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Dielectric susceptibility of III-V indium-compound semiconductors

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The dielectric constant $[\epsilon_1(0)]$ of InP, InAs, and InSb is calculated with use of a linear combination of hybrids model recently developed by us. Our expression for $\epsilon_1(0)$ is origin independent and is free from any scaling parameter, unlike the earlier theories. There is reasonably good agreement between our results and experiment.

The series of indium-based III-V-compound semiconductors is gaining attention because of their potential as device materials. InAs and InSb are good infrared detectors as a result of their small band gap. InP forms a lattice-matched basis for In-Ga-As high-electron-mobility transistors which have achieved higher speed[1] than comparable AlAs-GaAs structures. Several attempts have been made to investigate the electronic structure as well as physical properties of these semiconductors.[2] In recent years the chemical bond approach[3,4] has been utilized to calculate the electric, magnetic, and optical properties of tetrahedrally bonded solids. This approach, which is much simpler than the band theory, emphasizes the bond aspect of the crystal structure and is valuable in studying chemical trends. Recently, we have formulated a chemical bond theory to calculate the diamagnetic susceptibility[5] χ of InP, InAs, and InSb, using a linear combination of hybrids method developed by us.[6] We have constructed a basis set for the valence bands by taking linear combination of sp^3 hybrids forming a bond in which their relative phase factors, heretofore neglected, have been properly included. We have also constructed a basis set for conduction bands which are orthogonal to the valence-band functions. We have constructed localized (Wannier) functions[7] from our Bloch functions and have shown that the bond orbitals used in the earlier chemical bond theories[8,9] are not the proper choice for the Wannier functions of the valence band. We have shown that the basic assumption in the bond orbital models, i.e., that the localized Wannier functions have the character of the chemical bonds, is equivalent to ignoring the relative Bloch phase factor $e^{i\mathbf{k}\cdot\mathbf{d}_j}$ (where $\mathbf{d}_j$ is a bond length) between the hybrids forming a bond. However, since $\mathbf{d}_j-\mathbf{d}_{j'}$ is a lattice vector, the relative phase factor plays an important role in solids unlike in molecules where it could be neglected. We have used our basis states in our general expression[6] for χ and have calculated χ of InP, InAs, and InSb. The novelty of our formulation is that our results are origin independent and are free from any scaling parameter.

In the present paper we calculate the dielectric constant $[\epsilon_1(0)]$ of III-V indium compounds using our chemical bond formalism. We consider a zinc-blende structure, where each A atom is surrounded tetrahedrally by four B atoms and vice versa. The primitive cell contains two basic atoms, A and B. At each site i, we construct four sp^3 hybrids $\phi_j^B(\mathbf{r}-\mathbf{R}_i)$ pointing from the B atom to the nearest-neighbor A atoms along the direction j $(j=1,\ldots,4)$ and four other sp^3 hybrids $\phi_j^A(\mathbf{r}-\mathbf{R}_i-\mathbf{d}_j)$ pointing from these nearest neighbors to the B atom. We choose one of the B atomic sites as the origin. $\mathbf{R}_i$ is a lattice vector for site i and $\mathbf{d}_j$ is a nearest-neighbor vector. We construct Bloch-like tight-binding sums for valence-band basis functions by taking linear combination of hybrids forming a bond

$$\chi_j^v(\mathbf{r},\mathbf{k})=\frac{1}{\sqrt{N}}\sum_i C_j^v(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{R}_i}\times[\phi_j^B(\mathbf{r}-\mathbf{R}_i)+\lambda\phi_j^A(\mathbf{r}-\mathbf{R}_i-\mathbf{d}_j)e^{i\mathbf{k}\cdot\mathbf{d}_j}]\,, \tag{1}$$

where

$$C_j^v(\mathbf{k})=[1+\lambda^2+2\lambda S\cos(\mathbf{k}\cdot\mathbf{d}_j)]^{-1/2}\,. \tag{2}$$

S is the overlap integral between the two hybrids forming a bond. λ accounts for the partial ionic character of the compound via Coulson's ionicity parameter[7] f_c by the expression

$$f_c=\frac{(1-S^2)^{1/2}(1-\lambda^2)}{1+\lambda^2+2\lambda S}\,. \tag{3}$$

We obtain the basis functions for the conduction bands by constructing functions orthogonal to $\chi_j^v(\mathbf{r},\mathbf{k})$:

$$\chi_j^c(\mathbf{r},\mathbf{k})=\frac{1}{\sqrt{N}}\sum_i C_j^c(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{R}_i}[(\lambda+Se^{i\mathbf{k}\cdot\mathbf{d}_j})\phi_j^B(\mathbf{r}-\mathbf{R}_i)-(\lambda S+e^{i\mathbf{k}\cdot\mathbf{d}_j})\phi_j^A(\mathbf{r}-\mathbf{R}_i-\mathbf{d}_j)]\,, \tag{4}$$

where

$$C_j^c(\mathbf{k})=\left[\frac{\lambda+Se^{-i\mathbf{k}\cdot\mathbf{d}_j}}{(1-S^2)[1+\lambda^2+2\lambda S\cos(\mathbf{k}\cdot\mathbf{d}_j)](\lambda+Se^{i\mathbf{k}\cdot\mathbf{d}_j})}\right]^{1/2} . \tag{5}$$

The Bloch eigenfunctions for the valence and conduction bands are

$$|n\mathbf{k}\rangle=\sum_j \alpha_{jn}^v(\mathbf{k})\chi_j^v(\mathbf{r},\mathbf{k}) , \tag{6}$$

$$|m\mathbf{k}\rangle=\sum_j \alpha_{jm}^c(\mathbf{k})\chi_j^c(\mathbf{r},\mathbf{k}) , \tag{7}$$

where n and m denote valence and conduction bands, respectively. α's are elements of 4×4 unitary matrices which satisfy the unitary properties

$$\sum_n \alpha_{jn}^v(\mathbf{k})\alpha_{nj'}^{v\dagger}(\mathbf{k})=\delta_{jj'}$$

and

$$\sum_m \alpha_{jm}^c(\mathbf{k})\alpha_{mj'}^{c\dagger}(\mathbf{k})=\delta_{jj'} .$$

The dielectric constant is calculated by using an expression[10] which is derived from the Kramers-Kronig relation at $\omega=0$,

$$\epsilon_1(0)=1+\frac{8\pi e^2}{V}\sum_{\substack{n,m,\mathbf{k}\\(m\neq n)}}|\langle n\mathbf{k}|r^\gamma|m\mathbf{k}\rangle|^2/E_{mn} , \tag{8}$$

where $|n\mathbf{k}\rangle$ and $|m\mathbf{k}\rangle$ are Bloch functions [Eqs. (6) and (7)] representing filled valence-band and empty conduction-band states, respectively, $E_{mn}=E_{m\mathbf{k}}-E_{n\mathbf{k}}$ and r^γ is the component of the electron position vector in the direction of polarization. It may be noted that we have neglected the core contributions to the dielectric constant because they are small.[11] Further, the nature of the steep and narrow, curve between $\epsilon_2(w)$ and photon frequency[7,12] for tetrahedral semiconductors permits us to expand the energy denominator about an average energy gap (E_g) as

$$E_{mn}^{-1}=E_g^{-1}\sum_{p=0}^{\infty}(1-E_{mn}/E_g)^p , \tag{9}$$

where we keep only the first term in this expansion. In order to evaluate $\epsilon_1(0)$, we have used Hall-Weaire approximations,[13,14] i.e., we have calculated matrix elements between hybrids of the same site and hybrids of the same bond. Since the Hall-Weaire model yields a poor description of the conduction band, we have expressed Eq. (8) in terms of valence bands alone by assuming the completeness relation

$$\sum_{m,\mathbf{k}}|m\mathbf{k}\rangle\langle m\mathbf{k}|=\delta(\mathbf{r}-\mathbf{r}')-\sum_{n,\mathbf{k}}|n\mathbf{k}\rangle\langle n\mathbf{k}| . \tag{10}$$

Further, we note that for semiconductors, which contain high-lying core d states, the peaks in $\epsilon_2(\omega)$ are broader mainly because of the mixing of these core d states with the valence-band states.[11] Consequently, we introduce a dimensionless factor[11] D to correct for this effect.

Using Eq. (10) in Eq. (8) and after some algebra, we obtain

$$\epsilon_1(0)=1+\frac{64\pi e^2ND}{VE_g}T , \tag{11}$$

where

$$T=\left\{f_{1j}\left[\langle x^2\rangle_B+\lambda^2\langle x^2\rangle_A+\frac{\lambda^2 d}{\sqrt{3}}\left[\frac{d}{\sqrt{3}}-M_A\right]\right]+2f_{2j}\lambda\langle x^2\rangle_{BA}-4f_{3j}\lambda^2\langle x\rangle_{BA}^2\right.$$
$$\left.-4f_{4j}\lambda\langle x\rangle_{BA}\left[\frac{M_B-\lambda^2M_A}{2}+\frac{\lambda^2 d}{\sqrt{3}}\right]-f_{5j}\left[\frac{M_B-\lambda^2M_A}{2}+\frac{\lambda^2 d}{\sqrt{3}}\right]^2-\tfrac{1}{4}f_{6jj'}(M_B-\lambda^2M_A)^2\right\} . \tag{12}$$

TABLE I. Results of one-site and two-site integrals used in $\epsilon_1(0)$.

Solid	$\langle x^2\rangle_B$ (Å^2)	$\langle x^2\rangle_A$ (Å^2)	M_B (Å)	M_A (Å)	$\langle x^2\rangle_{BA}$ (Å^2)	$\langle x\rangle_{BA}$ (Å)	S
InP	0.549	1.38	0.625	0.924	0.486	0.396	0.598
InAs	0.627	1.38	0.659	0.924	0.542	0.426	0.611
InSb	0.829	1.38	0.771	0.924	0.703	0.496	0.633

TABLE II. Dielectric constant of InP, InAs, and InSb.

Solid	d^{a} (Å)	$E_g{}^{\text{a}}$ (eV)	λ^{a}	D^{b}	$e_1(0)$ (Theory)	$\epsilon_1(0)^{\text{b}}$ (Expt)
InP	2.54	4.84	0.222	1.19	7.71	9.6
InAs	2.61	4.6	0.258	1.33	8.86	12.3
InSb	2.81	4.08	0.267	1.42	10.52	15.7

[a] Reference 9.

[b] Reference 11.

Here $\langle O\rangle_\alpha=\langle\phi_j^\alpha(\mathbf{r})|O|\phi_j^\alpha(\mathbf{r})\rangle$ ($\alpha=A,B$), $\langle O\rangle_{BA}=\langle\phi_j^B(\mathbf{r})|O|\phi_j^A(\mathbf{r}-\mathbf{d}_j)\rangle$, and $M_\alpha=\langle s_\alpha|x|p_{x\alpha}\rangle$. We have chosen j along the (111) direction and $j'\neq j$, s_α and $p_{x\alpha}$ are the atomic orbitals and V is the volume of the solid. $f_{1j}, f_{2j}, \ldots$ are functions of λ, S, and $\cos(\mathbf{k}\cdot\mathbf{d}_j)$ involving summation, over $\mathbf{k}$. We note that in the expression for T [Eq. (12)] the first, fifth, and sixth terms are contributions due to the matrix elements between intrasite hybrids while the second, third, and fourth terms are contributions due to matrix elements between hybrids of adjacent sites forming a bond. In the case of homopolar semiconductors ($\lambda=1$, $\langle x^2\rangle_B=\langle x^2\rangle_A$, and $M_B=M_A$), the first part of the fourth and fifth terms and the sixth term vanish. In the case of heteropolar semiconductors,[15] such as III-V indium compounds, ionicity plays an important role in the results of $\epsilon_1(0)$. Due to specific dependence of λ of different terms in Eq. (12), the first term of the first group of terms predominates over all the other terms yielding maximum anionic contribution to the dielectric constant. We note that our expression for $\epsilon_1(0)$ is independent of the choice of the origin and is free from any scaling parameter. However, in the Harrison's bond orbital model[8,9] an arbitrary scaling factor γ has been used to fit with the experimental results.

We have calculated $\epsilon_1(0)$ of InP, InAs, and InSb, using Hartree-Fock atomic orbitals from Clementi's table.[16] We have used the spheroidal coordinate transformation technique[17] to calculate the two-site integrals. The coefficients $f_{1j}, f_{2j}, \ldots$ are evaluated by carrying out the $\mathbf{k}$ integration over a sphere of volume equal to that of the Brillouin zone. There is reasonably good agreement between our theoretical results and the experiment. In Table I we present our results of one-site and two-site integrals. In Table II we present the values of d, E_g, λ, and D together with our results for $\epsilon_1(0)$ and the experimental results.[11]

In order to analyze our results, we note that we have made an expansion of the energy gap denominator about the average-energy gap and kept only the first term in the expansion. This approximation, in fact, is a consequence of the steepness and narrowness of the $\epsilon_2(\omega)$ curve and the error involved here has been estimated[7] to be around 10%. In order to estimate the error due to the Hall-Weaire approximation, we note that we have considered the matrix elements between intrasite hybrids (N_i) and the matrix elements between hybrids on adjacent sites forming a bond (O_i). If we would calculate $\epsilon_1(0)$ in a more realistic method, we would have to consider the additional contributions such as matrix elements between hybrids on adjacent sites not forming a bond (P_i) and matrix elements between hybrids on further neighbors (Q_i). We note that in general $N_i > O_i > P_i > Q_i$, a trend which is confirmed by the earlier calculation of matrix elements of the Hamiltonian.[7,18] Since the contribution of O_i terms in the present calculation of $\epsilon_1(0)$ is only 8%, we estimate from the above analysis that the error due to neglect of P_i and Q_i terms, i.e., due to the Hall-Weaire approximation, is very small and would be around 1% or 2%. We further note that we have not considered the effect of local fields on $\epsilon_1(0)$. However, there is still controversy for[19] and against[20] inclusion of the local field correction to $\epsilon_1(0)$.

Finally we note that the effect of mixing of bonding and antibonding states in the construction of the valence-band states[7] is effective in the case of higher elements where the metallic character is comparatively large. The increasing discrepancy between our results and the experiment, as we go from InP,InAs to InSb, may be accounted for due to the fact that we have not considered band mixing in our formulation.

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