FINAL TECHNICAL REPORT BY OTTO F. SANKEY

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Theory of electronic states and formation energies of defect complexes, interstitial defects and crystal growth in semiconductors.

Introduction

It is interesting to look back and write this final report to see the variety of problems tackled, and re-live some of the breakthroughs that occurred.

I will briefly summarize ~~below~~ IS all the work that has been performed in this final report. The major accomplishments were (i) the determination of trends in defect concentration in III-V and II-VI semiconductors, and (ii) the development and deployment of a novel quantum molecular dynamics method which is far faster and can handler larger systems than any competing method. These topics will be marked ~~below~~ with a **** to indicate their importance.

The topics ~~which we covered in this work~~ are:

(1) Deep electronic levels of large chalcogenide defect complexes in Si,

(2) Atomic forces from electronic energies via the Hellmann-Feynman theorem with application to semiconductor (110) surface relaxation,

(3) Theoretical modeling of solid hydrogen halides under pressure,

(4) An abitio self-consistent tight-binding model for semiconductors,

(5) The prediction of near edge structure in electron energy loss experiments using the ab-initio model of section (4),

****(6) The prediction of equilibrium defect concentrations in II-VI and III-V semiconductor materials, and

****(7) An efficient method for performing quantum molecular dynamics calculation in covalent systems.

Keywords: Electronic states, semiconductors, Energy (CP)

Details of these topics can be found in earlier technical reports. The four earlier reports are reference 1, 2, 3, and 4. The following table shows where further details of the above seven (7) topics can be found in refs. 1-4.

	TOPIC	REFERENCE
	1	1
	2	1
	3	2
	4	2
	5	3
****	6	2, 3
****	7	3, 4

We now give a short report for each of the seven (7) topics.

(1) Deep electronic levels of large chalcogen defect complexes in Si

Calculations of the deep band-gap electronic states due to large substitutional complexes of the chalcogen impurities S, Se, and Te were performed [5]. The complexes considered are those consisting of neighboring impurities of up to five-atom clusters. It is found that the number of gap levels for a given charge state of the cluster is equal to the number of impurities in the complex. In addition, it is found the the electronically active level for a complex of three or more impurities is quite different in wave-function character from that of the isolated impurity, but rather similar to that of a nearest-neighbor pair. The theory predicts a continuous change from deep-level character to nearly-shallow effective-mass-like character as the size of the complex increases. In addition, the theory predicts that several new intracenter transitions between localized bound states are possible. Results are compared with recent experimental observations involving identified and unidentified chalcogen complexes.

We can summarize the results by Fig. 1 where we show the levels given by a single Sulfur (S_1) impurity in Si, and levels of a S_3 complex. The top of the figure is the conduction band edge and the bottom the valence band edge. We see that S_1 forms one deep level, while S_3 forms three deep levels. Only the upper level of S_3 has been seen experimentally. This has led to confusion in the past, as it looked like the S_3 level was higher in energy than S_1 level. In fact the S_3 level is lower if one follows the S_1 level down as 2 more S atoms are brought in. Two new levels appear from the conduction band and one of these is higher in energy than the original S_1 level.

(2) Atomic forces from electronic energies via the Hellmann-Feynman Theorem

In this work [6] we used a simplified tight-binding Hamiltonian, and computed forces via the Hellmann-Feyman theorem, then did a molecular dynamics simulation of the atoms at a (110) semiconductor surface. We have come a long way since this paper, since we used a very simplified Hamiltonian here. This work, to my knowledge, was the first work ever to do molecular dynamics in covalent system with forces determined by electronic structure. Today, many groups, including my own, are performing quantum molecular dynamics calculations. So I take pride in the knowledge that this was the first, although I did not appreciate the significance of this at the time.

(3) Theoretical modeling of solid hydrogen halides under pressure

The electronic and dynamic properties of the solid phases of HF, HCl and HBr under pressure have been studied theoretically [7]. A simple model is constructed so that the pressure dependent properties of these systems and possibly other hydrogen-bonded systems can be studied in terms of a few parameters. The model predicts quite simply the pressure dependence of the

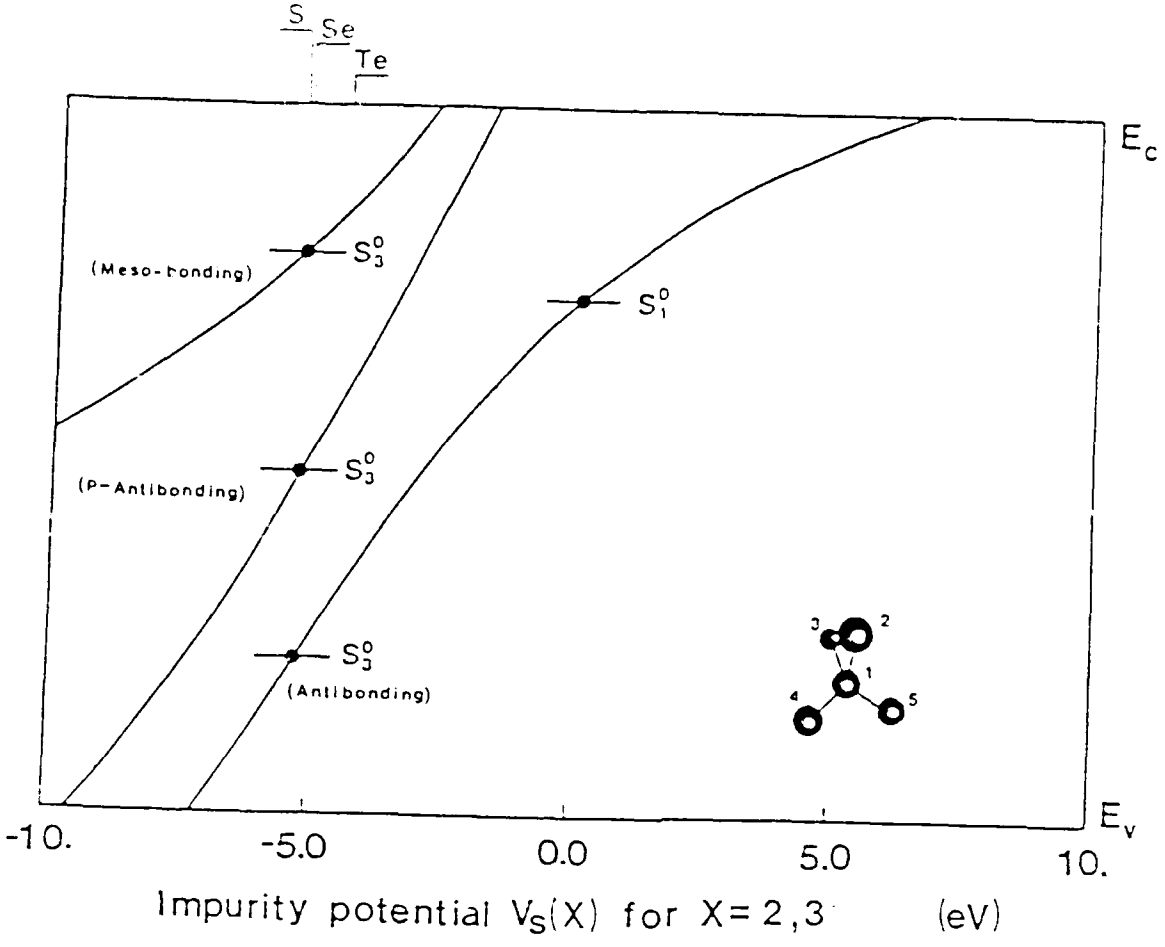


Fig. 1 Theoretical curve of energy level versus impurity potential for $(S,X_2)^0$ triplets. Atoms 4 and 5 (Fig. 1) are silicon atoms (V_S=0eV), atom 1 is fixed at the potential for sulfur (in the zero charge state), and atoms 2 and 3 have equal potentials which are varied to generate the curves. As for pairs, we fix the potential $V_S(1)$ such that the S_1^0 agrees with the data. When atoms 2 and 3 become sulfur atoms [$V_S(2)=V_S(3)=-5.31$eV], we find there are three states located in the gap-the highest- and the lowest-energy states is of B_2 (p-like) symmetry. Each of these three states can hold two of the six excess electrons so that no free electrons enter the conduction band.

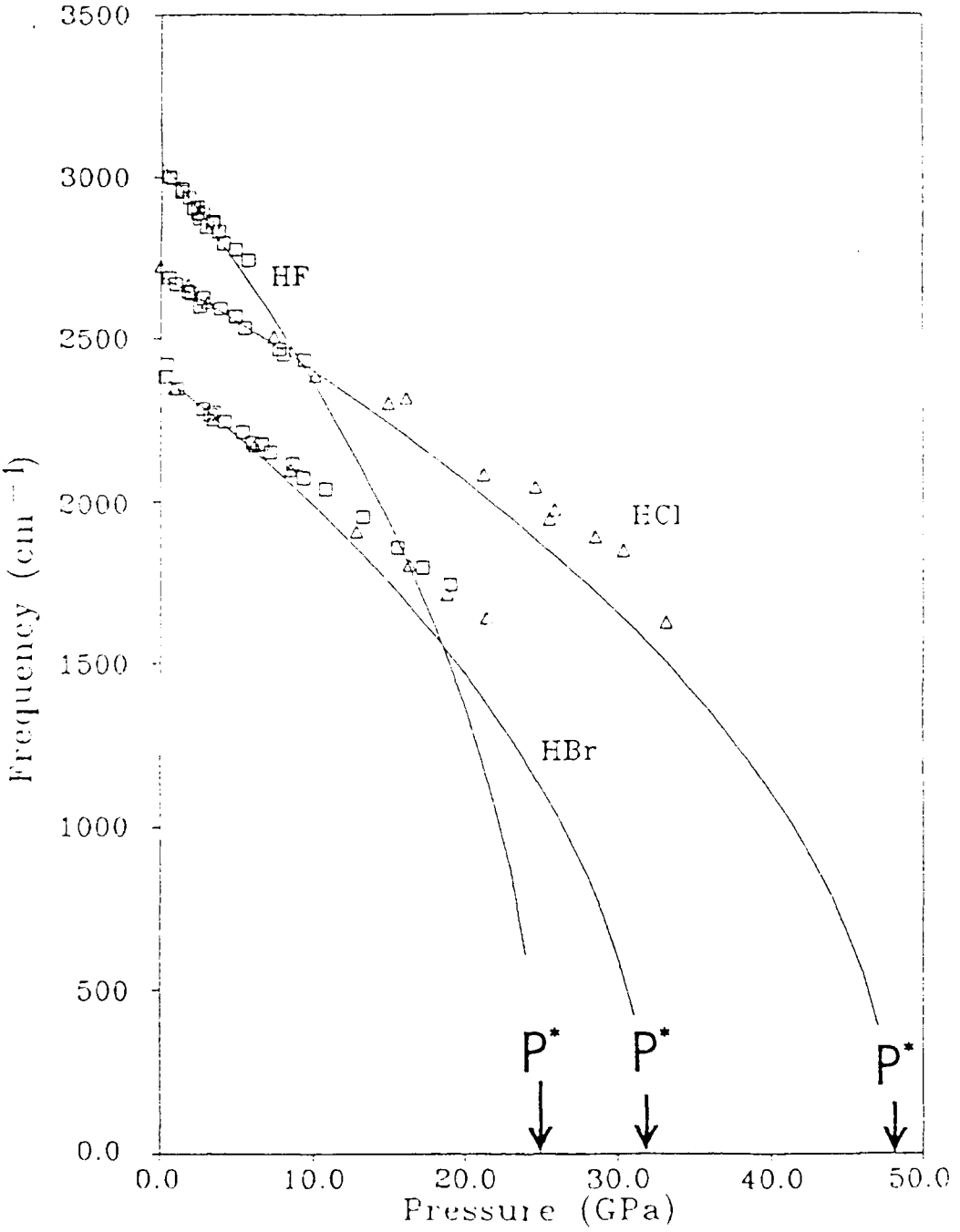
stretching mode frequency and the nature of the phase transition from the molecular hydrogen-bonded phases to a new symmetrical hydrogen bonded (non-molecular) phase. Quantum effects due to the light hydrogen atom are taken into account within a many-body Hartree approximation we have compared our theory with experimental data taken by Prof. R.C. Hanson at ASU. The data is mainly on the pressure dependence of the symmetric stretching mode frequency in HF. The possibility of soliton formation has been considered and it has been shown how pressure may act as a unique tuner to adjust the energetics of these non-linear excitation. We have performed ab-initio calculations of the total energy of ring-like structures of HF and the first ab-initio pseudopotential calculation of the band structure and total energy of solid HBr. The calculations for HF are within the Hartree-Fock approximation, while those of solid HBr are within the local density approximation and have been simplified by considering a linear instead of a zig-zag geometry.

A comparison of the theoretical scaling of the symmetric stretch optic node with experiment is shown in Fig. 2. Notice that the frequency goes down with pressure (indicating a softening, and suggesting a phase transition), and the theory predicts the phase transition pressure P^*, although no experiment has yet gone to high enough pressure to check these predictions. These calculations were the first application ever of the local density approximation on a hydrogen-bonded system.

(4) An ab-initio self-consistent tight-binding model for semiconductors

We have determined the band structure, charge density, and total-energy-related quantities such as equilibrium lattice constants, bulk moduli, and TO-phonon frequencies for a variety of different semiconducting materials, using a simple ab-initio self-consistent linear combination of pseudo-atomic-orbital

Fig. 2 Experimental Raman scattering A_1-mode frequencies (triangles [10] and squares [9][14]) for HF, HCl and HBr, compared with the pressure dependent classical frequencies ω_s of Eq. 13 (solid line). The predicted critical pressure P*, extrapolated from the low pressure slope, is shown for HF and HCl.



scheme (tight-binding-like model) [8]. The calculations are performed within the local-density approximation with an atomic pseudopotential and use a linear combination of sp^3 or sp^3d^5 pseudo-atomic-orbitals of the free atom. The method also allows for the possibility of orthogonalizing the pseudo-atomic-orbitals to a few low-energy plane waves. The results are compared to those of the rigorous plane-wave-basis expansion, and it is shown that for most properties, a pseudo-atomic-orbital formulation yields nearly identical results. The self-consistently determined Hamiltonian matrix in the pseudo-atomic-orbital representation is of the form obtained within the tight-binding approximation, but includes infinite neighbor interactions. The "tight-binding" Hamiltonian matrix elements with nearby atoms have been extracted.

(5) The prediction of near edge structure in electron energy loss experiments

The method of section 4 has been used to study the near edge structure in electron energy loss experiments [9]. The near-edge structure in inner-shell spectroscopy is a product of the slowly varying matrix element and the appropriate projected density of states. We have made use of the self-consistent pseudo-atomic-orbital band-structure-calculation method to produce accurate projected density of states. Our calculation is in good agreement with the K near-edge structure of diamond, silicon, cubic SiC, and Be_2C, and the L near-edge structure of Si and SiC. We found for the diamond K near-edge structure that the reported core exciton does not affect the near-edge structure at an energy resolution of about 1 eV. We also show, for the first time, that Si $L_{2,3}$ near-edge structure can be interpreted using a ground state model and that the s-projected density of states is significant near threshold.

This work in collaboration with Prof. Peter Rez of ASU, led to the Ph.D. thesis of Xudong Weng [10].

***(6) The prediction of equilibrium defect concentration in II-VI and III-V semiconductors

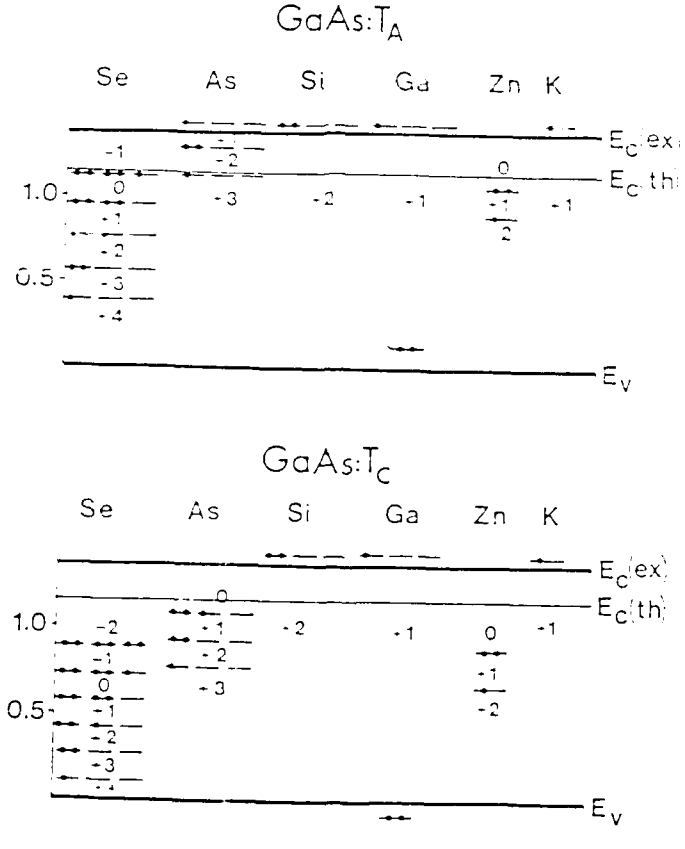
We wish to investigate trends in defect concentrations in semiconductors, and the electronic properties of these defects.

Our study began with the energetic of interstitial defects. We used the ab-initio pseudoatomic orbital method described in Section 4 to study chemical trends in the near band-gap deep levels and the total energies of interstitial impurities in GaAs, AlAs, ZnSe, and ZnTe. We investigate the impurities K, Zn, Ga, Si, As, Se, and Te at the two nonequivalent interstitial tetrahedral sites: The T_A site (surrounded by anions) and the T_C site (surrounded by cations). The interstitial site of lowest energy is determined primarily through a competition between two terms in the total energy--the band energy and the deep level energy. The band energy favors the T_A site, while the deep level energy favors the T_C site. Switching from one site to the other is predicted to occur in some cases due to changes in the Fermi level. Due to this mechanism, we predict a novel bistability of the native Zn interstitial in ZnSe. The derived deep levels associated with the interstitial defects exhibit chemical trends which closely parallel those found through empirical tight-binding methods.

As an example, we show the deep levels of interstitial defects in GaAs are shown in Fig. 3. We notice a number of levels in the gap which occur because each charge state has a different energy, and because the levels can have symmetries.

We then used these results and other results using the technique described in Section 4 and have made an extensive theoretical study [12] [13] [14] [15] [16] on the factors that influence the formation of native defects and extrinsic impurity incorporation in semiconductors. A complete set of reaction equations within equilibrium statistical mechanics is used to predict defect

Fig. 3 Transition state energy levels in the bandgap region for the interstitial impurities Se, As, Si, Ga, Zn, and K in GaAs at the two tetrahedral-interstitial sites T_A and T_C. The figure shows the valence band edge E_V and both the experimental and theoretical conduction band edges $E_C(ex)$ and $E_C(th)$ respectively. A single line represents an A_1 level while a triple dashed line indicates the level is derived from a triply degenerate T_2-symmetric state. The occupancies of the levels for the various charge states are indicated by dots. Notice the downward trend in the levels with increasing electronegativity of the interstitial atom. Notice also that the levels at the T_C site are consistently below the corresponding levels for the T_A site.



concentrations of intrinsic and extrinsic defects. The competing reactions involving host atoms include vacancies, antisites, and interstitial defects and the extrinsic impurity reactions include anion and cation site substitutional and interstitial site impurities. The extrinsic and intrinsic reaction form a coupled system. Examples are given to illustrate how various factors influence defect abundances, and such factors include temperature, stoichiometry, the host material, and the chemical potential of the electron/hole system. It is found that extrinsic impurities have a profound effect on native defect abundances. The defect formation energies used in the theory are obtained from a recently developed pseudoatomic-obital scheme using the local density approximation and pseudopotentials.

The reactions, their formation energies, and defect concentrations are shown in Fig. 4.

The native defects we consider are the simplest point defects consisting of vacancies, antisites, and interstitial defects. The extrinsic impurities we investigate are either substitutional or tetrahedral site interstitials. The compound semiconductors considered are the III-V materials GaAs and GaP, and the II-VI materials ZnTe and ZnSe. (The elemental semiconductor Si is also included for comparison.) The native defects are the anion and cation antisite defects (an anion occupying a cation site or vice versa) A_C and C_A, the anion and cation site vacancies V_A and V_C, and the anion and cation tetrahedral site interstitial defects $A(T_A)$, $A(T_C)$, $C(T_A)$, and $C(T_C)$ at the two nonequivalent tetrahedral sites T_A and T_C. The T_A (T_C) interstitial site is surrounded by anions (cations) and is at the position a/4(-1, -1, -1) in the zinc-blende lattice in which the anion (cation) atom is at (0,0,0) and the cation (anion) is at a/4(1,1,1). The extrinsic impurity X is allowed to occupy the anion or cation site, X_A or X_C, or the two tetrahedral interstitial sites $X(T_A)$ or $X(T_C)$.

Fig. 4 Reaction equations and stoichiometric constraints for native and extrinsic point defects in a compound semiconductor. The eight native defects considered are the anion and cation antisite defects, A_C and C_A, the anion- and cation- site vacancies, V_A and V_C, and the anion and cation interstitial defects at the two non-equivalent tetrahedral interstitial sites T_A (surrounded by anions) and T_C (surrounded by cations), A_{T_A}, A_{T_C}, C_{T_A}, and C_{T_C}. The extrinsic (for impurity X) defects considered are the anion and cation- site substitutional defects X_A and X_C, and the two tetrahedral site interstitial impurities X_{T_A} and X_{T_C}.

INTRINSIC DEFECTS: A_C. C_A. V_A. V_C. A_{T_A}. A_{T_C}. C_{T_A}. C_{T_C}

REACTION	EQUATION
$A_A + C_C \Longleftrightarrow A_C + C_A$	$[A_C][C_A] = e^{-\beta(E_{A_C} + E_{C_A})}$
$0 \Longleftrightarrow V_A + V_C$	$[V_A][V_C] = e^{-\beta(E_{V_A} + E_{V_C})}$
$A_A + V_C \Longleftrightarrow A_C + V_A$	$[V_A][A_C] = [V_C]e^{-\beta(E_{A_C} + E_{V_A} - E_{V_C})}$
$A_A \Longleftrightarrow V_A + A_{T_A}$.	$[V_A][A_{T_A}] = e^{-\beta(E_{V_A} + E_{A_{T_A}})}$
$A_A \Longleftrightarrow V_A + A_{T_C}$	$[V_A][A_{T_C}] = e^{-\beta(E_{V_A} + E_{A_{T_C}})}$
$C_C \Longleftrightarrow V_C + C_{T_A}$	$[V_C][C_{T_A}] = e^{-\beta(E_{V_C} + E_{C_{T_A}})}$
$C_C \Longleftrightarrow V_C + C_{T_C}$	$[V_C][C_{T_C}] = e^{-\beta(E_{V_C} + E_{C_{T_C}})}$

$$S = 2([A_C] - [C_A]) + ([V_C] - [V_A]) + ([A_{T_A}] + [A_{T_C}] - [C_{T_A}] - [C_{T_C}])$$
$$= (N_A - N_C)/N_L$$

EXTRINSIC DEFECTS: X_A. X_C. X_{T_A}. X_{T_C}

$X_A \Longleftrightarrow X_{T_A} + V_A$	$[X_{T_A}][V_A] = [X_A]e^{-\beta(E_{X_{T_A}} + E_{V_A} - E_{X_A})}$
$X_A \Longleftrightarrow X_{T_C} + V_A$	$[X_{T_C}][V_A] = [X_A]e^{-\beta(E_{X_{T_C}} + E_{V_A} - E_{X_A})}$
$X_C \Longleftrightarrow X_{T_A} + V_C$	$[X_{T_A}][V_C] = [X_C]e^{-\beta(E_{X_{T_A}} + E_{V_C} - E_{X_C})}$

$$S_X = [X_A] + [X_C] + [X_{T_A}] + [X_{T_C}]$$
$$= N_X/N_L$$

We have in total eight possible native defects [A_C, C_A, V_A, V_C, $A(T_A)$, $A(T_C)$, $C(T_A)$, and $C(T_C)$] and four possible extrinsic defects [X_A, X_C, $X(T_A)$, $X(T_C)$]. Of course, there could be many different atoms corresponding to X. We consider only one atom for X at a time. Our calculation give values for the reaction energies. These energies, when combined with the law of mass action determine the concentration of defects in equilibrium.

The so found defect concentrations as a function of stoichiometry are shown in Fig. 5 for GaAs. We see a very complicated behavior. If we consider stoichiometric material (S = 0, the center of each graph), we find the As on Ga antisite (As_{Ga}) to be the dominant defect in GaAs p-type material, while the vacancy on Ga defect (V_{Ga}) to be dominant defect in n-type material.

Calculations such as these have been performed on GaAs, ZnSe, ZnTe, and CaF. These are the only theoretical calculations ever done which have covered such a broad range of materials so that some trends become apparent. One such trend was immediately found. In III-V materials vacancies and antisites are the dominant types of defects, while interstitials rarely are important. For II-VII materials however we find vacancies are the most important, followed by interstitials, and finally antisites.

******(7) Quantum molecular dynamics**

Molecular dynamics is a technique which can be useful for simulating vibrations of molecules and solids, the growth of a crystal or interface, the interaction between an adatom and surface, defect reactions in crystals, migration of atoms in solids, and a wide range of other time-dependent phenomena. In this technique, the many-body classical equations of motion are solved as a function of time, and the physical process can be studied in real time. The equations of motion are prescribed once the instantaneous forces are given.

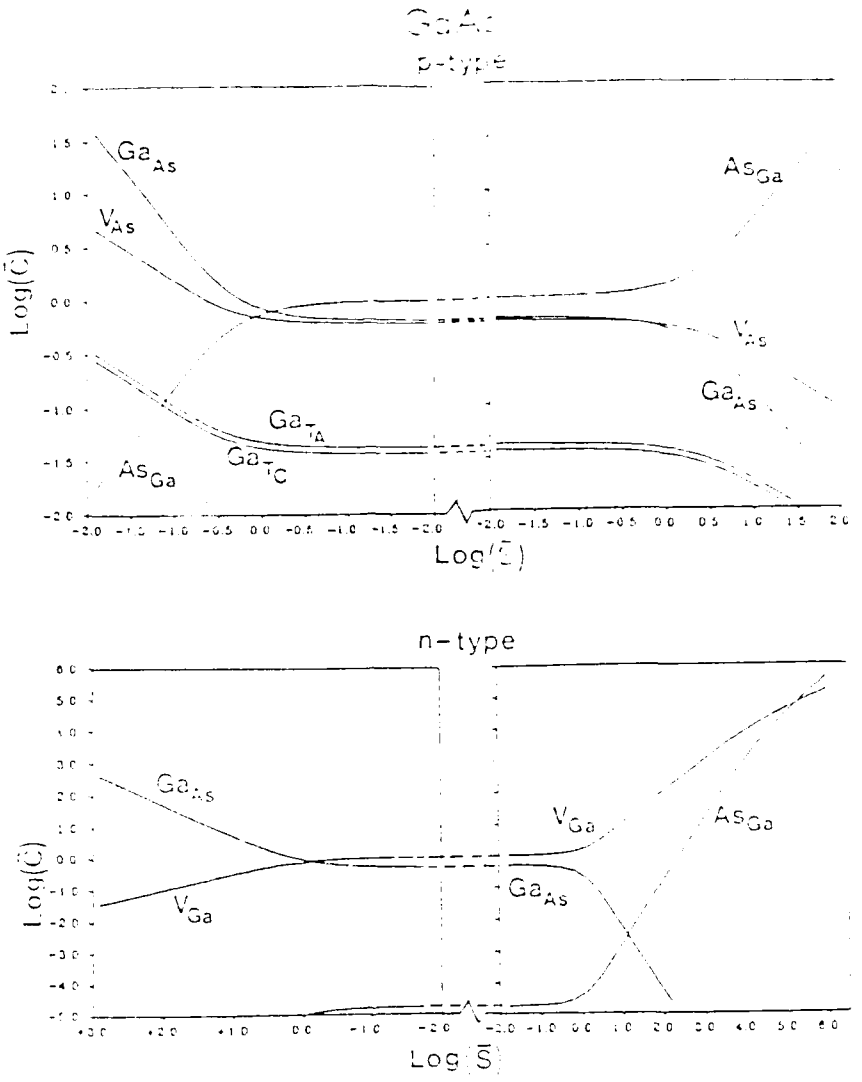


Fig. 5 Native defect concentrations as a function of stoichiometry for p- and n-type GaAs. The right panel is for positive stoichiometry $\bar{S}$ (excess As) and the left panel is for negative stoichiometry $\bar{S}$ (excess Ga). The center point between panels corresponds to perfect stoichiometry. A high temperature (corresponding to $\beta=7eV^{-1}$) was used, but this has no effect on the ordering.

The forces between atoms in covalent solids is more intricate than a sum of two-body forces because the strength of the covalent bond is quantum-mechanically derived and depends on the local environment. Potentials have been devised which mimic these nonlocal many-atom effects. However, the many-body effects are clearly rooted in the quantum electronic structure of the material and a superior method is to obtain these forces directly from the electronic structure.

We have developed a first-principles electronic-structure method which approximates very closely a rigorous calculation of these forces, yet is simple enough to be used for a wide variety of purposes, including molecular-dynamics simulations of covalent materials [17] [18] [19]. We have tested the static energetics thoroughly in Si, and have performed molecular-dynamics and molecular-dynamics simulated-annealing studies of small Si clusters. The method is framed within a first-principles tight-binding approximation, making it versatile and easy to use, and is executed entirely in real space, and so periodicity is not necessary. It can be adapted for use in supercells, slabs, clusters, or within a Green's-function technique.

Our approach is to use a number of physically motivated approximations within the framework of a well-established first-principles theory, to retain accuracy and transferability, yet still achieve the goal of simplifying the computation of the total energy and atomic forces. The theoretical foundation that we use is density-functional theory within the local-density and pseudopotential approximations in a tight-binding formation.

This work is a major breakthrough in the area, and will be pursued for years to come. It is currently my major research project, and the code that has been written is now being used in other groups on a wide variety of topics. These topics include surface reconstruction, surface adatom interactions, kinks

at surfaces, crack in bulk materials, dynamics of semiconductor clusters, melting, diffusion, construction of realistic models of amorphous Si, and defects in amorphous Si. Researchers who have used the method and the code include: Dr. John Dow, Arizona State University; Dr. David Drabold, University of Notre Dame; Dr. Peter Fedders, Washington University; Dr. Stefen Klemm, Minnesota Supercomputing; and Dr. John Spence, Arizona State University.

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Reference B

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