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16.Summary/Notes

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17.Remarks

INFLUENCE OF IONICITY ON THE BAND STRUCTURE OF III-V SEMICONDUCTORS WITH THE APW-$\vec{k}\cdot\vec{p}$ METHOD*

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The band structure calculation is performed on GaAs with the Augmented Plane Wave Method (APW) and $\vec{k}\cdot\vec{p}$ expansion, taking into account ionicity in addition to covalent bonding. Energy levels at the Γ point are also obtained for AlAs and the same behaviour for the variation with ionicity is observed. In both cases gaps decrease with increasing ionicity. For GaAs the value $E_g = 1.52$ eV is obtained for 10% of ionicity and for AlAs a 20% of ionicity is necessary to produce the direct gap $E_g = 2.50$ eV. The absolute value of the matrix elements of the momentum operator varies weakly with ionicity. Valence and lower conduction bands move almost rigidly, decreasing the gap.

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Nous avons calculé la structure des bandes du GaAs avec la méthode des Ondes Planes Augmentées (APW) et l'expansion $\vec{k}\cdot\vec{p}$ considerant l'ionization au même temps que la liaison covalente. Nous avons aussi obtenu les niveaux d'énergie pour le AlAs et nous avons observé qu'ils ont le même comportement en ce qui concerne la variation de l'ionization considerée comme un paramètre. Dans les deux cas on observe que le "gap" décroit au fûr et à mesure qu'on décroit l'ionization. Pour le GaAs nous avons obtenu la valuur $E_g = 1{,}52$ eV avec l'ionization 10%, et pour le AlAs un "gap" direct $E_g = 2{,}50$ eV avec l'ionization 20%. Les valeurs absolues des élements de matrice pour l'operateur momentum changent faiblement. Les bands de valence et de conduction se déplacent presque rigidement quand le "gap" décroit.

This paper deals with the problem of the influence of ionicity on the band structure calculation of III-V semiconductors as GaAs, AlAs, etc., using the Augmented Plane Wave (APW)[1] method and the $\vec{k}\cdot\vec{p}$ expansion[2]. Since the paper of Slater in 1973[3], the APW has been shown to be a very adequate method for semiconductors. After that paper many suggestions have been presented concerning the inclusion of relativistic corrections, improvements on the "muffin-tin" potential, etc. A $\vec{k}\cdot\vec{p}$ expansion was first utilized by Cardona and Pollak[2] and later formalized on a first principles basis by Parada[4], who has obtained the matrix elements of the momentum operator from his own results at the Γ Point. This expansion contributed to make the band structure calculation less time consuming since energy levels and wave functions had to be calculated only at high symmetry points where higher degeneracies occur.

From the $\vec{k}\cdot\vec{p}$ expansion, once we know the energy levels $E_n^{\Gamma\alpha}(\vec{k}_o)$ and their corresponding wave functions $\psi_{n\alpha,i}^{\Gamma}(\vec{k}_o,\vec{r})$ at a point $\vec{k}_o$ in the first Brillouin zone, energies and wave functions can be known everywhere. $\psi_{n,i}^{\Gamma\alpha}(\vec{k}_o,\vec{r})$ transforms like the i$^{\underline{th}}$ partner of the Γ_α irreducible representation of the group of $\vec{k}_o$, and n is the band index. The index Γ_α refers to the irreducible representation to which the state belongs, i and n represent respectively the partner and the band index. So

$$\psi_{n,i}^{\Gamma_\beta}(\vec{k},\vec{r}) = \sum_{m,j} A_{n;i}^{m;j}(\vec{k}-\vec{k}_o)\ x$$

$$\exp\left[i(\vec{k}-\vec{k}_o)\cdot\vec{r}\right]\psi_{m,j}^{\Gamma_\alpha}(\vec{k}_o, r) \qquad (1)$$

with coefficients to be determined. In what follows, the irreducible representation index will be included in the band index. When the above expressions are inserted in the one-electron Schrödinger equation for the $\vec{k}$ point, we obtain the secular determinant:

$$\det\left\{\left[E_m(\vec{k}_o)-E_n(\vec{k})+\frac{n^2\vec{K}^2}{2m}\right]\delta_{mn}\right.$$

$$\left.+\frac{n\vec{K}}{m}\cdot\vec{P}_{m,j}^{n,i}\right\} = 0 \qquad (2)$$

where $\vec{K} = \vec{k} - \vec{k}_o$ and

$$\vec{P}^{\,n,i}_{m,j} = \int \psi_{n,i}(\vec{k}_o, \vec{r})\,(-i\hbar\vec{\nabla})\,\psi_{m,j}(\vec{k}_o, \vec{r})\,d^3r \quad (3)$$

Bands are obtained by diagonalysing Eq. (2) for each point $\vec{k}$ in the Brillouin zone. In this paper, however, only results along symmetry axes will be presented.

It is known that semiconductors of the III-V group show some ionicity in addition to the covalent bonding, as mentioned by Demarco and Weiss[5] and also Phillips[6] who present some values for these ionicities. Kittel[7] assume 0.32 for GaAs which is a direct gap semiconductor with $E_g = 1.520$ eV for the transition $\Gamma_{15v} \rightarrow \Gamma_{1c}$.[8] According to Stukel and Euwema[9], AlAs has an indirect gap of $E_g = 2.38$ eV for the transition $\Gamma_{15} \rightarrow X_{1c}$ and a direct gap $E_g = 2.50$ eV corresponding to the transition $\Gamma_{15} \rightarrow \Gamma_{1c}$. For AlAs Phillips[7] assume an ionicity 0.274.

In a preliminary APW calculations we have obtained $E_g = 1.583$ eV for GaAs and $E_g = 2.650$ eV for AlAs, both with pure covalent bonding. But as we were interested to know the influence of ionicity we performed calculations with the Herman and Skilman[10] ionic potential in order to obtain the "muffin-tin" crystalline potential at different ionicities, namely 0.1, 0.2, 0.25 and 0.3 for GaAs and 0.1 and 0.2 for AlAs. In the first compound the experimental gap was found for an ionicity of 0.1, but calculations with greater values were performed in order to observe the characteristic behaviour. In the case of AlAs, the direct gap of 2.50 eV was obtained for an ionicity of 0.2.

The mean value of the crystalline potential (Coulomb + Slater's exchange)[1] in the plane wave regions have varied sensibly. Figure 1 shows that it decreases linearly with increasing ionicity. This seems to be the principal factor responsible for other behaviours as that of the gap, as we will discuss later.

Table Ia shows the levels obtained at the Γ point for GaAs and Table Ib for AlAs. Subindices characterize the irreducible representation of the group of the wave vector $\vec{k} = 0$. The left upper x zero indices order levels belonging to the same irreducible representation. $\overline{V}$ is the mean value of the potential in the region outside the "muffin-tin" spheres. It can be easily seen that the energy values increase with the ionicity.

Figure 2 shows the linear decrease of the gap as expected. Arsenium participates with five electrons to the covalent bond and galium with three. Ionicity in this mixed bonding occurs because negative charge flows to the atom which has less electrons in the valence shell. So Ga receives electrons from As and this tends to equalize the "muffin-tin" spheres. This reduces the mean value of the potential outside the spheres, thereby decreasing discontinuities between the potential on the surface of the sphere and outside region (shifted to be zero). This contributes to delocalize the highest valence level, which leads to a decrease of the energy gap. This behaviour was observed both in GaAs and AlAs.

Table II shows the absolute value of the matrix elements of the momentum operator for ionicities 0 and 0.1 in the case of GaAs. No large variation is observed. Figures 3 show tha bands calculated along symmetry axes Δ, Λ and Σ corresponding to directions 2π/a (1/2, 1/2, 1/2) and 2π/a (3/4, 3/4, 0) for GaAs with ionicity 0.1. In all the considered cases, bands were found to present almost the same variation as that shown by the direct gap.

Figure Captions

Figure 1: Mean value of the crystalline potential in the region outside spheres for several ionicities; Δ, results for GaAs; o, results for AlAs.

Figure 2: Variation of the energy gap with ionicity; Δ, results for GaAs; o, results for AlAs.

Figure 3a: Energy bands of GaAs in the Δ axis with ionicity 0.1.

Figure 3b: Energy bands of GaAs in the Σ axis with ionicity 0.1.

Figure 3c: Energy bands of GaAs in the Λ axis with ionicity 0.1.

TABLE Ia: Energy levels for GaAs obtained at the Γ point for several ionicities. $\overline{V}$ is the mean value of the crystalline potential outside the spheres

	Ionicity				
	0.0	010	0.20	0.25	0.30
Levels	$\overline{V} = -0.833$ Ry Gap = 1.58 eV	$\overline{V} = -0.874$ Ry Gap = 1.52 eV	$\overline{V} = -0.918$ Ry Gap = 1.44 eV	$\overline{V} = -0.941$ Ry Gap = 1.42 eV	$\overline{V} = -0.966$ Ry Gap = 1.38 eV
$^1\Gamma_1$	-0.695	-0.677	-0.661	-0.654	-0.647
$^2\Gamma_1$	0.319	0.332	0.344	0.345	0.355
$^3\Gamma_1$	0.792	0.801	0.810	0.814	0.817
$^4\Gamma_1$	1.242	1.244	1.246	1.247	1.248
$^1\Gamma_{12}$	-1.235	-1.208	-1.184	-1.161	-1.162
$^2\Gamma_{12}$	1.070	1.081	1.091	1.094	1.099
$^1\Gamma_{15}$	-1.219	-1.193	-1.168	-1.154	-1.146
$^2\Gamma_{15}$	0.202	0.221	0.238	0.246	0.253
$^3\Gamma_{15}$	0.678	0.690	0.700	0.705	0.709
$^4\Gamma_{15}$	1.136	1.140	1.144	1.146	1.147

TABLE Ib: Energy levels for AlAs obtained at the Γ point for several ionicities. $\overline{V}$ is the mean value of the crystalline potential outside spheres.

	Ionicity		
	0.0	0.1	0.2
Levels	$\overline{V}$ = -0.967 Ry Gap = 2.65 eV	$\overline{V}$ = -1.002 Ry Gap = 2.58 eV	$\overline{V}$ = -1.042 Ry Gap = 2.50 eV
$^1\Gamma_1$	-0.595	-0.582	-0.570
$^2\Gamma_1$	0.427	0.435	0.442
$^3\Gamma_1$	0.907	0.915	0.922
$^4\Gamma_1$	1.268	1.270	1.273
$^1\Gamma_{12}$	1.051	1.058	1.066
$^1\Gamma_{15}$	0.233	0.245	0.258
$^2\Gamma_{15}$	0.845	0.848	0.853
$^3\Gamma_{15}$	1.135	1.168	1.176

TABLE 2: Absolute value of matrix elements for GaAs of the momentum operator in atomic units. ${}^{n}\Gamma_{\alpha,i}$ means level n corresponding to representation α and partner i.

$A_{mn} = < {}^{m}\Gamma_{1}|p_{x}|\,{}^{n}\Gamma_{15,1} >$; $B_{mn} = < {}^{m}\Gamma_{12,1}|P_{x}|\,{}^{n}\Gamma_{15,1}>$; $D_{m,n} = < {}^{m}\Gamma_{15,1}|P_{x}|{}^{n}\Gamma_{15,2}>$

	Ionicity				
	0.0	0.1		0.0	0.1
A_{11}	0.0729	0.0724	B_{12}	0.0077	0.0071
A_{12}	0.5691	0.5637	B_{13}	0.3971	0.3957
A_{13}	0.1177	0.1152	B_{14}	0.0180	0.0192
A_{14}	0.0265	0.0259	B_{21}	0.0193	0.0192
A_{21}	0.1191	0.1203	B_{22}	0.9871	0.9818
A_{22}	0.9771	0.9816	B_{23}	0.2999	0.2079
A_{23}	0.3001	0.2848	B_{24}	1.3372	1.3300
A_{24}	0.0210	0.0262	D_{11}	0.0774	0.0782
A_{31}	0.0689	0.0667	D_{12}	1.1515	1.1465
A_{32}	0.1536	0.1432	D_{13}	2.2497	2.2261
A_{33}	1.0977	1.1028	D_{14}	2.0360	2.0351
A_{34}	0.0528	0.0485	D_{22}	0.0005	0.0005
A_{41}	0.0823	0.0820	D_{23}	1.0127	1.0145
A_{42}	0.1877	0.1881	D_{24}	0.2011	0.1968
A_{43}	0.0045	0.0006	D_{33}	0.0012	0.0011
A_{44}	1.2773	1.2782	D_{34}	0.6414	0.6407
B_{11}	0.0021	0.0021	D_{44}	0.0008	0.0008

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