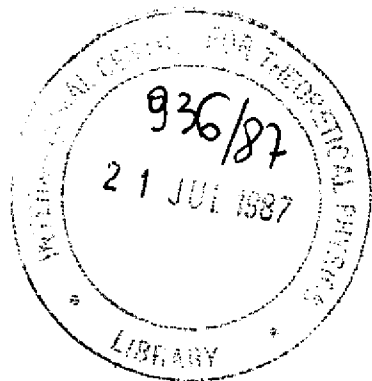


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A LOCALIZED ORBITAL DESCRIPTION
OF IDEAL VACANCIES IN GaP AND GaSb

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A LOCALIZED ORBITAL DESCRIPTION
OF IDEAL VACANCIES IN GaP AND GaSb *

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ABSTRACT

Gaussian orbitals of s and p symmetry and an empirical pseudopotential Hamiltonian is employed for the study of electronic structures of ideal vacancies in GaP and GaSb. A reasonably accurate description of band structures and densities of states are attained.

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I. INTRODUCTION

In recent years, the localized orbital method (LOM) has been developed as a powerful alternative approach to simple empirical tight-binding band structure calculational technique ¹⁾⁻⁵⁾. We have recently extended the method for a study of the electronic structure of ideal vacancies in semiconductors ⁶⁾.

The first part of a defect calculation is to determine the electronic structure of the perfect crystal. The procedure followed to calculate the band structure of the perfect semiconductor consists of the expansion of pseudowave functions in terms of Bloch sums of localized Gaussian orbitals and an empirical fitting of the orbital parameters to known features of the band structure. Thus, the most important feature of LOM is the parametrization of basis orbitals instead of the Hamiltonian matrix elements. The LOM offers some improvements over the matrix element parametrization. The improvements result mainly from the proper handling of the wave function overlap matrix and long range interactions. The good description of both the valance and conduction bands attained here is extremely important in the vacancy problem ⁷⁾.

II. THEORY

Bloch sums are formed from Gaussian orbitals $f_{\mathbf{l}}(\vec{r})$ as,

$$\chi_{\mathbf{l}}^m(\vec{k}, \vec{r}) = \sum_{\mathbf{j}} e^{-i\vec{k} \cdot (\vec{R}_{\mathbf{j}} + \vec{r}_{\mathbf{m}})} f_{\mathbf{l}}(\vec{r} - \vec{R}_{\mathbf{j}} - \vec{r}_{\mathbf{m}}). \quad (1)$$

The basis Bloch functions are expanded in plane waves where the expansion coefficients $\alpha_{\mathbf{l}}(\vec{k})$ turn out to be the Fourier transforms of the localized orbitals,

$$\alpha_{\mathbf{l}}(\vec{k}) = \Omega^{-1} \int e^{-i\vec{k} \cdot \vec{r}} f_{\mathbf{l}}(\vec{r}) d^3r. \quad (2)$$

Since the basis functions are not orthogonal, the eigenvalue equation to be solved is of the form,

$$(H_0 - ES)\lambda = 0, \quad (3)$$

where λ is a column vector whose elements are the expansion coefficients of the eigenfunction

$$\psi_0(\vec{k}, \vec{r}) = \sum_{\mathbf{l}} \lambda_{\mathbf{l}} \phi_{\mathbf{l}}(\vec{k}, \vec{r}), \quad (4)$$

and S is the overlap matrix. The eigenvalue equation (3) is solved by transforming to an orthogonal basis⁸⁾. The Gaussian orbitals,

$$f_s(r) = \left(\frac{2\alpha}{\pi}\right)^{3/4} \exp(-\alpha r^2) , \quad (5)$$

$$f_p(r) = \left(\frac{128\beta^5}{\pi^3}\right)^{1/4} (x,y,z) \exp(-\beta r^2) , \quad (6)$$

are employed in the analytical calculation of the Hamiltonian and overlap matrix elements and the exponents α and β are treated as empirical parameters.

The next step is to calculate the defect induced changes in the electronic structure in terms of the solution obtained above. For this purpose, the Koster-Slater method in the language of Green's functions and scattering theory is employed. The Schrödinger equation for the perturbed crystal is,

$$(H_0 + u)\psi = E\psi , \quad (7)$$

where u is the defect potential. For the states within the band gaps; the Green's operator for the perfect crystal is real and given by

$$G^0(E) = (E - H_0)^{-1} . \quad (8)$$

Eq. (7) can be rewritten in the form

$$[1 - G^0(E)u]\psi = 0 , \quad (9)$$

and it follows that nontrivial solution exists only when the determinant of the operator $1 - G^0U$ is zero.

For the states within the energy bands the definition of G^0 is generalized to

$$G^0(E) = \lim_{\epsilon \rightarrow 0} (E - H_0 + i\epsilon)^{-1} , \quad (10)$$

and the change in the density of states is given by

$$\Delta N(E) = \frac{1}{\pi} \frac{d\delta(E)}{dE} , \quad (11)$$

where the phase shift $\delta(E)$ is

$$\delta(E) = -\tan^{-1}[\text{Im}D(E)/\text{Re}D(E)] , \quad (12)$$

and $D(E)$ denotes the determinant

$$D(E) = \det \|1 - G^0(E)U\| . \quad (13)$$

The isolated vacancy is considered to be the absence of the appropriate atom in the unit cell in an otherwise perfect crystal. U represents a matrix which annuls all the interactions between the atom removed and the rest of the crystal. Thus, an ideal vacancy can be created by setting the diagonal energies corresponding to the atom to be removed to infinity. In this manner no electron is allowed to reach the site of the removed atom. The procedure is extensively discussed in the literature⁹⁾.

III. RESULTS AND CONCLUSIONS

The best converged results for the band structure determines the empirical parameters α and β . The exponent parameters for anions turn out to be larger than that for cations to fit well as can be seen from Table 1. The local pseudopotential form factors used are listed in Table 2. The reciprocal lattice summations are truncated at $G = \sqrt{12}$ in units of $2\pi/a$.

The resulting band structures are shown in Figs. 1 and 2. The corresponding density of states, obtained using tetrahedron method, are shown in Figs. 3 and 4. The results are in good agreement with the empirical pseudo-potential calculations^{10),11)}.

The real parts of s- and p-like Green function, and the vacancy induced changes in the corresponding density of states are calculated as described in Sec. II. The calculated cation and anion ideal vacancy levels A_1 and T_2 symmetry are shown in Table 3, which also includes a comparison with the results of Das Sarma and Madhukar¹²⁾ and Hemstreet¹³⁾. For GaP, there is an overall agreement on the position of Ga vacancy level of A_1 symmetry. Hemstreet finds Ga(T_2) level in the band gap while the present work is in agreement with Ref. 12 and locates this level in the valence band. $P(A_1)$ level is in the band gap, but $P(T_2)$ is found to be in the conduction band in contrast to Das Sarma and Madhukar who locates it within the band gap at 1.93 eV close to the conduction band. Our results for cation and anion vacancy levels in GaSb are in better agreement with Das Sarma and Madhukar.

It is thus reasonable to conclude that LOM is a useful technique to study the electronic structure of pure and doped semiconductors. Especially the resulting pseudopotential-like band structure is an important improvement for any defect calculation. In addition, one has the wavefunctions ready to be used in the calculation of other physical properties like the optical ones.

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TABLE 1

Orbital parameters in atomic units.
c: cation, a: anion

Element	α_c	β_c	α_a	β_a
GaP	0.080	0.070	0.117	0.107
GaSb	0.062	0.055	0.088	0.080

TABLE 2

Symmetric and antisymmetric pseudopotential form factors in Rydberg units. 3, 8, 11 refer to G^2 values in units of $(2\pi/a)^2$, where a is listed in the last column in Angstrom units.

Element	V_S^3	V_S^8	V_S^{11}	V_A^3	V_A^8	V_A^{11}	a
GaP	-0.225	0.038	0.070	0.122	0.070	0.025	5.45
GaSb	-0.220	0.008	0.047	0.050	0.040	0.005	6.09

TABLE 3

Ideal vacancy energy levels in eV, with respect to the top of valence band.

Element	Ga(A_1)	Ga(T_2)	P(A_1)	P(T_2)
GaP				
Ref. 12	v.b.	v.b.	1.75	1.93
Ref. 13	-0.60	0.50	-	-
Present	v.b.	-0.38	0.70	c.b.
GaSb				
Ref. 12	v.b.	v.b.	0.56	0.76
Present	-0.73	-0.04	0.02	0.75

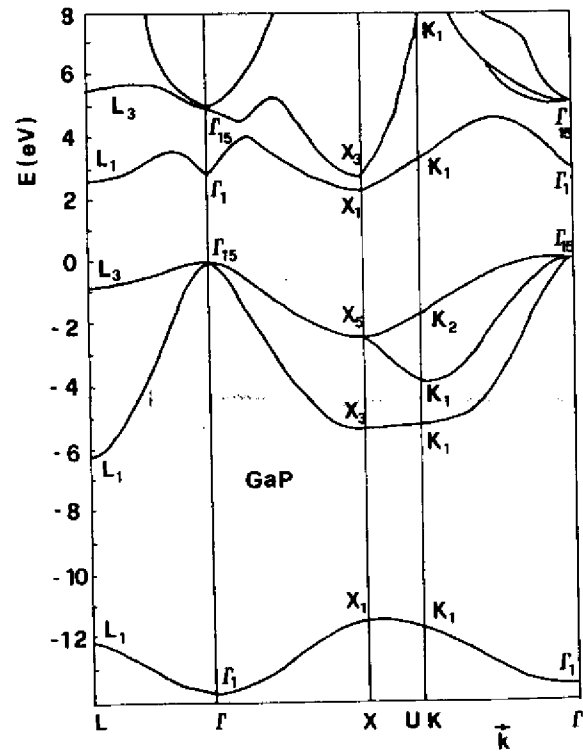


Fig. 1 The band structure of GaP.

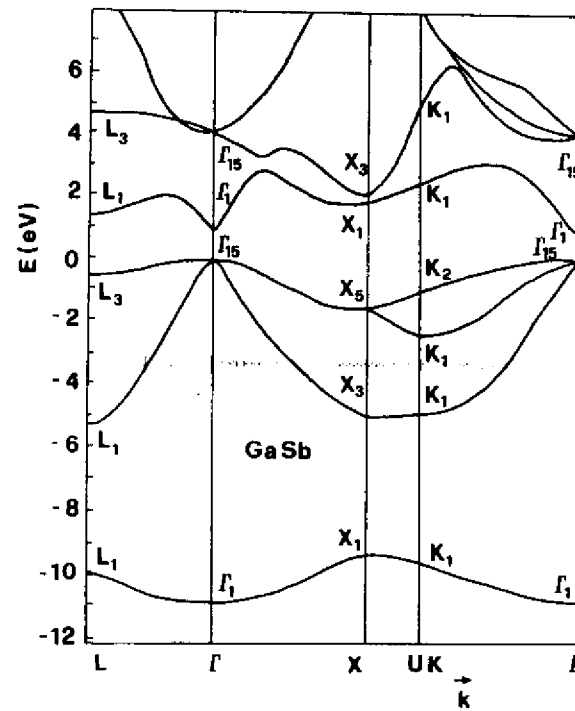


Fig. 2 The band structure of GaSb.

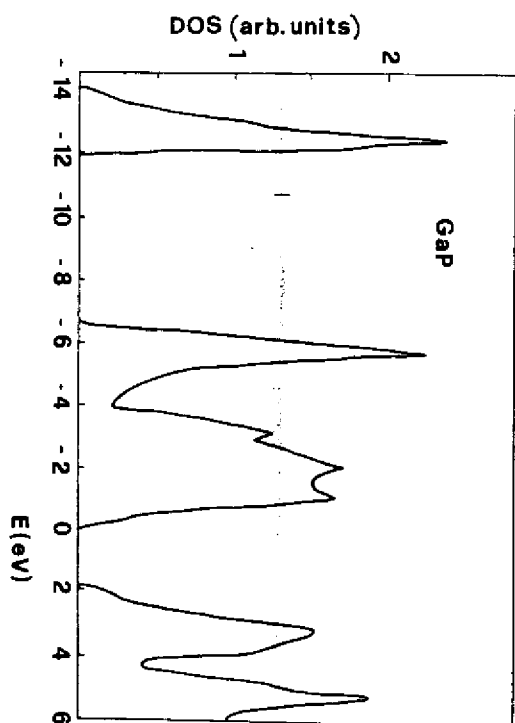


Fig. 3 The density of states of GAP.

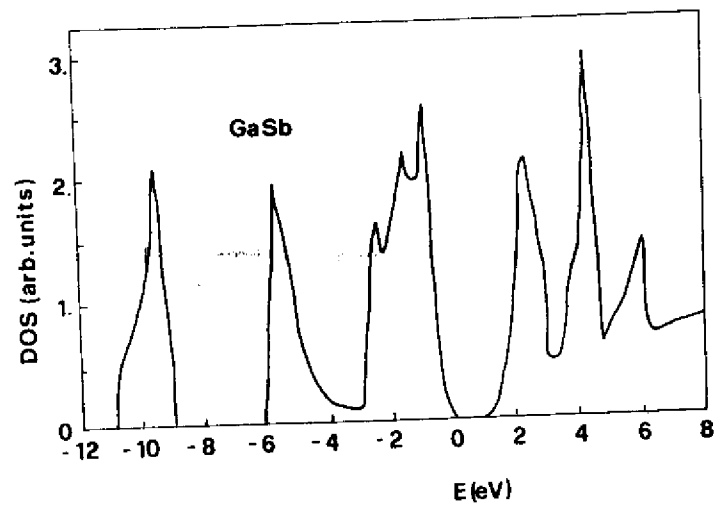


Fig. 4 The density of states of GaSb.