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Molecular-dynamics approach to lattice-relaxation effects on deep levels in semiconductors

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A tight-binding formalism for calculating the effects of lattice relaxation on deep levels due to substitutional impurities in semiconductors is presented. Molecular dynamics is used to calculate the lattice relaxation around an impurity, and its effects on the associated deep levels are computed using a Green's-function method. The results of applying this scheme to several impurities in GaP and Si are presented and compared with experiment.

There have been many theories of deep levels in semiconductors,[1–4] and they are of varying degrees of sophistication and accuracy. In this paper, we present a tight-binding formalism for calculating the effects of lattice relaxation on the deep levels produced by substitutional impurities. Molecular dynamics is used to calculate the relaxation around an impurity and its effects on the associated deep levels are computed using a Green's-function technique.[5] As a first application of our method, the deep levels produced by several impurities in GaP and Si are investigated.

A defect in a semiconductor will interact with the host, displacing the surrounding atoms.[6] Because deep levels are produced by a short-ranged potential,[1–4] this distortion will strongly affect them. First-principles theories have been used to study these effects in a few cases.[7] They have also been included phenomenologically within tight-binding theory.[5,8] While first-principles techniques produce the most reliable results, they require considerable computational effort, which is undesirable when the number of defects to be studied is large or when one desires to obtain trends in deep levels. On the other hand, while tight-binding approachs require comparatively little computational effort and can thus easily be used to study large classes of defects or trends, they are somewhat unsatisfying because of the necessity either to assume an amount of relaxation or to calculate it from a simple model.[5,8] Our theory is intermediate between these approaches. Since it is tight binding based, it retains much of the computational simplicity of this approach. However, lattice relaxation is calculated using molecular dynamics, so that the necessity to treat it phenomenologically is circumvented.

Our approach is based on our generalization[5] of the theory of Hjalmarson *et al.*[3] of deep levels to include lattice relaxation. In obtaining numerical results, we describe the host using the sp^3s^* tight-binding band structures of Vogl *et al.*[9] However, any other suitable choice of tight-binding band structures could also be used. The theory of Hjalmarson *et al.*[3] is a simple, yet widely used[10,11] theory in which lattice relaxation is neglected. It and its extensions have been successful in predicting trends in deep levels in numerous applications.[10,11] In Ref. 5, lattice-relaxation effects were incorporated into the theory of Hjalmarson *et al.*[3] by treating the off-diagonal elements of the defect potential with a generalization of the inverse-bond-length-scaling rule,[12] with the impurity bond length determined using a covalent radius model.[13] By contrast, in the present approach, molecular dynamics is used to determine this bond length. The attractive part of the force which enters the molecular-dynamics calculation is computed from the electronic structure using the Hellmann-Feynman theorem[14] and the repulsive part is obtained from a pair potential based on Harrison's overlap interaction.[12]

We consider the problem of the calculation of the deep levels produced by neutral, sp^3 bonded, substitutional impurities in zinc-blende and diamond structure hosts. The point group for such an impurity is T_d and the deep levels can thus be either of the A_1-symmetric (s-like) or the T_2-symmetric (p-like) type. In principle, our formalism could be generalized to include more complicated defects[10] and charge state effects.[11] In treating lattice relaxation, we include only those effects due to relaxations of the nearest neighbors. We show elsewhere[15] that second-neighbor relaxations have only a small effect on the deep levels. Our technique is applicable for a general distortion of the host atoms around an impurity. Here, however, we consider only T_d symmetry conserving breathing-mode distortions, which are thought to dominate for substitutional impurities in the materials of interest.[7,16,17]

The Koster-Slater[18] theory is convenient for calculating the bound-state energies ε produced in the band gap by a defect potential V. In this method, these energies are given by the solutions to

$$\det[1-G^0(\varepsilon)V]=0 , \tag{1}$$

where $G^0(\varepsilon)=(\varepsilon-H_0)^{-1}$ is the host Green's function, and H_0 is the host Hamiltonian. The advantage of this method is that Eq. (1) only needs to be solved in the subspace of V. In the present case, this yields a 20×20 determinant (five atoms, four orbitals per atom). For breathing-mode distortions, it is shown in Ref. 5 that symmetry allows Eq. (1) to factor into the product of four 5×5 determinants, one of which yields the A_1 states and three of which yield the T_2 states.

For an impurity on the anion site in a zinc-blende crystal, the defect potential can be written[5,15]

$$V=\sum_i V_i=\sum_i \left[|ia\mathbf{0}\rangle U_i \langle ia\mathbf{0}| + \sum_{\mathbf{d}} (|ia\mathbf{0}\rangle \alpha_i \langle ic\mathbf{d}| + \text{H.c.}) \right] , \tag{2}$$

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where i is a symmetry label corresponding to A_1 and T_2 states, a and c refer to the anion and the cation, **0** is the unit cell at the origin, the sum on **d** is taken over the four nearest-neighbor cations, U_i is the diagonal matrix element at the anion site, α_i is the off-diagonal element coupling the anion and cation sites, and H.c. is the Hermitian conjugate. For an impurity on the cation site, a and c are interchanged in Eq. (2). For U_i, we use the empirical rule[3] of proportionality to atomic energy differences. For α_i, we use a generalization[5] of the inverse-bond-length-squared scaling rule,[12] which gives[5]

$$\alpha_i = -C_i[(d_I)^{-2} - (d_H)^{-2}] , \quad (3)$$

where d_I and d_H are the bond lengths of the impurity and the host atoms and C_i is a constant[19] determined from the host band structures.[5,9] To calculate α_i, we use experimental values[12] for d_H and compute d_I by the molecular-dynamics method we now describe.

For an ideal impurity, the four nearest-neighbor host atoms remain in their perfect-crystal positions. In a more realistic treatment, these atoms experience a net force and the lattice distorts to a new configuration where that force is zero. The total force on one of these neighbors can be divided into repulsive and attractive parts, $F_x = F_x^r + F_x^a$, where x is the impurity-atom–host-atom bond direction. The origin of F_x^r is the repulsion between electrons in overlapping states. We compute it from a pair potential based on Harrison's overlap interaction,[12] which gives

$$F_x^r = -A/d_I^5 . \quad (4)$$

Here, A is a constant determined by requiring the total force to vanish when the impurity atom is replaced by a host atom ($d_I = d_H$). We find $A = 152.0$ eV Å^4 and 199.0 eV Å^4 for GaP and Si, respectively.

In our formalism, the attractive force F_x^a, which originates from the occupied one-electron levels, is computed from the electronic structure by use of the Hellman-Feynman theorem.[14] According this theorem,[14] if x is a component of the position coordinate of an atom, the x component of the force on that atom can be computed from the derivative of the total quantum-mechanical energy E as

$$F_x^a = -\frac{\partial E}{\partial x} = -\frac{\partial}{\partial x}\int_{-\infty}^{\varepsilon_F} \varepsilon\rho(\varepsilon)d\varepsilon , \quad (5)$$

where ε_F is the Fermi energy and $\rho(\varepsilon) = -(1/\pi)\mathrm{Im\,Tr}G(\varepsilon)$ is the electronic density of states. Here, G is the Green's-function matrix, including the impurity, which can be found from G^0 and V using the Dyson equation

$$G = G^0 + G^0VG = (1-G^0V)^{-1}G^0 . \quad (6)$$

By combining Eqs. (5) and (6), the attractive part of the force can be written as

$$F_x^a = \frac{1}{\pi}\mathrm{Im\,Tr}\int_{-\infty}^{\varepsilon_F} \varepsilon\frac{\partial G}{\partial x}d\varepsilon = \frac{1}{\pi}\mathrm{Im\,Tr}\int_{-\infty}^{\varepsilon_F} \varepsilon G\frac{\partial V}{\partial x}G\,d\varepsilon , \quad (7)$$

where the last equality is obtained from the first by combining Eq. (6) with its derivative.

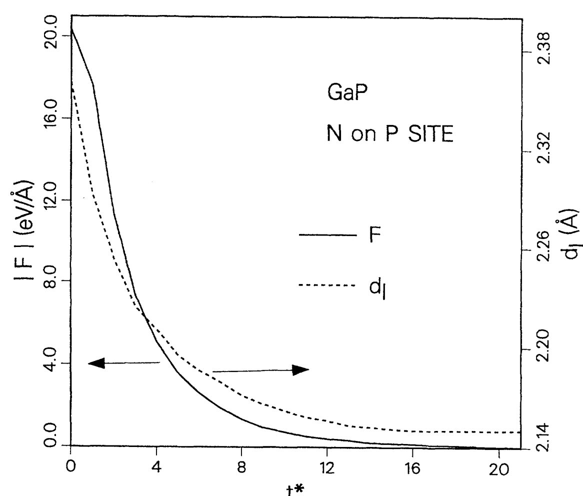

FIG. 1. Time dependence of the magnitude of the total force (solid curve) along an impurity-atom–host-atom bond and of the bond length (dashed curve) for N substitutional for P in GaP.

Using this formalism and beginning with the nearest-neighbor host atoms in their perfect-crystal positions, one can calculate the motion of each of these atoms for a small time interval, Δt, using Newton's second law along with standard "molecular-dynamics" methods.[20] In this way new atomic positions can be determined a new V and a new force can be computed. This process can be repeated for successive intervals Δt until the net force acting on each neighbor approaches zero. In this way, one can determine d_I and V for the relaxed lattice. Then, deep levels in the band gap are obtained from Eq. (1). Some representative results are presented in Figs. 1 and

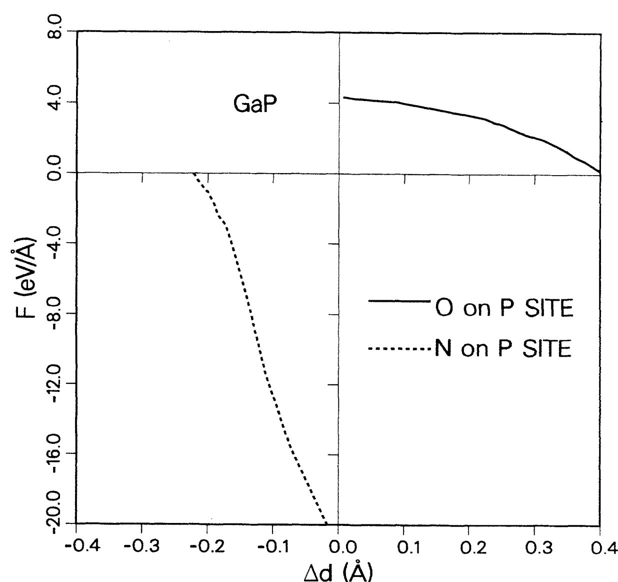

FIG. 2. Force on one of the four Ga nearest neighbors as a function of distortion distance for N (dashed curve) and O (solid curve) substitutional for P in GaP.

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In Fig. 1, we show the results for the time dependence both of the magnitude of the total force along an impurity-atom–host-atom bond and of d_I for N substitutional for P in GaP. These are plotted versus $t^*=t/(\Delta t)$, where $\Delta t=0.35\times10^{-14}$ s. This choice of Δt was obtained by trial and error. We have found that, while the best choice depends on the particular case, it is always of this order of magnitude. A smaller Δt uses considerably more computer time to achieve similar results and a larger value can cause an "overshoot" of the final equilibrium position and an oscillatory behavior of d_I versus t^*. As can be seen from Fig. 1, after about 16 time steps or about 0.06 ps, the force approaches zero. It can also be seen that, as the atoms approach their new equilibrium positions, the nearest-neighbor Ga atoms move inward by about 0.21 Å, or about 9% of the 2.36-Å GaP bond length. This result is in qualitative agreement with a covalent radius model.[5,13]

It is also of interest to study the relationship between the distortion distance, $\Delta d=d_I-d_H$, and the force. In Fig. 2 we show results for the total force on one of the four Ga nearest neighbors as a function of Δd for N and O substitutional for P in GaP. In agreement with Fig. 1, it can be seen that N induces an inward relaxation of the nearest-neighbor Ga atoms by about 0.21 Å. By contrast, O in GaP induces an outward relaxation, which contradicts an analysis based on covalent radii,[5,13] but which is in qualitative agreement with a model discussed by Morgan.[16] We note that Morgan's model[16] is similar to that proposed earlier by Baraff *et at.*[17] and that it contradicts an earlier calculation by Jaros,[21] who proposed an inward relaxation for GaP:O. We also note that a complete survey of the problem of GaP:O can be found in Ref. 22. In our calculations, the nearest-neighbor Ga atoms move away from the O impurity by about 0.42 Å or about 18% of the GaP bond length. The qualitative difference between the results for N and O in GaP is partially due to the fact that O is much more electronegative than *N* and partially due to the small radii of the O orbitals in comparison with those for Ga, which cause a small overlap between the Ga and O orbitals.[16,17] Thus, the Ga—O bond is much weaker than the Ga—N bond, so that the Ga atoms relax away from the O atom.[16,17] The fact that the magnitude of the initial force between Ga and N is almost five times as large as that between Ga and O (Fig. 2) also supports this conclusion.

Results obtained using our formalism to compute the A_1-symmetric deep levels produced by several impurities in GaP and in Si are shown in Table I. Also shown for the same impurities are the experimental deep levels,[4,23–25] the predictions of theory of Hjalmarson *et al.*,[3] and the results of our phenomenological treatment of lattice relaxation on deep levels.[5] The last column in Table I gives results for d_I calculated with our formalism. As can be seen from that table, our model predicts an inward relaxation for all impurities considered, except for O in GaP and Te in Si. In all cases except for O in GaP, our results are in qualitative agreement with a covalent radius model.[5,13] Also, in all cases considered, our deep-level predictions improve upon those of Ref. 3 in comparison with experiment. We note that other studies[1,7,26] of deep-level shifts with symmetric displacements of nearest-neighbor atoms in Si and GaP have found energy shift-to-displacement ratios, with respect to deep levels obtained in the absence of distortion, which are similar to those obtained from Table I by comparison of the present results with those of Ref. 3.

In this paper, only the effects of nearest-neighbor lattice relaxation on deep levels associated with substitutional impurities have been considered. We have recently generalized our formalism to include second-neighbor relaxation and preliminary results show that such effects cause the predicted deep levels to change by only a small amount.[15] The remaining discrepancies between theory and experiment might thus be attributable to other factors, including inaccuracies in the host band structures and charge state effects.

TABLE I. Deep energy levels of A_1 symmetry for various impurities in GaP and Si. All energies are in electron volts, measured from the top of the valence band. The bond lengths are in angstroms.

System	Present theory	Experiment	Hjalmarson[a]	Ref. 5	Bond length
GaP:N	2.25	2.34[b]	2.10	2.27	2.15
GaP:O	1.70	1.46[b]	1.85	2.08	2.78
GaP:P_{Ga}	1.09	1.10[c]	1.03	1.11	2.28
GaP:Ge	1.95	2.16[d]	1.85	1.90	2.24
GaP:Se	C.B.		2.32	C.B.	2.22
Si:S	0.63	0.85[e]	0.58	0.66	2.23
Si:Se	0.83	0.86[e]	0.65	0.70	2.03
Si:Te	1.05	1.01[e]	1.12	1.09	2.60
Si:C	C.B.		1.09	C.B.	1.98

[a]Reference 3 (*no* relaxation).
[b]Reference 23.
[c]Reference 24.
[d]Reference 25.
[e]Reference 4.

The results presented here depend on a generalization[5] of the inverse-bond-length-squared scaling rule[12] for the off-diagonal matrix elements [Eq. (3)], and on Harrison's model for the overlap interaction[12] [Eq. (4)]. However, the formalism outlined here can easily be utilized with any other reasonable assumptions for these quantities. To test the sensitivity of our results to these assumptions, we have repeated some of the above calculations assuming exponential dependences of these quantities on d_I, following Menon and Allen.[27] Results obtained in this manner both for d_I and for the deep levels differ by less than 1% from those presented above.

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