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Effects of lattice relaxation on deep levels in semiconductors

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A formalism for phenomenologically including the effects of nearest-neighbor lattice relaxation on deep levels associated with substitutional impurities in semiconductors is outlined and used to investigate such effects in GaP and Si. This approach is an extension of the theory of Hjalmarson *et al.* [Phys. Rev. Lett. **44**, 810 (1980)]. Lattice relaxation is accounted for by characterizing the nearest-neighbor off-diagonal matrix elements of the defect potential by parameters that depend on the impurity- and host-atom bond lengths. For symmetric, "breathing-mode" relaxations, only two parameters are needed, one each for the A_1-symmetric and the T_2-symmetric deep levels. By computing the A_1- or T_2-symmetric levels as a function of the appropriate parameter, the effects of varying amounts of lattice relaxation can be systematically explored. To determine these parameters for a specific impurity-host system, a variation of the inverse bond-length-squared scaling law is used. The results of applying this formalism to several impurities in GaP and Si are presented and compared with experimental data and with other theories.

I. INTRODUCTION

The properties of a semiconductor are influenced by defects which produce deep levels[1-6] in the band gap. Unlike shallow levels,[7] which primarily control the type and magnitude of the conductivity, and which are produced by the long-ranged Coulomb potential of a defect, deep levels primarily control the charge-carrier lifetime and are produced by the central-cell, atomiclike potential associated with a defect. Shallow levels are well described by effective-mass theory.[1,7] On the other hand, there have been many theories of deep levels in semiconductors[1-6] and they are of varying levels of sophistication and accuracy. Furthermore, many of these theories cannot be rigorously compared with experiment because of various simplifying assumptions. For example, the effect of lattice relaxation has often been neglected.[6] In this paper, we outline a simple phenomenological theory of this effect and use it to show how the deep levels of a substitutional impurity are changed by lattice relaxation.

A simple, yet widely used[8-14] deep-level theory was developed several years ago by Hjalmarson *et al.*[6] These workers have shown that the chemical trends in the deep levels of substitutional impurities can be understood using a Koster-Slater[15] model where only the central-cell part of the defect potential is treated and where this potential is modeled by the assumption that it is proportional to the atomic-energy differences of the defect and host atoms. This theory was designed to be a global theory capable of easily predicting trends in deep levels as a function of defect or host. Generalizations of the theory of Hjalmarson *et al.*[6] to treat various types of defects in the bulk and on the surface have been successful in their predictions of such chemical trends in the defect-related properties of numerous materials[8-14] and have often produced results which are in semiquantitative agreement with both experiment[8-14] and more sophisticated theories.[16] Nevertheless, this theory suffers from the drawback that it neglects the effects of lattice relaxation. Thus, while it is useful for predicting chemical trends, its quantitative accuracy is limited.

In the present work, we generalize the theory of Hjalmarson *et al.*[6] to include lattice-relaxation effects. A rigorous treatment of these effects would require a total-energy calculation. However, the necessity to perform such a calculation would destroy the simplicity and universality of the theory of Hjalmarson.[6] Our theory circumvents this problem by treating lattice relaxation phenomenologically. It thus requires that the amount of lattice relaxation be either guessed or easily computed from a simple model. The rigor of a total-energy calculation is sacrificed in this manner. In exchange, however, much of the complication of such a calculation is also eliminated. In fact, our formalism retains much of the simplicity and universality of the approach of Hjalmarson *et al.*,[6] while considerably improving its quantitative accuracy. It retains the ability to easily predict chemical trends by treating the diagonal matrix elements of the defect potential using the assumption of the Hjalmarson *et al.*[6] of proportionality to atomic-energy differences. The effects of lattice relaxation are included by characterizing the nearest-neighbor off-diagonal matrix elements of this potential by two phenomenological parameters, one for the A_1-symmetric states and one for the T_2-symmetric states. These parameters depend on the bond lengths of the impurity and host atoms. By computing deep levels of a particular symmetry as a function of the appropriate parameter, trends with varying amounts of lattice relaxation can be systematically explored. To determine these parameters for specific impurities, our formalism uses a generalization of Harrison's[17] inverse bond-length-squared scaling law for off-diagonal tight-binding matrix elements.

We compare the results of our theory to experimental data for the deep levels produced by N and O substitutional for P in GaP and for the S, Se, and Te deep levels in Si. We find that the inclusion of lattice-relaxation effects considerably improves the agreement between theory and experiment in comparison with the results obtained by the theory without lattice-relaxation included.[6]

Ideas, similar to those presented here, for incorporating lattice-relaxation effects into their theory were discussed by Hjalmarson *et al.*[6] in their original work. Further, they used these ideas to estimate such effects on the deep levels of a few impurities in a few hosts. In the present paper, these ideas are used to develop a general phenomenological theory of lattice-relaxation effects on deep levels and to systematically explore such effects for deep levels in GaP and Si.

A previous generalization of the theory of Hjalmarson *et al.*[6] to include lattice-relaxation effects was made by Talwar, Suh, and Tang[18] by combining ideas similar to those outlined here with a theory of total energies.[19] As just mentioned, inclusion of a total-energy calculation in the problem necessarily makes the theory of Ref. 18 more complicated than that outlined here. We note, however, that despite this fact and despite the fact that second-nearest-neighbor relaxation was included in the more sophisticated theory of Ref. 18, the resulting deep levels fail to improve on the results of Ref. 6 in comparison with experiment.[18]

II. THEORY

A. Background

Following previous work based on the theory of Hjalmarson *et al.*,[6,8–14] we describe the perfect-crystal host Hamiltonian H_0 by using the Vogl *et al.*[20] sp^3s^* semiempirical, nearest-neighbor, tight-binding band-structure model. This Hamiltonian has five states per atom (the four sp^3 states and an excited s^* state) with 13 parameters which were obtained by a fit to pseudopotential band structures.[21] These parameters may be found in Ref. 20. The use of an excited s^* state enables a description of the conduction band which can treat both direct- and indirect-band-gap semiconductors. This model reproduces the principal features of the Si and GaP conduction-band structures, particularly near the Γ and X points of the Brillouin zone. We note in passing that the band structures employed by Talwar, Suh, and Tang[18] were different than those used here.

Here we consider the problem of the calculation of the deep levels produced by neutral, sp^3-bonded, substitutional impurities only. In principle, our formalism could be generalized to treat lattice-relaxation effects for more complicated defects such as pairs[8] and complexes.[9] Also, a generalization to calculate the deep levels due to charged defects and the associated charge-state splittings[16,22] is possible but tedious.

In its original form, the deep-level theory of Hjalmarson *et al.*[6] makes the following approximations concerning the form of the localized, central-cell defect potential. (1) The on-site matrix elements are proportional to the atomic-energy differences of the impurity and the host atoms. (2) Only the nearest-neighbor host atoms around a substitutional impurity are affected by the potential. (3) The effects of lattice relaxation are usually small. As will be discussed in detail below, the off-diagonal matrix elements of the defect potential are a direct measure of this relaxation. This last assumption thus allowed Hjalmarson *et al.*[6] to neglect these matrix elements so that the defect potential became diagonal in the tight-binding basis. In this manner, a simple, global theory of deep levels which could be applied to a large number of defect-host systems and which was capable of predicting a wide variety of chemical trends was constructed. As mentioned above, this theory and its extensions have been successful in such predictions in numerous applications.[8–14,16] Hjalmarson *et al.*[6] estimated that the neglected lattice-relaxation effects should shift their predicted deep levels by a few tenths of an electron volt. The accuracy of their predictions for deep levels of specific defects was thus estimated to be in this range. In the results presented below, we show that lattice-relaxation effects indeed produce shifts in the predicted A_1-symmetric deep levels which are of this order of magnitude. (We also show that such effects are much smaller for T_2-symmetric levels.) Thus, in this sense, the results of the present theory show that the third assumption of the theory of Hjalmarson *et al.*[6] was justified in the context of the development of a global theory. We show below, however, that by treating the off-diagonal matrix elements of the defect potential with a generalization of Harrison's[17] inverse bond-length-squared scaling law combined with a simple covalent radius model,[23] the theory of Hjalmarson *et al.*[6] can be straightforwardly generalized to include lattice-relaxation effects. Further, we also show that the resulting theory retains much of the simplicity and universality of the Hjalmarson *et al.*[6] approach, while considerably improving its accuracy.

The theory of Hjalmarson *et al.*[6] also neglects the splittings produced by the different charge states of a defect. It has been generalized to include such charge-state splitting effects, which have also been found to be on the order of 0.1 eV for the impurities and host materials which have been studied.[16,22] Since we only consider neutral impurities here, such effects will not be considered further. Instead, we focus our attention on lattice-relaxation effects.

When a defect is added to a semiconductor, it will interact with the host, the lattice stability around it will be altered, and the surrounding host atoms will be displaced.[24] Because deep levels are produced by a short-ranged defect potential,[1–6] the distortion of the lattice around a defect will strongly affect them. For a realistic calculation, the effects of lattice relaxation clearly have to be included.

Such effects have been considered in previous tight-binding-based deep-level theories. In particular, as mentioned above, Talwar, Suh, and Tang[18] have generalized the theory of Ref. 6 using a similar approach to that outlined here. In their theory, the off-diagonal matrix elements of the defect potential, and thus the lattice distortions, are determined using a theory of total energies.[19] However, the results of this approach fail to improve upon those of Ref. 6 in comparison with experiment for deep levels in Si and Ge. As we discuss below, our approach uses a simpler method than that of Ref. 18 to determine the defect-potential off-diagonal matrix elements, yet it obtains considerable improvement upon the results of Ref. 6 for predicted deep levels in comparison with experiment. We also note that Singh and Madhukar[25] have developed a tight-binding-based deep-level theory with which one can include lattice-relaxation effects. This theory combines a transfer-matrix technique with ideas similar to those used here to treat the lattice relaxation. Singh and Madhukar[25] have studied the deep levels produced by the arsenic antisite defect in GaAs and by O on the anion site in $GaAs_{1-x}P_x$ using their method, and have found reasonable agreement with data for these cases.

Lattice-relaxation effects have also been included in several self-consistent pseudopotential calculations of deep levels and other defect properties.[26] This approach, while certainly more accurate than that outlined here, has the disadvantage that it requires considerably more computational effort than our formalism. In addition, it is difficult to predict trends with this type of theory. Our approach requires only slightly more computational effort than the original theory of Hjalmarson *et al.*,[6] so that it retains much of its simplicity and ability to predict global chemical trends. To treat substitutional impurities, the computational labor required to implement our theory is comparable to that which is necessary for the treatment of paired defects without lattice relaxation[8] and is less than that required for triplet defects[9] in the same approximation.

B. Deep levels with lattice relaxation

In order to generalize the theory of Hjalmarson *et al.*[6] to include lattice relaxation, we modify their third approximation and allow for nonzero off-diagonal matrix elements of the defect potential. The other two approximations of the theory of Ref. 6 are retained. Since only nearest-neighbor coupling is included in this way, our theory can only account for the relaxation of the nearest neighbors of an impurity. The relaxation of second and higher neighbors could, in principle, be included by a generalization of the present approach to allow for higher-neighbor matrix elements of the defect potential. In a tight-binding picture, where the defect potential formally corresponds to a difference between the matrix elements of the defect containing and perfect host crystals, the nearest-neighbor off-diagonal matrix elements of that potential correspond to differences in the transfer-matrix elements of these two Hamiltonians. Our method exploits this fact to phenomenologically determine the off-diagonal matrix elements of this potential.

For an impurity on the anion site at the origin in a zinc-blende crystal, the defect potential, including the off-diagonal matrix elements which can be used to describe the lattice relaxation, can formally be written as

$$V=\sum_i |ia\mathbf{0}> U_i^a < ia\mathbf{0}| + \sum_{i,j,\mathbf{d}} [\,|ia\mathbf{0}> V_{ij}^{ac} < jc\mathbf{d}| + \text{H.c.}\,] \;, \tag{1}$$

where a and c refer to the anion and cation, $\mathbf{R}=\mathbf{0}$ is the unit cell at the origin, i and j label the orbitals, the sum on $\mathbf{d}$ is taken over the four nearest-neighbor cations, U_i^a is the diagonal matrix element of the potential at the anion site for orbital i, V_{ij}^{ac} is the off-diagonal matrix element of the defect potential which couples the oribital i at the anion site to orbital j at the cation site, and H.c. denotes the Hermitian conjugate. Formally, U_i^a is a difference in the on-site matrix elements of the Hamiltonians for the defect containing and perfect crystals and V_{ij}^{ac} is a difference in transfer matrix elements. For a similar impurity on the cation site, the labels a and c are interchanged in Eq. (1). In Eq. (1), the sums on i and j are taken only over the s, p_x, p_y, and p_z orbitals following previous work.[6,8–14] Also following previous work, we assume that all orientations of the p orbitals have the same defect-potential energies. In the case of a diamond-structure semiconductor like Si, the labels a and c lose their meanings except to denote the atom at the origin and its nearest neighbor.

The Koster-Slater theory[15] is a convenient method for determining the bound-state energies E of the impurity which are produced by the defect potential of Eq. (1). In this method, these energies are given by the solutions to the determinantal equation

$$\det[I-G^0(E)V]=0 \;, \tag{2}$$

where

$$G^0(E)=(E-H_0)^{-1} \tag{3}$$

is the perfect-crystal Green's function, H_0 is the sp^3s^* host Hamiltonian, and I is the identity matrix. The advantage of the Koster-Slater[15] method is that the determinant of Eq. (2) only needs to be evaluated in the subspace of the defect potential. In the present case, this (in general) yields a 20×20 determinant (five atoms and four orbitals, one s and three p, per atom).

This determinant can be simplified by symmetry considerations. The point group for an isolated point defect in a zinc-blende-structure semiconductor is T_d. Point defects with sp^3 hybrid bonding can thus have defect states with either nondegenerate A_1 (s-like) or triply degenerate T_2 (p-like) symmetry. In this paper, we consider only the effects of symmetry conserving, "breathing mode" distortions of the host lattice around the impurity. That is, we assume that the four nearest neighbors to the impurity atom relax either inward or outward in a symmetric fashion so that the T_d symmetry is preserved. In this case, it is easy to show[27] that the block diagonalization of the host Green's function and the subsequent factoring of Eq. (2) into smaller determinants can be done in a manner identical to the procedure for a point defect in the absence of relaxation.[6] The results of this manipulation are that Eq. (2) becomes

$$\det[I_s-G_s^0(E)V_s]\{\det[I_p-G_p^0(E)V_p]\}^3=0 \;, \tag{4}$$

where for $i=s$ and p, $G_i^0(E)$, V_i and I_i are, respectively, the Green's-function submatrix, the defect-potential submatrix, and the unit matrix in the subspace i that results from these operations. In writing Eq. (4) and in what follows, the labels s and p are, respectively, shorthand notation for the A_1- and the T_2-symmetric states. Equation (4) enables one to calculate the deep levels for the A_1 and T_2 states separately. It can also be shown[27] that the defect-potential submatrix of symmetry i has the form

$$V_i = |ia\mathbf{0}> U_i < ia\mathbf{0}| + \sum_{\mathbf{d}} [\,|ia\mathbf{0}> \alpha_i < ic\mathbf{d}| + \text{H.c.}\,] \;, \tag{5}$$

where α_i is a linear combination of the V_{ij}^{ac27} and U_i is a shorthand notation for U_i^a. For impurities on the cation site, the labels a and c are interchanged in Eq. (5).

By combining Eqs. (4) and (5) and treating U_i and α_i as parameters, the deep-level energies for a substitutional impurity can be computed as a function of these quantities. For example, for $\alpha_i = 0$, which corresponds to the case of the theory of Hjalmarson *et al.*[6] with no lattice relaxation, one can use Eq. (4) to generate the deep-level energy E versus diagonal defect-potential energy U_i diagrams which are one of the common results of this theory. For fixed $\alpha_i \neq 0$, such a diagram can also be generated. Similarly, for fixed U_i, one can generate deep-level energy versus α_i diagrams using Eq. (4). As is discussed below, the parameters α_i represent the effects of lattice relaxation on the defect potential. Thus, the generation of such diagrams allows, as is the case with the theory of Hjalmarson *et al.*,[6] the exploration of chemical trends in the deep levels (by varying U_i for fixed α_i). However, it also allows one to explore the trends in the deep levels with varying amounts of lattice relaxation (by varying α_i for fixed U_i).

C. Deep levels for specific impurities

In order to calculate the deep levels of a particular impurity, the parameters U_i and α_i must be specified. For the diagonal-matrix elements, we use the empirical rule developed by Hjalmarson *et al.*[6] that these quantities are proportional to the atomic-energy differences of the impurity atom and the replaced host atom. That is,

$$U_i = \beta_i(\varepsilon_I^i - \varepsilon_H^i) \;, \tag{6}$$

where $i = s$ and p, ε_I^i and ε_H^i are the atomic energies of the impurity atom and the host atom for orbital i and β_i is a constant determined for orbital i by a fit to experimental data.[6] In Ref. 6 it is shown that $\beta_s = 0.8$ and $\beta_p = 0.6$.

Our model for the off-diagonal matrix elements of the defect potential is based upon Harrison's[17] model for the nearest-neighbor transfer-matrix elements of the host Hamiltonian. In this model, it is shown that these scale approximately as the inverse bond-length squared.[17] The transfer-matrix elements in the sp^3s^* model which we use to characterize the host crystal also have this property.[20] We assume that this same scaling rule holds for the transfer-matrix elements of both the defect containing and the perfect crystal. Since the off-diagonal matrix elements of the defect potential are differences in such transfer matrix elements, this allows them to be written as

$$\alpha_i = -C_i[(d_I)^{-2} - (d_H)^{-2}] \;, \tag{7}$$

where d_I and d_H are the bond lengths of the impurity and the host atoms, respectively, and the first minus sign has been chosen for convenience. A similar form for the off-diagonal matrix elements was assumed by Talwar, Suh, and Tang.[18] Following Vogl, Hjalmarson, and Dow,[20] C_i is a proportionality constant which depends on i but which is independent of the material. We assume that this quantity is the same for the imperfect and perfect crystals. The values of C_i, have been determined empirically in Ref. 20 to be $C_s = 10.5$ eV Å^2 and $C_p = -3$ eV Å^2.

It is clear from Eq. (7) that the off-diagonal matrix element α_i is a measure of the lattice relaxation produced in a state of symmetry i by an impurity. From that equation and the numerical values of the C_i, it can be seen that for outward relaxation ($d_H < d_I$), α_s (α_p) is positive (negative) while for inward relaxation ($d_H > d_I$) α_s (α_p) is negative (positive). Lattice relaxation can thus be completely characterized in both magnitude and direction by the two parameters α_s and α_p.

In order to calculate α_i for a particular impurity, the bond lengths d_I and d_H must be specified. The host bond length d_H is well known for all of the common semiconductors[17] and experimental data can thus be used for this purpose. Our model for the impurity bond length d_I utilizes the concept of covalent radius,[17,23] originally proposed by Pauling.[28] We assume that

$$d_I = r_I + r_H \;, \tag{8}$$

where r_I and r_H are, respectively, the covalent radii of the impurity atom and the *nearest-neighbor* host atom. Such radii are tabulated for most atoms.[17,23] We believe that Eq. (8) is a reasonable assumption for a number of reasons. First, a similar assumption for the host yields bond lengths within 1% of the experimental values. In addition, the d_I computed via Eq. (8) are within 1% of the experimental values for the appropriate solid (if it exists) formed from the impurity atom-host atom molecular unit. Furthermore, molecular-dynamics calculations, discussed elsewhere,[29] which use forces obtained from the electronic structure via the Hellmann-Feynman theorem[30] yield relaxed impurity bond lengths which are within 10% of those predicted by Eq. (8) for the impurity-host systems considered here. Finally, the values of d_I obtained from Eq. (8) are also within 5% of those obtained in the valence force model of Martins and Zunger.[31]

The special case of oxygen substitutional for P in GaP needs to be discussed. For this case, Eq. (8) gives $d_I = 1.92$ Å, similar to the Ga—O bond length in Ga_2O_3,[32] which corresponds to inward relaxation of the nearest-neighbor Ga atoms. However, several years ago, Morgan[33] argued that because of the weakness of the Ga—O bond in GaP:O, the Ga atoms relax away from the oxygen impurity. A similar model was proposed earlier by Jaros[2] and later given a semiquantitative justification by Baraff, Kane and Schlüter.[34] If the relaxation for GaP:O is indeed outward, one would clearly expect d_I for this impurity-host system to be greater than the simple covalent radii the model predicts. Morgan has estimated that the Ga—O bond in GaP:O is about 0.85 Å

TABLE I. Bond lengths, covalent radii, and parameters α for various impurities in GaP and Si.

Host-impurity system	d_H (Å)[a]	r_H (Å)[b]	r_I (Å)[b]	d_I (Å)	α_s (eV)	α_p (eV)
GaP:N	2.36	1.26	0.70	1.96	−0.85	0.24
GaP:C			0.77	2.03	−0.66	0.19
GaP:Sb			1.36	2.62	0.36	−0.10
GaP:O[c]			0.66	1.92	−0.96	0.27
GaP:O[d]			0.66	2.77	0.52	−0.15
Si:S	2.35	1.17	1.04	2.21	−0.25	0.07
Si:Se			1.14	2.31	−0.07	0.02
Si:Te			1.32	2.49	0.21	−0.06
Si:N			0.70	1.87	−1.10	0.31
Si:C			0.77	1.94	−0.89	0.25

[a]Reference 17.
[b]Refernece 23.
[c]Without correction from Ref. 33.
[d]With correction from Ref. 33.

larger than in Ga_2O_3, or $d_I = 2.77$ Å, which corresponds to outward relaxation. We have calculated deep levels for GaP:O using both the covalent radius model for d_I and the d_I with Morgan's[33] correction. As shown below, we find that the corrected bond length gives much better agreement with experiment. The molecular-dynamics calculations,[29] mentioned above, yield $d_I = 2.78$ Å, which also tends to support Morgan's model.[33]

In Table I, we show the values of the host and impurity bond lengths we have used and the resulting values for α_s and α_p for various impurities substitutional for P in GaP and for various impurities in Si. It can be seen, either from Table I or merely by noticing the relative sizes of C_s and C_p, that $|\alpha_p| \ll |\alpha_s|$ for all impurity-host systems considered. Since the α_i are a measure of the effect of lattice relaxation on deep levels, this effect should thus be much more important for s-like (A_1) states than for p-like (T_2) states. Due to this fact, only the results of the calculation of A_1-symmetric deep levels are discussed below and the T_2 states will not be discussed further.

III. RESULTS

A. Chemical trends and trends with varying amounts of relaxation

We have used the model described above to calculate the effects of lattice relaxation on the A_1-symmetric deep levels produced by substitutional impurities in GaP and Si. Typical results are shown in Figs. 1–4. Figures 1 and 2 display results for deep levels in GaP, while Figs. 3 and 4 show results for Si. In all figures, we have used the symbol α as an abbreviation for the parameter α_s discussed in Sec. II.

Figures 1–3 show diagrams for the deep-level energy E versus the diagonal impurity s potential U_s for the deep levels produced by impurities substitutional for the appropriate host atom. Such results for impurities on the anion site (substitutional for P) in GaP, for impurities on the cation site (substitutional for Ga) in GaP, and for impurities in Si are shown in Figs. 1, 2, and 3, respectively. The various curves in these figures correspond to results obtained for the various values of the parameter α shown in the labels. In Figs. 1–3, the zero of energy corresponds to the top of the valence band, and the horizontal scale and the labeled impurities on the top of the figures correspond to the appropriate values of U_s calculated from atomic-energy differences via Eq. (6). Chemical trends (variation in E, for fixed α, as the impurity is changed) can thus be obtained from these figures as is usual in the Hjalmarson *et al.*[6] approach. Since the parameter α is a measure of lattice relaxation, trends for varying amounts of relaxation (variation in E for fixed U_s, as α is changed) can also be extracted from the figures by comparing the E versus U_s curves for different values of α. The curves in Figs. 1–3 for $\alpha=0$, which correspond to the case of no lattice relaxation, are the same as the results obtained in Ref. 6.

The deep levels for a particular impurity with a particular value of α can be obtained from Figs. 1–3 by finding the intersection with the curve for that value of α of a vertical line drawn from the label for that impurity at the top of the figure. If there is no intersection for a particular case, no A_1-symmetric deep level is predicted in the band gap for that impurity with that value of α.

Inspection of Figs. 1–3 reveals the qualitative effects of lattice relaxation on A_1-symmetric deep levels. First, it can be seen that the $\alpha \neq 0$ curves all have chemical trends which are similar to the $\alpha=0$ (no lattice relaxation) curves. However, it can also be seen that the deep levels for a fixed U_s are shifted upward towards the conduction-band edge as α becomes increasingly negative and downward towards the valence-band edge as α becomes more positive. As was noted above [see Eq. (7)], for A_1 states, negative α corresponds to inward relaxation ($d_H > d_I$) and positive α corresponds to outward relaxation ($d_H < d_I$). These results thus show that inward relaxation about an impurity moves its A_1-symmetric deep level toward the conduction band, while outward relaxation moves it towards the valence band.

It is worth noting that one-dimensional model calculations for A_1symmetric antibonding states[27] yield similar results. In particular, in these model calculations, it was also found that such states are pushed towards the conduction band (valence band) for inward (outward) relaxation. Since Hjalmarson *et al.*[6] and others[35] have shown that the A_1-symmetric states associated with substitutional impurities are conduction-band derived, antibonding *hostlike* states, this simple model result lends support to the results of the present calculations. We note that the opposite trend has been predicted by Talwar, Suh, and Tang,[18] who included both first- and second-neighbor relaxation in their theory. It is possible that such higher-neighbor relaxation, neglected here, might reverse our predicted trend. However, we believe this is to be unlikely based on results obtained in molecular-dynamics simulations where second-neighbor relaxation was included.[29] Further, as is discussed below, the agreement of the present model with experimental data also tends to confirm our predicted trend.

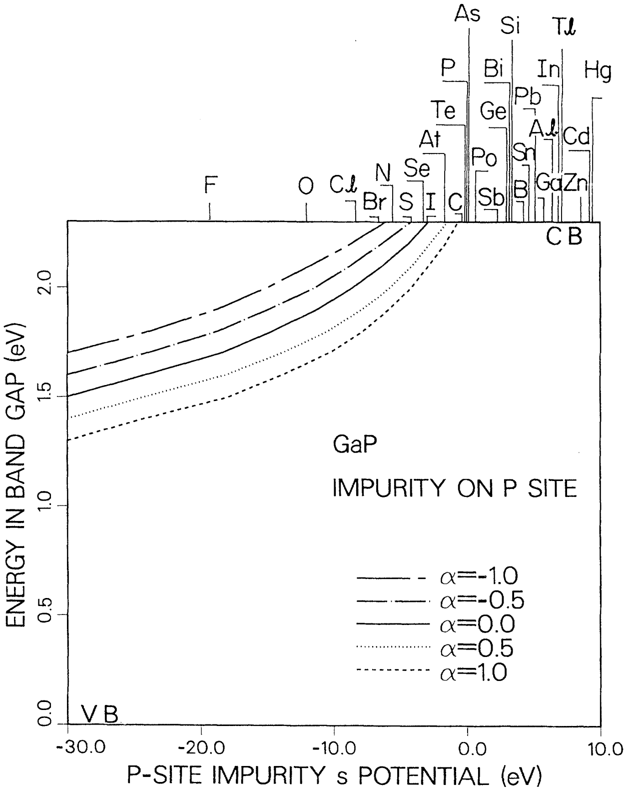

FIG. 1. Energy levels of A_1 symmetry produced by an impurity substitutional for P in GaP. The abscissa is the diagonal part of the s-orbital defect potential U_s. The ordinate is the band-gap energy with the zero equal to the top of the valence band. The sp^3-bonded impurities are shown at the top of the figure at the values of U_s obtained from atomic-energy differences. Results are shown for various values of the parameter α, which characterizes the off-diagonal matrix element of the defect potential. Since this parameter is a measure of the magnitude and direction of the nearest-neighbor lattice relaxation around the impurity, the dependence of the deep levels on this relaxation can be obtained by comparing curves for different α. The $\alpha=1.0$-, 0.5-, 0.0-, -0.5-, and -1.0-eV results are shown, respectively, as dashed, dotted, solid, dotted-dashed, and chained curves. These values of α correspond to impurity-bond-length to host-bond-length ratios d_I/d_H of 1.45, 1.17, 1.00, 0.89, and 0.81, respectively. The abbreviations CB and VB indicate the conduction-band and valence-band edges, respectively.

This trend can be illustrated by discussing a few specific cases in detail. For example, consider the N impurity, substitutional for P in GaP. From Fig. 1 it can be seen that this impurity is predicted to have a deep level which changes from about 1.88 eV above the valence band for $\alpha=1.0$ eV (corresponding to an outward relaxation with $d_I=1.46d_H$), to about 2.10 eV for $\alpha=0.0$ (no relaxation or $d_I=d_H$). Similarly, this deep level moves further toward the conduction band as α is decreased below zero, occurring in Fig. 1 at about 2.21 eV for $\alpha=-0.5$ eV (corresponding to an inward relaxation with $d_I=0.89d_H$) and becoming conduction-band resonant for $\alpha<-0.9$ eV ($d_I<0.82d_H$). Using our covalent radius model for d_I for this impurity (see Table I), we obtain $d_I=0.83d_H$, which yields $\alpha=-0.85$ eV. From Fig. 1, this predicts the N deep level at 2.27 eV, which compares quite favorably with the experimental value of 2.34 eV, or

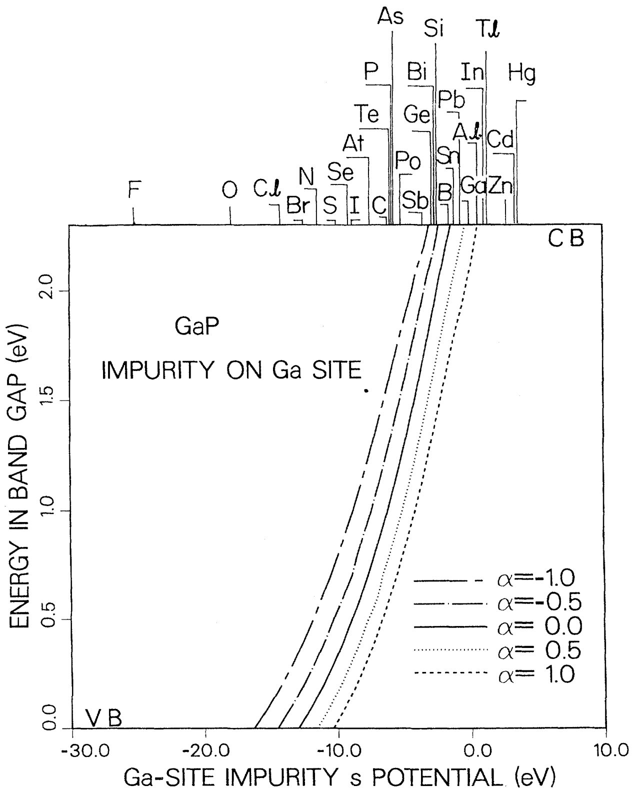

FIG. 2. Energy levels of A_1 symmetry produced by an impurity substitutional for Ga in GaP. The remainder of the interpretation is as in Fig. 1.

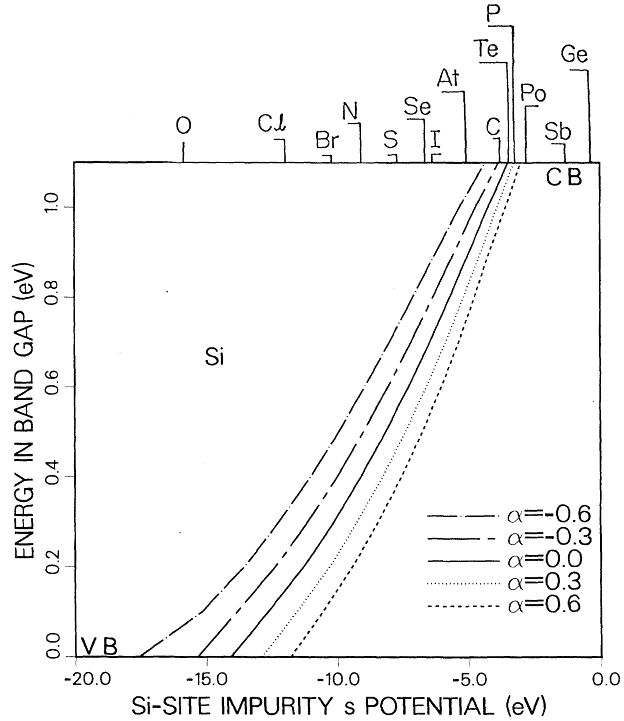

FIG. 3. Energy levels of A_1 symmetry produced by a substitutional impurity in Si. The α=0.6-, 0.3-, 0.0-, −0.3-, and −0.6-eV results are shown, respectively, as dashed, dotted, solid, chained, and dotted-dashed curves. These values of α correspond to impurity-bond-length to host-bond-length ratios d_I/d_H of 1.21, 1.09, 1.00, 0.93, and 0.87, respectively. The remainder of the interpretation is as in Fig. 1.

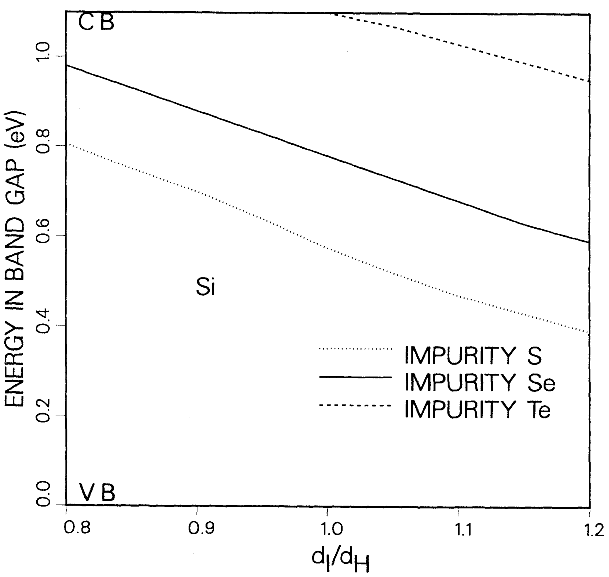

FIG. 4. Energy levels of A_1 symmetry produced by Te (dashed curve), Se (solid curve), and S (dotted curve) in Si. The abscissa is the ratio of d_I/d_H between the impurity and the host bond lengths. The ordinate is the band-gap energy with the zero of energy equal to the top of the valence band. Since d_I/d_H is a measure of the nearest-neighbor lattice relaxation around the impurity, this figure gives the dependence of the deep levels of the impurities mentioned on this relaxation. The abbreviations CB and VB indicate the conduction-band and valence-band edges, respectively.

just below the conduction-band edge.[36,37]

Similar trends can be obtained for Ga-site impurities in GaP by examination of Fig. 2. For example, consider the P on Ga antisite defect "impurity." From Fig. 2 it can be seen that a large variation in the associated deep level is predicted, depending on the amount of lattice relaxation. In fact, by varying α, this level can be made to move across a significant fraction of the band gap. Specifically, this level changes from about 0.71 eV for $\alpha=1.0$ eV (outward relaxation with $d_I=1.46d_H$) to about 1.10 eV for $\alpha=0.0$ (no relaxation, $d_I=d_H$), to about 1.63 eV for $\alpha=-1.0$ eV (inward relaxation with $d_I=0.81d_H$). Using the covalent radius model (see Ref. 23) yields a predicted inward relaxation with $d_I=0.93d_H$. This gives $\alpha=-0.3$ eV, which, from Fig. 2, predicts a deep level at about 1.24 eV. To our knowledge, no data exist with which to compare this prediction.

Similar trends for deep levels due to various impurities in Si can be obtained from Fig. 3. These trends are also illustrated in Fig. 4 for the A_1-symmetric deep levels produced by the S, Se, and Te impurities in Si. In that figure, the ordinate is the energy in the band gap, measured from the top of the valence band and the abscissa is the ratio d_I/d_H. The dependence of the deep levels on this ratio is shown for the impurities mentioned. As can be seen from the figure, this dependence is nearly linear for all cases considered. Further, these deep levels move towards the conduction band for inward relaxation and deeper into the band gap for outward relaxation, in agreement with the above-discussed trend. We note that this almost linear dependence of the deep levels on d_I/d_H differs from the results one would obtain from perturbation theory, which would, to lowest order, predict a linear dependence of the deep levels on α.

B. Specific impurities; comparisons with experiment and other theories

We have used our theory to compute the A_1-symmetric deep levels produced by several impurities in GaP and Si. These results are summarized in Table II. In the second column of that table, we display the results of these calculations for N, C, Sb, and O substitutional for P in GaP and for S, Se, Te, N, and C in Si. For the case of GaP:O, results obtained using both the covalent radius model for d_I and using Morgan's correction to this model[33] are shown. Shown for comparison in the third and fourth columns of Table II are the experimental deep levels (where data exists) for the same impurities, along with the predictions of the theory of Hjalmarson *et al.*[6] (no relaxation). For the impurities in Si considered in Ref. 18, the predictions of the Talwar, Suh, and Tang[18] theory both with and without lattice relaxation are

TABLE II. Deep energy levels for various impurities in GaP and Si. (All energies are in eV, CB means conduction-band resonant.)

Host-impurity system	Present theory (With relaxation)	Experiment[a]	Hjalmarson[b] (No relaxation)	Talwar[c] (With relaxation)	Talwar[c] (No relaxation)
GaP:N	2.27	2.34	2.10		
GaP:C	CB		CB		
GaP:Sb	CB		CB		
GaP:O[d]	2.08	1.46	1.85		
GaP:O[e]	1.75	1.46	1.85		
Si:S	0.66	0.85	0.57	0.46	0.51
Si:Se	0.70	0.86	0.65	0.59	0.64
Si:Te	1.09	1.01	1.18	1.18	1.18
Si:N	0.79		0.44		
Si:C	CB		1.09		

[a] References 36 and 37.
[b] Reference 6.
[c] Reference 18.
[d] Our prediction without the correction of Ref. 33.
[e] Our prediction with the correction of Ref. 33.

shown in the fifth and sixth columns of that table, respectively.

As can be seen from Table II, in all cases considered, the present theory improves the results of the theory of Hjalmarson *et al.*[6] in comparison with the experimental results. Further, for deep levels in Si, it does better in this regard than the model of Talwar, Suh, and Tang.[18] It can also be seen that the change in the predicted deep levels from those predicted by the theory of Hjalmarson *et al.*[6] with no relaxation is usually of the order of 10–15 % (with the exception of Si:N).

IV. SUMMARY AND CONCLUSIONS

In this paper we have presented a formalism for phenomenologically including the effects of nearest-neighbor lattice relaxation on deep levels associated with substitutional impurities in semiconductors. Our formalism is an extension of the theory of Hjalmarson *et al.*[6] to include such effects. Lattice relaxation is accounted for by characterizing the off-diagonal matrix elements of the defect potential by two parameters, one for A_1 states and one for T_2 states. Further, the bond-length dependence of these parameters is obtained by combining Harrison's[17] inverse bond-length-squared scaling rule for the host with a covalent radius model for the impurity. With this formalism, both chemical trends in the impurity-associated deep levels and trends with varying amounts of lattice relaxation can be explored.

We have applied this theory to A_1-symmetric deep levels in both GaP and Si. Among the interesting results predicted are that such levels move closer to the conduction-band edge for inward relaxation around the impurity, while they move deeper into the band gap for outward relaxation. Further, we find that the dependence of the deep-level energy on the impurity bond length is almost linear. For specific impurities we find that lattice-relaxation effects, as included in the present model, considerably improve the predictions of the theory of Hjalmarson *et al.*[6] in comparison with experiment and move the deep levels on the order of 10–15 %.

The remaining discrepancies between theory and experiment may be due to a number of factors. Among these are charge-state splittings,[16] inaccuracies in the band structures used in the calculations,[20] second-neighbor relaxation effects, and breakdown of the covalent radius model.

As mentioned in the Introduction, a rigorous theory of lattice-relaxation effects clearly requires a total-energy calculation. From such a calculation, one can take derivatives of the total energy with respect to atomic positions to determine interatomic forces. These, in turn, can be used to compute the lattice relaxation. The approach outlined above sacrifices this rigor in exchange for computational simplicity by treating the relaxation phenomenologically. It thus retains much of the simplicity and universality of the theory of Hjalmarson *et al.*[6] Recently, we have combined the formalism of Sec. II with a molecular-dynamics calculation of lattice relaxation.[29] In this scheme, the forces which enter the molecular-dynamics simulation are obtained from the electronic structure using the Hellmann-Feynman theorem.[30] This calculation obtains a relaxed impurity-host bond length that differs by about 10% from the covalent radius model results. The resulting values obtained for α yield deep levels in even better agreement between theory and experiment than the present theory. These calculations will be discussed elsewhere.[29]

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