CHEMICAL TRENDS FOR DEEP LEVELS ASSOCIATED WITH
VACANCY-IMPURITY COMPLEXES IN SEMICONDUCTORS

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ABSTRACT

Beginning with the theory of deep traps due to vacancy-impurity pairs, we have developed a theory of deep levels associated with vacancy-impurity complexes in zincblende hosts. We consider triplet complexes which consist of a vacancy that is a nearest-neighbor to two identical, substitutional impurities. Such defects are thought to play an important role in recombination processes in device materials. On the basis of this theory, the chemical trends in such deep levels are predicted for 12 semiconductors and for the semiconductor alloy $\text{GaAs}_{1-x}\text{P}_x$. These predictions show that a triplet complex may have deep levels which are very different from those of either the isolated impurity or the vacancy-impurity pair. For example, complexing with a second impurity can produce deep levels at energies where neither the pair nor the isolated impurity produce any. Examples of such effects are discussed for GaP and $\text{GaAs}_{1-x}\text{P}_x$.

CONTENTS

ACKNOWLEDGEMENTS	ii
ABSTRACT	iii
CHAPTER	
I. INTRODUCTION	1
II. SHALLOW AND DEEP LEVELS	7
III. VOGL-HJALMARSON THEORY	14
3.1 Vogl Bandstructures for the Host Semiconductors	14
3.2 Deep Level Theory for Substitutional Defects	18
IV. FORMALISM FOR THE TRIPLET COMPLEX	24
4.1 Defect Potential	24
4.2 Block-Diagonalization of the Perfect Crystal Green's Function G^0	32
V. RESULTS AND DISCUSSION	44
5.1 General Discussion of the Numerical Results	44
5.1.1 Results for GaP	46
5.1.2 Results for Other Semiconductors	58
5.2 Deep Acceptor-Like Levels in Ge	61
VI. ALLOY COMPOSITION DEPENDENCE OF DEEP LEVELS IN $\text{GaAs}_{1-x}\text{P}_x$	126
VII. SUMMARY AND CONCLUSIONS	137
REFERENCES	140

APPENDIX

A. THE BLOCK-DIAGONALIZATION OF PERFECT CRYSTAL GREEN'S FUNCTION G^0	144
B. THE RELATIONSHIP BETWEEN THE MATRIX ELEMENTS OF THE GREEN'S FUNCTION IN THE TWO COORDINATE SYSTEMS	162
C. COMPUTER CODE	169

LIST OF FIGURES

1. Figure 1. Structural schematic diagram of triplet of defects in the unit cell at $R=0$	26
2. Figure 2(a). Energy levels of a_1 and b_1 symmetries produced by a triplet cation (gallium) vacancy-impurity complex symbolized by $(V_{Ga}, 2X_p)$ in GaP (plus symbol curves)	58
3. Figure 2(b). Energy levels of a_1 and b_1 symmetries produced by a triplet anion (phosphorus site) vacancy-impurity complex $(2X_{Ga}, V_p)$ in GaP (plus symbol curves)	60
4. Figure 2(c). Energy levels of b_2 symmetry produced by a triplet vacancy-impurity complex for both a cation (gallium-site) vacancy $(V_{Ga}, 2X_p)$ and an anion (phosphorus-site) vacancy $(2X_{Ga}, V_p)$ in GaP (plus symbol curves)	62
5. Figure 3(a). Energy levels of a_1 and b_1 symmetries produced by a triplet vacancy-impurity $(2X, V)$ in Ge	64
6. Figure 3(b). Energy levels of b_2 symmetry produced by a triplet vacancy-impurity complex $(2X, V)$ in Ge	66
7. Figure 4(a). Energy levels of a_1 and b_1 symmetries produced by a triplet vacancy-impurity $(2X, V)$ in Si	68
8. Figure 4(b). Energy levels of b_2 symmetry produced by a triplet vacancy-impurity complex $(2X, V)$ in Si	70
9. Figure 5(a). Energy levels of a_1 and b_1 symmetries produced by a triplet cation (gallium-site) vacancy-impurity complex $(V_{Ga}, 2X_{As})$ in GaAs	72
10. Figure 5(b). Energy levels of a_1 and b_1 symmetries produced by a triplet anion (arsenic site) vacancy-impurity complex $(2X_{Ga}, V_{As})$ in GaAs	74

11. Figure 5(c). Energy levels of b_2 symmetry produced by a triplet vacancy-impurity complex for both cation vacancy ($V_{Ga}, 2X_{As}$) and anion vacancy ($2X_{Ga}, V_{As}$) triplet complexes in GaAs 76
12. Figure 6(a). Energy levels of a_1 and b_1 symmetries produced by a triplet cation (gallium-site) vacancy-impurity complex ($V_{Ga}, 2X_{Sb}$) in GaSb 78
13. Figure 6(b). Energy levels of a_1 and b_1 symmetries produced by a triplet anion (antimony-site) vacancy-impurity complex ($2X_{Ga}, V_{Sb}$) in GaSb 80
14. Figure 6(c). Energy levels of b_2 symmetry produced by a triplet vacancy-impurity complex for both cation vacancy ($V_{Ga}, 2X_{Sb}$) and anion vacancy ($2X_{Ga}, V_{Sb}$) triplet complexes in GaSb 82
15. Figure 7(a). Energy levels of a_1 and b_1 symmetries produced by a triplet cation (aluminium-site) vacancy-impurity complex ($V_{Al}, 2X_P$) in AlP 84
16. Figure 7(b). Energy levels of a_1 and b_1 symmetries produced by a triplet anion (phosphorus-site) vacancy-impurity complex ($2X_{Al}, V_P$) in AlP 86
17. Figure 7(c). Energy levels of b_2 symmetry produced by a triplet vacancy-impurity complex for both cation vacancy ($V_{Al}, 2X_P$) and anion vacancy ($2X_{Al}, V_P$) triplet complexes in AlP 88
18. Figure 8(a). Energy levels of a_1 and b_1 symmetries produced by a triplet cation (aluminium-site) vacancy-impurity complex ($V_{Al}, 2X_{As}$) in AlAs 90
19. Figure 8(b). Energy levels of a_1 and b_1 symmetries produced by a triplet anion (arsenic site) vacancy-impurity complex ($2X_{Al}, V_{As}$) in AlAs 92
20. Figure 8(c). Energy levels of b_2 symmetry produced by a triplet vacancy-impurity complex for both cation vacancy ($V_{Al}, 2X_{As}$) and anion vacancy ($2X_{Al}, V_{As}$) triplet complexes in AlAs 94

21. Figure 9(a). Energy levels of a_1 and b_1 symmetries produced by a triplet cation (indium-site) vacancy-impurity complex ($V_{In}, 2X_p$) in InP	96
22. Figure 9(b). Energy levels of a_1 and b_1 symmetries produced by a triplet anion (phosphorus-site) vacancy-impurity complex ($2X_{In}, V_p$) in InP	98
23. Figure 9(c). Energy levels of b_2 symmetry produced by a triplet vacancy-impurity complex for both cation vacancy ($V_{In}, 2X_p$) and anion vacancy ($2X_{In}, V_p$) triplet complexes in InP	100
24. Figure 10(a). Energy levels of a_1 and b_1 symmetries produced by a triplet cation (indium-site) vacancy-impurity complex ($V_{In}, 2X_{As}$) in InAs	102
25. Figure 10(b). Energy levels of a_1 and b_1 symmetries produced by a triplet anion (arsenic site) vacancy-impurity complex ($2X_{In}, V_{As}$) in InAs	104
26. Figure 10(c). Energy levels of b_2 symmetry produced by a triplet vacancy-impurity complex for both cation vacancy ($V_{In}, 2X_{As}$) and anion vacancy ($2X_{In}, V_{As}$) triplet complexes in InAs	106
27. Figure 11(a). Energy levels of a_1 and b_1 symmetries produced by a triplet cation (indium-site) vacancy-impurity complex ($V_{In}, 2X_{Sb}$) in InSb	108
28. Figure 11(b). Energy levels of a_1 and b_1 symmetries produced by a triplet anion (antimony-site) vacancy-impurity complex ($2X_{In}, V_{Sb}$) in InSb	110
29. Figure 11(c). Energy levels of b_2 symmetry produced by a triplet vacancy-impurity complex for both cation vacancy ($V_{In}, 2X_{Sb}$) and anion vacancy ($2X_{In}, V_{Sb}$) triplet complexes in InSb	112

30. Figure 12(a). Energy levels of a_1 and b_1 symmetries produced by a triplet cation (zinc-site) vacancy-impurity complex ($V_{Zn}, 2X_{Se}$) in ZnSe	114
31. Figure 12(b). Energy levels of a_1 and b_1 symmetries produced by a triplet anion (selenium-site) vacancy-impurity complex ($2X_{Zn}, V_{Se}$) in ZnSe	116
32. Figure 12(c). Energy levels of b_2 symmetry produced by a triplet vacancy-impurity complex for both cation vacancy ($V_{Zn}, 2X_{Se}$) and anion vacancy ($2X_{Zn}, V_{Se}$) triplet complexes in ZnSe	118
33. Figure 13(a). Energy levels of a_1 and b_1 symmetries produced by a triplet cation (zinc-site) vacancy-impurity complex ($V_{Zn}, 2X_{Te}$) in ZnTe	120
34. Figure 13(b). Energy levels of a_1 and b_1 symmetries produced by a triplet anion (tellurium-site) vacancy-impurity complex ($2X_{Zn}, V_{Te}$) in ZnTe	122
35. Figure 13(c). Energy levels of b_2 symmetry produced by a triplet vacancy-impurity complex for both cation vacancy ($V_{Zn}, 2X_{Te}$) and anion vacancy ($2X_{Zn}, V_{Te}$) triplet complexes in ZnTe	124
36. Figure 14. Composition dependences of the deep levels associated with triplet cation vacancy-anion impurity complexes in the alloy $GaAs_{1-x}P_x$	133
37. Figure 15. Composition dependences of the deep levels associated with triplet anion vacancy-cation impurity complexes in the alloy $GaAs_{1-x}P_x$	135
38. Figure A.1. The relationship between the new coordinate system and the zincblende coordinate system	150

CHAPTER I

INTRODUCTION

It is well known that semiconductors are very important materials for device applications. They are insulators at zero temperature and their energy gap is relatively narrow, with typical values being of the order of 1-2 eV. The characteristics of these materials are to a large extent determined by lattice imperfections. The performance characteristics of many semiconductor devices are thus severely limited by effects which are related to impurities, defects, and complexes in the materials from which such devices are manufactured. In particular, defects may form energy levels which lie within the fundamental band-gap of the semiconductor, and these levels can strongly affect both the electrical and the optical properties of such materials. These band-gap defect levels fall into two general classes. The first class consists of shallow levels, which are usually formed by substitutional impurities whose valence differs from that of the host by unity (1). These levels are produced by the long-ranged Coulomb potential of the defect and lie within ~ 0.1 eV from the valence- or conduction-band edges. The second class of defects produces "deep" levels lying well within the band gap (2-6). These

levels are controlled by the central-cell, atomic-like potential of the defects and they usually lie at energies greater than ~ 0.1 eV from a band edge.

Hjalmarson, Vogl, Wolford, and Dow (7) have shown that the chemical trends in the deep energy levels of isolated substitutional impurities can be understood using a Koster-Slater (8) 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 the host atoms. Sankey and co-workers (9-13) have generalized these ideas to treat paired substitutional impurities, and have predicted the chemical trends in deep pair levels in GaP, GaAs_{1-x}P_x, GaAs, Si, and InP. Myles and Sankey (14) have developed a theory of deep levels due to vacancies paired with nearest-neighbor sp^3 -bonded substitutional impurities in zincblende hosts, and have calculated the chemical trends in the deep levels associated with vacancy-impurity pairs in 12 different semiconductors.

The purpose of this work is to generalize the theory of Myles and Sankey (14) to treat the deep levels produced by more complicated vacancy-impurity complexes. In particular, in this dissertation we develop a theory of deep levels produced by triplet vacancy-impurity complexes in zincblende

semiconductor hosts. Specifically, we consider complexes which consist of a vacancy that is a nearest-neighbor to two identical substitutional impurities (hereafter such a complex will be called a "triplet complex"). Consideration of this type of complex is the simplest possible extension of the theory of Myles and Sankey (14). The theory which accomplishes this generalization is outlined in Chapter III, and some of the mathematical details are discussed in the appendices. On the basis of this theory, we calculate the chemical trends in the deep levels associated with such complexes in 12 different semiconductors and the alloy composition dependences of deep levels produced by such complexes in the alloy $\text{GaAs}_{1-x}\text{P}_x$. The results of calculations made using this new theory for such complexes in several semiconductor materials are presented in Chapters V and VI.

Vacancies are important native defects in semiconductor materials and will be present to a greater or lesser extent, depending on the material-preparation technique. Furthermore, vacancies are mobile and can thus migrate in the material and be trapped by impurities to form a vacancy-impurity complex. The existence of such complexes has been shown to have an important effect on the efficiency of radiative donor-acceptor recombination in silicon (15,16), GaP (17,18), GaAs (18), $\text{GaAs}_{1-x}\text{P}_x$ (18), ZnTe (19), and ZnSe

(20). Presumably, such complexes act as radiative "killer centers" in these materials. In addition, the hardening and other mechanical properties of silicon-doped GaP are known to be strongly affected by the presence of these complexes (21,22).

Myles and Sankey (14) have found that an impurity paired with an ideal vacancy (23-30) may have energy levels which are significantly altered in comparison with those of either isolated defect. Thus, the presence of vacancies in a material can greatly alter the position of deep levels associated with particular impurities. This finding, as well as the fact that there is evidence that triplet complexes might be experimentally important (18), motivates the present work. The theory presented here for deep levels due to triplet complexes should be viewed as a first step beyond the theory for the simplest complex treated by Myles and Sankey (14). These calculations will deepen our understanding of how the local environment of an impurity affects its deep levels. Furthermore, since, as already stated, vacancy-impurity complexes are thought to be important in recombination processes in device materials, the results we present here will have the potential to increase our understanding of the effect of such complexes on the electronic properties of device materials. This, in turn,

could potentially (although certainly indirectly) lead to improvement in device fabrication.

Our theory is based upon the semiempirical tight binding bandstructure model of Vogl, Hjalmarson, and Dow (31), the Hjalmarson, Vogl, Wolford, and Dow (7,32) theory of deep levels, and the Myles and Sankey vacancy-impurity pair theory (14). Our principal finding is that a triplet complex may have deep levels which are very different from those of either the isolated impurity or the vacancy-impurity pair. Our predictions of these levels will thus potentially be a valuable aid in the identification of the defect center which produces an observed deep energy level.

The remainder of this dissertation is organized as follows. In Chapter II, some background material is discussed, and the difference between shallow and deep levels in semiconductors is briefly reviewed (2). In Chapter III, we present a brief discussion of both the Vogl et al. (31) bandstructures with which we model our host semiconductors and the Hjalmarson et al. (32) theory of deep levels due to substitutional impurities, which forms the starting point for our theory. These two chapters are included mainly for completeness and as a review. In Chapter IV, we present an outline of the formalism we have developed for calculating the deep levels due to triplet complexes. Chapter V

contains our results, obtained using this formalism, for the chemical trends in the deep levels due to such complexes for 12 semiconductors. In that Chapter, we also present comparisons of these results with experimental data, where it is available, and discuss their implications for interpreting data on deep levels. Chapter VI contains our results for the alloy composition dependence of deep levels due to such triplet complexes in $\text{GaAs}_{1-x}\text{P}_x$. In that chapter, these results are compared with analogous results for vacancy-impurity pairs in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ obtained by Myles et al. (33). A summary and conclusions is presented in Chapter VII. Finally, the appendices discuss some of the calculational details and list the major computer programmes we have used in our calculations.

CHAPTER II

SHALLOW AND DEEP LEVELS

In this chapter, we briefly review the elementary theory of shallow levels in semiconductors and contrast the physics of these levels with what is currently understood about the basic physics of deep levels in semiconductors. This chapter is included by way of review for the reader already familiar with the field. However, it should also serve as a brief introduction for the reader unfamiliar with the theory of defects in semiconductors.

It is well known that shallow levels produced by substitutional impurities can be excellently explained by so called effective-mass theory, otherwise known as the hydrogenic model for impurities (2). Let us now describe qualitatively the elementary aspects of this model. According to band theory, at a temperature of 0K, the pure and perfect crystalline semiconductor has completely full valence bands, a forbidden energy gap, and completely empty conduction bands.

Let us assume that we replace one of the host atoms by an atom from the column of the periodic table to the right of the column of the host atom. The impurity atom thus has one extra valence electron which it can "donate" to the

conduction band. It is therefore called a donor impurity and the energy levels which are produced in the bandgap are thus called donor levels. Although all host atoms are on average electrically neutral, the positively charged impurity ion will set up a Coulomb field in addition to all of the crystal fields that existed before the introduction of the impurity. Since this positive charge is in a dielectric medium, the Coulomb potential for this charge will be screened by the medium and will thus be given by $U(r)=e/\epsilon r$, where ϵ is the dielectric constant of the material. On the other hand, the extra electron will occupy the lowest available energy state, i.e., the bottom of the conduction band. For the host bands, the energies of the states nearest the bottom of the conduction band can, at least near the Brillouin zone center ($k=0$), be approximated by the simple formula

$$E(k) = E_C + \hbar^2 k^2 / 2m_e^* \quad (2-1)$$

where E_C is the conduction band minimum, k is the modulus of the wave vector $\vec{k}$, and m_e^* is the effective mass of the electron at the bottom of the conduction band. This means that the dynamical behavior of an electron in the conduction bands is the same as that of a free electron with a mass m_e^* . Now the physical picture of the impurity charge becomes that of a free electron with mass m_e^* under the action of the

screened Coulombic potential $e/\epsilon r$. So the situation is exactly the same as for the hydrogen atom except that now the "proton" has a charge equal to e/ϵ and the electron has a mass equal to m_e^* . We can immediately conclude that the energy levels of the impurity are given by

$$E_n = E_C - e^4 m_e^* / 2\hbar^2 \epsilon^2 n^2, \quad (2-2)$$

or

$$E_n = E_C + E_n^H (m_e^* / m_0 \epsilon^2), \quad (2-3)$$

where

$$E_n^H = - e^4 m_0 / 2\hbar^2 n^2 \quad (2-4)$$

are the energy levels of the hydrogen atom. Here, m_0 is the mass of free electron, and $n=1,2,3,\dots,\infty$. Since typical experimentally determined values of ϵ are of the order of 10, and experimental values of m_e^* range from about $0.03m_0$ to about m_0 , Eq.(2-2) shows that the ionization energy of the donor energy levels ($n=1$) ranges from about 50 meV to about 130 meV. Compared with band gaps of the order of 1 eV, such levels are clearly "shallow."

The picture for acceptors (which are impurity atoms which come from the column in the periodic table to the left of the host atom) is analogous to that for donors. The only

change needed in the above discussion is the replacement of the electron by a hole and the bottom of the conduction band by the top of the valence band. Equation (2-3) becomes in this case

$$E_n = E_v - E_n^H(m_h^*/m_0 \xi^2) , \quad (2-5)$$

where E_v is the valence band maximum, m_h^* is the effective mass of a hole at the top of the valence band, and the E_n^H are again the energy levels of the hydrogen atom, expressed by Eq.(2-4). Numerical estimates for the binding energies of holes bound to acceptor impurities are similar to those described above for electrons bound to donor impurities.

The above discussion is an outline of the simplest version of a theory known as effective mass theory. Many more sophisticated versions of this theory have been developed and applied to the analysis of large quantities of data (2). The basic physics of these theories is, however, essentially the same as we have discussed above.

Effective mass theory works reasonably well for shallow donor and acceptor levels. In particular, for excited states of the impurities, it obtains excellent quantitative successes (2). For the ground states of the impurities, however, the agreement between the theoretical predictions and the experimental data is not as good as for the excited

states. To improve this situation, a considerable amount of work has been done (2). Since our interest is in deep levels, we will not discuss these more sophisticated shallow level theories here. The interested reader is referred to reference (2) for more details. We stress here that effective mass theory, even in its most sophisticated form, is known to be inadequate for describing even the qualitative features of deep levels in semiconductors (2,3,34). The basic reason for this is that the short-ranged central-cell potential of impurities, which was ignored in the shallow level theory, is known to play the primary role in producing deep levels (3,4-7,34). In fact, theorists often now use the definition that a deep level is one which is produced in the bandgap by this central-cell potential alone (neglecting the long ranged Coulomb potential), independent of the actual level depth (32). Unfortunately, this central-cell potential is difficult to understand and quantify because the electronic polarization and lattice distortion associated with it are very difficult to model.

Since deep traps (or deep levels) were discovered in 1952 (35), many theories have been presented to account for these phenomena. For example, cluster methods (36,24), extended Koster-Slater techniques (37,38), and other types of theories (39,40,3,4,5) have been developed and applied to

this problem. These early calculations suffered from lack of success in quantitatively relating the predicted defect energies to those observed in the perfect crystal bandgap. Modern theories of deep levels were only developed around 1978 and 1979 (2-5,33,34), so this field is still very young. There are two basic approaches to deep level theory, both of which have their uses for understanding the basic physics of these phenomena.

The first of these is "first-principles" deep level theories, such as pseudopotential (41) and local density (40) approaches. These theories concentrate on the accurate prediction of deep levels for a few specific defects in a few hosts. The advantages of these methods are that they can be made self-consistent and thus can relatively easily include lattice relaxation effects. Their disadvantages are that they require tremendous amounts of computer time and that they are not easily able to predict the trends ("chemical trends") in data because of their computational complexity.

The second approach to deep level theory uses semi-empirical tight-binding bandstructure theory as a starting point and empirically models the central cell potential. Several versions of this approach exist (7,30). We will discuss a particular version of this approach, known as

Vogl-Hjalmarson theory (7,31,32), in greater detail in Chapter III. The advantages of this general type of method and of the Vogl-Hjalmarson approach in particular, are (i) that one can use it to easily and inexpensively predict the trends in the trap depths as functions of both the defect and the host for numerous defect-host systems, (ii) that these trends are usually remarkably well predicted in comparison with experiment data, and (iii) that the deep trap energy one obtains by these methods is also qualitatively and often semi-quantitatively correct. However, because of its semi-empirical nature, absolute level depths obtained by this approach are not expected to be as reliable in comparison with experimental data as those obtained with "first principles" approaches. This is the main shortcoming of this approach. Despite their expected unreliability, the predictions obtained by this type of approach are often in semi-quantitative agreement both with experimental data and with more sophisticated theories (42). The latter fact lends support to the use of this type of theory to obtain an understanding of the deep levels due to defect complexes, such as the triplet vacancy-impurity complex we consider here.

CHAPTER III

VOGL-HJALMARSON THEORY

In this chapter, we briefly describe the Vogl et al. (31) nearest-neighbor, semi-empirical tight-binding theory of energy bands in zincblende and diamond structure materials and the Hjalmarson et al. (7) theory of deep levels due to substitutional impurities. These are often known collectively as the Vogl-Hjalmarson theory. We do this here because these theories form the starting point for our theory of deep levels due to triplet complexes which is developed in Chapter IV. We also include this chapter here as a review for the reader already familiar with deep level theory and as an introduction for the reader who is new to the field.

3.1 Vogl Bandstructures for the Host Semiconductors

One of the preconditions for a successful attempt at a theory of deep levels is the availability of a theory of the electronic bandstructure of the perfect host semiconductors which is as accurate as possible. Furthermore, for a successful theory of chemical trends in deep levels, as is desired in this work, the bandstructures must be

parameterized so that they are computationally easily and rapidly reproducible on a repeated basis for numerous defect calculations. The tight-binding approach to bandstructure theory is ideal for use in such calculations because the major bandstructure information for a given material may be reduced to only a few parameters. However, since tight-binding bandstructures are well-known to often contain inaccuracies, care must be taken that the parameters resulting from the application of such a theory should produce bandstructures which are accurate in comparison both with data and with very accurate bandstructures obtained by "first principles" techniques, such as self-consistent pseudopotential or local density functional techniques.

The Vogl et al. (31) sp^3s^* semi-empirical nearest-neighbor tight-binding bandstructure theory meets all of these criteria. In particular, it successfully reproduces the valence and lower conduction band structures of the major semiconductors in comparison with pseudopotential calculations (41). It thus forms a convenient and accurate parameterization with which to model the energy bands of the host crystal in a theory of deep levels. This model has the following properties: (i) the chemistry of sp^3 bonding is preserved (this is not always true for tight-binding theories); (ii) the diagonal matrix elements of the model

are related to the atomic energies of the chemical constituents, which permits the relatively easy exploration of chemical trends, simple treatment of alloys, and theories of semiconductors with defects; (iii) the off-diagonal matrix elements in the model scale as the inverse square of the bond length (the d^{-2} scaling role originally due to Harrison (43)), which allows (in principle) a treatment of lattice relaxation; (iv) the model employs a minimum number of parameters (13 independent parameters), and only nearest-neighbor matrix elements, so that the computation required to produce the energy bands, once the band parameters are fixed, is minimized; (v) the inclusion of excited s^* states (corresponding to the lowest excited states of the atoms) enables the theory to successfully reproduce not only the valence bands but also the lowest conduction bands, even in indirect gap semiconductors. Other empirical tight-binding theories lack one or more of these properties (30).

The perfect crystal Hamiltonian in this $sp\ s^*$ model is

$$H_0 = \sum_{i, \vec{R}} (|i\vec{a}\vec{R}\rangle E_i^a \langle i\vec{a}\vec{R}| + |i\vec{c}\vec{R}\rangle E_i^c \langle i\vec{c}\vec{R}|)$$

(3-1)

$$\sum_{\substack{i, j \\ \vec{R}, \vec{R}'}} [|i\vec{a}\vec{R}\rangle v_{ij}(\vec{R}, \vec{R}') \langle j\vec{c}\vec{R}'| + \text{h.c.}] ,$$

where $i=s, p_x, p_y, p_z$, or s^* labels the orbitals, a and c denote anion and cation, $\vec{R}$ specifies the unit cell, and h.c. denotes the Hermitian conjugate. The transfer-matrix elements V_{ij} are nonzero only between nearest-neighbors; namely when $|\vec{R} + \vec{\tau}_1 - \vec{R}'| = |\vec{\tau}_1|$, where $\vec{\tau}_1$ is the nearest-neighbor vector, $\vec{\tau}_1 = a_L(1,1,1)/4$. Here a_L is the cubic lattice constant. The states $|ia\vec{R}\rangle$ and $|ic\vec{R}\rangle$ are localized basis orbitals, called Lowdin orbitals (47), centered on the anion at $\vec{R}$ and the cation at $\vec{R} + \vec{\tau}_1$ respectively. The tight-binding parameters of the Vogl et al. Hamiltonian, Eq.(3-1), have the property that differences of the on-site matrix elements E_i^a and E_i^c are proportional to the corresponding atomic energy difference of the host atoms (7,32), as suggested earlier by Harrison (43). The nearest-neighbor transfer-matrix elements V_{ij} in this Hamiltonian are found to scale roughly according to the inverse square of the bond length d , following Harrison's d^{-2} scaling rule (43). The parameters E_i and V_{ij} for the semiconductors considered in this dissertation can be found in Table 1 of Ref.32, and were obtained by an empirical fit to accurate pseudopotential band structures (44). The use of an excited s^* orbital allows a description of the conduction bands that is flexible enough to treat both direct and indirect band-gap semiconductors. Figure 11 of Ref.32 displays the Vogl et al. sp^3s^* bandstructures for 15 major semiconductors, including the 12 we consider here.

3.2 Deep Levels Theory for Substitutional Defects

We now briefly discuss the Hjalmarson et al. (7) theory of deep levels due to substitutional impurities, which forms the starting point for the triplet complex theory we derive in Chapter IV. We emphasize, that while the calculations we do in this dissertation assume that the perfect crystal Hamiltonian H_0 is given by the Vogl et al. model, Eq.(3-1), the formalism outlined here and discussed in detail for triplet complexes in Chapter IV is independent of this particular choice and is valid for any bandstructure model. The numerical results one obtains, of course, do depend on the choice of H_0 . If we suppose that one atom of the perfect semiconductor is replaced by an impurity atom, the Schrodinger equation becomes

$$(H_0 + V)|\Psi\rangle = E |\Psi\rangle , \quad (3-2)$$

where H_0 is the Hamiltonian of the perfect semiconductor (given by Eq.(3-1) in our calculations). The defect potential V is formally given by

$$V = H - H_0 , \quad (3-3)$$

where H is the crystal Hamiltonian in the presence of the impurity. In Eq.(3-2), $|\Psi\rangle$ is the impurity wavefunction and

E is the deep level energy of interest. We seek solutions to Eq.(3-2) for the energy E (and also for the wavefunction $|\psi\rangle$) of the defect state in terms of the perfect-crystal Hamiltonian H_0 and the defect potential V . We are particularly interested in the case where the energy E occurs in the bandgap of the perfect crystal (i.e., where E is a deep level). In principle, the defect potential V describes the many-body interactions of an electron (or hole) with the host crystal and the impurity atom which, because of its size, slightly distorts its lattice environment (this effect is called "lattice relaxation") and because of its charge, slightly polarizes neighboring atoms (this effect is called "charge-state-splitting").

From Eq.(3-2), one formally obtains

$$[I - (E - H_0)^{-1}V] |\psi\rangle = 0 , \quad (3-4)$$

where I is a unit matrix. According to a standard algebraic theorem, the condition under which a set of homogeneous linear equations has non-trivial solutions is that the determinant of the coefficients must vanish. That is, Eq.(3-4) requires that

$$\det[I - (E - H_0)^{-1}V] = 0 . \quad (3-5)$$

Customarily, the concept of the Green's function is used, where the perfect crystal Green's function is defined as

$$G^O(E) = (E - H_O)^{-1} . \quad (3-6)$$

Equation (3-5) then becomes

$$\det[I - G^O(E)V] = 0 . \quad (3-7)$$

Using the point group symmetry of the defect can greatly simplify the calculations involved in finding solutions to Eq.(3-7). The determinant, Eq.(3-7) factors into a product of smaller determinantal equations labelled by symmetry. In general, this becomes

$$\det[I - G^O(E)V] = \prod_{r=1}^n \det[I^{(r)} - G^{O(r)}(E)V^{(r)}] = 0 , \quad (3-8a)$$

where the superscript r is the symmetry index, and n the number of irreducible representations contained in the point group for the lattice.

In the Hjalmarson et al. theory, both lattice relaxation and charge-state-splitting effects are ignored as a first approximation, in order to understand the dominating features of the problem. Such effects can, in principle, be included at a later stage of the calculation. Hjalmarson et al. also ignore the screened Coulomb potential of the defect and include the central cell defect potential only. Thus,

there are no shallow, effective mass-like levels (such as those previously discussed) in the Hjalmarson et al. theory, although they could be included by performing calculations similar to those discussed in Chapter II. In fact, use of the Hjalmarson et al. theory, which keeps only the central cell potential and ignores Coulomb effects, emphasizes the distinct physical difference between deep and shallow levels; the latter are produced by the Coulomb potential alone. Deep levels, by contrast, are those that are formed by the central cell potential alone. Thus, shallow and deep level theories are really the opposite limits of the theory of defects in semiconductors.

In the Hjalmarson et al. theory one makes two approximations about the form of the defect potential V , which are consistent with the neglect of charge state splittings and lattice relaxation. These are (i) that the atomic energy difference between two atoms in a solid is similar to that difference for two free atoms; and (ii) that, using the scaling with inverse bond length squared, the difference of interatomic matrix elements must be very small. In most cases, they are set to zero. Thus, the defect potential is diagonal in the appropriate representation. With these approximations, one then treats each equation resulting from the factorization of Eq.(3-8a) as an implicit equation for

the defect potential of symmetry r as a function of deep level energy E in the bandgap. This function is generated numerically, and a deep level energy versus defect potential energy diagram $V(E)$ or $E(V)$ is generated graphically from this function.

Finally, in order to relate these numerical results with specific atomic defects, Hjalmarson et al. make the assumption that, for symmetry r , the matrix elements of V , expressed in the same localized basis as the perfect crystal Hamiltonian H_0 , are proportional to the difference in the atomic energy of the impurity atom and that of the host atom it replaces.

For the isolated substitutional impurity case considered by Hjalmarson et al. (7), and for the zincblende lattice of interest, the symmetry index r has the values $r=A_1$, for s-like, non-degenerate states and $r=T_2$, for p-like, triply-degenerate states. Here A_1 and T_2 are, respectively, the group theoretical labels for the s-like and p-like states associated with the irreducible representations of the point group T_d of the zincblende lattice. In this case, Equation (3-8a) becomes two scalar equations

$$V(r) = 1/G^0(E) , \quad (3-8b)$$

where $r=A_1$ or T_2 . From this equation, an E versus V function can be generated as discussed above. In order to relate this to a specific atomic impurity, Hjalmarson et al. then assumed as mentioned above that

$$V^{(r)} = \beta_r (\epsilon_{\text{imp}}^{(r)} - \epsilon_{\text{host}}^{(r)}) , \quad (3-8c)$$

where $\epsilon_{\text{imp}}^{(r)}$ and $\epsilon_{\text{host}}^{(r)}$ are respectively the impurity and host atomic energies for states of symmetry r and β_r is an empirical parameter, which, for a fixed r , is a constant for all defect and host systems. By fitting to experimental data, Hjalmarson et al. have determined that $\beta_r=0.8$ for all s-like states and $\beta_r=0.6$ for all p-like states.

For the triplet vacancy-impurity complex we consider in the next chapter, we utilize many of the ideas of the Hjalmarson et al. substitutional defect theory. In particular, Eq.(3-8a) is still valid, but it does not reduce to the scalar equation Eq.(3-8b). Also, we still use eq.(3-8c) for the matrix elements of the defect potential. More details are discussed in the next chapter.

CHAPTER IV

FORMALISM FOR THE TRIPLET COMPLEX

4.1 Defect Potential

On basis of the Vogl et al. (31) bandstructure theory for the perfect crystal and Hjalmarson et al. (7,32) theory of deep levels, discussed in Chapter III, we now develop a formalism to treat the problem of deep levels associated with triplet vacancy-impurity complexes. As is briefly discussed in Chapter III, in the Hjalmarson et al. (7,32) theory, it is assumed that the on-site matrix elements of the defect potential are obtained from the atomic energy differences of the impurity and the host, and that the difference in the transfer-matrix elements between the impurity and the host are zero. As has already been mentioned, in the above localized basis representation and with these assumptions, the matrix of the defect potential is diagonal. This theory thus neglects both lattice relaxation and charge-state-splittings. The neglect of lattice relaxation around the vacancy appears, at first sight, to be a serious omission, and certainly is so if one desires sensitive predictions of absolute trap level depths. However, the neglect of both lattice relaxation and charge

state-splittings in a theory of chemical trends of deep levels has been justified in previous work (7,32), where it was argued that these effects tend to be monotonic functions of trap depth, and hence are not expected to greatly alter the order of the predicted deep levels. The resulting theory thus gives a global view of chemical trends, but is limited by uncertainties in absolute level depths as large as a few tenths of an electron volt. The long-ranged, dielectrically screened Coulomb interaction is also neglected in this model because it has a small effect on the energy scale of interest. Shallow impurities therefore have zero binding energy in this model.

The defect we consider here is shown schematically in Fig.1. This figure shows a structural representation of a triplet complex of nearest-neighbor impurities in the unit cell at $\vec{R}=\vec{0}$. This complex consists of an impurity at the center of a unit cell, complexed with two other impurities which are identical to each other. In this figure, $\otimes$ denotes the host atoms, $\odot$ denotes a cation impurity at the origin (which we later replace by a vacancy) and the two open circles $\bigcirc$ denote anion impurities. Occupying anion(1) and anion(2) are two identical impurity atoms with site indices $\vec{\tau}_1$ and $\vec{\tau}_2$, respectively, where $\vec{\tau}_1 = a_L(1,1,1)/4$, $\vec{\tau}_2 = a_L(-1,-1,1)/4$, and a_L is the cubic lattice constant.

Figure 1. Structural schematic diagram of a triplet of defects in the unit cell at $R=0$. $\otimes$ denotes the host atoms. $\odot$ denotes the cation at the origin. The two $\circ$ denote two identical impurity atoms anion(1) and anion(2) which occupy the sites $\vec{r}_1$ and $\vec{r}_2$, respectively.

It should be pointed out that this figure illustrates a more general case than the one we consider in this dissertation. Much of the formalism which follows can therefore be used to treat a triplet problem consisting of three impurities. However, here we consider only the triplet vacancy-impurity complex and will ultimately take the limit as the defect potential of the central impurity approaches that of a vacancy. This limiting process is described below. We illustrate the more general case here because most of the formalism we give below fits this case. The triplet vacancy-impurity complex is thus just a special case of the more general triplet defect. In addition, in this entire dissertation, all of our explicit equations are for the case illustrated in Fig.1; namely the case where the origin is taken to be the cation site. The opposite case, where the origin is taken to be an anion site and two of the nearest-neighbors are identical cation impurities can also easily be treated by our formalism. This merely requires the exchange of anion and cation labels in all equations. Thus, although we explicitly discuss the formalism only for the case where the origin is taken as a cation site, in Chapter V we present results for both types of triplet vacancy-impurity complexes, that is both for cation vacancy-two identical anion impurity complexes and for anion vacancy-two identical cation impurity complexes.

For the triplet complex with the cation at the origin, the defect potential is written as

$$V = \sum_i (|ic\vec{0}\rangle v_i^c \langle ic\vec{0}| + |ia\vec{\tau}_1\rangle v_i^a \langle ia\vec{\tau}_1| + |ia\vec{\tau}_2\rangle v_i^a \langle ia\vec{\tau}_2|) , \quad (4-1)$$

where a and c refer to the anion and cation sites, respectively. The states $|ic\vec{0}\rangle$, $|ia\vec{\tau}_1\rangle$, and $|ia\vec{\tau}_2\rangle$ are localized, Lowdin basis orbitals of type i for the cation c at the origin, for the anion(1) at the site $\vec{\tau}_1$, and for the anion(2) at the site $\vec{\tau}_2$, respectively. v_i^a and v_i^c are the anion and cation site defect potentials for orbital i. $\vec{\tau}_1$ and $\vec{\tau}_2$ are nearest-neighbor vectors shown in Fig.1. In writing Eq.(4-1), we have made the same approximations for the triplet defect potential as Hjalmarson et al. made for the isolated impurity potential. Namely, we have assumed that it is diagonal in the Lowdin basis (47) and that all orientations of p orbitals have the same defect energy. This is consistent with the assumptions made in pair calculations by Sankey et al. (9-13) and in the treatment of vacancy-impurity pairs by Myles and Sankey (14). We emphasize again that these approximations neglect both lattice relaxation and charge-state-splittings, but that they are useful for

obtaining a global theory of chemical trends. In Eq.(4-1), the sum on i is taken only over the s , p_x , p_y , and p_z orbitals. The excited s^* states which enter the Vogl et al. bandstructures are not included in this sum.

The reason for neglecting the s^* states in Eq.(4-1) is discussed in detail by Hjalmarson in his dissertation (32). Briefly it can be summarized as follows. The excited s^* states for all atoms in column II to VI of the periodic table lie within a very narrow range of energies with respect to the vacuum reference energy (see Table II in Ref.32). Thus, in the solid, the excited s^* states all lie at about the same energy--about 6 to 8 eV--because the solid state environment shifts all energies by approximately a constant amount. This means that substitution of an impurity atom for a host atom causes little change in either the excited s^* states of the host, which are located high in the conduction band, or the unoccupied nearest-neighbor-like impurity states. In other words, the defect potential will, to a good approximation, be determined by the s and p impurity potential energies only and not by the s^* impurity potential energy. This is not only because the s^* state does not couple strongly to the lower energy states, but also and most importantly because the s^* (and p^*) states are at about the same energies for all atoms.

The defect potential in Eq.(4-1) contains four independent parameters, namely v_s^a , v_s^c , v_p^a and v_p^c , since we assume that all orientations of the p orbitals have the same defect potential energies. Following Hjalmarson et al. (7,32) and in analogy with the discussion in the previous chapter, we take each of these four parameters to be proportional to an appropriate difference between defect and host atomic energies, as is illustrated for isolated impurities in Eq.(3-8c). For the case of interest in this dissertation, where the central site is occupied by an ideal vacancy, we take the appropriate defect potential matrix element to be infinite in magnitude, as has been done in numerous other studies of vacancies in semiconductors (23-30). This allows for the vacancy "atom" to be decoupled from the host since the net result of such an assumption is that no electron is allowed to reside at the vacancy site, which simulates the effect of a missing atom. Furthermore, Das Sarma and Madhukar (30) have shown that such an assumption is equivalent to the so-called bond-cutting method of creating an ideal vacancy. Thus, for a cation (anion) vacancy we take v_i^c (v_i^a) $\rightarrow \infty$ in Eq.(4-1).

Because the defect potential in Eq.(4-1) is local in the tight-binding basis, the Koster-Slater theory (8) is a convenient method for determining the bound state energies E

of the triplet complex. In this method these energies are given by solutions to the implicit Fredholm determinant equation (see Chapter III)

$$\det[I - G^0(E)V] = 0 , \quad (4-2)$$

where

$$G^0(E) = (E - H_0)^{-1} \quad (4-3)$$

is the perfect crystal Green's function, H is given by Eq.(3-1), and I is the identity matrix. The advantage of the Koster-Slater Green's function method is that the determinant in Eq.(4-2) only needs to be evaluated in the subspace of the perturbation. In the present case, this yields a 12x12 determinant (three atoms and four orbitals—one s and 3 p - per atom) before the vacancy limit is taken for the central site defect potential. When the vacancy limit is taken for that potential, this reduces to an 8x8 determinant, as is discussed below.

It should be pointed out that for the isolated impurities (32) and paired defects (9-14) in semiconductors, the block diagonalization of the host Green's function has been relatively straightforward because of the high symmetry of the defects. In the present case, however, the defect symmetry is reduced and the block diagonalization of the Green's function is non-trivial.

4.2. Block-Diagonalization of the Perfect Crystal Green's Function G^0

The Fredholm determinant in Eq.(4-2) can be simplified by symmetry considerations (45,46). The point group for an isolated point defect in a tetrahedrally symmetric zincblende 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, where the degeneracies referred to here and in the rest of this dissertation are understood to exclude spin degeneracy. From Fig.1 it can be seen that triplet complex defects in the same zincblende host are described by a reduced "molecular" symmetry group C_{2v} (45,46) (a twofold axis of rotation and two reflection planes containing the twofold axis and perpendicular to each other). This results in splittings of the T_2 levels and mixing of the "atomic" A_1 and T_2 levels on the three sites (46). Due to the fact that the point group C_{2v} has one-dimensional irreducible representations only (45,46), the T_2 level is completely split into three nondegenerate levels (46). 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),

In the zincblende coordinate system illustrated in Fig.1, the 12×12 matrix for the Green's function of the perfect crystal has the schematic form

$$G^O(E) = \begin{pmatrix} G^{aa} & G^{ac}(1) & G^{aa}(1,2) \\ G^{ca}(1) & G^{cc} & G^{ca}(2) \\ G^{aa}(2,1) & G^{ac}(2) & G^{aa} \end{pmatrix} \quad (4-4)$$

where we have defined the 4x4 submatrices

$$G^{aa} = \begin{pmatrix} G_{ss}^{aa} & 0 & 0 & 0 \\ 0 & G_{xx}^{aa} & 0 & 0 \\ 0 & 0 & G_{xx}^{aa} & 0 \\ 0 & 0 & 0 & G_{xx}^{aa} \end{pmatrix}, \quad (4-5)$$

$$G^{cc} = \begin{pmatrix} G_{ss}^{cc} & 0 & 0 & 0 \\ 0 & G_{xx}^{cc} & 0 & 0 \\ 0 & 0 & G_{xx}^{cc} & 0 \\ 0 & 0 & 0 & G_{xx}^{cc} \end{pmatrix}, \quad (4-6)$$

$$G^{ca}(1) = \begin{pmatrix} G_{ss}^{ca}(1) & G_{sx}^{ca}(1) & G_{sy}^{ca}(1) & G_{sz}^{ca}(1) \\ G_{xs}^{ca}(1) & G_{xx}^{ca}(1) & G_{xy}^{ca}(1) & G_{xz}^{ca}(1) \\ G_{ys}^{ca}(1) & G_{yx}^{ca}(1) & G_{yy}^{ca}(1) & G_{yz}^{ca}(1) \\ G_{zs}^{ca}(1) & G_{zx}^{ca}(1) & G_{zy}^{ca}(1) & G_{zz}^{ca}(1) \end{pmatrix}, \quad (4-7)$$

$$G^{ca}(2) = \begin{pmatrix} G_{ss}^{ca}(2) & G_{sx}^{ca}(2) & G_{sy}^{ca}(2) & G_{sz}^{ca}(2) \\ G_{xs}^{ca}(2) & G_{xx}^{ca}(2) & G_{xy}^{ca}(2) & G_{xz}^{ca}(2) \\ G_{ys}^{ca}(2) & G_{yx}^{ca}(2) & G_{yy}^{ca}(2) & G_{yz}^{ca}(2) \\ G_{zs}^{ca}(2) & G_{zx}^{ca}(2) & G_{zy}^{ca}(2) & G_{zz}^{ca}(2) \end{pmatrix}, \quad (4-8)$$

and

$$G^{aa}(2,1) = \begin{pmatrix} G_{ss}^{aa}(2,1) & G_{sx}^{aa}(2,1) & G_{sy}^{aa}(2,1) & G_{sz}^{aa}(2,1) \\ G_{xs}^{aa}(2,1) & G_{xx}^{aa}(2,1) & G_{xy}^{aa}(2,1) & G_{xz}^{aa}(2,1) \\ G_{ys}^{aa}(2,1) & G_{yx}^{aa}(2,1) & G_{yy}^{aa}(2,1) & G_{yz}^{aa}(2,1) \\ G_{zs}^{aa}(2,1) & G_{zx}^{aa}(2,1) & G_{zy}^{aa}(2,1) & G_{zz}^{aa}(2,1) \end{pmatrix}. \quad (4-9)$$

In the energy gap, $G^0(E)$ is a real symmetric matrix. We therefore have

$$G^{ac}(1) = [G^{ca}(1)]^T, \quad (4-10)$$

$$G^{ac}(2) = [G^{ca}(2)]^T, \quad (4-11)$$

$$G^{aa}(1,2) = [G^{aa}(2,1)]^T, \quad (4-12)$$

where the superscript T means the transpose of the matrix.

The matrix elements in Eqs.(4-5)-(4-9) are written in

suggestive notation. For example, in the Lowdin basis (47) discussed earlier, we have

$$G_{sx}^{ca}(1) = \langle sc\vec{0} | (E-H_0)^{-1} | p_x^a \vec{\tau}_1 \rangle, \quad (4-13)$$

$$G_{sx}^{ca}(2) = \langle sc\vec{0} | (E-H_0)^{-1} | p_x^a \vec{\tau}_2 \rangle, \quad (4-14)$$

$$G_{sx}^{aa}(2,1) = \langle sa \vec{\tau}_2 | (E-H_0)^{-1} | p_x^a \vec{\tau}_1 \rangle. \quad (4-15)$$

An important feature of these matrix elements is that they are evaluated using only the unperturbed Hamiltonian H_0 , and they thus depend only on the host band structure. Also, because the matrix elements of G^0 are taken between localized Lowdin orbitals (47), they include contributions from all of k space and from energetically distant bands.

It is worthwhile to point out that the matrix elements of perfect crystal Hamiltonian H_0 are nonzero only between nearest-neighbors in the present model. This does not mean that this is true for G^0 , however. For example, the matrix elements of G^0 between localized states on atoms which are second nearest-neighbors to each other may be nonzero, as is indicated in Eqs.(4-5)-(4-9).

After using the symmetric operations of the point group C_{2v} , the Green's function G^0 (12x12) can algebraically be block-diagonalized into the direct sum of four smaller

matrices. This is shown in more detail in Appendices A and B. The result of this manipulation is

$$G^O(E) = \left(\begin{array}{c|c|c|c} G_5^O(5 \times 5) & & & \\ \hline & G_4^O(4 \times 4) & & \\ \hline & & G_2^O(2 \times 2) & \\ \hline & & & G_1^O(1 \times 1) \end{array} \right) \quad (4-16)$$

The explicit expressions for the smaller submatrices shown schematically in Eq.(4-16) can be written as follows. The 5x5 submatrix has the form

$$G_5^O(5 \times 5) = \left(\begin{array}{ccccc} G_5^O(1,1) & G_5^O(1,2) & G_5^O(1,3) & G_5^O(1,4) & G_5^O(1,5) \\ G_5^O(1,2) & G_5^O(2,2) & G_5^O(2,3) & G_5^O(2,4) & 0 \\ G_5^O(1,3) & G_5^O(2,3) & G_5^O(3,3) & G_5^O(3,4) & G_5^O(3,5) \\ G_5^O(1,4) & G_5^O(2,4) & G_5^O(3,4) & G_5^O(4,4) & G_5^O(4,5) \\ G_5^O(1,5) & 0 & G_5^O(3,5) & G_5^O(4,5) & G_5^O(5,5) \end{array} \right) \quad (4-17)$$

where we have defined

$$G_5^O(1,1) = G_{ss}^{aa} + G_{ss}^{aa}(2,1) , \quad (4-17a)$$

$$G_5^O(2,2) = G_{ss}^{cc} , \quad (4-17b)$$

$$G_5^O(3,3) = G_{xx}^{aa} - G_{xx}^{aa}(2,1) - G_{xx}^{aa}(2,1) , \quad (4-17c)$$

$$G_5^O(4,4) = G_{xx}^{aa} + G_{zz}^{aa}(2,1) , \quad (4-17d)$$

$$G_5^O(5,5) = G_{xx}^{cc} , \quad (4-17e)$$

$$G_5^O(1,2) = \sqrt{2} G_{ss}^{ca} , \quad (4-17f)$$

$$G_5^O(1,3) = -\sqrt{2} G_{sx}^{aa}(2,1) , \quad (4-17g)$$

$$G_5^O(1,4) = G_{sz}^{aa}(2,1) , \quad (4-17h)$$

$$G_5^O(1,5) = \sqrt{2} G_{xs}^{ca} , \quad (4-17i)$$

$$G_5^O(2,3) = -2 G_{sx}^{ca} , \quad (4-17j)$$

$$G_5^O(2,4) = \sqrt{2} G_{xz}^{aa}(2,1) , \quad (4-17k)$$

$$G_5^O(3,4) = \sqrt{2} G_{xz}^{aa}(2,1) , \quad (4-17m)$$

$$G_5^O(3,5) = -2 G_{xy}^{ca} , \quad (4-17n)$$

and

$$G_5^O(4,5) = \sqrt{2} G_{xx}^{ca} , \quad (4-17p)$$

The 4x4 submatrix has the form

$$G_4^O(4 \times 4) = \begin{pmatrix} G_4^O(1,1) & G_4^O(1,2) & G_4^O(1,3) & G_4^O(1,4) \\ G_4^O(1,2) & G_4^O(2,2) & G_4^O(2,3) & G_4^O(2,4) \\ G_4^O(1,3) & G_4^O(2,3) & G_4^O(3,3) & G_4^O(3,4) \\ G_4^O(1,4) & G_4^O(2,4) & G_4^O(3,4) & G_4^O(4,4) \end{pmatrix}, \quad (4-18)$$

where we have defined

$$G_4^O(1,1) = G_{SS}^{aa} - G_{SS}^{aa}(2,1), \quad (4-18a)$$

$$G_4^O(2,2) = G_{XX}^{aa} + G_{XX}^{aa}(2,1) + G_{XY}^{aa}(2,1), \quad (4-18b)$$

$$G_4^O(3,3) = G_{XX}^{cc}, \quad (4-18c)$$

$$G_4^O(4,4) = G_{XX}^{aa} - G_{ZZ}^{aa}(2,1), \quad (4-18d)$$

$$G_4^O(1,2) = \sqrt{2} G_{SX}^{aa}(2,1), \quad (4-18e)$$

$$G_4^O(1,3) = -2 G_{XS}^{ca}, \quad (4-18f)$$

$$G_4^O(1,4) = - G_{SZ}^{aa}(2,1), \quad (4-18g)$$

$$G_4^O(2,3) = \sqrt{2} (G_{XX}^{ca} + G_{XY}^{ca}), \quad (4-18h)$$

$$G_4^O(2,4) = -\sqrt{2} G_{XZ}^{aa}(2,1), \quad (4-18i)$$

and

$$G_4^O(3,4) = -2 G_{xy}^{ca} . \quad (4-18j)$$

The 2x2 submatrix has the form

$$G_2^O(2x2) = \begin{pmatrix} G_2^O(1,1) & G_2^O(1,2) \\ G_2^O(1,2) & G_2^O(2,2) \end{pmatrix} , \quad (4-19)$$

where we have defined

$$G_2^O(1,1) = G_{xx}^{aa} + G_{xx}^{aa}(2,1) - G_{xy}^{aa}(2,1) , \quad (4-19a)$$

$$G_2^O(2,2) = G_{xx}^{cc} , \quad (4-19b)$$

and

$$G_2^O(1,2) = \sqrt{2} (G_{xx}^{ca} - G_{xy}^{ca}) . \quad (4-19c)$$

Finally, the 1x1 or scalar part of the Green's function has the form

$$G_1^O(1x1) = G_1^O(1,1) , \quad (4-20)$$

where we have defined

$$G_1^O(1,1) = G_{xx}^{aa} - G_{xx}^{aa}(2,1) + G_{xy}^{aa}(2,1) . \quad (4-20a)$$

In writing these expressions, we have used the shorthand notations.

$$G_{SS}^{ca} = G_{SS}^{ca}(1) , \quad (4-21)$$

$$G_{XX}^{ca} = G_{XX}^{ca}(1) , \quad (4-22)$$

$$G_{SX}^{ca} = G_{SX}^{ca}(1) , \quad (4-23)$$

$$G_{XS}^{ca} = G_{XS}^{ca}(1) , \quad (4-24)$$

and

$$G_{XY}^{ca} = G_{XY}^{ca}(1) . \quad (4-25)$$

The defect potential is diagonal, as has already been stated. It can thus be written as

$$V = V_5(5 \times 5) + V_4(4 \times 4) + V_2(2 \times 2) + V_1(1 \times 1) , \quad (4-26)$$

where we have defined the submatrices

$$V_5(5 \times 5) = \begin{pmatrix} v_s^a & 0 & 0 & 0 & 0 \\ 0 & v_s^c & 0 & 0 & 0 \\ 0 & 0 & v_p^a & 0 & 0 \\ 0 & 0 & 0 & v_p^a & 0 \\ 0 & 0 & 0 & 0 & v_p^c \end{pmatrix} , \quad (4-27)$$

$$V_4(4 \times 4) = \begin{pmatrix} v_x^a & 0 & 0 & 0 \\ 0 & v_p^a & 0 & 0 \\ 0 & 0 & v_p^c & 0 \\ 0 & 0 & 0 & v_p^a \end{pmatrix}, \quad (4-28)$$

$$V_2(2 \times 2) = \begin{pmatrix} v_p^a & 0 \\ 0 & v_p^c \end{pmatrix}, \quad (4-29)$$

and

$$V_1(1 \times 1) = v_p^a. \quad (4-30)$$

Finally, the Koster-Slater (8) eigenvalue determinant (12x12) factors to become

$$\det[I_5 - G_5^O(E)V_5] \times [I_4 - G_4^O(E)V_4] \times \quad (4-31)$$

$$\det[I_2 - G_2^O(E)V_2] \times [I_1 - G_1^O(E)V_1] = 0,$$

where the matrices I_5 , I_4 , I_2 , and I_1 are the unit matrices in the appropriate subspaces and the subscripts denote the dimensions of the subspaces.

As is mentioned above, for the case of interest here where we have a cation (anion) site at the origin occupied by a vacancy, we take the limits $V_S^C(V_S^a)$ and $V_P^C(V_P^a) \rightarrow \infty$. As is discussed by Myles and Sankey (14), this can be accomplished by at least two methods: (i) numerically, by allowing these quantities to become a sufficiently large numbers in Eq.(4-31), or (ii) analytically, by developing a slightly different formalism designed specially for the case where the origin site is occupied by a vacancy (for more detail, see Ref.14). It is both instructive and advantageous to take the analytic approach, since, in this way, the meaning of this limiting procedure becomes physically more transparent, and the 5x5, 4x4, and 2x2 determinantal equations are reduced respectively to 3x3, 3x3, and 1x1 determinants, thus saving both algebraic and computational efforts. For comparison and in order to check our calculation, we have done the calculation both ways, and achieve essentially the same results by either method. The details of the analytical approach are very similar to those for the case of the vacancy-impurity pair, discussed by Myles and Sankey (14). Thus, in the interest of brevity, they will not be shown here.

It should be noted that in the results presented below we have employed Hjalmarson's empirical rule (32) that the

diagonal p matrix elements of the impurity potential V_p are equal to one-half of the appropriate diagonal s matrix elements V_s . This simplification is not necessary but is both helpful for simplifying the computation and consistent with previous uses of the Hjalmarson et al. approach (32). In this approximation, the defect potential energies depend on only one parameter: either V_s or V_p , depending on the case of interest. Further details of and justification for the empirical rule may be found in Hjalmarson's dissertation (32).

It is worth noting that the predictions for the isolated cation or anion vacancy levels can be obtained in our formalism by setting the impurity potentials for the appropriate sites equal to zero. These isolated vacancy deep levels are identical to those obtained in the Hjalmarson et al.(7,32) theory of deep levels produced by substitutional defects.

Finally, we note in passing that the case of the tri-vacancy can also be obtained in our formalism by taking the limit as the appropriate impurity potentials approach infinity.

CHAPTER V

RESULTS AND DISCUSSION

5.1 General Discussion of the Numerical Results

We have used the above formalism to calculate the deep levels associated with a triplet vacancy-impurity complex in 12 different semiconductors. Furthermore, by exchanging anion and cation labels in this formalism we have done such calculations for both cation-vacancy and anion-vacancy complexes. The materials we have considered are Si, Ge, GaP, GaAs, GaSb, AlP, AlAs, InP, InAs, InSb, ZnSe, and ZnTe. We seek specifically the major chemical trends in the ordering of the levels. Owing to the neglect of lattice relaxation and charge-state-splitting effects, our results for the absolute level depths of deep levels associated with specific complexes should be viewed on a coarse scale of several tenths of an electron volt. As is stated above, however, based on past successes of the Hjalmarson et al. theory (7,9-14,32), we believe that the ordering we predict for the deep levels as the impurity in the complex is changed and the relative spacing between deep levels due to specific complexes should be correct. The results for the deep level energy E versus defect potential energy diagrams

obtained from the solution to Eq.(4-31) are summarized in Figs.2-13. For comparison, the deep levels for the corresponding isolated impurity are also shown in these figures. These should be compared to the corresponding figures for the deep levels produced by vacancy-impurity pairs, obtained by Myles and Sankey (14). The appropriate figures to use for comparison are Figs.1-4 of Ref.14. In Figs.2-13, the zero of energy on the vertical scale corresponds to the top of the valence band, and the horizontal scale and the labelled impurities on the top of the figures correspond to the s or p defect potentials of the impurity calculated from atomic energy differences, following Hjalmarson (7,32), as discussed above and as is shown in Eq.(3-8c).

The deep levels of a particular symmetry for a particular impurity 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 (in our theory) by the central cell potential alone for that impurity.

5.1.1 Results for GaP

A typical case is illustrated in Fig.2, where we display in detail all of the predicted results for both cation and anion vacancies complexed with two identical nearest-neighbor impurities in GaP. Plotted in Fig.2(a) are the a_1 -symmetric and b_1 -symmetric levels (plus symbols) for two P-site impurities $2X_P$ complexed with a Ga-site vacancy V_{Ga} . Figure 2(b) displays similar information for the levels of the $(2X_{Ga}, V_P)$ triplet. The A_1 -symmetric (s-like "atomic") levels for the corresponding isolated impurity (X_P or X_{Ga}) are shown in these figures as circular symbols. The b_2 -symmetric triplet complex levels for both the anion- and the cation-site vacancy triplet complexes are shown in Fig.2(c) (plus symbols), along with the corresponding T_2 -symmetric (p-like "atomic") levels of the appropriate isolated impurity (circular symbols). The zero of potential on the horizontal scale has been taken as the s potential of P in Fig.2(a), the s potential of Ga in Fig.2(b), and the p potential of P in Fig.2(c). The special case of an isolated vacancy can also be found from these figures by allowing the "impurity" atoms X to be the host semiconductor atoms, as is discussed in Chapter IV. The resulting predicted isolated vacancy levels in GaP (which are the same as those obtained earlier by Hjalmarson et al. (7,32)) are shown in Figs.2(a)-2(c) as solid circles with appropriate labels.

The general features which we now discuss for GaP will also hold qualitatively for the other semiconductors considered in this dissertation.

There are, in general, two varieties of levels for a given triplet vacancy-impurity complex (although, for a particular impurity one or both could be a band resonant state). One type of level has a wavefunction which is derived mainly from the impurity wavefunction, while the other type of level has a wavefunction which is derived mainly from the vacancy wavefunction. These will henceforth be referred to as impurity-like and vacancy-like levels, respectively. In some cases, however, hybridization effects can produce substantial mixing of these two types of levels.

The positions of the various vacancy complex associated levels with respect to the appropriate isolated impurity levels can be understood by first discussing the vacancy-impurity pair case and then generalizing the discussion to the present case of the triplet complex. For the vacancy-impurity pair, (which has C_{3v} symmetry in contrast to the present case of C_{2v} symmetry), as is discussed by Myles and Sankey (14), σ -bonded a_1 -pair levels are constructed by mixing the s-like A_1 and p-like T_2 states of both isolated defects. Because this mixing is strong for σ -bonded states, these levels may be at very different energies than the A_1

or T_2 levels of either isolated defect. But the π -like doubly degenerate e-symmetric levels of the vacancy-impurity pair have virtually identical energies to those of the impurity and vacancy point-defect T_2 levels (14). The π -like orbitals are constructed by mixing the p-like T_2 orbitals of the isolated defects and this mixing is much weaker than that which makes up the a_1 levels. Now, let us consider what happens when the second identical impurity is added to the complex. There are two effects. First, due to the strong mixing between the s-like A_1 and p-like T_2 states of the three isolated defects, the triplet complex in general has energy levels which are very different from those of either the isolated impurity or the vacancy-impurity pair (Figs.1-4 in Ref.14). Secondly, the π -like doubly degenerate e-symmetric levels of the vacancy-impurity pair are split due to the presence of the second impurity which perturbs them (Fig.2(c)). This splitting can also be explained from the group theoretical view point. When the second identical impurity is added to the complex, the C_{3v} symmetry of vacancy-impurity pair is reduced to C_{2v} symmetry. Since the point group C_{2v} has one-dimensional irreducible representations only (45,46), each energy level associated with such a triplet complex is nondegenerate, so that this causes the doubly degenerate e-symmetric levels belonging to the pair to split.

Several interesting trends and features can be obtained for specific impurities in GaP by a detailed examination of Figs.2(a)-2(c). For example, from Fig.2(a), the isolated nitrogen impurity, substitutional for P, produces a deep A_1 -symmetric level which is accidentally energetically shallow. When this impurity is complexed with another second nearest-neighbor P-site nitrogen and a nearest-neighbor vacancy on the gallium site, however, the impurity-like level is pushed out of the gap to become resonant with the conduction band (similar to the case of vacancy-impurity pair) (Ref.14, Fig.1(a)). Similar statements can be made about the isolated impurity and the triplet complex levels of Br, N, S, Se, and I substitutional for P in GaP. The P-site impurities F and O, however, produce deep levels in the band gap both as isolated impurities and as part of a triplet complex, but the impurity-like (a_1 and b_1) levels due to the triplet complex are much closer to the conduction band than the isolated impurity A_1 levels. Inspection of Fig.2(a) also shows that one member of the Ga vacancy T_2 manifold is drastically perturbed by complexing with the two P-site impurities for the cases of C through Zn (reading from left to the right at the top of the figure). In fact, the resulting a_1 -symmetric vacancy-like levels move from near the bottom of the gap (for C) to near the top (for Zn). A final

interesting prediction of Fig.2(a) is that , for the P-site impurities Zn, Cd and Hg, the central-cell potential alone does not produce a_1 -symmetric deep levels in the band gap in GaP either for the isolated impurities or for the corresponding (V_{Ga}, X_p) nearest-neighbor pair (Ref.14, Fig.1(a)). They, however, do produce deep levels in the gap near the valence band for the triplet complex.

Similar behavior of the triplet complex produced levels is found for the $(2X_{Ga}, V_p)$ complex, as is shown in Fig.2(b). Complexing two identical impurities with a phosphorous vacancy gives rise to deep levels which are very different from those due to either the pair (14) or the isolated impurity. For example, let us consider the a_1 and b_1 levels of the (vacancy, antisite defect) triplet $(2P_{Ga}, V_p)$. In Fig.2(b) we see that this complex produces a vacancy-like level at 2.1 eV, an impurity-like level at 1.8 eV (doubly accidentally degenerate), and a hybrid level at 1.3 eV. By contrast, the (P_{Ga}, V_p) pair, as has been shown by Myles and Sankey (14), is expected to produce an a_1 impurity-like level at 2.0 eV and a hybrid level at 1.2 eV; the isolated antisite defect P_{Ga} , as has been shown by Hjalmarson et al. (7,32), is predicted to produce an A_1 -symmetric level at 1.1 eV. Reading from left to right at the top of Fig.2(b), the vacancy-two impurity triplet for

the impurity F is predicted to produce three deep levels in the gap (one vacancy-like and two impurity-like). The complex containing the impurity O is predicted to produce four deep levels (one vacancy-like and three impurity-like). The complex containing the impurities Cl through I are all predicted to produce five deep levels (one vacancy-like, three impurity-like and one hybrid). The impurities At through Sb are predicted to produce four deep levels (one vacancy-like, two impurity-like and one hybrid) when incorporated in the triplet complex. However, the complexes containing the impurities In through Hg are predicted to produce only one vacancy-like level in the gap. These predictions should be contrasted with the predicted a_1 -symmetric levels of the (vacancy,Ga-site defect) pair (14) and the A_1 symmetric levels of the isolated Ga-site impurities (14). This comparison proves that the vacancy-two impurity triplet complex may have deep levels which are very different from those of either the isolated impurity or the vacancy-impurity pair.

Inspection of Fig.2(c) confirms the interesting fact discussed earlier that complexing with a second identical impurity causes the doubly degenerate e-symmetric level of the vacancy-impurity pair (14) to be split. The energy of this splitting is roughly equal to 0.2 eV.

2. Results for Other Semiconductors

In Figs.3-13 we present all of our predicted results for the deep levels associated with triplet complexes in the other 11 different semiconductors we consider here. In Figs.3(a) and 4(a), the zero on the abscissa is taken as the germanium s potential and the silicon s potential, respectively. In Figs.3(b) and 4(b), the zero on the abscissa is the germanium p potential and the silicon p potential, respectively. In Figs.5(a)-13(c) the defect potentials have been referenced to the appropriate (s or p) isolated-impurity potential of the perfect crystal cation (or anion). For example, in Figs.5(a) and 5(b), the zero on the abscissa is taken as the As s potential and the Ga s potential respectively, and in Fig.5(c) the zero on the abscissa is taken as As p potential.

An interesting phenomenon occurs in the case of the vacancy-like a_1 -symmetric levels (see Figs. 2(b), 5(b), 6(b), 7(b), and 8(b)) for the anion vacancy complexed with two cation impurities in GaP, GaAs, GaSb, AlP, and AlAs; the predicted curves for these levels have two hyperbola-like branches in the band gap, one attached to the conduction band and the other attached to the valence band. This is a consequence of Rayleigh's interlacing theorem (48,49). This theorem requires that perturbed levels of the same symmetry

lie between unperturbed levels. Although this theorem strictly applies for a single defect potential on each atom (the present case has two defect potentials, s and p), inspection of the figures listed above confirms this qualitative description. We can understand the above phenomenon using the following reasoning. For these materials, the A_1 -symmetric, isolated anion-vacancy level lies in the band gap. Also, an isolated cation-site impurity which is more electronegative than the atom it replaces will pull a deep level from the conduction band into the band gap. However, when the vacancy is complexed with two such identical impurities, this impurity level is prevented from crossing the A_1 -symmetric anion-vacancy level by the interlacing theorem. As a result, the conduction-band-attached hyperbola saturates, for large negative potential, to an energy slightly above the isolated anion-vacancy level (see, for example, the isolated V_{As} level for GaAs in Fig.5(b)). In this saturation region, this level has changed from predominantly impurity-like to predominantly vacancy-like. At the same time, a vacancy-like level has reappeared in a continuous fashion in the lower, valence-band-attached hyperbola.

An other interesting phenomenon is that the splitting of the e-symmetric, doubly degenerate level of the vacancy-impurity pair (14) in the cases of InP, ZnSe, and

ZnTe is much smaller than in the other materials (see Figs.9(c), 12(c) and 13(c)). Qualitatively, we can understand this as follows. From Eqs.(4-19a) and (4-20a), it is not difficult to see that for the cation-vacancy complexes (similar arguments hold for the anion-vacancy-complexes), the splitting amount is proportional to the difference between the Green's function matrix elements $G_{xx}^{aa}(2,1)$ and $G_{xy}^{aa}(2,1)$. In Table 1 we show a table, compiled by Phillips (50), of the fractional ionic character of the chemical bonds in the materials we have considered. From that table, it can be seen that the crystals InP, ZnTe, and ZnSe have more ionic character than the others. Thus the charge distribution of the valence electrons for these crystals show more spherical symmetry (51) (i.e., less difference between the x-direction and y-direction) than for the other materials. This means that the difference of the Green's function matrix elements above is smaller and therefore the splitting is smaller for these materials.

5.2 Deep Acceptor-Like Levels in Ge

Some of the predictions presented in Figs.2-13 have a bearing on experiment. Here we discuss the predictions and experimental comparisons for deep levels due to triplet vacancy-impurity complexes in Ge. Time did not permit the detailed analysis of the large quantities of data which

exist for defects in other materials.

Two deep hole trapping states have recently been observed at 0.23 eV (52,53) and 0.38 eV (52) (in Ref.53, it is quoted as 0.41 eV) above the valence- band edge in high purity p-type Ge. The experimental techniques used were gamma-irradiation (52) and quenching from temperatures in the range 500-700 C (53). The former deep level has tentatively been attributed to an oxygen-vacancy complex (52,53). Our predictions for the deep level due to the triplet vacancy-oxygen complex in Ge are in qualitative agreement with those data.

Figures 3(a) and 3(b) contain our explicit predictions for this complex. From those figures, it can be seen that this complex should produce one b_1 -symmetric and three a_1 -symmetric energy levels in the valence band, one b_1 -symmetric level near the valence-band edge, one impurity-like a_1 -symmetric deep level at 0.2eV above the valence band edge, one a_1 -symmetric conduction band resonant level, and two b_2 -symmetric levels at 0.5eV and 0.7eV above the valence band edge. The energy of the impurity-like a_1 -symmetric level at 0.2eV agrees with the first of the experimentally observed levels to within the accuracy of the theory. Furthermore, by electron-counting arguments, this complex should contain eight excess electrons. This electron number is arrived at as follows. When a vacancy replaces a Ge

atom, four electrons remain behind to preserve lattice neutrality. When a Ge atom is replaced by an oxygen atom (which has six valence electrons), two extra electrons are contributed. Thus, in undoped material, the four valence-band resonant levels would each be doubly occupied, the b_1 -symmetric level just near the valence-band edge would be empty, and the a_1 -symmetric level at 0.2eV would be empty and thus observable in the experiments.

On the basis of this analysis, we conclude that the results of the present calculations support the identification of the deep level observed at 0.2eV with the triplet vacancy-oxygen complex in Ge, and we predict that this level should be of the acceptor-like a_1 -symmetric type. It is worth noting in passing that inspection of Figs.2 and 4(c) in Ref.14 shows that neither the vacancy-oxygen pair nor the isolated oxygen impurity in Ge produces a deep level at 0.2eV. We also speculate on the basis of our theory that the observed level near 0.4eV may be due to this same complex, corresponding to our predicted 0.5eV b_2 -symmetric level.

TABLE 1

Fractional Ionic Character of Bonds
in Crystal(after Phillips(50))

Crystal	Factional Ionic Character
Si	0.00
Ge	0.00
GaSb	0.26
AlAs	0.27
GaAs	0.31
AlP	0.31
InSb	0.32
GaP	0.33
InAs	0.36
InP	0.42
ZnTe	0.61
ZnSe	0.63

Figure 2(a). Energy levels of a_1 and b_1 symmetries produced by a triplet cation (gallium) vacancy-impurity complex symbolized by $(V_{Ga}, 2X_p)$ in GaP (plus symbol curves). The abscissa is the s orbital potential of the phosphorus-site impurity X_p . In this and subsequent figures the ordinate is energy in the bandgap, with the zero equal to the top of the valence band and the maximum energy equal to the bandgap. The sp^3 -bonded impurities are shown at the top of the figures at their corresponding impurity potentials. For comparison, the A_1 levels of an isolated X_p impurity (Refs. 7 and 32) are shown as circular symbol curves. The predicted isolated-vacancy V_{Ga} levels are represented by solid circles and appropriately labeled in this and subsequent figures. The "impurity-like" and "vacancy-like" labels discussed in the text, as is the method for finding a deep level due to a particular impurity.

Energy in Bandgap (eV)
0.00
0.40
0.80
1.20
1.60
2.00

Figure 2(b). Energy levels of a_1 and b_1 symmetries produced by a triplet anion (phosphorus site) vacancy-impurity complex ($2X_{Ga}, V_p$) in GaP (plus symbol curves). The abscissa is the s-orbital potential of the gallium-site impurity X_{Ga} . The symbol V_p represents the phosphorus-site vacancy. The interpretation is otherwise as in Fig.2(a).

Energy in Bandgap (eV)
2.00
1.60
1.20
0.80
0.40
0.00
 E_{gap}

Figure 2(c). Energy levels of b_2 symmetry produced by a triplet vacancy-impurity complex for both a cation (gallium-site) vacancy ($V_{Ga}, 2X_p$) and an anion (phosphorus-site) vacancy ($2X_{Ga}, V_p$) in GaP (plus symbol curves). The abscissa is the p orbital potential of the impurity, with the zero equal to the p-orbital potential of phosphorus. For comparison, the T_2 levels of the isolated X_{Ga} and X_p impurities (Refs. 7 and 32) are shown as circular symbol curves. The vacancy-like b_2 levels are represented by almost horizontal lines which end with arrows and which branch from the discontinuity in the impurity-like levels. Such arrow in this and subsequent figures indicate that the curve is continuous to the edge of the figure and asymptotic to almost horizontal lines passing through the discontinuity. The remainder of the labels in this figure are interpreted as in fig. 2(a).

Energy in Bandgap (eV)
0.80
0.40
0.00

Figure 3(a). Energy levels of a_1 and b_1 symmetries produced by a triplet vacancy-impurity complex ($2X,V$) in Ge. The abscissa is the s-orbital potential of the impurity. The remainder of the interpretation is as in the Fig.2(a).

Figure 3(b). Energy levels of b_2 symmetry produced by a triplet vacancy-impurity complex ($2X,V$) in Ge. The abscissa is the p-orbital potential of the impurity. The remainder of the interpretation is as in Fig.2(a).

Figure 4(a). Energy levels of a_1 and b_1 symmetries produced by a triplet vacancy-impurity complex ($2X,V$) in Si. The abscissa is the s-orbital potential of the impurity. The remainder of the interpretation is as in the Fig.2(a).

Figure 4(b). Energy levels of b_2 symmetry produced by a triplet vacancy-impurity complex ($2X,V$) in Si. The abscissa is the p-orbital potential of the impurity. The remainder of the interpretation is as in Fig.2(a).

Energy in Bandgap (eV)
 0.00
 0.20
 0.40
 0.60
 0.80
 1.00
 E_{gap}

Figure 5(a). Energy levels of a_1 and b_1 symmetries produced by a triplet cation (gallium-site) vacancy-impurity complex ($V_{Ga}, 2X_{As}$) in GaAs. The symbols X_{As} and V_{Ga} represent respectively an impurity on the arsenic site and a gallium site vacancy. The interpretation is otherwise as in Fig.2(a).

Energy in Bandgap (eV)
 1.50
 1.25
 1.00
 0.75
 0.50
 0.25
 0.00

Figure 5(b). Energy levels of a_1 and b_1 symmetries produced by a triplet anion (arsenic-site) vacancy-impurity complex ($2X_{Ga}, V_{As}$) in GaAs. The symbols X_{Ga} and V_{As} represent respectively an impurity on the gallium site and an arsenic site vacancy. The interpretation is otherwise as in Fig.2(a).

Energy in Bandgap (eV)
 0.50 0.75 1.00 1.25 1.50

Figure 5(c). Energy levels of b_2 symmetry produced by a triplet vacancy-impurity complex for both cation vacancy ($V_{Ga}, 2X_{As}$) and anion vacancy ($2X_{Ga}, V_{As}$) triplet complexes in GaAs. The abscissa is the p-orbital potential of the impurity X with the zero equal to the p-orbital potential of arsenic. Aside from obvious notational changes, the interpretation is as in Fig.2(c).

Energy in Bandgap (eV)
 1.50
 1.25
 1.00
 0.75
 0.50
 0.25
 0.00

Figure 6(a). Energy levels of a_1 and b_1 symmetries produced by a triplet cation (gallium-site) vacancy-impurity complex ($V_{Ga}, 2X_{Sb}$) in GaSb. The symbols X_{Sb} and V_{Ga} represent respectively an impurity on the antimony site and a gallium site vacancy. The interpretation is otherwise as in Fig.2(a).

Figure 6(b). Energy levels of a_1 and b_1 symmetries produced by a triplet anion (antimony-site) vacancy-impurity complex ($2X_{Ga}, V_{Sb}$) in GaSb. The symbols X_{Ga} and V_{Sb} represent respectively an impurity on the gallium site and an antimony site vacancy. The interpretation is otherwise as in Fig.2(a).

Figure 6(c). Energy levels of b_2 symmetry produced by a triplet vacancy-impurity complex for both cation vacancy ($V_{Ga}, 2X_{Sb}$) and anion vacancy ($2X_{Ga}, V_{Sb}$) triplet complexes in GaSb. The abscissa is the p-orbital potential of the impurity X with the zero equal to the p-orbital potential of antimony. Aside from obvious notational changes, the interpretation is as in Fig.2(c).

Figure 7(a). Energy levels of a_1 and b_1 symmetries produced by a triplet cation (aluminium-site) vacancy-impurity complex ($V_{Al,2Xp}$) in AlP. The symbols X_p and V_{Al} represent respectively an impurity on the phosphorus site and an aluminium site vacancy. The interpretation is otherwise as in Fig.2(a).

Energy in bandgap (eV)

0.00 0.40 0.80 1.20 1.60 2.00 E_{gap}

Figure 7(b). Energy levels of a_1 and b_1 symmetries produced by a triplet anion (phosphorus-site) vacancy-impurity complex ($2X_{Al}, V_P$) in AlP. The symbols X_{Al} and V_P represent respectively an impurity on the aluminium site and a phosphorus site vacancy. The interpretation is otherwise as in Fig.2(a).

E_{ga}

2.00

Energy in Bandgap (eV)
1.60
1.20
0.80

0.40

0.00

Figure 7(c). Energy levels of b_2 symmetry produced by a triplet vacancy-impurity complex for both cation vacancy ($V_{Al}, 2X_p$) and anion vacancy ($2X_{Al}, V_p$) triplet complexes in AlP. The abscissa is the p-orbital potential of the impurity X with the zero equal to the p-orbital potential of phosphorus. Aside from obvious notational changes, the interpretation is as in Fig.2(c).

Figure 8(a). Energy levels of a_1 and b_1 symmetries produced by a triplet cation (aluminium-site) vacancy-impurity complex ($V_{Al,2X_{As}}$) in AlAs. The symbols X_{As} and V_{Al} represent respectively an impurity on the arsenic site and an aluminium site vacancy. The interpretation is otherwise as in Fig.2(a).

Figure 8(b). Energy levels of a_1 and b_1 symmetries produced by a triplet anion (arsenic-site) vacancy-impurity complex ($2X_{Al}, V_{As}$) in AlAs. The symbols X_{Al} and V_{As} represent respectively an impurity on the aluminium site and an arsenic site vacancy. The interpretation is otherwise as in Fig.2(a).

Energy in Bandgap (eV)

0.00 0.40 0.80 1.20 1.60 2.00 E_{gap}

.

Figure 8(c). Energy levels of b_2 symmetry produced by a triplet vacancy-impurity complex for both cation vacancy ($V_{Al}, 2X_{As}$) and anion vacancy ($2X_{Al}, V_{As}$) triplet complexes in AlAs. The abscissa is the p-orbital potential of the impurity X with the zero equal to the p-orbital potential of arsenic. Aside from obvious notational changes, the interpretation is as in Fig.2(c).

Figure 9(a). Energy levels of a_1 and b_1 symmetries produced by a triplet cation (indium-site) vacancy-impurity complex ($V_{In}, 2X_p$) in InP. The symbols X_p and V_{In} represent respectively an impurity on the phosphorus site and an indium site vacancy. The interpretation is otherwise as in Fig.2(a).

Energy in Bandgap (eV)	E_g
0.00	1.00
0.20	0.80
0.40	0.60
0.60	0.40
0.80	0.20
1.00	0.00

Figure 9(c). Energy levels of b_2 symmetry produced by a triplet vacancy-impurity complex for both cation vacancy ($V_{In}, 2X_p$) and anion vacancy ($2X_{In}, V_p$) triplet complexes in InP. The abscissa is the p-orbital potential of the impurity X with the zero equal to the p-orbital potential of phosphorus. Aside from obvious notational changes, the interpretation is as in Fig.2(c).

E_{gap}

1.20

1.00

Energy in Bandgap (eV)

0.80

0.60

0.40

0.20

0.00

Figure 10(a). Energy levels of a_1 and b_1 symmetries produced by a triplet cation (indium-site) vacancy-impurity complex ($V_{In}, 2X_{As}$) in InAs. The symbols X_{As} and V_{In} represent respectively an impurity on the arsenic site and an indium site vacancy. The interpretation is otherwise as in Fig.2(a).

Figure 10(b). Energy levels of a_1 and b_1 symmetries produced by a triplet anion (arsenic-site) vacancy-impurity complex ($2X_{In}, V_{As}$) in InAs. The symbols X_{In} and V_{As} represent respectively an impurity on the indium site and an arsenic site vacancy. The interpretation is otherwise as in Fig.2(a).

E_{gap}

0.35

Energy in Bandgap (eV)

0.21

0.28

0.07

0.00

Figure 10(c). Energy levels of b_2 symmetry produced by a triplet vacancy-impurity complex for both cation vacancy ($V_{In}, 2X_{As}$) and anion vacancy ($2X_{In}, V_{As}$) triplet complexes in InAs. The abscissa is the p-orbital potential of the impurity X with the zero equal to the p-orbital potential of arsenic. Aside from obvious notational changes, the interpretation is as in Fig.2(c).

E_{gap}

0.35

Energy in Bandgap (eV)
0.28
0.21
0.14

0.07

0.00

Figure 11(a). Energy levels of a_1 and b_1 symmetries produced by a triplet cation (indium-site) vacancy-impurity complex ($V_{In}, 2X_{Sb}$) in InSb. The symbols X_{Sb} and V_{In} represent respectively an impurity on the antimony site and an indium site vacancy. The interpretation is otherwise as in Fig.2(a).

E_{gap}

0.20

Energy in Bandgap (eV)
0.16
0.12
0.08

0.04

0.00

Figure 11(b). Energy levels of a_1 and b_1 symmetries produced by a triplet anion (antimony-site) vacancy-impurity complex ($2X_{In}, V_{Sb}$) in InSb. The symbols X_{In} and V_{Sb} represent respectively an impurity on the indium site and an antimony site vacancy. The interpretation is otherwise as in Fig.2(a).

E_{ga}

5
c

Energy in Bandgap (eV)
0.16

0.12

0.08

0.04

0.00

Figure 11(c). Energy levels of b_2 symmetry produced by a triplet vacancy-impurity complex for both cation vacancy ($V_{In}, 2X_{Sb}$) and anion vacancy ($2X_{In}, V_{Sb}$) triplet complexes in InSb. The abscissa is the p-orbital potential of the impurity X with the zero equal to the p-orbital potential of antimony. Aside from obvious notational changes, the interpretation is as in Fig.2(c).

E_{gap}

0.20

Energy in Bandgap (eV)

0.16

0.12

0.08

0.04

0.00

Figure 12(a). Energy levels of a_1 and b_1 symmetries produced by a triplet cation (zinc-site) vacancy-impurity complex ($V_{Zn}, 2X_{Se}$) in ZnSe. The symbols X_{Se} and V_{Zn} represent respectively an impurity on the selenium site and a zinc site vacancy. The interpretation is otherwise as in Fig.2(a).

E_{ga}

5
2

2.00

Energy in Bandgap (eV)
1.60
1.20
0.80

0.40

0.00

Figure 12(b). Energy levels of a_1 and b_1 symmetries produced by a triplet anion (selenium-site) vacancy-impurity complex ($2X_{Zn}, V_{Se}$) in ZnSe. The symbols X_{Zn} and V_{Se} represent respectively an impurity on the zinc site and a selenium site vacancy. The interpretation is otherwise as in Fig.2(a).

Energy in bandgap (eV)
 0.80 1.20 1.60
 0.40
 0.00

Figure 12(c). Energy levels of b_2 symmetry produced by a triplet vacancy-impurity complex for both cation vacancy ($V_{Zn}, 2X_{Se}$) and anion vacancy ($2X_{Zn}, V_{Se}$) triplet complexes in ZnSe. The abscissa is the p-orbital potential of the impurity X with the zero equal to the p-orbital potential of selenium. Aside from obvious notational changes, the interpretation is as in Fig.2(c).

120

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Figure 13(a). Energy levels of a_1 and b_1 symmetries produced by a triplet cation (zinc-site) vacancy-impurity complex ($V_{Zn}, 2X_{Te}$) in ZnTe. The symbols X_{Te} and V_{Zn} represent respectively an impurity on the tellurium site and a zinc site vacancy. The interpretation is otherwise as in Fig.2(a).

Energy in bandgap (eV)
0.00
0.40
0.80
1.20
1.60
2.00
2.40
2.80
3.20
3.60
4.00
4.40
4.80
5.20
5.60
6.00
6.40
6.80
7.20
7.60
8.00
8.40
8.80
9.20
9.60
10.00

Figure 13(b). Energy levels of a_1 and b_1 symmetries produced by a triplet anion (tellurium-site) vacancy-impurity complex ($2X_{Zn}, V_{Te}$) in ZnTe. The symbols X_{Zn} and V_{Te} represent respectively an impurity on the zinc site and a tellurium site vacancy. The interpretation is otherwise as in Fig.2(a).

E_g

Energy in bandgap (eV)
0.80
0.40
0.00

Figure 13(c). Energy levels of b_2 symmetry produced by a triplet vacancy-impurity complex for both cation vacancy ($V_{Zn}, 2X_{Te}$) and anion vacancy ($2X_{Zn}, V_{Te}$) triplet complexes in ZnTe. The abscissa is the p-orbital potential of the impurity X with the zero equal to the p-orbital potential of tellurium. Aside from obvious notational changes, the interpretation is as in Fig.2(c).

E_c

Energy in Bandgap (eV)

CHAPTER VI

ALLOY COMPOSITION DEPENDENCE OF DEEP LEVELS IN $\text{GaAs}_{1-x}\text{P}_x$

We have calculated the composition dependences of the deep levels produced by triplet vacancy-impurity complexes in the alloy $\text{GaAs}_{1-x}\text{P}_x$. The formalism we have used is the same as above. To model the effect of alloying, we have combined the host Hamiltonians given by Eq.(3-1) for GaAs and GaP in the virtual crystal approximation (54), which is the simplest theory for the electronic structure of alloys. The tight binding Hamiltonian we use in this case is thus

$$H_{\text{alloy}} = (1-x) H_{\text{O}}^{\text{GaAs}} + x H_{\text{O}}^{\text{GaP}} , \quad (7-1)$$

where $H_{\text{O}}^{\text{GaAs}}$ and $H_{\text{O}}^{\text{GaP}}$ are the Vogl et al. Hamiltonians for GaAs and GaP, and x is the alloy composition. We note that this model does not include any effects of alloy disorder. We thus neglect these effects in our discussion of deep levels in the alloy. Such effects have recently been shown experimentally (55) and theoretically (56) to be of potential importance for understanding deep levels in semiconductor alloys. They should thus be included in any detailed analysis of experimental data. Therefore, the results presented below should be applied to the analysis of such data with caution.

The results of our calculations for $\text{GaAs}_{1-x}\text{P}_x$ are shown in Figs.14 and 15. These figures were obtained by generating figures similar to Figs.2-13 for both the cation vacancy complex and the anion vacancy complex at several values of x . The deep levels for selected impurities were then found from these figures at each of these composition values. The resulting deep levels were then plotted as functions of x . In these figures, the abscissa denotes the alloy composition x , the vertical axis denotes the energy E in the band gap measured from the valence band maximum, and the upper cross hatched region represents the conduction band, with the "kink" indicating the cross over from the direct bandgap of GaAs to the indirect bandgap of GaP. The impurity-like deep levels and vacancy-like deep levels are shown as dashed and solid lines, respectively. Figure 14 shows the deep levels produced by several cation-vacancy plus two anion-impurity complexes, and Fig.15 shows the deep levels produced by complexes containing an anion-vacancy plus two cation-impurities.

Briefly summarized, these results, along with results obtained by others for isolated impurities (32) and vacancy-impurity pairs (33,57), show that (i) the alloy composition (x) dependence (slope or dE/dx) of deep levels due to triplet complexes in this material depends on the

impurity site and the state symmetry, (ii) the vacancy-like and the impurity-like levels for a particular complex have very different slopes, and (iii) the vacancy-like levels have very different slopes than the corresponding isolated defect levels. Thus, we suggest that the dE/dx of a defect level is not only indicative of the site the impurity occupies, but that it also might be used, in favorable cases, to help to distinguish between observed levels due to point defects and those due to complexes. We further propose that these results could be used, in conjunction with experimental data on the composition dependence of deep levels in $\text{GaAs}_{1-x}\text{P}_x$, to obtain site and symmetry information about the defects which produce particular observed levels of unknown origin in this material. In particular, we suggest that in the case of vacancy-like levels, it is possible to distinguish experimentally between isolated defect levels and levels produced by vacancy-impurity complexes by using the different slopes (dE/dx) for these two cases. A similar scheme has been proposed and successfully tested in analysis of data for deep levels in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ by Myles et al.(33). The calculations in that work were, however, for vacancy-impurity pairs.

As is mentioned in previous chapters, most theories of deep level defects cannot accurately predict absolute depths

of defect energy levels. The scheme we discuss here for possible correlation of theoretical predictions with experimentally observed levels does not require such absolute level predictions; instead it requires only that the theory correctly predict the variation of defect energy levels with x . The composition dependences (dE/dx) of such levels can then be used, in conjunction with data, to obtain information about the defect which produces an observed level.

We now discuss the results presented in Figs.14 and 15 in more detail. Examination of these figures shows that the composition dependence (dE/dx) of an energy level, which is associated with a particular complex, depends on whether the impurity occupies the cation or the anion site of the host crystal. For example, the slopes of the impurity-like energy levels for the triplet cation vacancy-oxygen complex, in which two oxygen impurity atoms occupy the anion sites, are greater than those produced by an anion vacancy complex with two oxygen impurity atoms occupying the cation sites. By contrast, the dE/dx of the vacancy-like energy levels for the triplet cation vacancy-boron complex in which two boron impurity atoms occupy the anion sites is smaller than that produced by the anion vacancy complex with two boron impurity atoms occupying the cation sites. These results are in qualitative agreement with the results of Kobayashi

et al.(58) for isolated point defects in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ and of Myles et al.(33) for vacancy-impurity pairs in the same material.

Another significant finding of our calculations is that the dE/dx for the energy levels whose wavefunctions are primarily vacancy-like (e.g., the solid line 0 in Fig.15) can be greatly different from those whose wavefunctions are primarily impurity-like (e.g. refer to the dashed lines 0 in Fig.15). We also find that for both vacancy-like and impurity-like levels, the slope of an energy level is almost independent of which impurity is present in the vacancy-impurity complex, even though the absolute energy of such a level certainly does depend on the impurity. Both of these results are also in agreement with the results of Myles et al. for vacancy-impurity pairs in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$.

The final finding of our calculations is that the dE/dx of the vacancy-like energy levels associated with complexes containing anion-site impurities is almost equal to that of the impurity-like energy levels associated with such complexes containing cation-site impurities. The opposite case is also valid. That is, the dE/dx of the impurity-like energy levels associated with complexes containing anion-site impurities is almost equal to that of the vacancy-like deep energy levels associated with triplet complexes

containing cation-site impurities. Unfortunately, this result means that it will be difficult to distinguish between certain kinds of levels on the basis of their dE/dx .

In summary, our findings for the composition dependences of deep levels due to complexes in $\text{GaAs}_{1-x}\text{P}_x$, taken together with the results of Myles (57) for deep levels due to vacancy-impurity pairs and Hjalmarson (7,32) for deep levels due to isolated substitutional impurities in the same material, indicate that the slopes of such energy levels could be used, in conjunction with experimental data, to aid in the identification of the defect center which produces an observed level. In particular, site and symmetry information can be obtained from such slopes and, in favorable cases, complexes and isolated impurities can be distinguished by the slopes of the associated deep levels. These results correlate well with similar findings for deep levels in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$, thus indicating that such results should hold qualitatively for other semiconductor alloys.

Unfortunately, data on the x dependence of deep levels in $\text{GaAs}_{1-x}\text{P}_x$ (or for that matter in other semiconductor alloys) is scarce, so that it is difficult to test our conjectures in comparison with experiment. However, some data, taken by Bylander and Chapman using photoluminescence, do exist (18). A detailed analysis of these data in

comparison both with our theory and with that of Myles (57) for vacancy-impurity pairs will be presented elsewhere. We do, however, hope that the predictions we make here will aid in the identification of the defect centers producing observed deep levels in $\text{GaAs}_{1-x}\text{P}_x$.

Figure 14. Composition dependences of the deep levels associated with triplet cation vacancy-anion impurity complexes in the alloy $\text{GaAs}_{1-x}\text{P}_x$.

Figure 15. Composition dependences of the deep levels associated with triplet anion vacancy-cation impurity complexes in the alloy $\text{GaAs}_{1-x}\text{P}_x$.

Energy in bandgap (eV)

CHAPTER VII

SUMMARY AND CONCLUSIONS

We have calculated the deep levels associated with vacancy-impurity complexes in 12 semiconductor materials. Our theory uses the Vogl et al.(31) sp^3s^* semi-empirical, nearest-neighbor, tight-binding bandstructures for perfect semiconductors as input and is a generalization of the Hjalmarson et al.(7,32) theory of deep levels due to substitutional impurities. In developing our theory, we have adopted the framework introduced by Myles and Sankey (14) for the extension of the Vogl-Hjalmarson theory to treat vacancy-impurity pairs and have further generalized this theory to our triplet complex problem. We stress that in these theories lattice relaxation and charge-state-splitting effects are ignored. Our results thus should be viewed as the predictions of the global chemical trends of deep levels rather than the predictions of their absolute energies. One of the main findings of this work is that a triplet vacancy-impurity complex may have deep levels which are significantly different from those either the isolated impurity or the vacancy-impurity pair. We hope that our predictions will be useful in assisting in the identification of defects which produce observed deep levels in the materials we consider.

We have also calculated the composition dependences of the deep levels due to triplet complexes in the semiconductor alloy $\text{GaAs}_{1-x}\text{P}_x$. We find that the slope (dE/dx) of the energy levels depends on the site occupied by an associated impurity, on the symmetry of the state, and on whether the wavefunction of the deep level belongs mainly to the impurities ("impurity-like") or mainly to the vacancy ("vacancy-like"). Furthermore, the energy level slope for a given type of level is almost independent of which impurity is present in the complex. These properties are in qualitative agreement with the results obtained by Myles et al.(33) in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$. We propose that these properties could be used in conjunction with experimental data to help to identify the defect centers which give rise to observed deep levels in $\text{GaAs}_{1-x}\text{P}_x$. We also speculate that these properties are general enough that they might be qualitatively independent of the semiconductor alloy materials one considers.

It is worthwhile to point out that the formalism developed by us is general enough to treat a complex consisting of three impurities, two of which are identical. However, we have only calculated the deep levels associated with a vacancy plus two identical impurities. It should be straightforward to predict the deep levels associated with either an impurity plus two identical impurities or an

impurity plus a di-vacancy. This type of calculation will be carried out later and the results will be presented elsewhere.

Finally, we should stress again that in order to improve the accuracy of absolute depths of the deep levels which we predict, the Hjalmarson et al. theory that we use as a basis must be generalized to include such effects as lattice relaxation in the neighborhood of the defect, and charge-state-splittings of the deep levels. In more general terms, more accurate calculations require that this theory be generalized to improve the defect potential which it uses. Lee, Dow, and Sankey (42) have recently generalized this method to include the charge-state-splittings of deep levels produced by substitutional impurities in Si. In principle, this new theory could be applied to the treatment of the type of vacancy complexes we have considered in this dissertation.

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APPENDIX A

THE BLOCK-DIAGONALIZATION OF PERFECT CRYSTAL GREEN'S FUNCTION G^0

As is discussed in Chapter IV, the 12×12 perfect crystal Green's function G^0 can be block-diagonalized into the direct sum of 4 smaller matrices after using the symmetric operations of the point group C_{2v} . Details concerning this point group may be found in Refs. 45 and 46. In this Appendix, we show the detailed procedures of this block-diagonalization. Here and in the rest of this Appendix, the Green's functions referred to are those of the perfect crystal.

In the zincblende coordinate system, displayed in Fig.1, the matrix elements of the Green's function G^0 are given by Eqs.(4-5)-(4-13). There are four symmetric operations in the group C_{2v} . They are E , $C_2(z)$, $\sigma_d^+(z)$, and $\sigma_d^-(z)$ where E is the identity element, $C_2(z)$ is a rotation through π along the z -axis, $\sigma_d^+(z)$ is the reflection operation in a plane σ_d^+ passing through the z axis and direction $(1,1,0)$, and $\sigma_d^-(z)$ is the reflection operation in a plane σ_d^- passing through the z axis and perpendicular to the plane σ_d^+ (see Fig.1). The vectors $\vec{\tau}_1$, $\vec{\tau}_2$ and the atomic-like basis functions transform according to the following table:

	τ_1	τ_2	p_x	p_y	p_z
$c_2(z)$	τ_2	τ_1	$-p_x$	$-p_y$	p_z
$q_d^+(z)$	τ_1	τ_2	p_y	p_x	p_z
$q_d^-(z)$	τ_2	τ_1	$-p_y$	$-p_x$	p_z

In this table, p_x , p_y , and p_z are the three p-like localized Lowdin orbital wave functions in the zincblende coordinate system.

It can be shown, using the above table, that the matrix elements of the Green's functions G (see Eqs.(4-5)-(4-13)) transform according to the following tables:

	$G_{ss}^{ca}(1)$	$G_{sx}^{ca}(1)$	$G_{sy}^{ca}(1)$	$G_{sz}^{ca}(1)$
$c_2(z)$	$G_{ss}^{ca}(2)$	$-G_{sx}^{ca}(2)$	$-G_{sy}^{ca}(2)$	$G_{sz}^{ca}(2)$
$q_d^+(z)$	$G_{ss}^{ca}(1)$	$G_{sy}^{ca}(1)$	$G_{sx}^{ca}(1)$	$G_{sz}^{ca}(1)$
$q_d^-(z)$	$G_{ss}^{ca}(2)$	$-G_{sy}^{ca}(2)$	$-G_{sx}^{ca}(2)$	$G_{sz}^{ca}(2)$

	$G_{xs}^{ca}(1)$	$G_{xx}^{ca}(1)$	$G_{xy}^{ca}(1)$	$G_{xz}^{ca}(1)$
$c_2(z)$	$-G_{xs}^{ca}(2)$	$G_{xx}^{ca}(2)$	$G_{xy}^{ca}(2)$	$-G_{xz}^{ca}(2)$
$q_d^+(z)$	$G_{ys}^{ca}(1)$	$G_{yy}^{ca}(1)$	$G_{yx}^{ca}(1)$	$G_{yz}^{ca}(1)$
$q_d^-(z)$	$-G_{ys}^{ca}(2)$	$G_{yy}^{ca}(2)$	$G_{yx}^{ca}(2)$	$-G_{yz}^{ca}(2)$

	$G_{ys}^{ca}(1)$	$G_{yx}^{ca}(1)$	$G_{yy}^{ca}(1)$	$G_{yz}^{ca}(1)$
$c_2(z)$	$-G_{ys}^{ca}(2)$	$G_{yx}^{ca}(2)$	$G_{yy}^{ca}(2)$	$-G_{yz}^{ca}(2)$
$q_d^+(z)$	$G_{xs}^{ca}(1)$	$G_{xy}^{ca}(1)$	$G_{xx}^{ca}(1)$	$G_{xz}^{ca}(1)$
$q_d^-(z)$	$-G_{xs}^{ca}(2)$	$G_{xy}^{ca}(2)$	$G_{xx}^{ca}(2)$	$-G_{xz}^{ca}(2)$

	$G_{zs}^{ca}(1)$	$G_{zx}^{ca}(1)$	$G_{zy}^{ca}(1)$	$G_{zz}^{ca}(1)$
$c_2(z)$	$G_{zs}^{ca}(2)$	$-G_{zx}^{ca}(2)$	$-G_{zy}^{ca}(2)$	$G_{zz}^{ca}(2)$
$q_d^+(z)$	$G_{zs}^{ca}(1)$	$G_{zy}^{ca}(1)$	$G_{zx}^{ca}(1)$	$G_{zz}^{ca}(1)$
$q_d^-(z)$	$G_{zs}^{ca}(2)$	$-G_{zy}^{ca}(2)$	$-G_{zx}^{ca}(2)$	$G_{zz}^{ca}(2)$

	$G_{ss}^{aa}(2,1)$	$G_{sx}^{aa}(2,1)$	$G_{sy}^{aa}(2,1)$	$G_{sz}^{aa}(2,1)$
$c_2(z)$	$G_{ss}^{aa}(1,2)$	$-G_{sx}^{aa}(1,2)$	$-G_{sy}^{aa}(1,2)$	$G_{sz}^{aa}(1,2)$
$\sigma_d^+(z)$	$G_{ss}^{aa}(2,1)$	$G_{sy}^{aa}(2,1)$	$G_{sx}^{aa}(2,1)$	$G_{sz}^{aa}(2,1)$
$\sigma_d^-(z)$	$G_{ss}^{aa}(1,2)$	$-G_{sy}^{aa}(1,2)$	$-G_{sx}^{aa}(1,2)$	$G_{sz}^{aa}(1,2)$

	$G_{xs}^{aa}(2,1)$	$G_{xx}^{aa}(2,1)$	$G_{xy}^{aa}(2,1)$	$G_{xz}^{aa}(2,1)$
$c_2(z)$	$-G_{xs}^{aa}(1,2)$	$G_{xx}^{aa}(1,2)$	$G_{xy}^{aa}(1,2)$	$-G_{xz}^{aa}(1,2)$
$\sigma_d^+(z)$	$G_{ys}^{aa}(2,1)$	$G_{yy}^{aa}(2,1)$	$G_{yx}^{aa}(2,1)$	$G_{yz}^{aa}(2,1)$
$\sigma_d^-(z)$	$-G_{ys}^{aa}(1,2)$	$G_{yy}^{aa}(1,2)$	$G_{yx}^{aa}(1,2)$	$-G_{yz}^{aa}(1,2)$

	$G_{ys}^{aa}(2,1)$	$G_{yx}^{aa}(2,1)$	$G_{yy}^{aa}(2,1)$	$G_{yz}^{aa}(2,1)$
$c_2(z)$	$-G_{ys}^{aa}(1,2)$	$G_{yx}^{aa}(1,2)$	$G_{yy}^{aa}(1,2)$	$-G_{yz}^{aa}(1,2)$
$\sigma_d^+(z)$	$G_{xs}^{aa}(2,1)$	$G_{xy}^{aa}(2,1)$	$G_{xx}^{aa}(2,1)$	$G_{xz}^{aa}(2,1)$
$\sigma_d^-(z)$	$-G_{xs}^{aa}(1,2)$	$G_{xy}^{aa}(1,2)$	$G_{xx}^{aa}(1,2)$	$-G_{xz}^{aa}(1,2)$

and

	$G_{zs}^{aa}(2,1)$	$G_{zx}^{aa}(2,1)$	$G_{zy}^{aa}(2,1)$	$G_{zz}^{aa}(2,1)$
$c_2(z)$	$G_{zs}^{aa}(1,2)$	$-G_{zx}^{aa}(1,2)$	$-G_{zy}^{aa}(1,2)$	$G_{zz}^{aa}(1,2)$
$\sigma_d^+(z)$	$G_{zs}^{aa}(2,1)$	$G_{zy}^{aa}(2,1)$	$G_{zx}^{aa}(2,1)$	$G_{zz}^{aa}(2,1)$
$\sigma_d^-(z)$	$G_{zs}^{aa}(1,2)$	$-G_{zy}^{aa}(1,2)$	$-G_{zx}^{aa}(1,2)$	$G_{zz}^{aa}(1,2)$

In these tables, the notation is the same as that used in Eqs.(4-13)-(4-15). In addition, for the perfect crystal, we must have

$$G_{sz}^{ca}(1) = G_{sx}^{ca}(1) , \quad (A-1)$$

$$G_{zs}^{ca}(1) = G_{xs}^{ca}(1) , \quad (A-2)$$

and

$$G_{zz}^{ca}(1) = G_{xx}^{ca}(1) . \quad (A-3)$$

We now write the explicit expressions for the submatrices $G^{ca}(1)$, $G^{ca}(2)$, and $G^{aa}(2,1)$ in the zincblende coordinate system using the symmetries required by the above discussed C_{2v} point group operations. These are

$$G^{ca}_{(1)} = \begin{pmatrix} G^{ca}_{ss}(1) & G^{ca}_{sx}(1) & G^{ca}_{sx}(1) & G^{ca}_{sx}(1) \\ G^{ca}_{xs}(1) & G^{ca}_{xx}(1) & G^{ca}_{xy}(1) & G^{ca}_{xy}(1) \\ G^{ca}_{xs}(1) & G^{ca}_{xy}(1) & G^{ca}_{xx}(1) & G^{ca}_{xy}(1) \\ G^{ca}_{xs}(1) & G^{ca}_{xy}(1) & G^{ca}_{xy}(1) & G^{ca}_{xx}(1) \end{pmatrix}, \quad (A-4)$$

$$G^{ca}_{(2)} = \begin{pmatrix} G^{ca}_{ss}(1) & -G^{ca}_{sx}(1) & -G^{ca}_{sx}(1) & G^{ca}_{sx}(1) \\ -G^{ca}_{xs}(1) & G^{ca}_{xx}(1) & G^{ca}_{xy}(1) & -G^{ca}_{xy}(1) \\ -G^{ca}_{xs}(1) & G^{ca}_{xy}(1) & G^{ca}_{xx}(1) & -G^{ca}_{xy}(1) \\ G^{ca}_{xs}(1) & -G^{ca}_{xy}(1) & -G^{ca}_{xy}(1) & G^{ca}_{xx}(1) \end{pmatrix}, \quad (A-5)$$

and

$$G^{aa}_{(2,1)} = \begin{pmatrix} G^{aa}_{ss}(2,1) & G^{aa}_{sx}(2,1) & G^{aa}_{sx}(2,1) & G^{aa}_{sz}(2,1) \\ -G^{aa}_{sx}(2,1) & G^{aa}_{xx}(2,1) & G^{aa}_{xy}(2,1) & G^{aa}_{xz}(2,1) \\ -G^{aa}_{sx}(2,1) & G^{aa}_{xy}(2,1) & G^{aa}_{xx}(2,1) & G^{aa}_{xz}(2,1) \\ G^{aa}_{sz}(2,1) & -G^{aa}_{xz}(2,1) & -G^{aa}_{xz}(2,1) & G^{aa}_{zz}(2,1) \end{pmatrix}. \quad (A-6)$$

It is not difficult to see from Fig.1 that the zincblende coordinate system is not the best one to use to fully take advantage of the symmetry of the triplet complex. In order to choose a better coordinate system in which the symmetry of the triplet complex defect can be presented so that more zero matrix elements can be expected, the following coordinate transformation is made. We define a new coordinate system (x',y',z') , displayed in Fig.A.1.

Figure A.1 The relationship between the new coordinate system and the zincblende coordinate system.

In that figure, x' , y' , and z' are new axes such that anion(1) and anion(2) lie in the x -plane (see Fig.1.). From Fig.A.1, it is easily seen that the primed and unprimed vectors are related by

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = M \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \quad (\text{A-7})$$

where

$$M = \begin{pmatrix} 1/\sqrt{2} & 1/\sqrt{2} & 0 \\ -1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (\text{A-8})$$

In the new system, the four elements of the group C_{2v} are E , $C_2(z')$, $\sigma(x')$, and $\sigma(y')$, where E is the identity element, $C_2(z')$ is a rotation through π about the z' axis, $\sigma(x')$ is a reflection operation in a plane passing through the z' and x' axes, and $\sigma(y')$ is a reflection operation in a plane passing through the z' and y' axes.

As above, the vectors $\vec{\tau}_1$, $\vec{\tau}_2$ and the atomic-like p-like wavefunctions in the new coordinate system transform according to the following table:

	τ_1	τ_2	$p_{x'}$	$p_{y'}$	$p_{z'}$
$c_2(z')$	τ_2	τ_1	$-p_{x'}$	$p_{y'}$	$p_{z'}$
$\sigma(x')$	τ_1	τ_2	$-p_{x'}$	$-p_{y'}$	$p_{z'}$
$\sigma(y')$	τ_2	τ_1	$-p_{x'}$	$p_{y'}$	$p_{z'}$

Here $p_{x'}$, $p_{y'}$, and $p_{z'}$ are the three atomic-like p-like wavefunctions in the new coordinate system.

Similar to the discussion above, by carrying out the group symmetric operations in the new coordinate system, we can simplify the matrix elements of the Green's function in this system. Here we ignore the detailed steps and just write down the results.

In the new coordinate system, the Green's function submatrices defined by Eqs.(4-5)-(4-9) can be rewritten as

$$G^{aa} = \begin{pmatrix} G_{s's'}^{a a} & 0 & 0 & 0 \\ 0 & G_{x'x'}^{a a} & 0 & 0 \\ 0 & 0 & G_{x'x'}^{a a} & 0 \\ 0 & 0 & 0 & G_{x'x'}^{a a} \end{pmatrix}, \quad (A-9)$$

$$G^{CC} = \begin{pmatrix} G_{S'S'}^{CC} & 0 & 0 & 0 \\ 0 & G_{X'X'}^{CC} & 0 & 0 \\ 0 & 0 & G_{X'X'}^{CC} & 0 \\ 0 & 0 & 0 & G_{X'X'}^{CC} \end{pmatrix}, \quad (A-10)$$

$$G^{ca}_{(1)} = \begin{pmatrix} G_{S'S'}^{ca}(1) & G_{S'X'}^{ca}(1) & 0 & G_{S'Z'}^{ca}(1) \\ G_{X'S'}^{ca}(1) & G_{X'X'}^{ca}(1) & 0 & G_{X'Z'}^{ca}(1) \\ 0 & 0 & G_{Y'Y'}^{ca}(1) & 0 \\ G_{Z'S'}^{ca}(1) & G_{Z'X'}^{ca}(1) & 0 & G_{Z'Z'}^{ca}(1) \end{pmatrix}, \quad (A-11)$$

$$G^{ca}_{(2)} = \begin{pmatrix} G_{S'S'}^{ca}(1) & -G_{S'X'}^{ca}(1) & 0 & G_{S'Z'}^{ca}(1) \\ -G_{X'S'}^{ca}(1) & G_{X'X'}^{ca}(1) & 0 & -G_{X'Z'}^{ca}(1) \\ 0 & 0 & G_{Y'Y'}^{ca}(1) & 0 \\ G_{Z'S'}^{ca}(1) & -G_{Z'X'}^{ca}(1) & 0 & G_{Z'Z'}^{ca}(1) \end{pmatrix}, \quad (A-12)$$

and

$$G'^{aa}(2,1) = \begin{pmatrix} G_{S'S'}^{a,a}(2,1) & G_{S'X'}^{a,a}(2,1) & 0 & G_{S'Z'}^{a,a}(2,1) \\ -G_{S'X'}^{a,a}(2,1) & G_{X'X'}^{a,a}(2,1) & 0 & G_{S'Z'}^{a,a}(2,1) \\ 0 & 0 & G_{Y'Y'}^{a,a}(2,1) & 0 \\ G_{S'Z'}^{a,a}(2,1) - G_{X'Z'}^{a,a}(2,1) & 0 & 0 & G_{Z'Z'}^{a,a}(2,1) \end{pmatrix}. \quad (A-13)$$

The relationships between the matrix elements in the two coordinate systems is given in Appendix B.

In order to further simplify the Green's function G^0 , a second coordinate transformation is made. In particular, it is convenient to introduce symmetric and anti-symmetric representations. We define the symmetric and anti-symmetric basis functions as follows.

$$S_S = 1/\sqrt{2} (s'_1 + s'_2) \quad (A-14)$$

$$X_S = 1/\sqrt{2} (x'_1 + x'_2) \quad (A-15)$$

$$Y_S = 1/\sqrt{2} (y'_1 + y'_2) \quad (A-16)$$

$$Z_S = 1/\sqrt{2} (z'_1 + z'_2) \quad (A-17)$$

$$S_A = 1/\sqrt{2} (s'_2 - s'_1) \quad (A-18)$$

$$X_A = 1/\sqrt{2} (x'_2 - x'_1) \quad (\text{A-19})$$

$$Y_A = 1/\sqrt{2} (y'_2 - y'_1) \quad (\text{A-20})$$

and

$$Z_A = 1/\sqrt{2} (z'_2 - z'_1) \quad (\text{A-21})$$

where s'_i , x'_i , y'_i , and z'_i are the s' , p_x' , p_y' , and p_z' orbitals in the primed coordinate system and $i=1,2$ refers to atoms number 1 and 2 in Fig.1.

In order to obtain the matrix elements of the Green's function between these symmetric and anti-symmetric basis function, we make the following orthonormal transformation.

$$G_{SA} = U G' U^{-1} \quad (\text{A-22a})$$

where

$$U = \begin{pmatrix} 1/\sqrt{2} & 0 & 1/\sqrt{2} \\ 0 & 1 & 0 \\ -1/\sqrt{2} & 0 & 1/\sqrt{2} \end{pmatrix} . \quad (\text{A-22b})$$

Writing G' as

$$\begin{pmatrix} G',aa & [G',ca(1)]^T & [G',aa(2,1)]^T \\ G',ca(1) & G',cc & G',ca(2) \\ G',aa(2,1) & [G',ca(2)]^T & G',aa \end{pmatrix}, \quad (A-23)$$

where G' is a 12×12 matrix, each sub-matrix of G' is a 4×4 matrix, described by Eqs.(A-9)-(A-13), and T is the transpose operation.

We then have

$$G_{SA} = U G U^{-1} = \begin{pmatrix} G^{aa} + 1/2[G^{aa}(2,1) + G^{aa}(2,1)]^T & 1/\sqrt{2}[G^{ca}(1) + G^{ca}(2)]^T & 1/\sqrt{2}[G^{aa}(2,1) - G^{aa}(2,1)]^T \\ 1/\sqrt{2}[G^{ca}(1) + G^{ca}(2)] & G^{cc} & 1/\sqrt{2}[G^{ca}(2) - G^{ca}(1)] \\ 1/\sqrt{2}[G^{aa}(2,1) - G^{aa}(2,1)]^T & 1/\sqrt{2}[G^{ca}(2) - G^{ca}(1)]^T & G^{aa} - 1/\sqrt{2}[G^{aa}(2,1) + G^{aa}(2,1)]^T \end{pmatrix}.$$

(A-24)

Thus, we obtain the 12x12 matrix of the Green's function in the basis of the symmetric and anti-symmetric functions. For the sake of brevity, we will not write down the explicit expression for this 12x12 matrix. Instead we manipulate the resulting function further. Specifically, upon rearranging the basis, we obtain a block-diagonalized Green's function matrix which has the schematic form

$$G_{SA} = \left(\begin{array}{c|c|c|c} G1(5 \times 5) & 0 & 0 & 0 \\ \hline 0 & G2(4 \times 4) & 0 & 0 \\ \hline 0 & 0 & G3(2 \times 2) & 0 \\ \hline 0 & 0 & 0 & G4(1 \times 1) \end{array} \right) \quad (A-25)$$

In this matrix we have defined the following submatrices.

$$\begin{array}{c}
S_S \\
s' \\
G1 = X_A \\
Z_S \\
z'
\end{array}
\begin{array}{c}
S_S \\
s' \\
X_A \\
Z_S \\
z'
\end{array}
\begin{array}{c}
s' \\
Z_S \\
z'
\end{array}
\begin{array}{c}
G_{S'S'}^a a + G_{S'S'}^a a, (2,1) \\
\sqrt{2} G_{S'S'}^C a \\
- G_{S'X'}^a a, (2,1) \\
- G_{S'X'}^a a, (2,1) \\
G_{S'Z'}^a a, (2,1) \\
\sqrt{2} G_{Z'S'}^C a
\end{array}
\begin{array}{c}
s' \\
X_A \\
Z_S \\
z'
\end{array}
\begin{array}{c}
G_{S'S'}^C a \\
- \sqrt{2} G_{S'X'}^C a \\
G_{S'X'}^a a - G_{X'X'}^a a, (2,1) \\
G_{X'Z'}^a a, (2,1) \\
- \sqrt{2} G_{Z'X'}^C a \\
0
\end{array}
\begin{array}{c}
Z_S \\
z'
\end{array}
\begin{array}{c}
G_{S'Z'}^a a, (2,1) \\
\sqrt{2} G_{S'Z'}^C a \\
G_{X'Z'}^a a + G_{Z'Z'}^a a, (2,1) \\
\sqrt{2} G_{Z'Z'}^C a \\
G_{X'X'}^C a
\end{array}
\begin{array}{c}
Z_S \\
z'
\end{array}
\begin{array}{c}
G_{S'Z'}^a a, (2,1) \\
\sqrt{2} G_{S'Z'}^C a \\
G_{X'Z'}^a a + G_{Z'Z'}^a a, (2,1) \\
\sqrt{2} G_{Z'Z'}^C a \\
G_{X'X'}^C a
\end{array}$$

(A-26)

$$G3 = \begin{matrix} & Y_S & & y' \\ Y_S & \left(G_{x',x'}^{a,a} + G_{y',y'}^{a,a}(2,1) \right) & \sqrt{2} G_{y',y'}^{c,a} \\ & & & \\ y' & \sqrt{2} G_{y',y'}^{c,a} & G_{x',x'}^{c,a} \end{matrix} \quad (A-28)$$

and

$$G4 = \begin{matrix} & Y_A \\ Y_A & (G_{x',x'} - G_{y',y'}(2,1)) \end{matrix} . \quad (A-29)$$

Using the results of Appendix B, the primed matrix elements can now be transformed back to the unprimed, or zinc-blende coordinate system. The results of this manipulation are explicitly displayed in Eqs.(4-17)-(4-20).

APPENDIX B

THE RELATIONSHIP BETWEEN THE MATRIX ELEMENTS OF THE GREEN'S FUNCTION IN THE TWO COORDINATE SYSTEMS

The relationship between two vectors in the primed and unprimed coordinate systems defined in Appendix A is given by Eqs.(A.7) and (A.8). Let us now include the s orbital part of the basis so that the dimensions of this subspace are extended from three to four. We then have

$$\begin{pmatrix} s' \\ x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 0 & -1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} s \\ x \\ y \\ z \end{pmatrix} . \quad (\text{B-1})$$

We now define

$$M = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 0 & -1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} . \quad (\text{B-2})$$

Obviously,

$$M M^T = M^T M = I . \quad (\text{B-3})$$

That is, M is an orthonormal matrix.

Since the Green's function matrices in the subspaces described by Eqs.(A-4)-(A-6) and Eqs.(A-9)-(A-13) are 4x4 matrices, they transform as tensors under the above coordinate transformation. Namely, in the new coordinate system,

$$G' = M G M^T . \quad (B-4)$$

Or explicitly,

$$\begin{pmatrix} G_{s's'} & G_{s'x'} & G_{s'y'} & G_{s'z'} \\ G_{x's'} & G_{x'x'} & G_{x'y'} & G_{x'z'} \\ G_{y's'} & G_{y'x'} & G_{y'y'} & G_{y'z'} \\ G_{z's'} & G_{z'x'} & G_{z'y'} & G_{z'z'} \end{pmatrix} = M \begin{pmatrix} G_{ss} & G_{sx} & G_{sy} & G_{sz} \\ G_{xs} & G_{xx} & G_{xy} & G_{xz} \\ G_{ys} & G_{yx} & G_{yy} & G_{yz} \\ G_{zs} & G_{zx} & G_{zy} & G_{zz} \end{pmatrix} M^T . \quad (B-5)$$

This yields

$$G' = \begin{pmatrix} G_{ss} & 1/\sqrt{2} (G_{sx} + G_{sy}) & 1/\sqrt{2} (G_{sy} - G_{sx}) & G_{sz} \\ 1/\sqrt{2} (G_{xs} + G_{ys}) & 1/2 (G_{xx} + G_{yy} + G_{xy} + G_{yx}) & 1/2 (G_{yy} - G_{xx} + G_{xy} - G_{yx}) & 1/\sqrt{2} (G_{xz} + G_{yz}) \\ 1/\sqrt{2} (G_{ys} - G_{xs}) & 1/2 (G_{yy} - G_{xx} + G_{yx} - G_{xy}) & 1/2 (G_{xx} + G_{yy} - G_{xy} - G_{yx}) & 1/\sqrt{2} (G_{yz} - G_{xz}) \\ G_{zs} & 1/\sqrt{2} (G_{zx} + G_{zy}) & 1/\sqrt{2} (G_{zy} - G_{zx}) & G_{zz} \end{pmatrix} .$$

(B-6)

Since

$$\begin{pmatrix} G_{s's'}^{a a} & 0 & 0 & 0 \\ 0 & G_{x'x'}^{a a} & 0 & 0 \\ 0 & 0 & G_{x'x'}^{a a} & 0 \\ 0 & 0 & 0 & G_{x'x'}^{a a} \end{pmatrix} = \begin{pmatrix} G_{ss}^{aa} & 0 & 0 & 0 \\ 0 & G_{xx}^{aa} & 0 & 0 \\ 0 & 0 & G_{xx}^{aa} & 0 \\ 0 & 0 & 0 & G_{xx}^{aa} \end{pmatrix} . \quad (\text{B-7})$$

We obtain

$$G_{s's'}^{a a} = G_{ss}^{aa} , \quad (\text{B-8})$$

and

$$G_{x'x'}^{a a} = G_{xx}^{aa} . \quad (\text{B-9})$$

Similarly we have,

$$\begin{pmatrix} G_{s's'}^{c c} & 0 & 0 & 0 \\ 0 & G_{x'x'}^{c c} & 0 & 0 \\ 0 & 0 & G_{x'x'}^{c c} & 0 \\ 0 & 0 & 0 & G_{x'x'}^{c c} \end{pmatrix} = \begin{pmatrix} G_{ss}^{cc} & 0 & 0 & 0 \\ 0 & G_{xx}^{cc} & 0 & 0 \\ 0 & 0 & G_{xx}^{cc} & 0 \\ 0 & 0 & 0 & G_{xx}^{cc} \end{pmatrix} . \quad (\text{B-10})$$

It is also true that

$$G_{S'S'}^{C\ C} = G_{SS}^{CC} , \quad (B-11)$$

and

$$G_{X'X'}^{C\ C} = G_{XX}^{CC} . \quad (B-12)$$

From Eqs.(A-11),(B-6) and (A-5), we have

$$\begin{pmatrix} G_{S'S'}^{C\ a} & G_{S'X'}^{C\ a} & 0 & G_{S'Z'}^{C\ a} \\ G_{X'S'}^{C\ a} & G_{X'X'}^{C\ a} & 0 & G_{X'Z'}^{C\ a} \\ 0 & 0 & G_{Y'Y'}^{C\ a} & 0 \\ G_{Z'S'}^{C\ a} & G_{Z'X'}^{C\ a} & 0 & G_{Z'Z'}^{C\ a} \end{pmatrix} = \begin{pmatrix} G_{SS}^{ca}\sqrt{2} & G_{SX}^{ca} & 0 & G_{SX}^{ca} \\ \sqrt{2} G_{XS}^{ca} & G_{XX}^{ca} + G_{XY}^{ca} & 0 & \sqrt{2} G_{XY}^{ca} \\ 0 & 0 & G_{XX}^{ca} - G_{XY}^{ca} & 0 \\ G_{XS}^{ca}\sqrt{2} & G_{XY}^{ca} & 0 & G_{XX}^{ca} \end{pmatrix} . \quad (B-13)$$

This means that

$$G_{S'S'}^{C\ a} = G_{SS}^{ca} , \quad (B-14)$$

$$G_{S'X'}^{C\ a} = \sqrt{2} G_{SX}^{ca} , \quad (B-15)$$

$$G_{S'Z'}^{C\ a} = G_{SX}^{ca} , \quad (B-16)$$

$$G_{X'S'}^{C\ a} = \sqrt{2} G_{XS}^{ca} , \quad (B-17)$$

$$G_{X'X'}^{C\ a} = G_{XX}^{ca} + G_{XY}^{ca} , \quad (B-18)$$

$$G_{X'Z'}^{C\ a} = \sqrt{2} G_{XY}^{ca} , \quad (B-19)$$

$$G_{S'S'}^{a\ a}(2,1) = G_{SS}^{aa}(2,1) , \quad (B-20)$$

$$G_{Z'S'}^{c\ a} = G_{XS}^{ca} , \quad (B-21)$$

$$G_{Z'X'}^{c\ a} = 2 G_{XY}^{ca} , \quad (B-22)$$

and

$$G_{Z'Z'}^{c\ a} = G_{XX}^{ca} . \quad (B-23)$$

Similarly, from Eqs.(A-13), (B-6) and (A-6), we have

$$\begin{pmatrix} G_{S'S'}^{a\ a}(2,1) & G_{S'X'}^{a\ a}(2,1) & 0 & G_{S'Z'}^{a\ a}(2,1) \\ -G_{S'X'}^{a\ a}(2,1) & G_{X'X'}^{a\ a}(2,1) & 0 & G_{X'Z'}^{a\ a}(2,1) \\ 0 & 0 & G_{Y'Y'}^{a\ a}(2,1) & 0 \\ G_{S'Z'}^{a\ a}(2,1) & -G_{X'Z'}^{a\ a}(2,1) & 0 & G_{Z'Z'}^{a\ a}(2,1) \end{pmatrix}$$

$$= \begin{pmatrix} G_{SS}^{aa}(2,1) & \sqrt{2} G_{SX}^{aa}(2,1) & 0 & G_{SZ}^{aa}(2,1) \\ -\sqrt{2} G_{SX}^{aa}(2,1) & G_{XX}^{aa}(2,1) + G_{XY}^{aa}(2,1) & 0 & \sqrt{2} G_{XZ}^{aa}(2,1) \\ 0 & 0 & G_{XX}^{aa}(2,1) - G_{XY}^{aa}(2,1) & 0 \\ G_{SZ}^{aa}(2,1) & -\sqrt{2} G_{XZ}^{aa}(2,1) & 0 & G_{ZZ}^{aa}(2,1) \end{pmatrix} . \quad (B-24)$$

This means that

$$G_{S,S}^{a,a}(2,1) = G_{SS}^{aa}(2,1) , \quad (B-25)$$

$$G_{S,X}^{a,a}(2,1) = G_{SX}^{aa}(2,1) , \quad (B-26)$$

$$G_{S,Z}^{a,a}(2,1) = G_{SZ}^{aa}(2,1) , \quad (B-27)$$

$$G_{X,X}^{a,a}(2,1) = G_{XX}^{aa}(2,1) + G_{XY}^{aa}(2,1) , \quad (B-28)$$

$$G_{Y,Y}^{a,a}(2,1) = G_{XX}^{aa}(2,1) - G_{XY}^{aa}(2,1) , \quad (B-29)$$

$$G_{X,Z}^{a,a}(2,1) = \sqrt{2} G_{XZ}^{aa}(2,1) , \quad (B-30)$$

and

$$G_{Z,Z}^{a,a}(2,1) = G_{ZZ}^{aa}(2,1) . \quad (B-31)$$

With Eqs.(B-8)-(B-9), (B-11)-(B-12), (B-14)-(B-23), and (B-24)-(B-31) we have established the relationship between the matrix elements of the Green's function in the two coordinate systems.

APPENDIX C
COMPUTER CODE

C ROUTINE TRIPLET.FOR
C THIS PROGRAM COMPUTES THE DEEP LEVELS ASSOCIATED
C WITH TRIPLET COMPLEX. THIS COMPLEX CONSISTS OF
C THREE IMPURITY ATOMS, WHERE THE ORIGIN IS TAKEN
C TO BE THE CATION SITE AND TWO OF THE NEAREST-
C NEIGHBORS ARE IDENTICAL ANION IMPURITY ATOMS.
C THE OPPOSITE CASE, WHERE THE ORIGIN IS TAKEN
C TO BE AN ANION SITE AND TWO OF THE NEAREST-
C NEIGHBORS ARE IDENTICAL CATION IMPURITY ATOMS,
C CAN ALSO EASILY BE COMPUTED BY THIS PROGRAM.
C THE CHANGES ARE IN LINE 30 (REPLACE TBPRA2 BY
C TBPRA1) AND IN LINE 40 (REPLACE TBPRA1 BY
C TBPRA2).
C OF COURSE, THIS PROGRAM CAN BE USED TO CALCULATE
C THE DEEP LEVELS ASSOCIATED WITH TRIPLET VACANCY-
C IMPURITY COMPLEX. THIS COMPLEX CONSISTS OF ONE
C VACANCY PLUS TWO IDENTICAL IMPURITIES. ONLY THING
C NEEDED TO DO IS TO SET VSI IN LINE 25 AS A LARGE
C ENOUGH NUMBER(FOR EXAMPLE, SET VS1=1000).
C IF WE SET VS1=0, THIS IS CORRESPONDING TO TWO
C IDENTICAL IMPURITY PAIR(THE ORIGIN IS A HOST
C ATOM NOW).

C*****

C WARNING:

C IF WE TAKE CATION SITE AS THE ORIGIN, THE

C AL(1,1,1)/4 AS ANION(1), AND AL(-1,-1,1)/4

C AS ANION(2), FOR NN=1 AND WITH TBPRA2 AS THE

C INPUT OF DENSPR, THE OUTPUTS OF DENSPEP AND

C GRNPAR ARE DIRECTLY CORRESPONDING TO THE MATRIX

C ELEMENTS OF GCA(1), NOT GAC(1). OF COURSE,

C GAC(1) IS THE TRANSPOSE OF GCA(1).

C SIMILARLY, FOR NN=2 AND WITH TBPRA1 AS THE INPUT

C OF DENSPR, THE OUTPUTS OF DENSPR AND GRNPAR ARE

C DIRECTLY CORRESPONDING TO THE MATRIX ELEMENTS

C OF GAA(2,1), NOT GAA(1,2). OF COURSE, GAA(1,2) IS

C THE TRANSPOSE OF GAA(2,1).

C*****

C VS0 IS THE S DEFECT POTENTIAL FOR THE ANION SITE

C VP0 IS THE P DEFECT POTENTIAL FOR THE ANION SITE

C VS1 IS THE S DEFECT POTENTIAL FOR THE CATION SITE

C VP1 IS THE P DEFECT POTENTIAL FOR THE CATION SITE

C WE USE THE EMPIRICAL RELATION

C VP0=BETA*VS0 (BETA ABOUT 0.5)

C VP1=GAMMA*VS1 (GAMMA ABOUT 0.5)

C DIMENSION P(13),AA(3),BB(3),P2(13),AA2(3),BB2(3)

C DIMENSION G1(14),G1I(14),G2(14),G2I(14)

C DIMENSION G5(5,5),GG4(4,4),XCOF(4),X2COF(4)

```

        DIMENSION X3COF(2),GGG2(2,2)
        DIMENSION SROOTR(3),SROOTI(3),WA(4)
        DIMENSION SRTR(3),SRTI(3),WB(4)
DATA EGAP,BETA,GAMMA,VS1/2.35,.5,.5,1000./
        WRITE(6,77)
77      FORMAT(' INSERT EGAP =BAND GAP -.05')
        WRITE(6,79)
79      FORMAT(' INSERT BETA=VP0/VS0')
C READ DATA FILE GRN, OUTPUT BY DENSPR FOR NN=1 AND WITH
C TBPRA2 AS INPUT, WHICH CONTAINS VARIOUS PARAMETERS
        READ(23,705) (P(I),I=1,9)
        READ(23,710) (P(I),I=10,13)
        READ(23,711) COMP,AA,BB
        READ(23,712) EGRID,EI,EF,EMIN,EMAX,NN,IMAX
705     FORMAT(9F8.4)
710     FORMAT(4F8.4)
711     FORMAT(F8.4,6A5)
712     FORMAT(5F11.5,2I3)
C READ DATA FILE G2RN, OUTPUT BY DENSPR FOR NN=2 AND WITH
C TBPRA1 AS INPUT, WHICH CONTAINS VARIOUS PARAMETERS
        READ(22,705) (P2(I),I=1,9)
        READ(22,710) (P2(I),I=10,13)
        READ(22,711) COMP2,AA2,BB2
        READ(22,712) EGRID2,EI2,EF2,EMIN2,EMAX2,NN2,IMAX2
        WRITE(6,10)

```



```

10      FORMAT(' ES1 EP1 ES2 EP2 VSS VXX VXY VSP1 VSP2')
        WRITE(6,705) (P(I),I=1,9)
        WRITE(6,11)
11      FORMAT(' ES3 ES4 VSP3 VSP4')
        WRITE(6,710) (P(I),I=10,13)
        WRITE(6,711) COMP,AA,BB
        WRITE(6,12) EGRID,EI,EF,NN,IMAX
12      FORMAT(' EGRID EI EF=',3E14.4,2X,'NN=',I3,2X,
1      ' IMAX=',I3)
        WRITE(6,13)
13      FORMAT(' ES1 EP1 ES2 EP2 VSS VXX VXY VSP1 VSP2')
        WRITE(6,705) (P2(I),I=1,9)
        WRITE(6,14)
14      FORMAT(' ES3 ES4 VSP3 VSP4')
        WRITE(6,710) (P2(I),I=10,13)
        WRITE(6,711) COMP2,AA2,BB2
        WRITE(6,15) EGRID2,EI2,EF2,NN2,IMAX2
15      FORMAT(' EGRID2 EI2 EF2=',3E14.4,2X,'NN2=',I3,2X,
1      ' IMAX2=',I3)
        NPTS=INT((EF-EI)/EGRID)+1
        NPTS2=NPTS-2
        ILOW=INT((0.-EI)/EGRID)+1+1
        IHI=INT((EGAP-EI)/EGRID)+1
        IBOT=((-1.-EI)/EGRID)+1
        ITOP=((EGAP+.4-EI)/EGRID)+1

```

```

C WRITE VARIOUS PARAMETERS INTO DATA FILE VACANT
      WRITE(26,80) NN,AA,BB,BETA,EGAP
80      FORMAT(I3,6A5,2F11.4)
      WRITE(6,800) BETA,EGAP
      800 FORMAT(2X,'BETA=',F11.4,2X,'EGAP=',F11.4)
      WRITE(26,81) EGRID,EI,EF,IMAX,IMAX2
81      FORMAT(3F8.4,2I3)
C
      IGAP=IHI-ILOW+1
C THE VARIOUS GREEN'S FUNCTIONS ARE READ FROM FILE GREENS,
C WHICH IS OUTPUT BY GRNPAR
      DO 103 I=3,NPTS2,2
      READ(24,123) (G1(J),G1I(J),J=1,IMAX),EN
123      FORMAT(6E11.4,/,6E11.4,/,6E11.4,/,E11.4)
      READ(25,124) (G2(J),G2I(J),J=1,IMAX2),EN2
124      FORMAT(6E11.4,/,6E11.4,/,6E11.4,/,5E11.4)
C
      IF(I.LT.IBOT.OR.I.GT.ITOP) GO TO 103
      CALL FORMG1(G1,G2,G5,GG4,GGG2,GGGG1)
C  FOR G5(5X5)
      G11=G5(1,1)
      G22=G5(2,2)
      G33=G5(3,3)
      G44=G5(4,4)
      G55=G5(5,5)

```

G12=G5(1,2)

G13=G5(1,3)

G14=G5(1,4)

G15=G5(1,5)

G23=G5(2,3)

G24=G5(2,4)

G25=G5(2,5)

G34=G5(3,4)

G35=G5(3,5)

G45=G5(4,5)

A34=G33+G44

B12=G11*G22-G12**2

B13=G11*G33-G13**2

B14=G11*G44-G14**2

B15=G11*G55-G15**2

B23=G22*G33-G23**2

B24=G22*G44-G24**2

B34=G33*G44-G34**2

B35=G33*G55-G35**2

B45=G44*G55-G45**2

C FOR G4(4X4)

GG11=GG4(1,1)

GG22=GG4(2,2)

GG33=GG4(3,3)

GG44=GG4(4,4)

```

GG12=GG4(1,2)
GG13=GG4(1,3)
GG14=GG4(1,4)
GG23=GG4(2,3)
GG24=GG4(2,4)
GG34=GG4(3,4)
AA24=GG22+GG44
BB12=GG11*GG22-GG12**2
BB13=GG11*GG33-GG13**2
BB14=GG11*GG44-GG14**2
BB23=GG22*GG33-GG23**2
BB24=GG22*GG44-GG24**2
BB34=GG33*GG44-GG34**2
C  FOR G2(2X2)
    GGG11=GGG2(1,1)
    GGG22=GGG2(2,2)
    GGG12=GGG2(1,2)
C  FOR G1(1X1)
    GGGG11=GGGG1
C  FOR DET(I-G5(5X5)V5)=0
C  THE COEFFICIENTS OF THE POLYNOMIAL ORDERED FROM
C  SMALLEST TO LARGEST POWER
C  THE COEFFICIENT OF ZEROth POWER
    XCOF(1)= 1.
1          -VS1*G22

```

```

1      -GAMMA*VS1*G55
1      +GAMMA*VS1**2*G22*G55

```

C THE COEFFICIENT OF FIRST POWER

```

      XCOF(2)=-G11
1      -BETA*A34
1      +VS1*B12
1      +GAMMA*VS1*B15
1      +BETA*VS1*(B23+B24)
1      +BETA*GAMMA*VS1*(B35+B45)
1      +GAMMA*VS1**2*(G12**2*G55-G22*B15)
1      +BETA*GAMMA*VS1**2*(G22*G45**2+G55*G24**2
1      -g22*G55*a34+G22*G35**2+G55*G23**2)

```

C THE COEFFICIENT OF SECOND POWER

```

      XC31=BETA*(B13+B14)
1      +BETA**2*B34
      XC32=BETA*VS1*(G12**2*A34+G13**2*G22+G14**2*G22
1      -G11*(B23+B24)
1      -2*G12*G13*G23-2*G12*G14*G24)
1      +BETA*GAMMA*VS1*(G15**2*A34+G13**2*G55
1      +g14**2*g55-G11*(B35+B45)
1      -2*G13*G15*G35-2*G14*G15*G45)
1      +BETA**2*VS1*(G22*G34**2+G33*G24**2+G44*G23**2
1      -G22*G33*G44-2*G23*G24*G34)
1+BETA**2*GAMMA*VS1*(G33*G45**2+G44*G35**2+G55*G34**2
1      -G33*G44*G55-2*G34*G35*G45)

```

```

XC33=BETA*GAMMA*VS1**2*(G15**2*G24**2+G12**2*G45**2
1      -G22*(G11*G45**2+G55*G14**2)
1      -A34*(G12**2*G55+G15**2*G22)
1      +G22*G55*B13+G11*G55*B24
1      -2.*G12*G15*G24*G45
1      +2.*G12*G14*G24*G55+2.*G14*G15*G22*G45)
1      +BETA*GAMMA*VS1**2*(G12*G35*(G12*G35-G15*G23)
1      +G12*G55*G13*G23+G15*G22*G13*G35
1      +G22*G35*(G13*G15-G11*G35)
1      +G23*G15*(G15*G23-G12*G35)
1      +G23*G55*(G12*G13-G11*G23))
1      +BETA**2*GAMMA*VS1**2*(G22*G33*B45
1      -G55*(G22*G34**2+G33*G24**2)
1      +G22*G35*(G34*G45-G35*G44)
1      +G22*G45*G34*G35+G24*G55*G23*G34
1      +G23*G45*(G23*G45-G24*G35)
1      +G23*G55*(G24*G34-G23*G44)
1      +G24*G35*(G24*G35-G23*G45))

```

XC0F(3)=XC31+XC32+XC33

C THE COEFFICIENT OF 3RD POWER

```

XC41=BETA**2*(G13**2*G44+G14**2*G33-G11*B34
1      -2*g13*g14*g34)
XC42=BETA**2*VS1*(G11*(G22*G33*G44+2*G23*G24*G34
1      -G22*G34**2-G33*G24**2-G44*G23**2)
1      +G12*(G12*G34**2+G13*G23*G44+G14*G24*G33

```

```

1      -G12*G33*G44-G13*G24*G34-G14*G23*G34)
1      +G13*(G12*G23*G44+G13*G24**2+G14*G22*G34
1      -G12*G24*G34-G13*G22*G44-G14*G23*G24)
1      +G14*(G12*G24*G33+G13*G22*G34+G14*G23**2
1      -G12*G23*G34-G13*G23*G24-G14*G22*G33))

```

XC43=BETA**2*GAMMA*VS1*

```

1      (G11*(G33*G44*G55+2*G34*G35*G45
1      -G33*G45**2-G44*G35**2-G55*G34**2)
1      +G13*(G13*G45**2+G14*G34*G35+G15*G35*G44
1      -G13*G44*G55-G14*G35*G45-G15*G34*G45)
1      +G14*(G13*G34*G55+G14*G35**2+G15*G33*G45
1      -G13*G35*G45-G14*G33*G55-G15*G34*G35)
1      +G15*(G13*G35*G44+G14*G33*G45+G15*G34**2
1      -G13*G34*G45-G14*G34*G35-G15*G33*G44))

```

XC44=BETA**2*GAMMA*VS1**2*(G15**2*G22*B34

```

1      +g13**2*g55*b24
1      +G12**2*G55*B34+G45**2*G22*B13
1      +G24**2*G33*B15-G11*G22*G55*B34
1      +G14**2*G22*G33*G55-G12**2*G33*G45**2
1      +2.*G15*G33*G45*(G12*G24-G14*G22)
1      +2.*G13*G22*G34*(G15*G45-G14*G55)
1      +2.*G12*G24*G55*(G13*G34-G14*G33))

```

XC45=BETA**2*GAMMA*VS1**2

```

1      *(G12*G35*(G12*G34*G45+G15*G23*G44+G14*G24*G35
1      -G15*G24*G34-G12*G35*G44-G14*G23*G45)

```

```

1          +G12*G45*(G12*G34*G35+G13*G23*G45
1          -G13*G24*G35-G15*G23*G34)
1          +G12*G55*(G14*G23*G34-G13*G23*G44)
1          +G22*G15*(G14*G34*G35-G13*G35*G44)
1      +G22*G35*(G11*G35*G44+G13*G14*G45+G14*G15*G34
1          -G11*G34*G45-G13*G15*G44-G14**2*G35)
1          +G22*G45*(G13*G14*G35-G11*G34*G35))

```

XC46=BETA**2*GAMMA*VS1**2

```

1      *(G23*G15*(G12*G35*G44+G14*G23*G45+G15*G24*G34
1          -G12*G34*G45-G14*G24*G35-G15*G23*G44)
1          +G23*G45*(G11*G24*G35+G12*G13*G45+G14*G15*G23
1          -G11*G23*G45-G12*G14*G35-G13*G15*G24)
1          +G23*G55*(G11*G23*G44+G12*G14*G34+G13*G14*G24
1          -G11*G24*G34-G12*G13*G44-G14**2*G23)
1          +G24*G15*(G13*G24*G35+G15*G23*G34
1          -G12*G34*G35-G13*G23*G45)
1          +G24*G35*(G11*G23*G45+G12*G14*G35+G13*G15*G24
1          -G11*G24*G35-G12*G13*G45-G14*G15*G23)
1          +G24*G55*(G13*G14*G23-G11*G23*G34))

```

XCOF(4)=XC41+XC42+XC43+XC44+XC45+XC46

C FOR DET(I-G4(4X4)V)=0

C THE COEFFICIENT OF THE ZEROth POWER

X2COF(1)=1.

```

1          -GAMMA*VS1*GG33

```

C THE COEFFICIENT OF THE FIRST POWER

$$X2COF(2) = -GG11 - BETA * AA24$$

$$1 \quad +GAMMA * VS1 * BB13$$

$$1 \quad +BETA * GAMMA * VS1 * (BB23 + BB34)$$

C THE COEFFICIENT OF THE SECOND POWER

$$X2COF(3) = BETA * (BB12 + BB14)$$

$$1 \quad +BETA ** 2 * BB24$$

$$1 \quad +BETA * GAMMA * VS1 * (GG23 * (GG11 * GG23 - GG12 * GG13))$$

$$1 \quad -GG33 * (BB12 + BB14)$$

$$1 \quad +GG13 * (GG13 * GG22 + GG13 * GG44 - GG12 * GG23 - GG14 * GG34)$$

$$1 \quad +GG34 * (GG11 * GG34 - GG13 * GG14))$$

$$1 \quad +BETA ** 2 * GAMMA * VS1 * (GG23 * (GG44 * GG23 - GG24 * GG34))$$

$$1 \quad -GG33 * BB24 + GG34 * (GG22 * GG34 - GG23 * GG24))$$

C THE COEFFICIENT OF THE THIRD POWER

$$X2COF(4) = BETA ** 2 * (GG11 * GG24 ** 2 + GG22 * GG14 ** 2$$

$$1 \quad +GG44 * GG12 ** 2$$

$$1 \quad -GG11 * GG22 * GG44 - 2 * GG12 * GG14 * GG24)$$

$$1 \quad +BETA ** 2 * GAMMA * VS1$$

$$1 \quad * (GG13 * (GG12 * GG23 * GG44 + GG13 * GG24 ** 2$$

$$1 \quad +GG14 * GG22 * GG34 - GG12 * GG24 * GG34$$

$$1 \quad -GG13 * GG22 * GG44 - GG14 * GG23 * GG24)$$

$$1 \quad +GG23 * (GG11 * GG24 * GG34 + GG12 * GG13 * GG44$$

$$1 \quad +GG14 ** 2 * GG23 - GG11 * GG23 * GG44$$

$$1 \quad -GG12 * GG14 * GG34 - GG13 * GG14 * GG24)$$

$$1 \quad +GG33 * (GG11 * GG22 * GG44 + 2 * GG12 * GG14 * GG24$$

$$1 \quad -GG11 * GG24 ** 2 - GG12 ** 2 * GG44 - GG14 ** 2 * GG22)$$

```

1          +GG34*(GG11*GG23*GG24+GG12**2*GG34
1          +GG13*GG14*GG22-GG11*GG22*GG34
1          -GG12*GG13*GG24-GG12*GG14*GG23))
C FOR DET(I-G2(2X2)V2)=0
      X3COF(1)=1.-GAMMA*VS1*GGG22
      X3COF(2)=-BETA*GGG11+BETA*GAMMA*VS1*(GGG11*GGG22
1          -ggg12**2)
C FOR DET(I-G1(1X1)V1)=0
      M=3
      CALL POLRT(XCOF,WA,M,SROOTR,SROOTI,IER)
      CALL POLRT(X2COF,WB,M,SRTR,SRTI,IER)
C ORDER THE ROOTS IN ASCENDING ORDER
      M1=M-1
      DO 30 II=1,M1
      LL=II+1
      DO 30 JJ=LL,M
      IF(SROOTR(II)-SROOTR(JJ)) 30,30,16
16    TEMP=SROOTR(II)
      SROOTR(II)=SROOTR(JJ)
      SROOTR(JJ)=TEMP
30    CONTINUE
      DO 31 III=1,M1
      LLL=III+1
      DO 31 JJJ=LLL,M
      IF(SRTR(III)-SRTR(JJJ)) 31,31,17

```

```
17  TEMP1=SRTR(III)
    SRTR(III)=SRTR(JJJ)
    SRTR(JJJ)=TEMP1
31  CONTINUE
    VSNN0=1./G1(3)
    VPNN0=1./G1(4)
    SRT3R=-(X3COF(1)/X3COF(2))
    SRT4R=-(1./X4COF)
    SRT3R=BETA*SRT3R
    SRT4R=BETA*SRT4R
C  WRITE THE VS AND VX POTENTIALS IN DATA FILE TRIPLET
C      NN=1    6X6 + 6X6
    WRITE(26,741) EN,VSNN0,VPNN0
    WRITE(26,741) SROOTR
    WRITE(26,741) SRTR
    WRITE(26,742) SRT3R,SRT4R
    WRITE(6,741) EN,VSNN0,VPNN0
    WRITE(6,741) SROOTR
    WRITE(6,741) SRTR
    WRITE(6,742) SRT3R,SRT4R
103  CONTINUE
741  FORMAT(1X,3E11.4)
742  FORMAT(1X,2E11.4)
    STOP
    END
```

```

C      IN FILE FORMG1.FOR
      SUBROUTINE FORMG1(G1,G2,G5,GG4,GGG2,GGGG1)
C      SUBROUTINE COMPUTES THE NEEDED MATRIX
C      ELEMENTS OF GREEN'S FUNCTION
C      FOR TRIPLET (IMPURITY COMPLEXED WITH TWO IDENTICAL
C      IMPURITIES). THE SYMMETRIC GROUP IS C2V.
C      THE MATRIX G5(5X5) IS 5*5.
C      THE MATRIX G4(4X4) IS 4*4.
C      THE MATRIX G2(2X2) IS 2*2.
C      THE MATRIX G1(1X1) IS 1*1.
      DIMENSION G1(14),G2(14),G5(5,5),GG4(4,4),GGG2(2,2)
      DO 1 I=1,5
      DO 1 J=1,5
      G5(I,J)=0.
1      CONTINUE
      DO 2 I=1,4
      DO 2 J=1,4
      GG4(I,J)=0.
2      CONTINUE
      DO 3 I=1,2
      DO 3 J=1,2
3      GGG2(I,J)=0.
C      FOR G5(5X5)
      G5(1,1)=G1(3)+G2(5)
      G5(2,2)=G1(1)

```

G5(3,3)=G1(4)-G2(6)-G2(10)

G5(4,4)=G1(4)+G2(7)

G5(5,5)=G1(2)

G5(1,2)=SQRT(2.)*G1(5)

G5(1,3)=-SQRT(2.)*G2(8)

G5(1,4)=G2(9)

G5(1,5)=SQRT(2.)*G1(8)

G5(2,3)=-2.*G1(7)

G5(2,4)=SQRT(2.)*G1(7)

G5(3,4)=SQRT(2.)*G2(11)

G5(3,5)=-2.*G1(9)

G5(4,5)=SQRT(2.)*G1(6)

C FOR G4(4X4)

GG4(1,1)=G1(3)-G2(5)

GG4(2,2)=G1(4)+G2(6)+G2(10)

GG4(3,3)=G1(2)

GG4(4,4)=G1(4)-G2(7)

GG4(1,2)=SQRT(2.)*G2(8)

GG4(1,3)=-2.*G1(8)

GG4(1,4)=-G2(9)

GG4(2,3)=SQRT(2.)*(G1(6)+G1(9))

GG4(2,4)=-SQRT(2.)*G2(11)

GG4(3,4)=-2.*G1(9)

C FOR G2(2X2)

GGG2(1,1)=G1(4)+G2(6)-G2(10)

```
      GGG2(2,2)=G1(2)
      GGG2(1,2)=SQRT(2.)*(G1(6)-G1(9))
C   FOR G1(1X1)
      GGGG1=G1(4)-G2(6)+G2(10)
      DO 801 I=1,5
      DO 801 J=I,5
      G5(J,I)=G5(I,J)
801   CONTINUE
      DO 802 I=1,4
      DO 802 J=1,4
      GG4(J,I)=GG4(I,J)
802   CONTINUE
      DO 803 I=1,2
      DO 803 J=1,2
      GGG2(J,I)=GGG2(I,J)
803   CONTINUE
      RETURN
      END
```