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Deep levels associated with triplet impurity complexes in GaP

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A theory of the deep energy levels produced by triplet impurity complexes in semiconductors is outlined and applied to GaP. Results are presented for the chemical trends in the deep levels of a_1 and b_1 symmetry for selected complexes in this material. Among the interesting results predicted are that, by selected complexing of impurities, the deep levels of a particular impurity can be significantly altered from their isolated impurity values.

I. INTRODUCTION

Defects that produce deep levels¹⁻⁶ in the band gap of a semiconductor can greatly influence the material optoelectronic properties. Unlike shallow levels,⁷ which are produced by the long-ranged Coulomb potential of the defect, deep levels¹⁻⁶ are controlled by the central-cell, atomlike potential associated with the defect. Hjalmarson *et al.*⁶ have shown that the chemical trends in the deep levels of substitutional impurities can be understood using a Koster-Slater⁸ 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. Sankey and co-workers⁹⁻¹⁴ have generalized these ideas to treat paired defects and have predicted the chemical trends in the deep pair levels in several materials. The latter theory was modified by Shen and Myles¹⁵ to treat triplet vacancy-impurity complexes and used to predict chemical trends in the deep levels due to such defects in several materials.

In this paper, we extend the Shen-Myles¹⁵ theory to treat deep levels associated with triplet impurity complexes in semiconductors and present predictions for the chemical trends in these levels due to selected complexes in GaP. The terminology "triplet impurity complex" is used here and in what follows to denote a complex consisting of three sp^3 -bonded, substitutional impurities, one of which is a nearest neighbor to two others which are identical to each other. This type of complex can be thought of as the triplet vacancy-impurity complex of Ref. 15 with the vacancy replaced by an impurity. It is one of the simplest impurity complexes containing three constituents. Because our theory is only a slight modification of that of Shen and Myles,¹⁵ it will only briefly be discussed here.

The motivation for considering triplet-impurity-complex-produced deep levels is that impurities are mobile and can migrate in the material to form complexes, which are thought to have important effects on the efficiency of radiative recombination in a number of materials.^{2,16-20}

Our theory is based upon the Hjalmarson *et al.* theory of deep levels^{6,21} and the Vogl, Hjalmarson, and Dow²² sp^3s^* tight-binding band-structure model. The Hjalmarson *et al.* theory^{6,21} and generalizations of it, when used with the Vogl, Hjalmarson, and Dow²² band structures, have been successful in their predictions of chemical trends in the defect-related properties of numerous materials.^{9-15,23-25} Furthermore, generalizations of this theory have often produced results which are in semi-quantitative agreement both with experiment^{9-15,23-25} and with more sophisticated theories.²⁴ Therefore, we have confidence that this theory can predict the major chemical trends in the energies of triplet-impurity-complex levels in GaP. Following previous work,^{6,9-15} our primary interest is in obtaining such trends and not in the prediction of absolute energy levels.

Our principal finding is that by selected complexing with an identical pair of impurities, the deep levels of a particular impurity can be greatly altered from their isolated impurity values. This result is similar to that found by Sankey and co-workers⁹⁻¹⁴ for paired defects. Our predictions of such impurity-complex-associated levels will hopefully serve as a guide to experimentalists attempting to interpret data.

II. THEORY

The Hamiltonian for GaP which we use is the sp^3s^* nearest-neighbor semiempirical tight-binding model of Vogl, Hjalmarson, and Dow.²² The parameters describing this Hamiltonian can be found in Ref. 22. The use of an excited s^* state enables a description of the conduction bands that is flexible enough to treat both direct and indirect band-gap semiconductors. This model successfully reproduces the principal features of the GaP conduction-band structure,²² particularly near the Γ and X points of the Brillouin zone.

We follow Hjalmarson *et al.*⁶ in constructing the defect potential. The on-site matrix elements of this potential are obtained from the atomic-energy differences of the impurity and the host and the off-diagonal matrix elements are set to zero, so that the defect potential for the

triplet complex is diagonal in the tight-binding basis. Both charge-state splittings and lattice relaxation are thus neglected. The neglect of such effects in a theory of chemical trends has been justified in previous work,^{6,9-15} where it was argued that they are not expected to greatly alter the ordering of the predicted levels. The resulting global theory of chemical trends is limited by uncertainties as large as a few tenths of an electron volt. The long-ranged Coulomb potential is also neglected, so that shallow impurities⁷ have zero binding energy in this simple model.

For a defect which consists of an impurity on the cation site and two other impurities, which are identical to each other and located at two of the nearest-neighbor anion sites, the defect potential in our model is

$$U = \sum_i (|ic\mathbf{0}\rangle U_i^c \langle ic\mathbf{0}| + |ia\mathbf{d}\rangle U_i^a \langle ia\mathbf{d}| + |ia\mathbf{d}'\rangle U_i^a \langle ia\mathbf{d}'|), \quad (1)$$

where c and a refer to cation and anion sites, respectively, \mathbf{d} and \mathbf{d}' are nearest-neighbor vectors $\mathbf{d} = a_L(1, 1, 1)/4$ and $\mathbf{d}' = a_L(-1, -1, 1)/4$, and U_i^c and U_i^a are the cation and anion-site defect potentials for orbital i . The states $|ic\mathbf{0}\rangle$ and $|ia\mathbf{d}\rangle$ are localized basis orbitals centered on the cation at the origin and the anion at \mathbf{d} , respectively. For a similar defect with the anion site at the origin, the labels a and c are interchanged in Eq. (1). In what follows we shall refer to these two types of complexes as type c (cation at the origin) and type a (anion at the origin) complexes. In Eq. (1), the sum on i is taken only over the s , p_x , p_y , and p_z orbitals.^{6,9-14} Also, we assume that all orientations of the p orbitals have the same defect potential energies.^{6,9-16} Thus, there are only four independent parameters in the defect potential; U_s^c , U_p^c , U_s^a , and U_p^a . Following Hjalmarson *et al.*,⁶ we take each of these parameters to be proportional to an appropriate difference between defect and host atomic energies.

The Koster-Slater theory⁸ is convenient for determining the bound-state energies E of the triplet complex. In this method, these energies are given by solutions to

$$\det[I - G^0(E)U] = 0, \quad (2)$$

where

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

is the perfect-crystal Green's function, H_0 is the sp^3s^* Hamiltonian, and I is the identity matrix. The advantage of this method is that the determinant in Eq. (2) only needs to be evaluated in the subspace of U . In the present case, this yields a 12×12 determinant (three impurity sites and four orbitals—one s and three p —per site).

For the cases of isolated impurities^{6,21} and paired defects,⁹⁻¹⁴ the block diagonalization of $G^0(E)$ and the subsequent factoring and simplification of Eq. (2) was relatively straightforward because of the high symmetry of the defects. In the present case, however, the defect symmetry is reduced and block diagonalization is nontrivial but still possible.¹⁵ Details of this procedure are given in Ref. 15. A summary of the group-theoretical considera-

tions needed for this procedure follows. The point group for a point defect in a zinc-blende semiconductor is T_d , so that point defects with sp^3 hybrid bonding have defect states with either nondegenerate A_1 (s -like) or triply degenerate T_2 (p -like) symmetry. Triplet impurity complexes in the same host are described by a reduced "molecular" symmetry group C_{2v} .²⁶ This results in splittings of the T_2 levels and mixing of the "atomic" A_1 and T_2 levels on the three sites.²⁶ The point group C_{2v} has one-dimensional irreducible representations only,²⁶ so that the T_2 level is split into three nondegenerate levels. The resulting "molecular" states are denoted as a_1 symmetric (s, p_z -like), b_1 symmetric (p_x -like), and b_2 symmetric (p_y -like). The a_1 and b_1 orbitals result from the strong overlap and mixing of the A_1 levels and the p_x and p_z components of the T_2 levels on the three sites. Thus, their energies may be very unlike those of either isolated defect. Therefore, they are the most interesting of the triplet-impurity-complex levels and are the ones for which we present results below. On the other hand, the b_2 states correspond to admixtures of the p_y orbitals on the three sites. Since these mix only weakly due to the orientation of the complex, the corresponding levels are relatively unaffected by complexing and are very close to both the levels of the T_2 states of the isolated defects^{6,21} and those of the e -symmetric levels of the corresponding vacancy-impurity pairs.¹⁴ Due to this fact, results for these levels will not be presented here.

In the results presented below we have employed Hjalmarson's empirical rule^{6,21} that for the impurity sites of the complex the diagonal p -matrix elements of the impurity potential U_p are equal to one-half of the appropriate diagonal s -matrix elements U_s . This simplification is not necessary to solve Eq. (4), but is both helpful for simplifying the computation and consistent with previous uses of the Hjalmarson and co-workers approach.^{6,9-15,23-25} In this approximation, the deep level energies depend only on the two parameters U_s^c and U_s^a .

III. RESULTS AND DISCUSSION

We have calculated the deep levels associated with several triplet impurity complexes in GaP. By exchanging anion and cation labels in our formalism, we have done calculations for both type- c and type- a complexes. We seek the major chemical trends in the ordering of the levels. Due to the neglect of lattice relaxation and charge-state-splitting effects, our results for the absolute level depths should be viewed on a coarse scale of several tenths of an electron volt. Based on past successes of similar approaches,^{6,9-15,20-25} we believe that the ordering we predict for the deep levels as the complex is changed should be correct.

To obtain the chemical trends in the a_1 and b_1 deep levels for the type- c complex we have computed the deep level energies E as functions of anion impurity s potential U_s^a for fixed cation impurity s potential U_s^c . That is, we have chosen particular impurities on the cation site and allowed the impurity on the anion sites to vary. For the type- a complex, we have computed E as a function of U_s^c for fixed U_s^a .

Typical results of our calculations are illustrated in Figs. 1–4 (solid curves). Figure 1 shows the deep level E versus U_s^a diagram for two anion (P-site) impurities complexed with C ($U_s^c = -6.12$ eV) on the cation (Ga) site. Figure 2 displays similar information for Ge ($U_s^c = -2.80$ eV) on the Ga site. In Figs. 3 and 4, the analogous results are shown for E versus U_s^c for two Ga-site impurities complexed with N ($U_s^a = -7.02$ eV) and O ($U_s^a = -11.92$ eV), respectively, on the P site. The deep level versus defect potential-energy curves for the A_1 levels of the appropriate isolated impurity (P site in Figs. 1 and 2 and Ga site in Figs. 3 and 4) are shown in these figures as dashed curves. These are the same as those obtained in Ref. 6.

In Figs. 1–4, the zero of energy on the vertical scale 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 defect potential of the impurity calculated from atomic energy differences.^{6,21} The deep levels for a particular complex are obtained from these figures by finding the intersection with the appropriate curve of a vertical line drawn from the label for that impurity at the top of the figure. If there is no such intersection for a particular case, no deep level of that symmetry is predicted to be formed for that complex.

The special cases of the A_1 and T_2 levels produced by the isolated Ga-site impurities C and Ge can also be obtained from Figs. 1 and 2, respectively, by allowing the identical pair of impurities to become the appropriate host atoms (by setting $U_s^a = 0$ in Figs. 1 and 2). Similarly, the A_1 and T_2 levels of the isolated P-site impurities N and O can be obtained from Figs. 3 and 4, respectively, by setting $U_s^c = 0$ in those figures. In all cases, the isolated impurity levels are the same as those obtained in Ref. 6, and, when they are predicted to be in the band gap, they are shown in the figures as solid circles with appropriate labels.

Several interesting trends and features can be obtained for specific triplet impurity complexes by a detailed examination of Figs. 1–4, which are very rich in information content.

For example, from either Fig. 1 or Fig. 3, the isolated N impurity, substitutional for P, is predicted by the Hjalmarson *et al.* theory⁶ to produce an A_1 -symmetric level near the conduction-band edge. When, as part of a type-*c* complex, this common GaP impurity is complexed with another, second-nearest-neighbor P-site nitrogen and a nearest-neighbor C on the Ga site, however, it is predicted (Fig. 1) to produce two deep levels of a_1 symmetry and one of b_1 symmetry which are 0.3, 1.5, and 1.8 eV, respectively, above the valence-band edge. Complexing thus pushes the isolated N level deeper into the band gap and produces two more deep levels. It should be pointed out that these three levels are also very different from the predicted A_1 and T_2 symmetric levels of isolated C on the Ga site, as can also be seen from either Fig. 1 or Fig. 3. From Fig. 1, it can be seen that similar statements can be made about the isolated impurity levels and the levels produced by type-*c* complexes containing C on the Ga

site and F, O, Cl, Br, S, Se, and I substitutional for P. Other P-site impurities, predicted in Ref. 6 to produce no deep levels in the band gap as isolated impurities, are predicted by Fig. 1 to produce one or more such levels when part of a type-*c* complex containing C on the Ga site. For example, reading from left to right across the top of the figure, the P-site impurities At–Si and Ga–Hg are predicted to produce three deep levels each as part of such a complex, while complexes containing B through Pb are predicted to produce only one level. Thus complexing can drastically alter the deep level properties of a given impurity and can produce deep levels where the isolated impurity has none.

The case of the type-*c* triplet impurity complex with Ge on the cation site, illustrated in Fig. 2, is qualitatively similar to the case of C on the cation site. However, some of the complex associated levels in this case tend to be closer to the conduction-band edge than for the C complex. This is caused by the fact that the Ge defect potential on the Ga site is weaker than that for C.

Similar analyses can be made about the type-*a* complexes containing N (Fig. 3) and O (Fig. 4) on the P site. For example, from Fig. 3 it can be seen that such a complex with N on the P site complexed with two antisite defect P “impurities” on the Ga site is predicted to produce one a_1 and two b_1 deep levels which are much nearer to the conduction band than the isolated antisite A_1 level. These levels are also very different from the predicted isolated A_1 symmetric level of N on the P site. Also, several Ga-site impurities which are predicted by Hjalmarson *et al.*⁶ to produce no deep levels when isolated are predicted in Fig. 3 to produce four deep levels as part of a type-*a* complex containing N on the P site. Among these are Cl, Br, N, and S. An examination of the deep levels predicted in Fig. 3 for other type-*a* complexes containing N yields similar information. Thus, type-*a* complexes can have deep levels which are very different from those of either isolated impurity and participation in such a complex can drastically alter the deep level properties of a given impurity.

The case of the type-*a* triplet impurity complex containing O on the anion site, illustrated in Fig. 4, is qualitatively similar to the case of the complex containing N, and similar deep levels are predicted. However, the analogous levels are pushed deeper into the band gap for the case of O, due to the fact that the O defect potential is stronger than that for N.

IV. SUMMARY

Using an extension of the Hjalmarson *et al.* theory⁶ we have predicted the chemical trends in the a_1 and b_1 symmetric deep levels produced by selected triplet impurity complexes in GaP. Among the interesting results predicted are that, by selected complexing of impurities, the deep levels of a particular impurity can be significantly altered from their isolated impurity values. While these

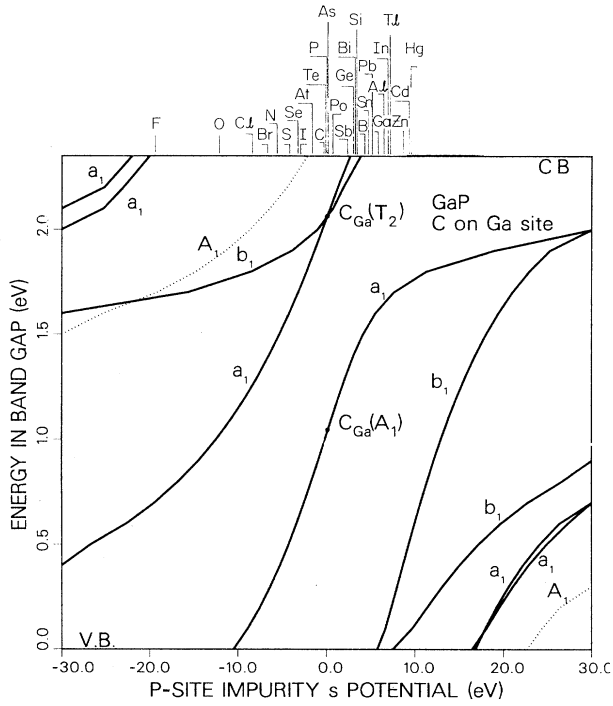


FIG. 1. Energy levels of a_1 and b_1 symmetry produced by a triplet impurity complex ($C_{Ga}, 2X_P$) containing carbon on the gallium site C_{Ga} and two identical phosphorous-site impurities X_P in GaP.

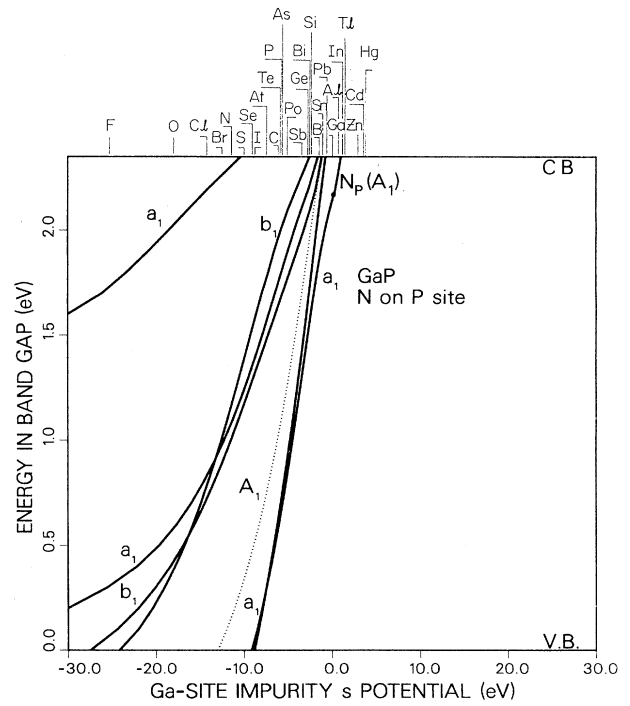


FIG. 3. Energy levels of a_1 and b_1 symmetry produced by a triplet impurity complex ($2X_{Ga}, N_P$) containing nitrogen on the phosphorous site N_P and two identical Ga-site impurities X_{Ga} in GaP.

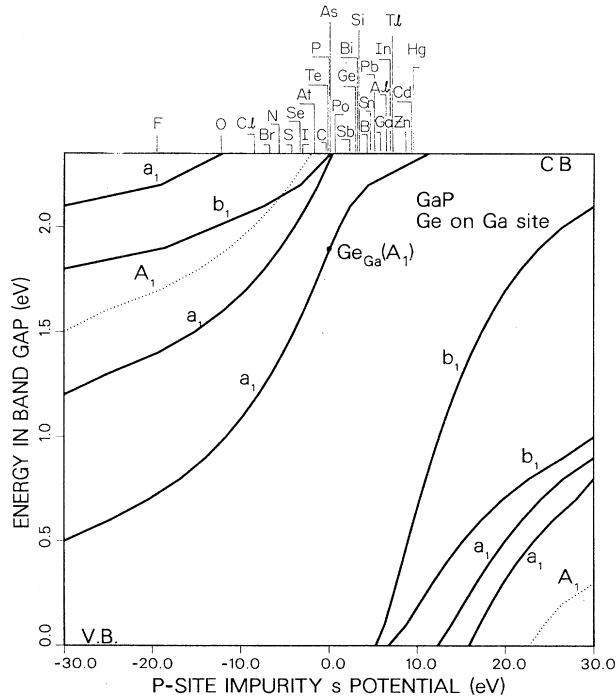


FIG. 2. Same as Fig. 1 except for germanium on the gallium site, Ge_{Ga} .

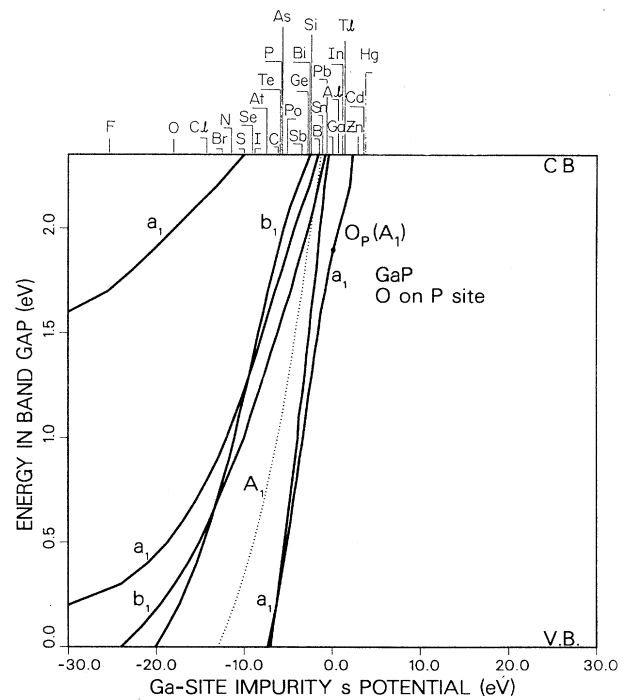


FIG. 4. Same as Fig. 3 except for oxygen on the phosphorous site, O_P .

results are not profound or surprising, our theory provides a quantitative means of systematically exploring the trends in the modifications of the deep level properties which are induced by such complexing.

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