseudopotential method without spin-orbit coupling [14], 2) relativistic LMTO method including spin-orbit coupling [15], 3) EPM (Empirical Pseudopotential Method) with spin-orbit coupling [11, 15] and 4) EPM without spin-orbit coupling (our calculation). Our results are in good agreement with references [11, 14, 16], although they used EPM with spin-orbit coupling in ref 16 we found for the case of GaP compound better results.

We notice that there is much more charge at X^C than at Γ^C; this difference has immediate consequences for the effect of interstitial impurities on the electronic structures of $Ga_{1-x}Al_xP$. As first studied by Rompa, Schuurmans, and Williams for GaAs [13], and later investigated by Wood, Zinger, and de Groot (WZG) for GaP [17] and other so-called "filled tetrahedral semiconductors" (FTS) [18, 19], the substitution of the interstitial sites of tetrahedral compounds with atoms possessing repulsive S and attractive non-S effective potentials (e.g., H, He, Li) can raise (lower) the energy of the lowest conduction-band-state at X^C if that state has S (non-S) charge density character at the interstitial site. Therefore, GaP, AlP and even $Ga_{1-x}Al_xP$ could be turned into the FTS, $V_CGa_{1-x}Al_xP\ V_a$, where V_C is the interstitial site nearest the cation (Ga, Al), and V_a is the interstitial site nearest the anion P. By inserting He atoms at each of the V_C and V_a sites of the crystal, we predict that $Ga_{1-x}Al_xP$ could be transformed from an indirect-gap semiconductor to direct-gap semiconductor $HeGa_{1-x}Al_xP\ He$.

TABLE 2. Energy splitting $E(X_3)$ - $E(X_1)$ in eV and percentage decomposition of angular momentum character of the first conduction eigenstates at the X point (001) in the BZ of GaP, AlP and GaAlP (x = 0.5).

	$E(X_3)$ - $E(X_1)$ (in eV)				Group-III atom		Group-V atom	
	1	2	3	4	P_Z	d_{xy}	S	d_{3z-1}^{2}
GaP	0.21	0.12	0.55	0.37	27	27	11	35
AlP	0.88	0.90		0.63	28	29	8	35
GalP x = 0.5				0.50				

[1] ab initio relativistic pseudopotential method without spin-orbit coupling.

[2] Dirac-relativistic LMTO.

[3] EPM including spin orbit-coupling.

[4] EPM without spin-orbit coupling.

As we observe from the charge-density plot for $Ga_{1-x}Al_xP$ at X_1^C in (Fig. 5, 8), there is an abundance of s-like charge density at V_C while there is a local minimum of charge density at V_a. Because these interstitial sites contain more s-character charge density than those at Γ^C, the insertion of He atoms at V_C raises the X_1^C conduction-band state more than that at Γ^C, thus forcing both GaP, AlP and $Ga_{1-x}Al_xP$ systems to become direct gap at Γ.

On the other band, this method will modify a particular semiconductor by altering its direct-indirect gap and can be very useful for superlattices systems. These structures have various applications in both microelectronic and optoelectronic fields.

For GaP/$Ga_{1-x}Al_xP$ superlattices the relative position of the bands in $Ga_{1-x}Al_xP$ wells and the GaP barriers can lead to several plausible configurations of the quantizing superpotentials which are shown in (Fig. 10).

Owing to the different band gaps of the host semiconductors, a superpotential is created in the Z direction perpendicular to the plane of the layers and tends to confine both electrons and holes in the smaller gap material, i.e., in the Gap layers. This usually is said to be of type I (Fig. 10-a).

Since of the confinement is also shown by the dependence of the energy of these states on the width of the wells, the value of x could change the way that interstitial impurities modify the electronic band structure of the $Ga_{1-x}Al_xP$ alloy.

As a result, electron are mainly localized in the GaP layers while holes are confined in the GaAlP ones. Such systems, where electrons and holes are spatially separated, is said to be of type II (Fig. 10-b).

The problem of finding the changes induced in the electronic structure by insertion of He atom in the empty interstitial sites is now mapped into the more transparent problem of calculating the response of the host electronic structure to electron-repelling potential wells at these sites. One expects the principal effect of insertion of closed-shell atom on a given state to be simply expulsion from the Pauli exclusion volume of its contribution to the valence charge density (thereby raising the kinetic energy of the corresponding orbitals, and hence the single-particle band eigenvalue for this state). Consequently, insertion of He

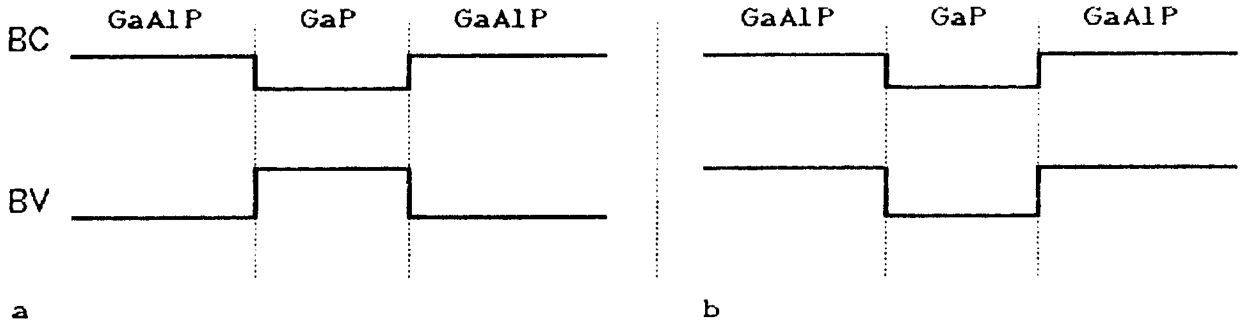


Fig. 10. Representation of the relative position of the bands in GaP/$Ga_{1-x}Al_xP$ superlattices.

into the two interstitial sites in Gap (HeGaPHe) dilates the lattice by 5.3% [17]. At The experimental bulk lattice constants the qualitative features change little with the lattice parameter a. Hence the strain induced in the HeGaPHe/GaAlP system do not shift the band edges enough to destroy the straggered band alignment of the type-II structure. It is seen in the work of Wood et al. [17] that He expels charge from the interstitial channels, and place some extra charge on the covalent bonds, suggestive of the formation of He-host "antibonds" by He[20] without formation of He-He bonds. This fact does not destroy the structure but destabilizes it by ~0.9eV per he atom in the host crystal.

Thus theories of superlattice electronic structure are band-edge theories. It is seldom of interest to describe superlattices on the scale of bonding and antibonding band widths. Instead, one cares about a detailed description of the band edges. Since the filled tetrahedral semiconductors ion tuned the electronic band gaps by lowering or raising the conduction band edges. Therefore we may have a new class of superlattice as HeGaPHe/GaAlP.

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