

CHANGING IN THE DENSITY OF STATES CAUSED BY VACANCY IN GaP AND InP

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A study of ideal-vacancy induced deep levels and changing in the density of states in two III—V compound semiconductors (GaP and InP) is presented. The Koster-Slater Green's-function technique is used in conjunction with a linear combination of atomic orbitals description of the electronic structure of the perfect solid.

Introduction

The electronic structure of localized defects in pure and III—V compound semiconductors is of crucial interest in the understanding of optical and electrical properties of a class of materials of major importance in most field of pure and applied solid-state physics. Excellent review of the various methods for the study of deep-level impurities and defects has been published by PANTELIDES [1].

In this paper the Green's-function method has been used to study the ideal-vacancy-induced deep levels and the change in the density of states in GaP and InP for both cation and anion vacancy.

In the calculation Koster and Slater method has been applied. They showed [2] that the electronic energy levels introduced in the band gaps by a localized perturbation could be calculated from a knowledge of the Green's function for the perfect crystal and the matrix elements of the potential, both calculated in the Wannier representation.

The method was developed further by CALLAWAY [3] and calculations of the electronic states in the band gap have been performed for the vacancy [4] and divacancy [5] of Si in the Wannier representation. The numerical determination of Wannier function turned out to be very tedious and difficult and for this reason only a few subsequent calculations have been made [6].

LANOO AND LENGART [7] observed that the Koster—Slater method can be applied using a conveniently chosen localized basis set. They performed a semiempirical tight binding band structure calculation for Si. The ideal vacancy was defined by removing all the Hamiltonian matrix elements between orbitals localized about the central atom with all basis states describing the system.

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This method has been extended by BERNHOLC and PANTELIDES [8], and our calculation is based on this technique.

The outline of the development is as follows. In section A the tight binding formalism is described. Section B contains the Green's function in LCAO-basis. In section C the ideal vacancy potential is defined and section D contains the numerical results.

A. Tight binding formalism

A brief review of the Linear Combination of Atomic Orbitals (LCAO) Tight Binding Method will be given because the bulk solid electronic structure is calculated within the framework of this approximation [9].

Atomic orbitals are symbolized by $\varphi_\mu(\vec{r} - \vec{R}_n^\alpha)$ where μ signifies both angular and spin angular momentum quantum numbers of the atomic wave function and \vec{R}_n^α is the position of the α th atom in the n th primitive cell. Bloch sums, $\Phi_\mu^\alpha(\vec{k}, \vec{r})$ are formed by taking combinations of each of these atomic orbitals in each primitive cell, with the coefficients being fixed by the periodicity of the lattice:

$$\Phi_\mu^\alpha(\vec{k}, \vec{r}) = N^{-1/2} \sum_{n=1}^N e^{i\vec{k}\cdot\vec{R}_n^\alpha} \varphi_\mu(\vec{r} - \vec{R}_n^\alpha), \quad (1)$$

where the summation is over primitive cells. The perfect crystal wave functions, $\Psi_j^0(\vec{k}, \vec{r})$ are then linear combinations of the above Bloch functions:

$$\Psi_j^0(\vec{k}, \vec{r}) = \sum_{\mu, \alpha} C_\mu^\alpha(j, \vec{k}) \Phi_\mu^\alpha(\vec{k}, \vec{r}), \quad (2)$$

where j signifies the band index and $C_\mu^\alpha(j, \vec{k})$ are determined by minimizing the expectation value of the Hamiltonian. Solving the resulting secular equations,

$$\sum_{\mu, \alpha} \left(\sum_n e^{-i\vec{k}(\vec{R}_n^\alpha - \vec{R}_1^\beta)} \langle \varphi_\mu(\vec{r} - \vec{R}_n^\alpha) | H^0 | \varphi_\nu(\vec{r} - \vec{R}_1^\beta) \rangle - E_j(\vec{k}) \delta_{\alpha\beta} \delta_{\mu\nu} \right) C_\mu^\alpha(j, \vec{k}) = 0 \quad (3)$$

we get the j th band energy at wave vector \vec{k} , $E_j(\vec{k})$ and the expansion coefficients, $C_\mu^\alpha(j, \vec{k})$.

B. Green's function

Let H^0 be the perfect crystal Hamiltonian and V the vacancy potential, then the Hamiltonian of the crystal consisting of the vacancy can be written as

$$H = H^0 + V. \quad (4)$$

The Green operator of the perfect crystal's Schrödinger equation is:

$$G^0(E) = \lim_{\epsilon \rightarrow 0^+} (E - H^0 + i\epsilon)^{-1}. \quad (5)$$

The Schrödinger equation for the imperfect crystal can then be replaced by the Lippmann—Schwinger [10] equation

$$\Psi_j(\vec{k}, \vec{r}) = \Psi_j^0(\vec{k}, \vec{r}) + G^0(E)V\Psi_j(\vec{k}, \vec{r}), \quad (6)$$

or equivalently

$$[1 - G^0(E)V]\Psi_j(\vec{k}, \vec{r}) = \Psi_j^0(\vec{k}, \vec{r}). \quad (7)$$

In the band gap $\Psi_j^0(\vec{k}, \vec{r}) \equiv 0$, therefore the condition for the existence of a bound state becomes

$$D = \det \|1 - G^0(E)V\| = 0. \quad (8)$$

Within the energy bands of the perfect crystal D is nonzero and a phase shift [3] can be defined as follows:

$$\delta(E) = -\tan^{-1} \frac{\text{Im } D(E)}{\text{Re } D(E)}. \quad (9)$$

It can be shown [3] that the change in the density of states is given by

$$\Delta N(E) = \pi^{-1} \frac{d\delta(E)}{dE}. \quad (10)$$

$G^0(E)$ can also be expanded in the $\Psi_j^0(\vec{k}, \vec{r})$ basis set:

$$G^0(E) = \sum_{j, \vec{k}} \frac{|j, \vec{k}\rangle \langle j, \vec{k}|}{E - E_j(\vec{k}) + i\epsilon}. \quad (11)$$

Using Eq. (2) an expansion in the (μ, α) basis set is

$$G_{\mu\alpha n, \nu\beta m}^0 = N^{-1} \sum_{j, \vec{k}} \frac{C_{\mu}^{\alpha}(j, \vec{k}) C_{\nu}^{\beta*}(j, \vec{k}) e^{-ik(R_m^{\beta} - R_n^{\alpha})}}{E - E_j(\vec{k}) + i\epsilon}, \quad (12)$$

where N is the number of the unit cells.

C. The Ideal Vacancy Potential

The ideal vacancy is viewed as the absence of the appropriate atom in the n th unit cell leaving all other atoms at the same positions, the atomic-like orbitals are retained on all other atoms, and their interactions are assumed unaltered. As we have seen in part B Eq. (8) is the condition that must be satisfied for a bound state to exist. In the (μ, α) LCAO basis it becomes

$$\det \|\delta_{\mu\alpha, \nu\beta} - \sum_{\mu'\alpha'} G_{\mu\alpha, \mu'\alpha'}^0 V_{\mu'\alpha', \nu\beta}\| = 0 \quad (13)$$

If the functions φ_{μ}^{α} are localized about atomic site and the perturbation potential V has a finite range the matrix element $V_{\mu'\alpha', \nu\beta}$ will be nonzero if both φ_{μ}^{α} and φ_{ν}^{β} overlap with the potential and the size of the determinant reduces to the size of the nonzero part of the potential matrix [2]. The V for ideal vacancy within the tight-binding description using large cluster [11] represents a matrix which annuls all the interaction between the atom placed at vacancy site and all other atoms of the solid. In this method the perfect crystal Hamiltonian's matrix form is sheared four blocks (Fig. 1.a) where the vacancy site is taken to be X and \mathbf{H}_X^0 is the $m * m$ submatrix and m is the number of orbitals chosen for atom removed to form vacancy, and the imperfect crystal Hamiltonian is $\mathbf{H} = \mathbf{H}_1$. To achieve that let \mathbf{H} and \mathbf{H}^0 be of the same size,

\mathbf{H} is rewritten in the form of Fig 1b, where E_0 is arbitrary chosen outside the range of interest and since $\mathbf{V}=\mathbf{H}-\mathbf{H}^0$, \mathbf{V} has the form of Fig. 1c. An equivalent way to obtain a matrix representation of \mathbf{V} is to take the limit $E_0 \rightarrow \infty$ and use arbitrary matrices in the off-diagonal blocks. This can't change the eigenvalues of \mathbf{H} [8]. Choosing \mathbf{H} in the form of Fig. 1.d where $\mathbf{M}=\mathbf{H}_x^0+E_0\mathbf{1}$ with $E_0 \rightarrow \infty$, we obtain for \mathbf{V} (Fig. 1.e.)

$$\begin{array}{ccc} \mathbf{H}^0 = \begin{pmatrix} \mathbf{H}_x^0 & \mathbf{H}_A^0 \\ \mathbf{H}_A^0 & \mathbf{H}_1^0 \end{pmatrix} & \mathbf{H} = \begin{pmatrix} E_0\mathbf{1} & 0 \\ 0 & \mathbf{H}_1 \end{pmatrix} & \mathbf{V} = \begin{pmatrix} -\mathbf{H}+E_0\mathbf{1} & -\mathbf{H}_A^0 \\ -\mathbf{H}_A^0 & 0 \end{pmatrix} \\ a & b & c \end{array}$$

$$\begin{array}{cc} \mathbf{H} = \begin{pmatrix} \mathbf{M} & \mathbf{H}_A^0 \\ \mathbf{H}_A^0 & \mathbf{H}_1 \end{pmatrix} & \mathbf{V} = \begin{pmatrix} E_0\mathbf{1} & 0 \\ 0 & 0 \end{pmatrix} \\ d & e \end{array}$$

Fig. 1.

The net result is that no electron is allowed to reach the site of this atom. Since the perturbation matrix has the above form and the matrix of the Green's operator is

$$\mathbf{G}^0 = \begin{pmatrix} \mathbf{G}_x^0 & \mathbf{G}_A^0 \\ \mathbf{G}_A^0 & \mathbf{G}_1^0 \end{pmatrix},$$

the matrix of the operator $\mathbf{1}-\mathbf{G}^0\mathbf{V}$ becomes

$$\mathbf{1}-\mathbf{G}^0\mathbf{V} = \begin{pmatrix} \mathbf{1}-\mathbf{G}_x^0 E_0 & 0 \\ \mathbf{G}_A^0 E_0 & \mathbf{1} \end{pmatrix}$$

From this it follows that

$$\det \|\mathbf{1}-\mathbf{G}^0\mathbf{V}\| = \det \|\mathbf{1}-\mathbf{G}_x^0 E_0\|, \quad (14)$$

so that the size of the determinant reduces to the size of the nonzero part of the potential matrix.

D. Calculations and results

In the present study s , p_x , p_y , p_z atomic orbitals were used, which, combined with the fact that GaP and InP have two atoms in the unit cell, yield an 8×8 secular matrix for the calculation of the band structure for the ideal crystal (Four valence and the four lowest conduction bands can be obtained).

For numerical calculations of the energy levels of the ideal vacancy we need to compute the Green's-function matrix elements $G_{\mu\mu}^0(E)$ on the atom X where $\mu=s$ or p and

$$G_{\mu\mu}^0(E) = \lim_{\epsilon \rightarrow 0^+} \sum_{j,\bar{k}} \frac{C_\mu(j,\bar{k})C_\mu^*(j,\bar{k})}{E-E_j(\bar{k})+i\epsilon}. \quad (15)$$

This expression can also be written as follows

$$G_{\mu\mu}^0(E) = \lim_{\varepsilon \rightarrow 0^+} \int \frac{dE'}{E - E' + i\varepsilon} C_{\mu\mu}(E'), \quad (16)$$

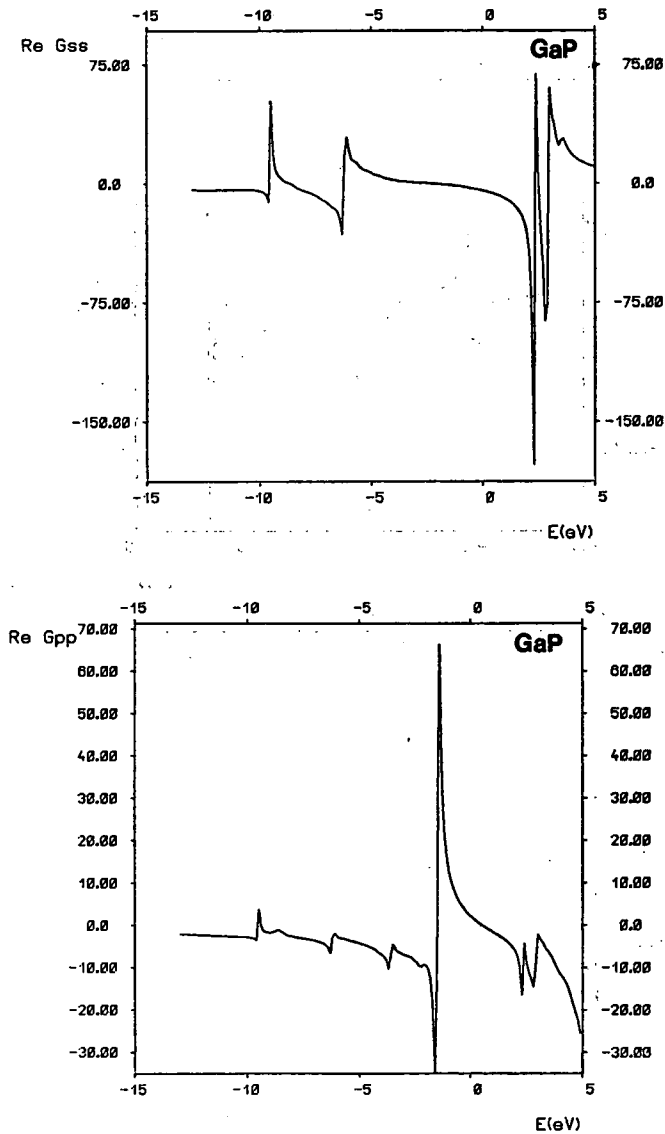


Fig. 2. Real parts of $G_{ss}^0(E)$ and $G_{pp}^0(E)$ of GaP in the case of cation vacancy.

where the quantity $C_{\mu\mu}(E')$ is given by

$$C_{\mu\mu}(E') = \sum_{j,\vec{k}} C_{\mu}(j, \vec{k}) C_{\mu}^*(j, \vec{k}) \delta(E' - E(j, \vec{k})). \quad (17)$$

Using the Dirac identity (15) becomes

$$G_{\mu\mu}^0(E) = P \int \frac{C_{\mu\mu}(E')}{E - E'} dE' - i\pi C_{\mu\mu}(E). \quad (18)$$

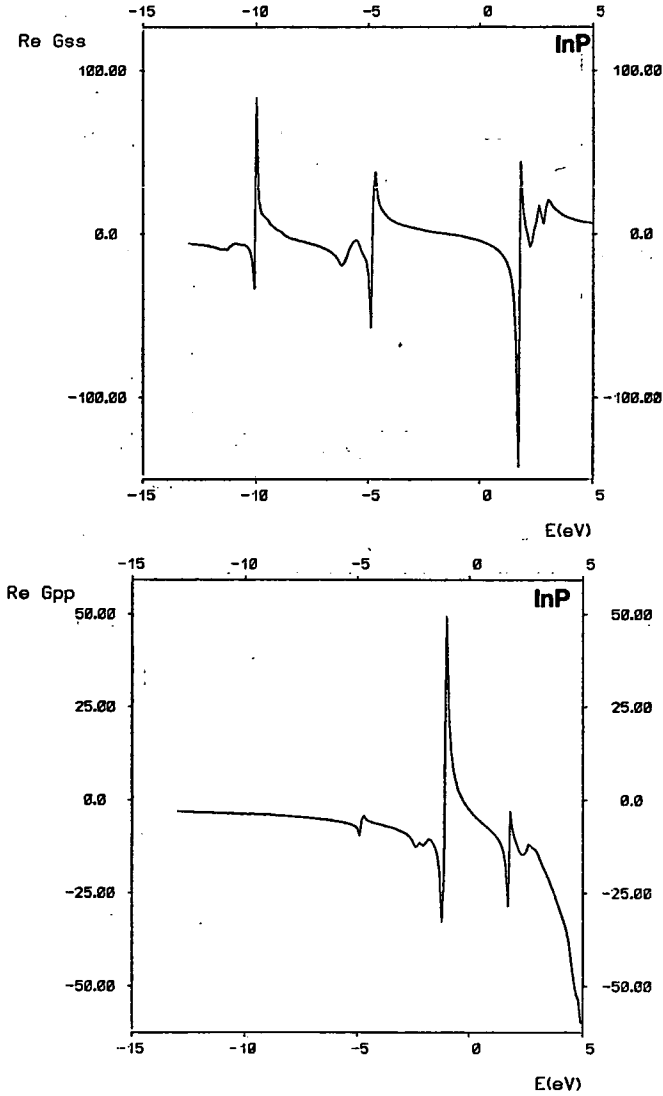


Fig. 3. Real parts of $G_{ss}^0(E)$ and $G_{pp}^0(E)$ of InP in the case of cation vacancy.

For our present calculations we have used the method of GILAT and RAUBENHEIMER [12] to evaluate the integral (17) for $C_{\mu\mu}(E')$. Principal value integrals were evaluated using the identity [13]

$$P \int_a^b \frac{g(E')}{E-E'} dE' = \int_a^b \frac{g(E')-g(E)}{E-E'} dE' - g(E) \ln \frac{b-E}{E-a}. \quad (19)$$

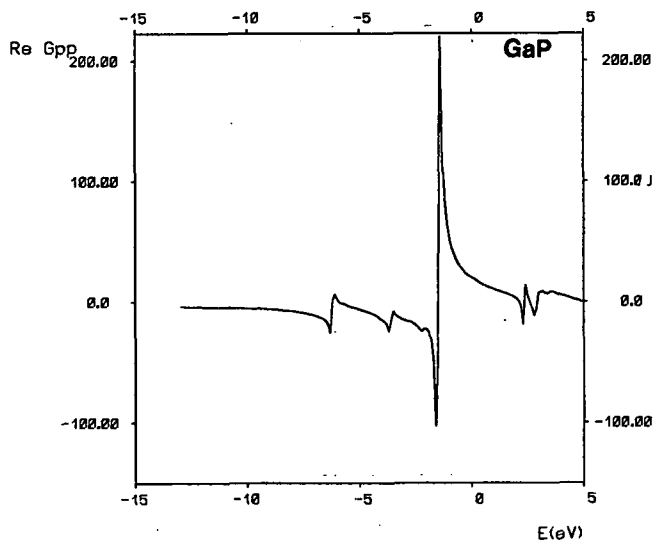
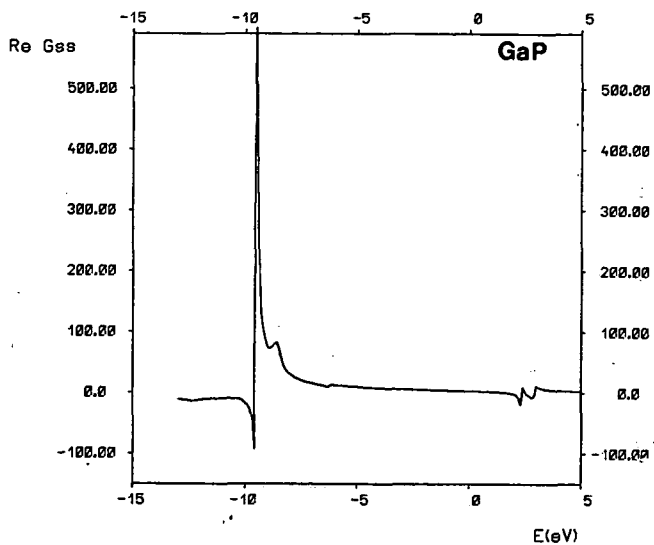


Fig. 4. Real parts of $G_{ss}^0(E)$ and $G_{pp}^0(E)$ of GaP in the case of anion vacancy.

Having evaluated the real parts of $G_{\mu\mu}^0(E)$, their zeros within the band gaps were located and identified as bound states. The changes in the densities of states within the energy bands were then evaluated using Eq. (10).

Calculations have been carried out for the ideal vacancy in GaP and InP. The parameterization of the energy bands of these materials is that of das SARMA and MADHUKAR [14] which retains the first and second nearest-neighbor interactions.

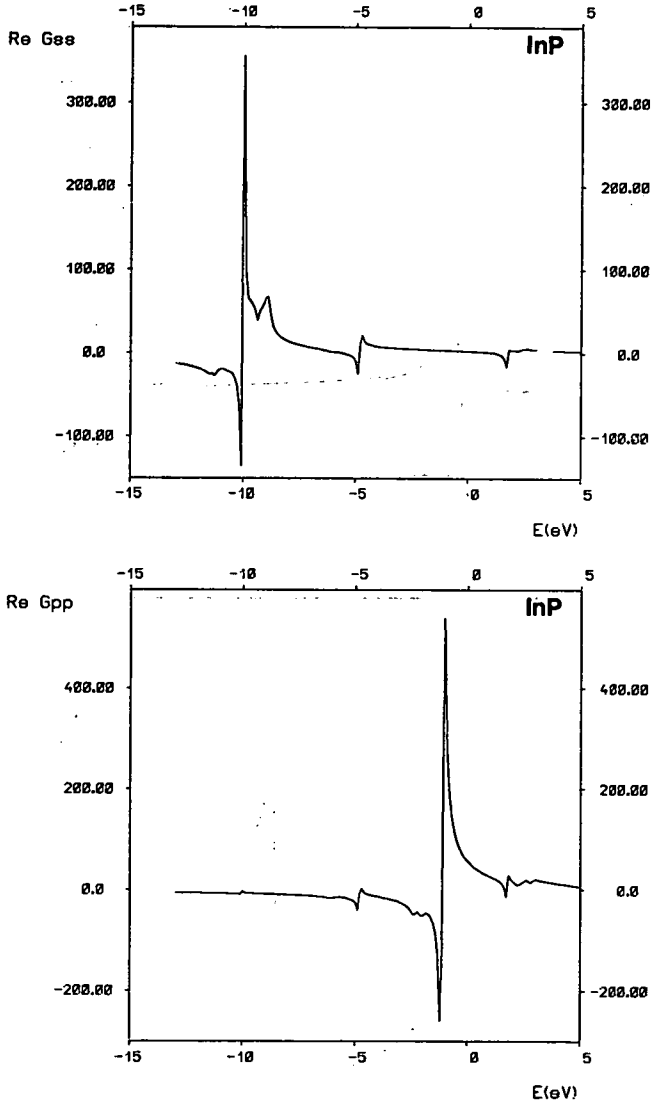


Fig. 5. Real parts of $G_{ss}^0(E)$ and $G_{pp}^0(E)$ of InP in the case of anion vacancy.

This parameterization were used to describe only the vacancy bound states of the same materials.

Figs. 2—3 show the real parts of Green's functions for GaP and for InP in the case of Ga and In vacancies, respectively. Figs. 4—5 show the real parts of Green's functions for GaP and for InP in the case of anion vacancies, respectively. The zeros

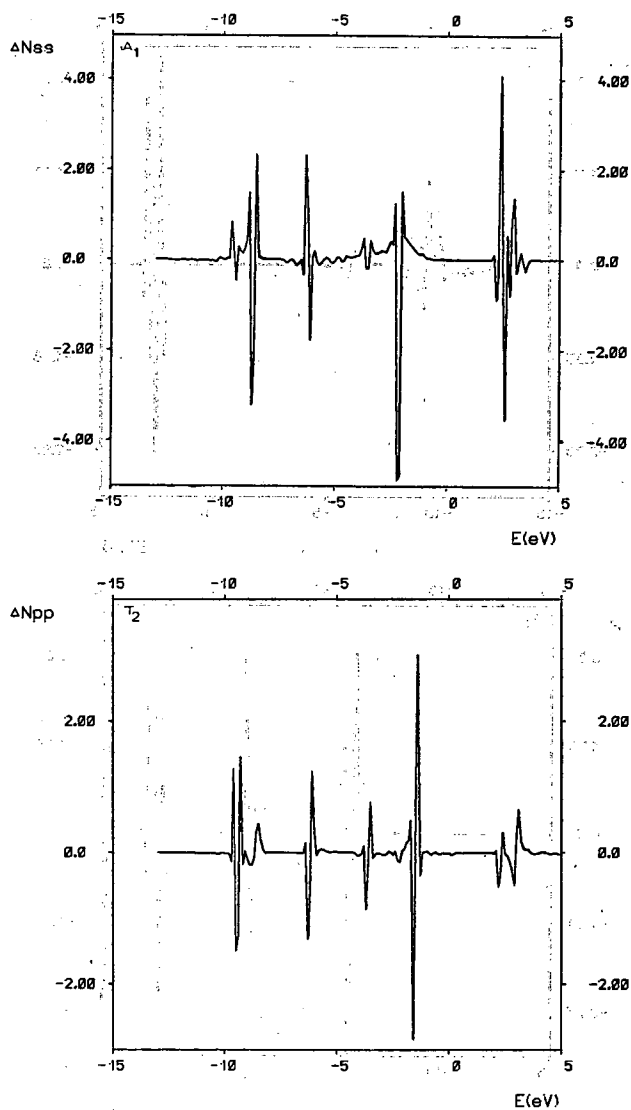


Fig. 6. A_1 and T_2 contributions to the change in density of states induced by an Ga vacancy in GaP.

of G_{ss}^0 in the regions of band gaps correspond to bound states of A_1 symmetry and the zeros of G_{pp}^0 in the regions of the band gaps correspond to bound states of T_2 symmetry.

The positions of the bound states within the gaps of materials are given in Table I. The changes in the densities of states are given in Figs. 6—9.

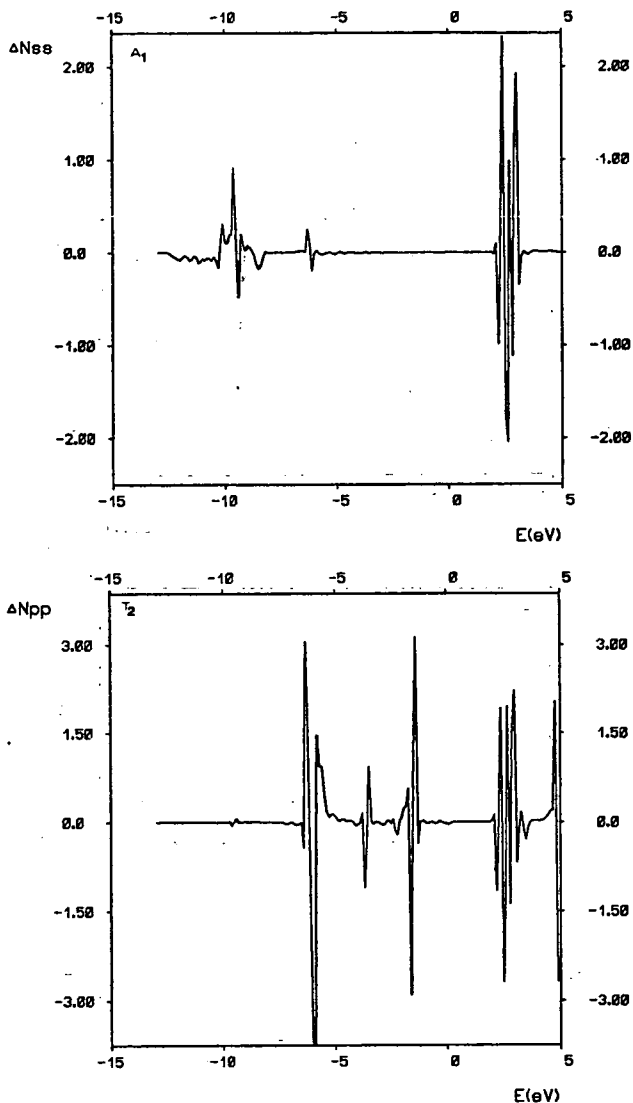


Fig. 7. A_1 and T_2 contributions to the change in density of states induced by an P vacancy in GaP.

Conclusion

The modified Koster-Slater technique has recently been widely used to calculate localized deep levels in semiconductors. A related quantity, the change in the density of states is investigated in this paper. The optical properties of the deep levels, which are of most important in many measurements and applications do depend on the

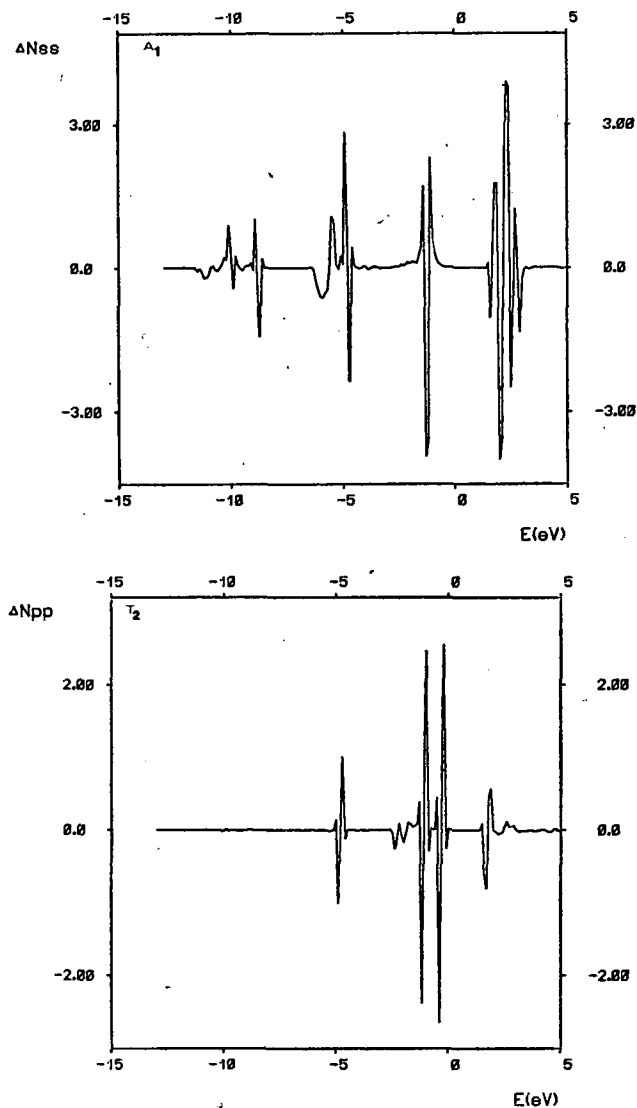


Fig. 8. A_1 and T_2 contributions to the change in density of states induced by an In vacancy in InP.

band states too from where transition takes place. From our calculations it is seen that in case of a reasonable "localized" transition significant structure can occur due to the sharp peaks in the change of the density of states. This, similarly to the "internal" transitions of the d-electrons in the crystal field for transition metal impurities might rise to unexpected structures even in case of an ordinary deep level if this energy difference is smaller than the forbidden gap. It remains to find an appropriate system where this effect should be seen experimentally.

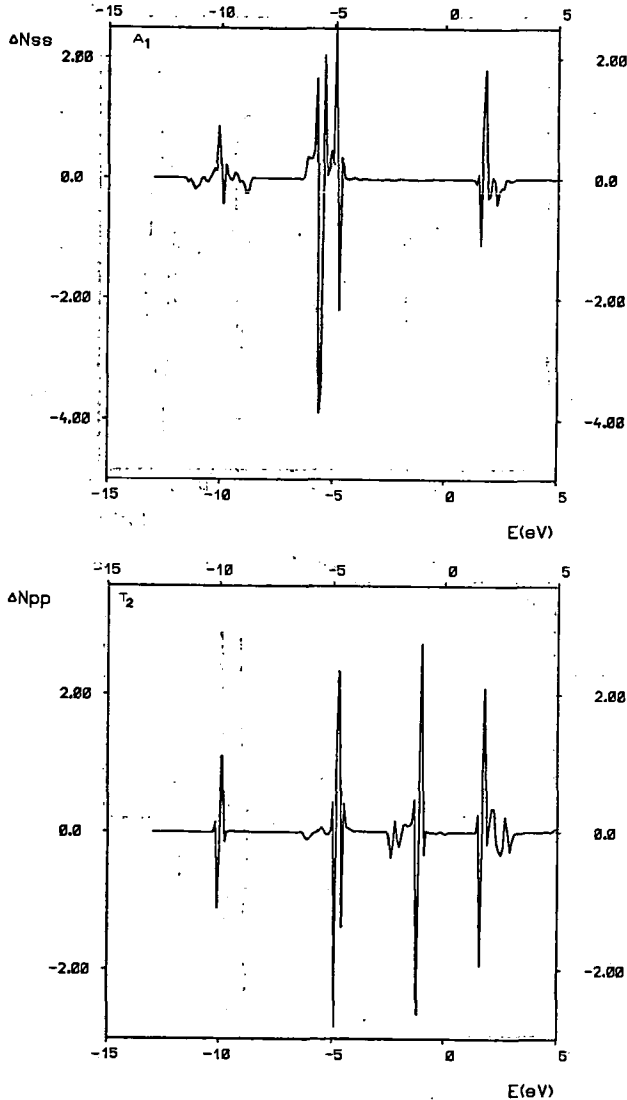


Fig. 9. A_1 and T_2 contributions to the change in density of states induced by a P vacancy in InP.

Table I

A_1 and T_2 levels obtained in this work. Energy in eV.
(The energy zero is at the top of the valence band)

	GaP		InP	
	A_1	T_2	A_1	T_2
V_{anion}	1.70	2.0	1.36	1.66
V_{cation}	—	0.5	—	—

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ИЗМЕНЕНИЯ В ПЛОТНОСТИ СОСТОЯНИЙ ВСЛЕДСТВИЕ ВАКАНСИЙ В GaP и InP

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Исследуются глубокие уровни, созданные идеальной вакансией и изменения в плотности состояний в двух III—V полупроводниках (GaP и InP). Используется техника гриновских функций Костера—Слетера вместе с ЛКАО для электронной структуры идеального твердого тела.