

Alloy broadening of the deep electronic levels associated with the As vacancy in $\text{Al}_x\text{Ga}_{1-x}\text{As}$

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The inhomogeneous alloy broadening of the deep electronic levels produced by the ideal anion (As) vacancy in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ is investigated using the embedded-cluster method to describe the disordered alloy host and the theory of deep levels to compute the defect energies. Results are presented for the composition dependences of the center, width, and component levels of the alloy-broadened spectra produced by both the *s*-like and the *p*-like vacancy-associated levels.

I. INTRODUCTION

In previous papers,¹⁻⁴ we have presented a microscopic theory of the effects of alloy disorder on the deep electronic energy levels associated with substitutional impurities in ternary semiconductor alloys (so-called "alloy-broadening" effects). The theory described in those articles accounts for local chemical environment effects in a realistic manner, employs a version of deep-level theory^{5,6} which has been shown to accurately predict the chemical trends in deep-level energies, and utilizes realistic band structures for the alloy constituents. In this paper, we extend this theory to treat vacancy-associated levels and apply it to the investigation of the alloy broadening of the deep levels produced by the ideal anion (As) vacancy in $\text{Al}_x\text{Ga}_{1-x}\text{As}$. As in our previous work,¹⁻⁴ our primary interest here is in obtaining estimates of the size of the alloy broadening and in predicting trends in this broadening as a function of alloy composition.

The physics of the inhomogeneous alloy broadening of deep levels in semiconductor alloys can be qualitatively understood in a straightforward manner. It is well known that the properties of deep levels are strongly affected by local environment effects.^{5,6,7} In an elemental or compound semiconductor, different defects of the same type are all surrounded by similar local chemical environments so that their associated deep levels will occur at nearly the same energy. However, in a disordered semiconductor alloy, different defects of the same type can be surrounded by different local configurations of alloy constituents. Such variations in the local chemical environment give rise to an effect where a given type of defect can produce numerous deep levels in the band gap, one for each possible distinct configuration which can surround it. In recent years, several workers have observed and studied these inhomogeneous alloy-broadening effects in optical absorption and luminescence from excitons bound to impurities in III-V semiconductor alloys.⁸⁻¹¹

To our knowledge, such effects have not been observed for vacancy-associated deep levels. Thus, an estimate of

the size of the alloy broadening of such levels might be useful as a guide in the interpretation of data on such levels. The results presented below show that alloy disorder can have a non-negligible effect on the anion vacancy-associated levels in $\text{Al}_x\text{Ga}_{1-x}\text{As}$. Based on our previous work,¹⁻⁴ we expect qualitatively similar results for other vacancy-associated levels in other semiconductor alloys. We have chosen $\text{Al}_x\text{Ga}_{1-x}\text{As}$ for the present study because of its technological importance. Furthermore, we treat only the As vacancy because the first-neighbor shell of atoms surrounding that defect is disordered so that the alloy-broadening effects are expected to be larger than for the cation (Al or Ga) vacancy, where the second-neighbor shell is disordered.⁴ In the present work, only the alloy disorder in the nearest-neighbor shell of atoms to the vacancy is accounted for by the theory. We emphasize, however, that our method can, in principle, be applied to investigate the effects of alloy disorder on any deep-level defect in any semiconductor alloy and can be extended to include the alloy disorder in higher-neighbor shells.

II. THEORY

In previous work,¹⁻⁴ we have presented some of the details of our theory. However, for completeness, we briefly outline our method below, with emphasis on the aspects that are unique to the treatment of vacancy-associated levels, which were not treated previously. As in our previous papers,¹⁻⁴ the present theory is based on the embedded-cluster method¹²⁻¹⁴ and the Hjalmarson *et al.*^{5,6} theory of deep levels. As is argued in Refs. 1-4, the combination of these two techniques is ideally suited for obtaining the estimates and trends that we seek here.

For both conceptual and calculational purposes, it is convenient to divide the problem into two parts: the problem of obtaining a description of the alloy host and the problem of the calculation of the deep levels. The description of the alloy host can itself be further subdivided into the problems of obtaining the global or average properties and of obtaining the local, alloy-configuration-dependent properties.

In our approach, the average properties of the alloy host are described using the nearest-neighbor sp^3s^* tight-binding band structures of Vogl *et al.*¹⁵ in the virtual-crystal approximation (VCA).¹⁶ Although the results presented below were obtained using these band structures and this alloy effective medium, our *formalism* is independent of the choice of these two inputs into the theory. We utilize the sp^3s^* band structures¹⁵ because they have recently been shown to compare favorably with experiment for $\text{Al}_x\text{Ga}_{1-x}\text{As}$ (Ref. 17) and because they have proven accurate and useful in numerous applications.^{1,3-6,15,18} We use the VCA for our effective medium rather than the coherent-potential approximation (CPA)¹⁶ because $\text{Al}_x\text{Ga}_{1-x}\text{As}$ has a relatively small disorder parameter,^{19,20} which places it into the category of weak scattering alloys. Thus, the VCA is expected to adequately describe the global properties of this material.¹⁶ In fact, calculations^{19,20} utilizing the CPA for $\text{Al}_x\text{Ga}_{1-x}\text{As}$ have shown that the corrections to the VCA generated by this approximation are small for this alloy. Formally, the global properties of the alloy in our approximation are contained in the VCA Green's function, which is defined as

$$g(E) = (E - H_v)^{-1}, \quad (1)$$

where E is an energy and H_v is the sp^3s^* Hamiltonian¹⁵ for $\text{Al}_x\text{Ga}_{1-x}\text{As}$, calculated in the VCA.

As in previous papers,¹⁻⁴ we describe the local properties of the alloy host using the embedded-cluster method.¹²⁻¹⁴ As is noted above, in the present application, we only account for the alloy disorder in the nearest-neighbor shell of atoms surrounding the vacancy site. To simulate this for a particular alloy configuration, a five-atom cluster, consisting of a central anion (As, to be replaced by the vacancy later in the calculation) tetrahedrally surrounded by four nearest-neighbor cations (either Al or Ga) in a particular configuration, is embedded in the VCA medium. For this configuration, the alloy host is described by the cluster Green's function, which satisfies the Dyson equation

$$G(E) = g(E) + g(E)V G(E) = [1 - g(E)V]^{-1}g(E), \quad (2)$$

where V is the cluster potential for the configuration under consideration and is defined as

$$V = H_c - H_v \quad (3)$$

for sites inside the cluster. For sites outside the cluster, V vanishes. In Eq. (3), H_c is the sp^3s^* Hamiltonian¹⁵ for that particular cluster configuration.

The vacancy-associated deep levels are determined by replacing the central As atom of the cluster by an ideal vacancy,²¹⁻²⁵ and calculating the persistent deep levels using the Hjalmarson *et al.*⁵ theory. In this approach, the diagonal matrix elements of the defect potential are taken to be infinite in magnitude and the off-diagonal matrix elements are taken to be zero. This is very similar to the use of an infinite potential for an ideal vacancy which has been made in numerous previous studies.²¹⁻²⁵ This approximation allows the vacancy "atom" to be decoupled from the host, since the result of this assumption is

that no electron is allowed to reside at the vacancy site, simulating the effect of a missing atom. This theory neglects lattice relaxation, which should certainly be expected to be important in the case of a vacancy. Furthermore, vacancies in semiconductors are well known to trap charge and to exist in several charge states. Thus, the potential of a vacancy clearly cannot be infinite, as in the ideal-vacancy approximation, but must be some finite value which depends on the amount of charge trapped at the vacancy site. Such effects can shift the vacancy-associated deep levels from the values predicted in the ideal-vacancy approximation, and such shifts may be comparable to those introduced by lattice relaxation. Also, the different charge states of a vacancy are each expected to produce a different deep level. All of these charging and charge-state effects are also neglected in the present theory because of the ideal-vacancy assumption. However, the use of this approximation and the related neglect of lattice relaxation, charging effects, and charge-state splittings have been justified in previous work,^{18,23,24} where it was argued that such effects do not appreciably affect the chemical trends in the vacancy-associated deep levels. Since in the present paper we are primarily interested in investigating such trends for the alloy broadening of the vacancy-produced deep levels in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ (specifically, we are interested in obtaining trends for the x dependence of this broadening), we feel that the ideal-vacancy assumption is a reasonable first approximation. Clearly, however, lattice relaxation, charging effects, and charge-state splittings could have a significant effect on the size of the predicted alloy broadening. Thus, such effects should be included before any meaningful comparison between theory and experiment can be made.

Just as for most deep-level theories based on the Green's-function technique,²²⁻²⁵ for the case of the ideal vacancy, the deep-level energies E in the Hjalmarson *et al.*⁵ theory are solutions to the determinantal equation⁷

$$\det[G(E)] = 0. \quad (4)$$

In the present theory, $G(E)$ is the cluster Green's function, Eq. (2), for the particular cluster configuration under consideration. The combination of Eqs. (2), (3), and (4) make it clear that one should expect different deep levels E for each distinct cluster configuration. It is worth noting that Eq. (4) need only be solved in the subspace of the ideal vacancy, so that it reduces to a 4×4 determinant in the tight-binding basis (for the four orbitals at the vacancy site). There are thus four solutions to Eq. (4). One of them gives the s -like deep level of the vacancy, and the other three are triply degenerate and give the p -like deep level.²⁶

The procedure described above is repeated for each distinct cluster configuration.²⁶ This results in both s -like and p -like vacancy-induced deep-level spectra in the band gap of the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ host. In the present theory, both of these spectra are a series of delta-function lines, one for each configuration.²⁷ In these spectra, each delta-function line is weighted by the probability of occurrence of the cluster configuration which produced it.²⁸ For all

of the results presented below, we have assumed that this probability is given by the binomial distribution,²⁸ and thus that the alloy under consideration is completely random. This assumption, however, affects only the moments of the *s*- and *p*-like spectra, and not the component levels computed via Eqs. (2)–(4). In principle, our method could be applied to nonrandom alloys by replacing the binomial distribution²⁸ with one chosen to reflect the nonrandomness. This clearly would affect the results of the moment calculations presented below.

The delta-function spectra associated with the vacancy-induced deep levels can be characterized by their configuration-averaged moments as well as by their component levels. Of particular interest are the composition dependences of the first moments or average energies and the widths of both the *s*-like and the *p*-like spectra. The first moment of one of these spectra is clearly the center of the spectrum and the corresponding width (or square root of the second moment about the mean) is a measure of the strength of the alloy broadening. For delta function spectra, these quantities are easily calculated. Their relationship to an experimentally measured alloy-broadened deep-level spectrum can be subtle, however. The latter point is discussed in some detail in Ref. 3.

III. RESULTS AND DISCUSSION

The results for the *s*-like and *p*-like alloy-broadened deep-level spectra obtained for the ideal As vacancy in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ by the procedure outlined above are summarized in Figs. 1 and 2.

In Fig. 1, we show the composition dependences of the

component levels for each of the five unique cluster configurations for both the *s*-like and the *p*-like vacancy-associated deep-level spectra. Also shown in this figure are the composition dependences of the first moments or average energies of these spectra. As is clear from the figure, the *s*-like deep-level spectrum lies closer to the valence-band edge than does the *p*-like spectrum, in general agreement with results obtained earlier by Ho and Dow,²⁴ using the same band structures we use here, but characterizing the alloy with the VCA. It is clear from the figure that all of the component levels are independent of the conduction-band edge as *x* is varied, as is characteristic of deep levels in general.⁶ Furthermore, they are not equally spaced, unlike the results of calculations of similar levels made using perturbation theory.²⁹ The unequal level spacing is attributable to the differences in the off-diagonal matrix elements of the sp^3s^* Hamiltonians for AlAs and GaAs which enter the calculation.

The behavior of the first moments as a function of *x* may be understood by considering the behavior of the component levels whose configuration average produce it. In the present case, the first moments we find are very close to the results obtained in the VCA for the A_1 - and T_2 -symmetric vacancy levels by Ho and Dow.²⁴ This is an indication that the centers of the alloy-broadened vacancy-associated deep-level spectra are relatively insensitive to the theory used to characterize the alloy host. In this regard, it is worth noting that the VCA does not yield any information concerning the deep levels produced by the different local environments. Thus, the additional computational effort needed to implement the

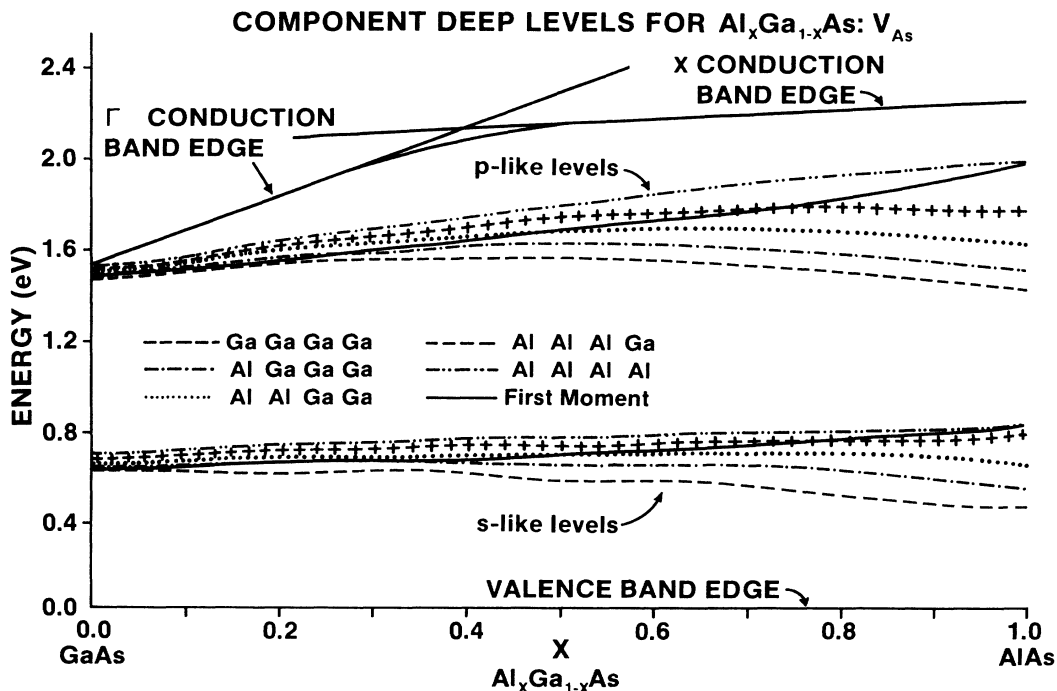


FIG. 1. Composition dependences of the component levels and the average energies for the alloy-broadened deep-level spectra produced by the ideal As vacancy in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ for both the *s*-like and the *p*-like vacancy-associated states.

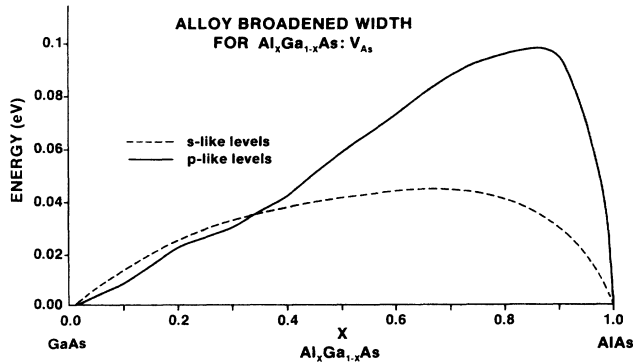


FIG. 2. Composition dependences of the widths of the alloy-broadened deep-level spectra produced by the ideal As vacancy in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ for both the s -like (dashed curve) and the p -like (solid curve) vacancy-associated states.

embedded-cluster method is rewarded with additional information which the VCA (or any other single-site effective medium theory) is incapable of producing.

In Fig. 2, we illustrate the computed spectrum widths as functions of x for both the s -like and the p -like deep-level spectra. The dashed curve is the width of the s -like spectrum, while the solid curve is the width for the p -like states. In contrast to some of the cases considered in our earlier work,¹⁻⁴ in the present case all of the component deep levels for both the s -like and the p -like states lie in the band gap for all alloy compositions. Thus, they all contribute to the spectrum width for all x . Therefore, these width versus x curves are smoother than analogous results found earlier for substitutional impurities.¹⁻⁴ In qualitative agreement with previous results, however, the spectrum widths shown in Fig. 2 show marked asymmetries about $x=0.5$. This should be contrasted with similar results obtained using perturbation theory,²⁹ where such widths are always symmetric about $x=0.5$. More important than the specific shape of the width versus x curves, however, are their magnitudes, which are estimates of the importance of inhomogeneous alloy broadening for the vacancy-associated deep levels in

$\text{Al}_x\text{Ga}_{1-x}\text{As}$. For the s -like deep-level spectrum, the present theory predicts that the spectrum width should be of the order of 20–45 meV for most compositions, while for the p -like spectrum, a width ranging from nearly 25 to about 100 meV is predicted, depending on the composition. Thus, the inhomogeneous broadening of the anion vacancy-associated deep levels due to nearest-neighbor disorder in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ is certainly non-negligible and could even be a potentially important effect for understanding such levels in this material.

In summary, we have extended our previous theory of the inhomogeneous alloy broadening of deep levels due to substitutional impurities in semiconductor alloys¹⁻⁴ to treat vacancy-associated levels in such materials. Using this technique, we have investigated the effects of alloy disorder on the ideal anion-site vacancy in $\text{Al}_x\text{Ga}_{1-x}\text{As}$. The results of our investigation predict that both the s -like and the p -like vacancy-associated deep levels in this material should experience appreciable alloy broadening. Although the present technique includes only the effects of alloy disorder in the nearest-neighbor environment of the vacancy, it is, in principle, generalizable to account for such disorder in the second³ and higher-neighbor environments of the vacancy. The method is also, in principle, generalizable to account for lattice relaxation and short-range-order effects, which can also contribute to observed widths of deep-level spectra. It should be noted that lattice relaxation effects are expected to be significant for the vacancy levels treated here. Therefore, such effects should be included in the theory before a meaningful comparison with experiment can be made.

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- ²⁷The total number of configurations is given by the sum of the binomial coefficients
- $$n = \sum_{N_{\text{Ga}}=0}^{N_c} \binom{N_c}{N_{\text{Ga}}},$$
- where $N_c = N_{\text{Ga}} + N_{\text{Al}}$ is the total number of cations in the cluster. In our five-atom cluster approximation, $N_c = 4$. Thus $n = 16$ in our approach. Not all configurations are distinct, however. It can be easily shown that only five distinct configurations exist—all Ga, one Al plus three Ga, two Al plus two Ga, three Al plus one Ga, and all Al.
- ²⁸The probability of occurrence of the *i*th cluster configuration is assumed to be given by the binomial distribution
- $$P_i = \binom{N_c}{N_{\text{Ga}}^i} x^{N_{\text{Al}}^i} (1-x)^{N_{\text{Ga}}^i},$$
- which implicitly assumes that the alloy is completely random.
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