

Bondlength distortion of atomic substitutions in semiconductors

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Abstract. The distortion in bondlength is calculated for a wide range of impurities, both isovalent and heterovalent, in all I–VII, II–VI and III–V compound semiconductors and in elemental semiconductors, silicon and germanium. Universal parameter tight binding (UPTB) theory of Harrison combined with the spring constant model is used. The results agree well with earlier theoretical estimates and also with the available extended X-ray absorption fine structure (EXAFS) data. A systematic behaviour of the bondlength distortion of impurities in semiconductors with respect to (i) the difference in covalent energy of the host-impurity bond, (ii) the difference in electronegativity between the host and that of the impurity atom and (iii) the change in covalency of the bond when the impurity replaces the host is observed.

Keywords. Semiconductors; impurities; bondlength; distortion.

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1. Introduction

Study of crystalline solid solutions and super lattice structures of II–VI and III–V compounds has been increasingly interesting due to their technological applications such as optoelectronics, IC technology, etc [1]. Structural information on such semiconducting materials is of fundamental importance in predicting and understanding their properties. The effects such as bowing and broadening of band gaps [2] and asymmetry in the first order Raman scattering experiments [1] are thought to be partly due to the change in the bond lengths consequent to the addition of impurities in the host crystals. The study of bondlength distortion in semiconductor-impurity systems is important not only because of their practical applications but also because of the fundamental problem in condensed matter physics of the formation of various crystals from atoms [3].

With the advent of extended X-ray absorption fine structure (EXAFS) techniques [4–6] the study of bondlength distortion due to impurities in semiconductors has generated widespread interest [7,8]. EXAFS experiments are very useful for characterising lattice

distortions around impurity atoms as they can probe one particular element at a time and provide information about the number, distance and chemical identity with an accuracy of 0.005 Å in the nearest neighbour distance [1].

On the theoretical side, there exist two tractable approaches to the problem of lattice distortions around simple defects in semiconductors. First, self consistent pseudopotential methods based on the calculation of electronic charge density at the defect site and evaluation of the force constant variation using the Hellmann–Feynman theorem [9–11]. Second, macroscopic theories based on the elastic and bonding properties of solids have been used to extract the energy associated with the bond relaxation [12–14]. Though the first principle study of the electronic structure of localised defects in semiconductors is expected to yield more reliable results, it requires considerable computational effort [15,8] and thus making it quite intricate and undesirable to be extended to a great variety of defects in a large number of semiconducting systems. The elementary tight binding scheme of Harrison [16], after a very simple modification of the overlap interaction, intended to improve the description of the bond energy has been used by Baranowski [13] to predict the equilibrium spacing for a number of semiconductor systems in good accordance with experiment. In his study of local distortion of various impurities in GaAs and GaP, it is observed that if an impurity forms an sp^3 bond with the host atom with larger average hybrid energy than that for the host-host atom, the resulting distortion of the nearest neighbours will be inward and vice-versa. Following the ideas of Baranowski [13], and with the revised Hartree Fock atomic term values, Talwar *et al* [1] have investigated the lattice relaxation around isovalent impurities for eighty cases of impurity host systems in nineteen elemental and compound semiconductors. By comparing their results with that of Martins and Zunger [12] they conclude that despite the simplified assumptions made in defining the bond energy, the bond orbital model is well suited to study the equilibrium spacing in the host systems and lattice distortion around isovalent impurities in semiconductors.

When the impurity atom is not isovalent (heterovalent) with that of the host semiconductor, as is the case for example when germanium is doped in gallium arsenide, these simple models do not work. Germanium-Arsenic bonds are formed which do not exist in pure zinc-blende structure compounds. Kraut and Harrison [17] have suggested a relatively simple procedure for obtaining natural bondlengths for heterovalent substitutions in semiconducting compounds.

Combining Harrison's universal parameter tight binding (UPTB) theory, with the spring constant model suggested by Shih *et al* [18], Kraut and Harrison [17] have estimated the displacement of the neighbours in selected semiconductor-impurity systems already investigated by Martins and Zunger [12] for the purpose of comparison. In all the above attempts the lattice distortion has been estimated only for few impurities, that too limited to atoms from the same column or column adjacent to that of the host atom replaced.

In the present work the ideas of Kraut and Harrison [17] have been used to estimate the natural bondlengths and lattice distortion of all possible (both isovalent and heterovalent) substitutional impurities in a large number of semiconductor systems, which are isoelectronic with Si, Ge and Sn, for the first time. Herman–Skillman atomic term values [16] of free atoms are used in the calculations. The estimated bondlength distortion for various impurity-host systems are compared with the existing theoretical and the available experimental EXAFS data. A study of schematic behaviour of lattice distortion with respect to some of the chemical parameters such as covalency difference and electronegativity difference between the impurity atom and the host atom and the change in covalent energy of the

bond when the impurity replaces the host is also attempted for the first time.

2. Theory

2.1 Natural bondlengths

In the bond orbital model [16] for polar semiconductors, the bond energy can be approximated by calculating the four major components in the energy as

$$E_{\text{bond}} = E_{\text{pro}} + E_{\text{sig}} + E_{\text{over}} + E_{\text{met}} \quad (1)$$

where E_{pro} is the promotion energy, E_{sig} is the bond formation energy, E_{over} is the overlap energy and E_{met} is the metallization energy. As the promotion energy E_{pro} is independent of bondlength, it is of no interest here. The energy gained in forming the σ bonds between the hybrids on neighbouring atoms is

$$E_{\text{sig}} = -2(V_2^2 + V_3^2)^{1/2}, \quad (2)$$

where $V_2 = (-3.22\hbar^2/md^2)$ is the covalent energy, m is the mass of the electron and d is the bondlength and $V_3 = (\epsilon_{hA} - \epsilon_{hB})/2$ is the polar energy equal to half the difference between the two hybrid energies in an AB compound. The hybrid energies can be readily calculated from the atomic term values as $\epsilon_h = (\epsilon_s + 3\epsilon_p)/4$. The overlap interaction takes the form

$$E_{\text{over}} = \frac{2\eta_0 V_2^2}{|\epsilon_{hA} + \epsilon_{hB}|} \quad (3)$$

arising from the nonorthogonality of the orbitals on neighbouring atoms. Here η_0 is a constant and has the same value for any AB compound formed by elements from the same row of the periodic table. The metallization energy is arising from the coupling between the bond and the neighbouring antibonds through the hybrids sharing the end atoms as

$$E_{\text{met}} = -\frac{3(V_{1A}^2 + V_{1B}^2)V_2^2}{4(V_2^2 + V_3^2)^{3/2}} \quad (4)$$

where V_{1A} or V_{1B} is equal to $(\epsilon_s - \epsilon_p)/4$ for the A or B atom. The total energy per bond may be written explicitly as

$$E_{\text{bond}} = E_{\text{pro}} - 2(V_2^2 + V_3^2)^{1/2} + \frac{2\eta_0 V_2^2}{|\epsilon_{hA} + \epsilon_{hB}|} - \frac{3(V_{1A}^2 + V_{1B}^2)V_2^2}{4(V_2^2 + V_3^2)^{3/2}} \quad (5)$$

At this point it is worth mentioning the use of the numerical coefficient -3.22 in the covalent energy V_2 for sp^3 hybrids, instead of -4.373 used by Baranowski [13] and Talwar *et al* [1]. This numerical coefficient is estimated using interatomic matrix elements $V_{ss\sigma}$, $V_{sp\sigma}$ and $V_{pp\sigma}$. The covalent energy is given by Harrison [16]

$$V_2 = (-V_{ss\sigma} + 2\sqrt{3}V_{sp\sigma} + 3V_{pp\sigma})/4$$

with $V_{ss\sigma} = (\eta_{ss\sigma}\hbar^2/md^2)$, $V_{sp\sigma} = (\eta_{sp\sigma}\hbar^2/md^2)$ and $V_{pp\sigma} = (\eta_{pp\sigma}\hbar^2/md^2)$, where $\eta_{ss\sigma}$, $\eta_{sp\sigma}$ and $\eta_{pp\sigma}$ are dimensionless coefficients. There are two choices of the dimensionless coefficients according to Harrison [16] as given in table 1. In both these choices,

Table 1. Choice of the parameters used in calculating covalent energy.

Dimensionless coefficients	Harrison [16]	Harrison [16]
$n_{ss\sigma}$	-1.40	-1.32
$n_{sp\sigma}$	1.84	1.42
$n_{pp\sigma}$	3.24	2.22
$n_{pp\pi}$	-0.81	-0.63
$n_{sp\pi}$	0	-0.63

the interatomic matrix elements were derived by requiring consistency between the tight binding bands and the free electron bands. In the first choice of the tight binding formulation, the interatomic matrix elements were based on a minimal basis set of atomic orbitals, and the nearest neighbour interatomic interactions are estimated from the Chadi Cohen fit [19]. In the second choice, Louie [20] has redetermined the interatomic matrix elements by including additional orbitals to the basis set as perturbation. The smaller the number of atomic orbitals used, greater will be the simplification and lesser will be the accuracy [16]. Hence, the use of larger number of atomic orbitals leads to greater accuracy. This has led Kraut and Harrison [17] to choose the second choice where the numerical coefficient is taken as -3.22 and is also followed in the present work.

With proper choice of η_0 the natural bondlengths of host system can be accurately obtained by minimising the bond energy with respect to 'd'. But as the only dependence upon 'd' comes through the covalent energy V_2 , the total energy per bond (eq. 5) can be minimised with respect to V_2 . As suggested by Harrison [16], η_0 has been adjusted to give the correct equilibrium spacing for the homopolar semiconductors and then taken to be the same for compounds from the same row of the periodic table; a geometric mean is used for skew compounds. This procedure [17] has been constructed to give values of natural bondlengths close to the observed internuclear distances in the pure semiconductor systems that is the systems where the average valence of the constituents is four. They have also suggested a procedure for obtaining natural bondlengths when the average valence of the elements forming the bond is not four, that is compounds of type I-II, I-III, I-IV, I-V, I-VI, I-VII, etc. In order to calculate the natural bondlengths of such systems, with suitable modifications, Kraut and Harrison [17] have obtained a more general expression for the bond energy of any tetrahedral compound as

$$E_{\text{bond}} = 2V_2 + 2 \frac{\eta_0 V_2^2}{|\epsilon_{hA} + \epsilon_{hB}|} - \frac{3(V_{1A}^2 + V_{1B}^2 - V_{1IV(A)}^2 - V_{1IV(B)}^2)V_2^2}{4(V_2^2 + V_3^2)^{\frac{3}{2}}} \quad (6)$$

where $V_{1IV(A)}$ and $V_{1IV(B)}$ are the V_1 values for the column IV element from the row of atoms A and B respectively.

The natural bondlengths for any pair of elements in a tetrahedral compound could be calculated by the minimisation of bond energy given in eq. (6) with respect to V_2 . Thus

$$\frac{\delta E_{\text{bond}}}{\delta V_2} = 2 + 4 \frac{\eta_0 V_2}{|\epsilon_{hA} + \epsilon_{hB}|} - \frac{3}{2}(V_{1A}^2 + V_{1B}^2 - V_{1IV(A)}^2 - V_{1IV(B)}^2) \times \left[\frac{V_2^1}{(V_2^2 + V_3^2)^{\frac{3}{2}}} - \frac{3V_2^3}{2(V_2^2 + V_3^2)^{\frac{5}{2}}} \right] = 0. \quad (7)$$

In the above equation it is noted that for a column IV semiconductor, A and B are identically the same, so that the metallization term vanishes. Thus the equilibrium condition for the homopolar system yields $\eta_0 = \epsilon_h/V_2$. Assuming the experimental equilibrium spacing for the homopolar semiconductors and by making use of Herman Skillman atomic term values, η_0 can be calculated for each row in the periodic table. The values of η_0 are taken to be the same for compounds from the same row of the periodic table. The geometric mean ($\eta = \sqrt{\eta_1\eta_2}$) is to be taken for the skew compounds. In order to estimate the natural bondlength of any compound AB corresponding η_0 values are used in eq. 7, and the relevant V_2 values are obtained. Hence the natural bondlength d_0 of the compound AB is deduced from the relation,

$$d_0 = \left(\frac{-mV_2}{3.22\hbar^2} \right)^{-\frac{1}{2}}. \quad (8)$$

Thus the natural bondlengths are calculated as if all the bonds in the system were of the same AB type and all AB pairs were tetrahedrally coordinated, using the universal parameter tight binding (UPTB) theory of Kraut and Harrison [17].

2.2 Lattice distortion of atomic substitution

Following the ideas of the simple force constant model suggested by Shih *et al* [18], Kraut and Harrison [17] have also described a method to estimate the local relaxation around impurities in semiconductors using just the natural bondlengths. In this model the second neighbour relaxation is neglected, resulting in a symmetric radial relaxation of the nearest neighbours. Thus the bondlength distortion Δd due to the size difference between the impurity and host atom in any defect system is given as three fourths the difference of the natural bondlengths of impurity-host bond and host-host bond:

$$\Delta d = \frac{3}{4}(d_{\text{impurity-host}} - d_{\text{host-host}}). \quad (9)$$

The positive distortion $+\Delta d$ corresponds to the nearest neighbours relaxing outwards and the negative distortion $-\Delta d$ corresponds to the nearest neighbours relaxing inwards.

In discussing the bonding properties it is also convenient to define a quantity covalency as [16]

$$\alpha_c = \frac{V_2}{(V_2^2 + V_3^2)^{\frac{1}{2}}}, \quad (10)$$

where V_2 and V_3 are covalent and polar energies.

3. Numerical results and discussions

3.1 Natural bondlengths for perfect compounds

In order to calculate the natural bondlengths of perfect systems, it becomes necessary to fix the values of the constant η_0 for the homopolar systems. Using the experimental equilibrium spacing [13] for C, Si, Ge, Sn and Pb as 1.544, 2.352, 2.440, 2.810 and 3.410 Å

Table 2. Predicted values of the natural bondlengths of perfect semiconducting systems.

System	V_2 eV	Covalency α_c	bondlength d_0 in Å	
			calculated	experimental†
C	-10.295	1.0000	1.544	1.544
Si	-4.440	1.0000	2.351	2.352
Ge	-4.095	1.0000	2.448	2.449
Sn	-3.110	1.0000	2.809	2.810
SiC	-6.835	0.9792	1.895	1.887
BN	-10.385	0.9576	1.537	1.565
AlN	-7.215	0.8697	1.844	1.904
GaN	-7.005	0.8725	1.872	1.953
InN	-6.285	0.8340	1.976	2.163
BP	-6.605	0.9838	1.927	1.965
AIP	-4.465	0.8990	2.344	2.367
GaP	-4.355	0.9086	2.374	2.358
InP	-3.870	0.8657	2.518	2.541
BA _s	-6.235	0.9855	1.984	2.068
AlAs	-4.205	0.8992	2.416	2.442
GaAs	-4.100	0.9095	2.446	2.448
InAs	-3.645	0.8656	2.595	2.623
AlSb	-3.610	0.9254	2.607	2.657
GaSb	-3.535	0.9380	2.635	2.639
InSb	-3.115	0.8963	2.807	2.805
BeO	-10.645	0.8582	1.518	1.650
ZnO	-7.625	0.7549	1.794	1.992
BeS	-6.360	0.8538	1.964	2.100
ZnS	-4.510	0.7372	2.333	2.341
CdS	-4.110	0.6976	2.443	2.526
HgS	-3.410	0.6316	2.682	2.543
BeSe	-5.860	0.8559	2.049	2.200
ZnSe	-4.140	0.7370	2.435	2.455
CdSe	-3.770	0.6965	2.551	2.620
HgSe	-3.130	0.6309	2.800	2.635
BeTe	-4.920	0.8702	2.233	2.400
MgTe	-3.440	0.7132	2.671	2.760
ZnTe	-3.430	0.7481	2.675	2.642
CdTe	-3.120	0.7060	2.804	2.805
HgTe	-2.580	0.6403	3.084	2.797
CuCl	-4.800	0.6157	2.261	2.345
CuBr	-4.290	0.6104	2.392	2.464
CuI	-3.470	0.6010	2.660	2.622
CuF	-8.480	0.6740	1.701	1.840
AgI	-3.210	0.5726	2.765	2.808

† As reported in Baranowski [13]

and by making use of Herman Skillman atomic term values ϵ_s and ϵ_p , the hybrid energy ϵ_h and hence $\eta_0 (= \epsilon_h/V_2)$ for the corresponding rows are calculated to be 1.079, 1.866, 2.044, 2.439 and 3.625 respectively. For any compound AB , the bond energy is minimised with respect to V_2 and the relevant natural bondlengths (equilibrium spacing - d_0) for 40 semiconducting systems are estimated. They are given in table 2. It is seen that the agreement between the experimental d_0 values [13] and those calculated in the present work using the UPTB model of Kraut and Harrison [17] for all III-V, II-VI and I-VII compounds is within

few per cent for most cases. Even in ZnO, BeO, CuCl and CuBr, in which Baranowski [13] has noted the largest deviation of about 10% the present estimates provide relatively better results. It is also to be noted that the calculated covalency α_c comes out to be unity for homopolar semiconductors. For polar semiconductors the covalency decreases as the hybrid polarity increases and reaches the limit of ≈ 0.5 for I–VII compounds [16].

3.2 Lattice distortions for impurity systems

Using the UPTB theory of Kraut and Harrison [17], the natural bondlengths of systems formed from all possible combinations of elements taken from the periodic table are estimated. These natural bondlengths are used in the spring model of Shih *et al* [18] and the resulting bondlength distortions are calculated for a large number of impurities in 19 perfect semiconducting systems. The ratio of bondlength distortion to host bondlength ($\Delta d/d_0$) for impurities in elemental semiconductors silicon and germanium, III–V compounds, II–VI compounds and I–VII compounds are given in tables 3–6 respectively. In every compound semiconducting system the cationic substitution of groups I to IV impurities is followed by the anionic substitution of group IV to VII impurities. The estimates of ($\Delta d/d_0$) reported by Talwar *et al* [1] are also given for comparison. The difference in covalency ($\Delta\alpha_c$) between host-host bond and host-impurity bond are calculated for all host-impurity systems. The ratio $\Delta d/\Delta\alpha_c$, the covalent energy V_2 of the host-impurity bond and the difference in electronegativity [21] ($\Delta\chi = \chi_{\text{host}} - \chi_{\text{imp}}$) of the host and that of the impurity replacing it are also given in tables 3 to 6.

It is noted that the present results agree with the observation of Cappelletti *et al* [22] that the local deformation is clearly not the actual difference of tetrahedral radii of impurity and host atoms.

Tables 3 to 6 reveal a clear dependence of the sign and extent of bondlength distortion of various impurities in different host systems, on (i) change in covalent energy V_2 of the host-impurity bond with respect to that of host-host bond, (ii) the difference in electronegativity, $\Delta\chi$, between the host and that of the impurity atom and (iii) the change in covalency, $\Delta\alpha_c$, of the bond when the impurity replaces the host. The trend in the dependence of the bondlength distortion on covalent energy shows a resemblance to that on the hybrid energy as pointed out by Talwar *et al* [1] an impurity forming a covalent bond with the neighbouring hosts with a covalent energy smaller in magnitude than that of the host-host bond causes an outward distortion $+\Delta d$ and vice-versa. The variation of fractional distortion $\Delta d/d_0$ with the difference in covalent energy between the host-impurity bond and the host-host bond ΔV_2 for impurities in InSb and ZnS is shown in figure 1. These two host systems are chosen for display in the figure, as they respectively have the smallest and the largest covalent energy, among the host systems considered in the present work. It is interesting to note that the corresponding variation for impurities in all other host systems lies within the narrow region between these two curves.

Tables 3 to 6 also exhibit a strong dependence of $\Delta d/d_0$ on the difference in electronegativity, $\Delta\chi$, between the host and the impurity atoms. It is striking to note that for all the impurities in 19 semiconducting systems considered in the present work, the sense of distortion $\Delta d/d_0$ is decided by the sign of the difference in electronegativity between the host and the impurity atom: (viz) an impurity with a higher electronegativity than the host atom it is replacing, results in a contraction and vice-versa. This is in agreement with the

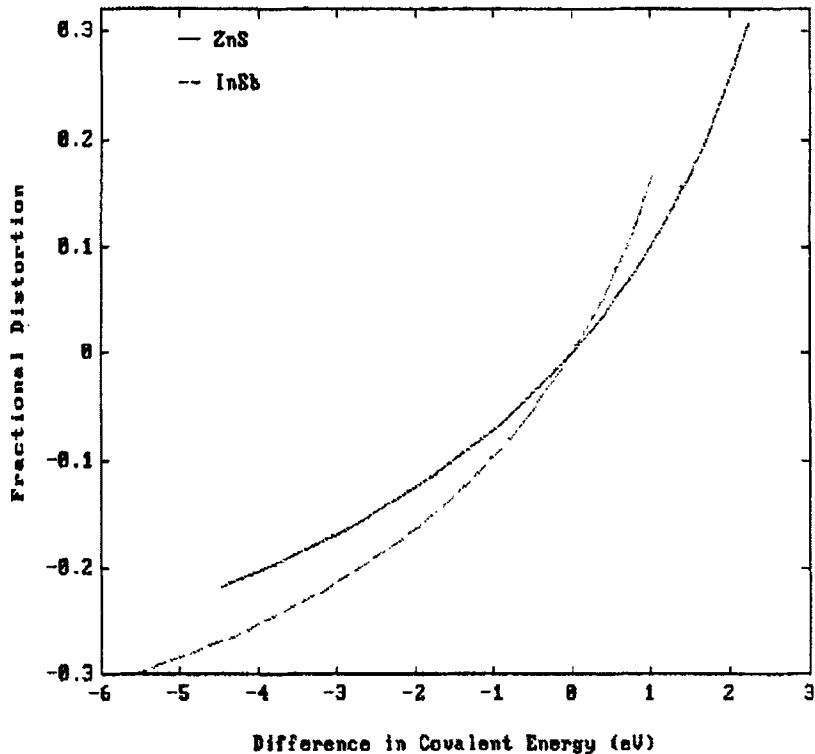


Figure 1. Variation of the fractional distortions $\Delta d/d_0$, with respect to the change in covalent energy ΔV_2 in InSb and ZnS host systems. The dotted line represents InSb host system having the smallest covalent energy V_2 and the continuous line represents ZnS host system having the largest covalent energy among the systems under study.

suggestion made by Scheffler *et al* [9] for the case of Ge replacing Ga in GaP. An increase in magnitude of $\Delta\chi$, leading to an increase in the magnitude of $\Delta d/d_0$ is also noted. This may be inferred from a comparison of $\Delta d/d_0$ values of the same impurities in both silicon and germanium host systems. The $\Delta d/d_0$ values are uniformly higher for impurities in the host system silicon which is more electronegative than germanium.

The change in covalency of the bond when the impurity replaces the host is another important factor which explains the nature of distortions produced due to atomic substitutions in semiconducting systems. From tables 4 to 6 it is clear that for cationic substitutions $\Delta d/\Delta\alpha_c$ is uniformly positive and for anionic substitutions it is uniformly negative. Deviations are noted for cases where either Δd is very small, or the covalent energy V_2 or covalency, α_c , of the host-impurity bond is nearly equal to that of the host system. Impurities from the C row and Pb row in the host systems under study are also found to violate the observation related to the change in covalency. This may be attributed to the fact that atoms from the C row differ drastically in size from that of the other rows, while atoms in Pb row do not hybridise well enough to form covalent structure [21].

It also becomes necessary to compare the results of the present study with the available experimental and theoretical results. As already observed by Kraut and Harrison [17] the

Table 3. Bondlength distortion of impurities in elemental semiconductors.

Impuri- ties	V_2 in eV		$\Delta d/d_0$		$\Delta d/\Delta\alpha_c$ Å	Δx
	ps	†	ps	†		
Silicon: Bondlength = 2.3508 Å; Covalency=1.000; $V_2 = -4.44$ eV						
Li	-3.35	0.113	0.878	0.41
Na	-2.52	0.246	1.389	0.69
Cu	-2.87	0.183	0.098	...	1.671	0.62
Ag	-2.64	0.223	1.847	0.84
Au	-2.20	0.315	2.249	0.77
Be	-4.90	-0.036	-1.789	-0.09
Mg	-3.30	0.120	1.727	0.46
Zn	-3.37	0.111	2.167	0.50
Cd	-3.01	0.161	2.483	0.58
Hg	-2.46	0.258	2.961	0.62
B	-5.93	-0.101	***	-0.59
Al	-3.97	0.043	3.038	0.23
Ga	-3.90	0.050	4.816	0.28
In	-3.42	0.105	4.990	0.42
Tl	-2.78	0.198	5.939	0.47
C	-6.84	-0.146	-0.149	...	-16.523	-1.09
Ge	-4.26	0.016	0.017	...	***	0.06
Sn	-3.72	0.069	0.055	...	37.353	0.26
Pb	-3.01	0.161	32.093	0.32
N	-7.89	-0.187	-0.191	...	-6.578	-1.59
P	-4.94	-0.039	-0.043	...	-3.686	-0.23
As	-4.65	-0.017	-0.017	...	-1.824	-0.16
Sb	-4.00	0.040	0.021	...	16.774	0.10
Bi	-3.19	0.135	***	0.17
O	-9.13	-0.227	-4.641	-2.09
S	-5.56	-0.080	-2.446	-0.46
Se	-5.13	-0.052	-1.840	-0.38
Te	-4.34	0.009	0.540	-0.06
Po	-3.43	0.103	6.578	-
F	-10.52	-0.263	-3.939	-2.59
Cl	-6.28	-0.119	-2.161	-0.69
Br	-5.68	-0.087	-1.785	-0.60
I	-4.74	-0.024	-0.704	-0.22
At	-3.74	0.067	1.796	-
Germanium: Bondlength=2.4478 Å; Covalency=1.000; $V_2 = -4.095$ eV						
Li	-3.22	0.096	0.727	0.35
Na	-2.43	0.224	1.261	0.63
Cu	-2.75	0.165	1.458	0.56
Ag	-2.54	0.202	1.635	0.78
Au	-2.11	0.295	2.050	0.71
Be	-4.71	-0.051	-2.311	-0.15
Mg	-3.16	0.104	1.413	0.40
Zn	-3.23	0.094	1.726	0.44
Cd	-2.88	0.144	2.051	0.52
Hg	-2.35	0.240	2.609	0.56
B	-5.71	-0.115	***	-0.65
Al	-3.82	0.027	1.674	0.17
Ga	-3.75	0.034	2.846	0.22
In	-3.28	0.088	3.773	0.36
Tl	-2.67	0.179	4.883	0.41
C	-6.56	-0.157	-0.163	...	-18.215	-1.15
Si	-4.26	-0.015	-0.016	...	***	-0.06
Sn	-3.57	0.053	0.041	...	21.766	0.20
Pb	-2.89	0.143	22.967	0.26
N	-7.56	-0.198	-6.879	-1.65
P	-4.73	-0.052	-5.099	-0.29
As	-4.45	-0.031	-3.392	-0.22
Sb	-3.84	0.025	12.182	0.04
Bi	-3.06	0.118	***	0.11
O	-8.75	-0.237	-4.772	-2.15
S	-5.33	-0.093	-2.837	-0.52
Se	-4.92	-0.066	-2.328	-0.44
Te	-4.16	-0.006	-0.381	-0.12
Po	-3.29	0.087	5.807	-
F	-10.09	-0.272	-4.025	-2.65
Cl	-6.02	-0.131	-2.361	-0.75
Br	-5.45	-0.100	-2.044	-0.66
I	-4.54	-0.038	-1.103	-0.28
At	-3.59	0.051	1.385	-

ps: present study; †: Talwar *et al.* [1]

Table 4. Bondlength distortion of impurities in III-V compounds.

Impuri- ties	V_2 in eV	ps	$\Delta d/d_0$	$\Delta d/\Delta\alpha_c$ Å	Δx
GaP; Bondlength=2.3736 Å; Covalecity=0.9086; $V_2=-4.355$ eV					
Li ^c	-4.18	0.016	...	0.158	0.13
Na ^c	-3.17	0.129	...	0.894	0.41
Cu ^c	-3.48	0.089	...	0.941	0.34
Ag ^c	-3.21	0.124	...	1.162	0.56
Au ^c	-2.69	0.204	...	1.587	0.49
Be ^c	-5.57	-0.087	-0.115	-25.903	-0.37
Mg ^c	-3.88	0.045	...	0.729	0.18
Zn ^c	-3.88	0.045	0.038	0.946	0.22
Cd ^c	-3.52	0.084	0.068	1.325	0.30
Hg ^c	-2.91	0.168	0.068	1.876	0.34
B ^c	-6.61	-0.141	...	4.456	-0.87
Al ^c	-4.47	-0.010	...	-2.451	-0.05
In ^c	-3.87	0.046	0.038	2.525	0.14
Tl ^c	-3.17	0.129	...	3.117	0.19
C ^c	-7.54	-0.180	-0.212	4.713	-1.37
Si ^c	-4.94	-0.046	-0.064	1.634	-0.28
Ge ^c	-4.73	-0.030	-0.043	1.085	-0.22
Sn ^c	-4.16	0.017	...	-1.207	-0.02
Pb ^c	-3.37	0.103	...	59.717	-0.04
Ca	-5.98	-0.110	-0.098	10.437	-0.86
Si ^a	-3.90	0.043	0.051	-1.510	0.23
Ge ^a	-3.75	0.058	0.064	-2.216	0.29
Sn ^a	-3.30	0.112	...	-3.366	0.49
Pb ^a	-2.71	0.201	...	-5.961	0.55
Na ^a	-7.01	-0.159	...	-10.494	-1.36
As ^a	-4.10	0.023	0.021	-59.318	0.07
Sb ^a	-3.54	0.082	0.064	-6.573	0.33
Bi ^a	-2.85	0.177	...	-19.379	0.40
O ^a	-8.21	-0.204	-0.225	-5.601	-1.86
S ^a	-4.96	-0.047	-0.042	-1.655	-0.23
Se ^a	-4.57	-0.018	-0.013	-0.700	-0.15
Te ^a	-3.86	0.047	0.030	3.654	0.17
Po ^a	-3.07	0.143	...	6.707	-
Fr ^a	-9.55	-0.244	...	-4.601	-2.36
Cl ^a	-5.64	-0.091	...	-1.761	-0.46
Br ^a	-5.09	-0.056	...	-1.194	-0.37
I ^a	-4.22	0.012	...	0.332	0.01
At ^a	-3.35	0.105	...	2.186	-
GaAs; Bondlength=2.4463 Å; Covalecity=0.9095; $V_2=-4.1$ eV					
Li ^c	-3.90	0.019	...	0.186	0.13
Na ^c	-2.96	0.133	...	0.904	0.41
Cu ^c	-3.25	0.092	...	0.952	0.34
Ag ^c	-3.01	0.125	...	1.161	0.56
Au ^c	-2.52	0.207	...	1.593	0.49
Be ^c	-5.24	-0.087	-0.114	-19.411	-0.37
Mg ^c	-3.64	0.046	...	0.732	0.18
Zn ^c	-3.64	0.046	0.041	0.950	0.22
Cd ^c	-3.30	0.086	0.074	1.326	0.30
Hg ^c	-2.73	0.169	0.074	1.881	0.34
B ^c	-6.24	-0.142	...	4.573	-0.87
Al ^c	-4.21	-0.010	...	-2.385	-0.05
In ^c	-3.65	0.045	0.041	2.518	0.14
Tl ^c	-2.98	0.130	...	3.164	0.19
C ^c	-7.12	-0.181	-0.217	4.985	-1.37
Si ^c	-4.65	-0.046	-0.065	1.636	-0.28
Ge ^c	-4.45	-0.030	-0.045	1.075	-0.22
Sn ^c	-3.91	0.018	...	-1.214	-0.02
Pb ^c	-3.17	0.103	...	***	0.04
Ca	-5.98	-0.129	-0.127	13.088	-0.93
Si ^a	-3.90	0.019	0.025	-0.704	0.16
Ge ^a	-3.75	0.034	0.041	-1.362	0.22
Sn ^a	-3.30	0.086	...	-2.704	0.42
Pb ^a	-2.71	0.173	...	-5.339	0.48
Na ^a	-7.01	-0.176	...	-11.718	-1.43
As ^a	-4.36	-0.023	-0.025	-72.643	-0.07
Sb ^a	-3.54	0.057	0.041	-4.877	0.26
Bi ^a	-2.85	0.150	...	-17.596	0.33
O ^a	-8.21	-0.220	-0.253	-6.168	-1.93
S ^a	-4.96	-0.068	-0.065	-2.428	-0.30
Se ^a	-4.57	-0.040	-0.037	-1.578	-0.22
Te ^a	-3.86	0.023	0.008	1.801	0.10
Po ^a	-3.07	0.117	...	5.534	-
Fr ^a	-9.55	-0.259	...	-4.999	-2.43
Cl ^a	-5.64	-0.111	...	-2.189	-0.53
Br ^a	-5.09	-0.077	...	-1.669	-0.44
I ^a	-4.22	-0.011	...	-0.305	-0.06
At ^a	-3.35	0.080	...	1.695	-

GaSb: Bondlength=2.6346 Å; Covalency=0.9380; $V_2 = -3.535$ eV		InP: Bondlength=2.518 Å; Covalency=0.8657; $V_2 = -3.87$ eV	
Li ^c	-3.20	0.038	0.13
Na ^c	-2.43	0.155	0.41
Cu ^c	-2.70	0.108	0.34
Ag ^c	-2.50	0.142	0.56
Au ^c	-2.09	0.225	0.49
Be ^c	-4.49	-0.085	-0.37
Mg ^c	-3.05	0.057	0.18
Zn ^c	-3.08	0.053	0.22
Cd ^c	-2.78	0.096	0.30
Hg ^c	-2.29	0.182	0.34
B ^c	-5.42	-0.144	-0.87
Al ^c	-3.61	-0.008	-0.05
In ^c	-3.12	0.048	0.14
Tl ^c	-2.54	0.135	0.19
C ^c	-6.19	-0.183	-1.37
Si ^c	-4.00	-0.045	-0.28
Ge ^c	-3.84	-0.030	-0.22
Sn ^c	-3.35	0.020	-0.02
Pb ^c	-2.70	0.108	0.04
Ca ^a	-5.98	-0.173	-1.19
Si ^a	-3.90	-0.036	-0.10
Ge ^a	-3.75	-0.022	-0.04
Sn ^a	-3.30	0.026	0.16
Pb ^a	-2.71	0.107	0.22
N ^a	-7.01	-0.217	-1.69
Pa ^a	-4.36	-0.075	-0.33
As ^a	-4.10	-0.054	-0.26
Bi ^a	-2.85	0.085	0.07
O ^a	-8.21	-0.258	-2.19
S ^a	-4.96	-0.117	-0.56
Se ^a	-4.57	-0.090	-0.48
Te ^a	-3.86	-0.032	-0.16
Po ^a	-3.07	0.055	-
F ^a	-9.55	-0.294	-2.69
Cl ^a	-5.64	-0.156	-0.79
Br ^a	-5.09	-0.125	-0.70
I ^a	-4.22	-0.064	-0.32
At ^a	-3.35	0.020	-
Li ^c	-0.373
Na ^c	0.660
Cu ^c	0.567
Ag ^c	0.883
Au ^c	1.434
Be ^c	8.996
Mg ^c	-0.024
Zn ^c	-0.036
Cd ^c	0.849
Hg ^c	1.712
B ^c	3.755
Al ^c	3.920
In ^c	...	-0.059	2.540
Tl ^c	...	-0.047	3.576
C ^c	4.010
Si ^c	1.983
Ge ^c	1.650
Sn ^c	0.870
Pb ^c	-3.483
Ca ^a	7.454
Si ^a	-1.415
Ge ^a	-2.109
Sn ^a	-2.986
Pb ^a	-5.445
N ^a	-12.942
As ^a	...	0.024	***
Sb ^a	...	0.063	-6.956
Bi ^a	-35.700
O ^a	-6.255
S ^a	-1.777
Se ^a	-0.843
Te ^a	2.979
Po ^a	5.208
F ^a	-5.064
Cl ^a	-1.876
Br ^a	-1.292
I ^a	0.206
At ^a	1.900

contd....

Impuri- ties	V_2 in eV	ps	$\Delta d/d_0$	†	$\Delta d/\Delta\alpha_c$ Å	Δx
InAs: Bondlength=2.5945 Å ; Covalency=8656; $V_2=-3.645$ eV						
Li ^c	-3.90	-0.025	-0.314	-0.01
Na ^c	-2.96	0.082	0.677	0.27
Cu ^c	-3.25	0.044	0.593	0.20
Ag ^c	-3.01	0.075	0.888	0.42
Au ^c	-2.52	0.152	1.442	0.35
Be ^c	-5.24	-0.124	9.789	-0.51
Mg ^c	-3.64	0.001	0.012	-0.04
Zn ^c	-3.64	0.001	0.018	-0.08
Cd ^c	-3.30	0.038	0.865	0.16
Hg ^c	-2.73	0.117	1.719	0.20
B ^c	-6.24	-0.177	3.826	-1.01
Al ^c	-4.21	-0.052	-0.057	...	4.003	-0.19
Ga ^c	-4.10	-0.043	-0.046	...	2.530	-0.14
Ti ^c	-2.98	0.079	3.656	0.05
C ^c	-7.12	-0.213	4.173	-1.51
Si ^c	-4.65	-0.086	1.986	-0.42
Ge ^c	-4.45	-0.071	1.644	-0.36
Sn ^c	-3.91	-0.026	0.836	-0.16
Pb ^c	-3.17	0.054	-3.296	-0.10
C ^a	-5.31	-0.129	8.978	-0.93
Si ^a	-3.42	0.024	-0.740	0.16
Ge ^a	-3.28	0.041	-1.364	0.22
Sn ^a	-2.88	0.094	-2.414	0.42
Pb ^a	-2.35	0.184	-4.856	0.48
N ^a	-6.29	-0.179	-14.813	-1.43
Pa ^a	-3.87	-0.022	-0.023	...	***	-0.07
Sb ^a	-3.12	0.061	0.042	...	-5.081	0.26
Bi ^a	-2.50	0.156	-31.017	0.33
O ^a	-7.42	-0.224	-6.947	-1.93
S ^a	-4.46	-0.072	-2.569	-0.30
Se ^a	-4.11	-0.044	-1.710	-0.22
Te ^a	-3.44	0.022	1.491	0.10
Po ^a	-2.74	0.115	4.375	-
F ^a	-8.66	-0.263	-5.533	-2.43
Cl ^a	-5.09	-0.115	-2.322	-0.53
Br ^a	-4.59	-0.082	-1.774	-0.44
I ^a	-3.79	-0.014	-0.392	-0.06
At ^a	-3.01	0.075	1.470	-
InSb: Bondlength=2.8066 Å ; Covalency=0.8963; $V_2=-3.115$ eV						
Li ^c	-3.20	-0.010	-0.108	-0.01
Na ^c	-2.43	0.099	0.753	0.27
Cu ^c	-2.70	0.056	0.681	0.20
Ag ^c	-2.50	0.087	0.958	0.42
Au ^c	-2.09	0.166	1.516	0.35
Be ^c	-4.49	-0.125	19.718	-0.51
Mg ^c	-3.05	0.008	0.167	0.04
Zn ^c	-3.08	0.004	0.135	0.08
Cd ^c	-2.78	0.044	0.944	0.16
Hg ^c	-2.29	0.125	1.835	0.20
B ^c	-5.42	-0.181	5.125	-1.01
Al ^c	-3.61	-0.053	-0.048	...	5.147	-0.19
Ga ^c	-3.54	-0.046	-0.046	...	3.115	-0.14
Ti ^c	-2.54	0.081	4.557	0.05
C ^c	-6.19	-0.218	6.709	-1.51
Si ^c	-4.00	-0.088	2.523	-0.42
Ge ^c	-3.84	-0.075	2.117	-0.36
Sn ^c	-3.35	-0.027	0.964	-0.16
Pb ^c	-2.70	0.056	-2.933	-0.10
C ^a	-5.31	-0.176	76.204	-1.19
Si ^a	-3.42	-0.034	1.764	-0.10
Ge ^a	-2.88	0.030	1.227	-0.04
Sn ^a	-2.88	0.030	-1.201	0.16
Pb ^a	-2.35	0.113	-4.708	0.22
N ^a	-6.29	-0.222	-10.049	-1.69
Pa ^a	-3.87	-0.077	-0.060	...	-7.079	-0.33
As ^a	-3.65	-0.057	-0.043	...	-5.273	-0.26
Bi ^a	-2.50	0.087	13.836	0.07
O ^a	-7.42	-0.264	-6.474	-2.19
S ^a	-4.46	-0.123	-3.345	-0.56
Se ^a	-4.11	-0.097	-2.809	-0.48
Te ^a	-3.44	-0.036	-1.476	-0.16
Po ^a	-2.74	0.050	1.409	-
F ^a	-8.66	-0.300	-5.463	-2.69
Cl ^a	-5.09	-0.163	-2.873	-0.79
Br ^a	-4.59	-0.132	-2.471	-0.70
I ^a	-3.79	-0.070	-1.555	-0.32
At ^a	-3.01	0.013	0.222	-

AIP: Bondlength=2.3442 Å ; Covalency=0.8990; V ₂ =-4.465 eV		AIA: Bondlength=2.4156 Å ; Covalency=0.8992; V ₂ =-4.205 eV			
Li ^c	-4.18	0.025	0.262	0.18	0.290
Na ^c	-3.17	0.140	0.986	0.46	0.996
Cu ^c	-3.48	0.100	1.086	0.39	1.096
Ag ^c	-3.21	0.135	1.299	0.61	1.299
Au ^c	-2.69	0.216	1.713	0.54	1.721
Be ^c	-5.57	-0.079	***	-0.32	***
Mg ^c	-3.88	0.055	0.943	0.23	0.945
Zn ^c	-3.88	0.055	1.250	0.27	1.253
Cd ^c	-3.52	0.095	1.572	0.35	1.574
Hg ^c	-2.91	0.179	2.075	0.39	2.083
B ^c	-6.61	-0.134	3.692	-0.82	3.761
Ga ^c	-4.36	0.009	-2.162	0.05	-2.233
In ^c	-3.87	0.056	3.916	0.19	3.987
Tl ^c	-3.17	0.140	3.703	0.24	3.782
C ^c	-7.54	-0.173	4.042	-1.32	4.234
Si ^c	-4.94	-0.037	1.138	-0.23	1.129
Ge ^c	-4.73	-0.021	0.658	-0.17	0.642
Sn ^c	-4.16	0.027	-1.446	0.03	-1.440
Pb ^c	-3.37	0.113	-48.095	0.09	-30.226
C ^a	-6.13	-0.110	8.988	-0.86	10.932
Si ^a	-3.97	0.045	-1.574	0.23	-0.784
Ge ^a	-3.82	0.061	-2.293	0.29	-1.437
Sn ^a	-3.35	0.116	-3.411	0.49	-2.745
Pb ^a	-2.75	0.206	-6.101	0.55	-5.437
N ^a	-7.22	-0.160	-12.875	-1.36	-14.611
As ^a	-4.21	0.022	***	0.07	***
Sb ^a	-3.61	0.084	-7.475	0.33	-5.486
Bi ^a	-2.91	0.179	-28.999	0.40	-25.653
O ^a	-8.48	-0.206	-6.340	-1.86	-7.025
S ^a	-5.11	-0.049	-1.797	-0.23	-2.628
Se ^a	-4.70	-0.019	-0.763	-0.15	-1.676
Te ^a	-3.96	0.046	3.421	0.17	1.725
Po ^a	-3.15	0.143	5.967	-	4.995
F ^a	-9.87	-0.246	-5.100	-2.36	-5.564
Cl ^a	-5.81	-0.093	-1.877	-0.46	-2.336
Br ^a	-5.24	-0.058	-1.270	-0.37	-1.769
I ^a	-4.34	0.011	0.301	0.01	-0.339
At ^a	-3.44	0.104	2.109	-	1.645

contd...

Impuri- ties	V_2 in eV		$\Delta d/d_0$		$\Delta d/\Delta\alpha_c$ Å	Δx	Impuri- ties	V_2 in eV		$\Delta d/d_0$		$\Delta d/\Delta\alpha_c$ Å	Δx
	ps	†	ps	†				ps	†				
AlSb: Bondlength=2.6071 Å; Covalency=0.9254; $V_2=-3.61$ eV													
Li ^c	-3.20	0.047	0.420	0.18	C ^a	-6.13	-0.174	***	-1.19
Na ^c	-2.43	0.164	1.073	0.46	Si ^a	-3.97	-0.035	2.203	-0.10
Cu ^c	-2.70	0.117	1.184	0.39	Ge ^a	-3.82	-0.021	1.523	-0.04
Ag ^c	-2.50	0.151	1.385	0.61	Sn ^a	-3.35	0.029	-1.398	0.16
Au ^c	-2.09	0.236	1.830	0.54	Pb ^a	-2.75	0.109	-5.415	0.22
Be ^c	-4.49	-0.078	-17.941	-0.32	N ^a	-7.22	-0.220	-10.307	-1.69
Mg ^c	-3.05	0.066	1.057	0.23	Pa ^a	-4.47	-0.076	-7.564	-0.33
Zn ^c	-3.08	0.062	1.374	0.27	As ^a	-4.21	-0.056	-5.564	-0.26
Cd ^c	-2.78	0.105	1.709	0.35	Bi ^a	-2.91	0.085	18.652	0.07
Hg ^c	-2.29	0.192	2.273	0.39	O ^a	-8.48	-0.261	-6.630	-2.19
B ^c	-5.42	-0.138	5.119	-0.82	S ^a	-5.11	-0.120	-3.457	-0.56
Ga ^c	-3.54	0.007	-1.505	0.05	Se ^a	-4.70	-0.093	-2.853	-0.48
In ^c	-3.12	0.057	...	0.050	5.131	0.19	Te ^a	-3.96	-0.034	-1.520	-0.16
Tl ^c	-2.54	0.144	4.773	0.24	F ^a	-9.87	-0.296	-5.549	-2.69
C ^c	-6.19	-0.177	7.444	-1.32	Cl ^a	-5.81	-0.159	-2.917	-0.79
Si ^c	-4.00	-0.038	1.418	-0.23	Br ^a	-5.24	-0.127	-2.501	-0.70
Ge ^c	-3.84	-0.023	0.854	-0.17	I ^a	-4.34	-0.066	-1.565	-0.32
Sn ^c	-3.35	0.029	-1.523	0.03	At ^a	-3.44	0.018	0.335	-
Pb ^c	-2.70	0.117	-12.695	0.09							

c-cationic substitution; a-anionic substitution; ps: present study; †: Talwar *et al.* [1]

Table 5. Bondlength distortion of impurities in II-VI compounds.

Impuri- ties	V_2		$\Delta d/d_0$	$\Delta d/\Delta\alpha_c$	Δx	Impuri- ties	V_2		$\Delta d/d_0$	$\Delta d/\Delta\alpha_c$	Δx
	in eV	ps					in eV	ps			
ZnS: Bondlength=2.3325 Å; Covalency=0.7372; $V_2=-4.51$ eV											
Li ^c	-5.05	-0.041	...	-1.228	-0.09	Li ^c	-4.59	-0.038	...	-1.005	-0.09
Na ^c	-3.85	0.062	...	0.779	0.19	Na ^c	-3.50	0.066	...	0.807	0.19
Cu ^c	-4.13	0.034	...	0.849	0.12	Cu ^c	-3.77	0.036	...	0.875	0.12
Ag ^c	-3.81	0.066	...	1.263	0.34	Ag ^c	-3.48	0.068	...	1.284	0.34
Au ^c	-3.19	0.142	...	1.841	0.27	Au ^c	-2.92	0.143	...	1.882	0.27
Be ^c	-6.36	-0.118	...	2.369	-0.59	Be ^c	-5.86	-0.120	...	2.448	-0.59
Mg ^c	-4.55	-0.003	...	-0.321	-0.04	Mg ^c	-4.17	-0.003	...	-0.245	-0.04
Cd ^c	-4.11	0.036	...	2.099	0.08	Cd ^c	-3.77	0.036	0.037	2.161	0.08
Hg ^c	-3.41	0.113	0.043	2.484	0.12	Hg ^c	-3.13	0.113	0.041	2.584	0.12
B ^c	-7.37	-0.163	...	1.781	-1.09	B ^c	-6.82	-0.166	...	1.830	-1.09
Al ^c	-5.11	-0.045	-0.056	1.081	-0.27	Al ^c	-4.70	-0.046	...	1.083	-0.27
Ga ^c	-4.96	-0.035	-0.038	0.784	-0.22	Ga ^c	-4.57	-0.036	...	0.792	-0.22
In ^c	-4.46	0.004	0.009	-0.175	-0.08	In ^c	-4.11	0.003	...	-0.106	-0.08
Tl ^c	-3.68	0.080	...	17.223	-0.03	Tl ^c	-3.38	0.080	...	39.757	-0.03
C ^c	-8.30	-0.197	...	1.789	-1.59	C ^c	-7.70	-0.200	...	1.871	-1.59
Si ^c	-5.56	-0.075	...	0.934	-0.50	Si ^c	-5.13	-0.076	...	0.946	-0.50
Ge ^c	-5.33	-0.060	...	0.766	-0.44	Ge ^c	-4.92	-0.062	...	0.779	-0.44
Sn ^c	-4.75	-0.019	...	0.331	-0.24	Sn ^c	-4.37	-0.020	...	0.334	-0.24
Pb ^c	-3.90	0.057	...	-1.707	-0.18	Pb ^c	-3.59	0.055	...	-1.500	-0.18
C ^a	-5.32	-0.059	...	1.184	-0.63	C ^a	-5.32	-0.088	...	1.834	-0.71
Si ^a	-3.37	0.118	...	-1.925	0.46	Si ^a	-3.37	0.081	...	-1.386	0.38
Ge ^a	-3.23	0.136	...	-2.467	0.52	Ge ^a	-3.23	0.099	...	-1.870	0.44
Sn ^a	-2.82	0.198	...	-3.102	0.72	Sn ^a	-2.82	0.159	...	-2.586	0.64
Pb ^a	-2.26	0.309	...	-5.992	0.78	Pb ^a	-2.26	0.265	...	-5.348	0.70
N ^a	-6.40	-0.120	...	4.762	-1.13	N ^a	-6.40	-0.147	...	6.039	-1.21
Pa	-3.88	0.059	0.051	-2.298	0.23	Pa	-3.88	0.025	...	-1.008	0.15
As ^a	-3.64	0.085	0.077	-3.674	0.30	As ^a	-3.64	0.050	...	-2.245	0.22
Sb ^a	-3.08	0.158	0.124	-5.205	0.56	Sb ^a	-3.08	0.120	...	-4.110	0.48
Bi ^a	-2.44	0.270	...	-24.073	0.63	Bi ^a	-2.44	0.227	...	-20.984	0.55
O ^a	-7.63	-0.173	...	22.536	-1.63	O ^a	-7.63	-0.198	...	26.503	-1.71
Se ^a	-4.14	0.033	0.034	***	0.08	Se ^a	-4.51	-0.031	-0.367	***	-0.08
Te ^a	-3.43	0.110	0.085	-23.537	0.40	Te ^a	-3.43	0.074	0.053	-16.221	0.32
Po ^a	-2.71	0.218	...	12.954	-	Po ^a	-2.71	0.177	...	11.058	-
F ^a	-8.97	-0.218	...	-40.739	-2.13	F ^a	-8.97	-0.240	...	-47.625	-2.21
Cl ^a	-5.18	-0.050	...	-2.695	-0.23	Cl ^a	-5.18	-0.080	...	-4.476	-0.31
Br ^a	-4.66	-0.012	...	-0.697	-0.14	Br ^a	-4.66	-0.043	...	-2.588	-0.22
I ^a	-3.81	0.066	...	4.570	0.24	I ^a	-3.81	0.032	...	2.312	0.16
At ^a	-2.99	0.171	...	4.539	-	At ^a	-2.99	0.133	...	3.677	-

contd...

Impuri- ties	V_2 in eV	ps	$\Delta d/d_0$	$\Delta d/\Delta\alpha_c$ Å	Δx	Impuri- ties	V_2 in eV	ps	$\Delta d/d_0$	$\Delta d/\Delta\alpha_c$ Å	Δx
ZnTe: Bondlength=2.6746 Å; Covalency=0.7481; $V_2=-3.43$ eV						CdS: Bondlength=2.4433 Å; Covalency=0.6976; $V_2=-4.110$ eV					
Li ^c	-3.71	-0.029	...	-0.610	-0.09	Li ^c	-5.05	-0.073	...	-4.626	-0.17
Na ^c	-2.83	0.076	...	0.866	0.19	Na ^c	-3.85	0.025	...	0.419	0.11
Cu ^c	-3.09	0.040	...	0.910	0.12	Cu ^c	-4.13	-0.002	...	-0.083	0.04
Ag ^c	-2.86	0.071	...	1.309	0.34	Ag ^c	-3.81	0.029	...	0.860	0.26
Au ^c	-2.39	0.148	...	1.975	0.27	Au ^c	-3.19	0.101	...	1.769	0.19
Be ^c	-4.92	-0.124	...	2.712	-0.59	Be ^c	-6.36	-0.147	...	2.300	-0.67
Mg ^c	-3.44	-0.001	...	-0.084	-0.04	Mg ^c	-4.55	-0.037	...	5.839	-0.12
Cd ^c	-3.12	0.036	0.038	2.310	0.08	Zn ^c	-4.51	-0.034	-0.048	2.100	-0.08
Hg ^c	-2.58	0.115	0.042	2.848	0.12	Hg ^c	-3.41	0.073	0.004	2.716	0.04
B ^c	-5.84	-0.175	...	2.056	-1.09	B ^c	-7.37	-0.190	...	1.830	-1.17
Al ^c	-3.96	-0.052	...	1.167	-0.27	Al ^c	-5.11	-0.077	...	1.374	-0.35
Ga ^c	-3.86	-0.043	...	0.884	-0.22	Ga ^c	-4.96	-0.067	...	1.147	-0.30
In ^c	-3.44	-0.001	...	0.037	-0.08	In ^c	-4.46	-0.030	...	0.770	-0.16
Tl ^c	-2.82	0.077	...	-14.127	-0.03	Tl ^c	-3.68	0.043	...	-3.625	-0.11
C ^c	-6.63	-0.211	...	2.239	-1.59	C ^c	-8.30	-0.222	...	1.831	-1.67
Si ^c	-4.34	-0.083	...	1.038	-0.50	Si ^c	-5.56	-0.105	...	1.138	-0.58
Ge ^c	-4.16	-0.069	...	0.862	-0.44	Ge ^c	-5.33	-0.091	...	1.004	-0.52
Sn ^c	-3.68	-0.026	...	0.404	-0.24	Sn ^c	-4.75	-0.052	...	0.732	-0.32
Pb ^c	-3.00	0.052	...	-1.125	-0.18	Pb ^c	-3.90	0.020	...	-0.417	-0.26
C ^a	-5.32	-0.148	...	3.720	-1.03	C ^a	-4.80	-0.056	...	1.098	-0.63
Si ^a	-3.37	0.007	...	-0.135	0.06	Si ^a	-3.01	0.126	...	-2.102	0.46
Ge ^a	-3.23	0.023	...	-0.519	0.12	Ge ^a	-2.88	0.146	...	-2.741	0.52
Sn ^a	-2.82	0.077	...	-1.492	0.32	Sn ^a	-2.49	0.214	...	-3.483	0.72
Pb ^a	-2.26	0.174	...	-4.247	0.38	Pb ^a	-1.98	0.331	...	-7.300	0.78
N ^a	-6.40	-0.201	...	11.179	-1.53	N ^a	-5.82	-0.120	...	4.566	-1.13
Pa ^a	-3.88	-0.045	...	2.469	-0.17	Pa ^a	-3.52	0.060	...	-2.455	0.23
As ^a	-3.64	-0.022	...	1.367	-0.10	As ^a	-3.30	0.087	...	-3.990	0.30
Sb ^a	-3.08	0.041	...	-1.858	0.16	Sb ^a	-2.78	0.162	...	-5.807	0.56
Bi ^a	-2.44	0.139	...	-24.455	0.23	Bi ^a	-2.21	0.273	...	-35.522	0.63
O ^a	-7.63	-0.247	...	93.813	-2.03	O ^a	-6.96	-0.174	...	19.066	-1.63
S ^a	-4.51	-0.096	-0.098	-23.515	-0.40	S ^a	-3.77	0.033	0.036	74.946	0.08
Se ^a	-4.14	-0.067	-0.053	-16.288	-0.32	Te ^a	-3.12	0.111	0.087	-32.333	0.40
Po ^a	-2.71	0.094	...	5.009	-	Po ^a	-2.47	0.217	...	11.818	-
F ^a	-8.97	-0.286	...	-32.724	-2.53	F ^a	-8.20	-0.219	...	-65.200	-2.13
Cl ^a	-5.18	-0.140	...	-6.876	-0.63	Cl ^a	-4.73	-0.051	...	-2.879	-0.23
Br ^a	-4.66	-0.107	...	-5.520	-0.54	Br ^a	-4.26	-0.013	...	-0.800	-0.14
I ^a	-3.81	-0.038	...	-2.303	-0.16	I ^a	-3.48	0.065	...	4.511	0.24
At ^a	-2.99	0.053	...	1.442	-	At ^a	-2.74	0.169	...	4.532	-

CdSe: Bondlength=2.5511 Å; Covalency=0.6965; $V_2=-3.77$ eV		CdTe: Bondlength=2.8043 Å; Covalency=0.7060; $V_2=-3.120$ eV						
Li ^c	-4.59	-0.070	-3.526	Li ^c	-3.71	-0.062	-2.068	-0.17
Na ^c	-3.50	0.028	0.459	Na ^c	-2.83	0.037	0.549	0.11
Cu ^c	-3.77	0.000	0.001	Cu ^c	-3.09	0.004	0.134	0.04
Ag ^c	-3.48	0.031	0.884	Ag ^c	-2.86	0.033	0.903	0.26
Au ^c	-2.92	0.102	1.804	Au ^c	-2.39	0.107	1.886	0.19
Be ^c	-5.86	-0.148	2.375	Be ^c	-4.92	-0.153	2.609	-0.67
Mg ^c	-4.17	-0.037	6.925	Mg ^c	-3.44	-0.036	13.973	-0.12
Zn ^c	-4.14	-0.034	2.157	Zn ^c	-3.43	-0.035	2.311	-0.08
Hg ^c	-3.13	0.073	2.846	Hg ^c	-2.58	0.075	3.192	0.04
B ^c	-6.82	-0.192	1.881	B ^c	-5.84	-0.202	2.096	-1.17
Al ^c	-4.70	-0.078	1.385	Al ^c	-3.96	-0.084	1.466	-0.35
Ga ^c	-4.57	-0.069	1.158	Ga ^c	-3.86	-0.076	1.232	-0.30
In ^c	-4.11	-0.032	0.786	In ^c	-3.44	-0.036	0.826	-0.16
Tl ^c	-3.38	0.042	-3.017	Tl ^c	-2.82	0.039	-1.923	-0.11
C ^c	-7.70	-0.225	1.910	C ^c	-6.63	-0.235	2.250	-1.67
Si ^c	-5.13	-0.107	1.154	Si ^c	-4.34	-0.114	1.247	-0.58
Ge ^c	-4.92	-0.093	1.017	Ge ^c	-4.16	-0.100	1.100	-0.52
Sn ^c	-4.37	-0.053	0.730	Sn ^c	-3.68	-0.059	0.779	-0.32
Pb ^c	-3.59	0.019	-0.364	Pb ^c	-3.00	0.015	-0.252	-0.26
C ^a	-4.80	-0.085	1.732	C ^a	-4.80	-0.145	3.509	-1.03
Si ^a	-3.01	0.089	-1.540	Si ^a	-3.01	0.014	-0.275	0.06
Ge ^a	-2.88	0.108	-2.102	Ge ^a	-2.88	0.031	-0.706	0.12
Sn ^a	-2.49	0.173	-2.922	Sn ^a	-2.49	0.090	-1.776	0.32
Pb ^a	-1.98	0.285	-6.504	Pb ^a	-1.98	0.191	-5.251	0.38
Na ^a	-5.82	-0.146	5.730	Na ^a	-5.82	-0.201	10.119	-1.53
P ^a	-3.52	0.026	-1.091	P ^a	-3.52	-0.044	2.378	-0.17
As ^a	-3.30	0.052	-2.423	As ^a	-3.30	-0.021	1.296	-0.10
Sb ^a	-2.78	0.123	-4.547	Sb ^a	-2.78	0.045	-2.091	0.16
Bi ^a	-2.21	0.230	-29.484	Bi ^a	-2.21	0.141	-38.187	0.23
O ^a	-6.96	-0.198	21.630	O ^a	-6.96	-0.248	50.170	-2.03
S ^a	-4.11	-0.032	73.315	S ^a	-4.11	-0.097	-32.237	-0.40
Te ^a	-3.12	0.074	-20.045	Te ^a	-3.77	-0.068	-20.030	-0.32
Po ^a	-2.47	0.177	10.271	Po ^a	-2.47	0.093	4.884	-
F ^a	-8.20	-0.241	-86.667	F ^a	-8.20	-0.287	-48.525	-2.53
Cl ^a	-4.73	-0.080	-4.876	Cl ^a	-4.73	-0.141	-7.660	-0.63
Br ^a	-4.26	-0.044	-2.867	Br ^a	-4.26	-0.108	-6.184	-0.54
I ^a	-3.48	0.031	2.289	I ^a	-3.48	-0.040	-2.560	-0.16
At ^a	-2.74	0.130	3.687	At ^a	-2.74	0.050	1.421	-

c- cationic substitution; a- anionic substitution; ps: present study; †: Talwar *et al* [1]

Table 6. Bondlength distortion of impurities in I-VII compounds.

Impurities	V_2 in eV	$\frac{\Delta d/d_0}{ps}$	$\frac{\Delta d/\Delta\alpha_c}{\text{Å}}$	Δx	Impurities	V_2 in eV	$\frac{\Delta d/d_0}{ps}$	$\frac{\Delta d/\Delta\alpha_c}{\text{Å}}$	Δx
CuBr: Bondlength=2.3915 Å; Covalency=0.6104; $V_2=-4.29$ eV					AgI: Bondlength=2.7647 Å; Covalency=0.5726; $V_2=-3.21$ eV				
Li ^c	-5.29	-0.075	7.220	-0.21	Li ^c	-4.23	-0.097	6.968	-0.43
Na ^c	-4.04	0.023	0.674	0.07	Na ^c	-3.22	-0.001	-0.046	-0.15
Ag ^c	-3.96	0.031	2.484	0.22	Cu ^c	-3.47	-0.029	2.791	-0.22
Au ^c	-3.32	0.103	2.794	0.15	Au ^c	-2.68	0.071	3.384	-0.07
Be ^c	-6.53	-0.142	1.615	-0.71	Be ^c	-5.39	-0.171	1.824	-0.93
Mg ^c	-4.71	-0.034	1.255	-0.16	Mg ^c	-3.84	-0.064	1.721	-0.38
Zn ^c	-4.66	-0.030	0.844	-0.12	Zn ^c	-3.81	-0.062	1.300	-0.34
Cd ^c	-4.26	0.003	-0.136	-0.04	Cd ^c	-3.48	-0.030	0.914	-0.26
Hg ^c	-3.53	0.077	8.264	0.00	Hg ^c	-2.88	0.042	-5.422	-0.22
B ^c	-7.46	-0.181	1.377	-1.21	B ^c	-6.29	-0.214	1.577	-1.43
Al ^c	-5.24	-0.071	0.937	-0.39	Al ^c	-4.34	-0.105	1.195	-0.61
Ga ^c	-5.09	-0.061	0.788	-0.34	Ga ^c	-4.22	-0.096	1.057	-0.56
In ^c	-4.59	-0.025	0.439	-0.20	In ^c	-3.79	-0.060	0.838	-0.42
Tl ^c	-3.79	0.048	-1.793	-0.15	Tl ^c	-3.12	0.011	-0.236	-0.37
C ^c	-8.33	-0.212	1.360	-1.71	C ^c	-7.08	-0.245	1.599	-1.93
Si ^c	-5.68	-0.098	0.853	-0.62	Si ^c	-4.74	-0.133	1.059	-0.84
Ge ^c	-5.45	-0.085	0.749	-0.56	Ge ^c	-4.54	-0.119	0.960	-0.78
Sn ^c	-4.88	-0.047	0.519	-0.36	Sn ^c	-4.05	-0.082	0.785	-0.58
Pb ^c	-4.03	0.024	-0.381	-0.30	Pb ^c	-3.33	-0.014	0.165	-0.52
C ^a	-4.77	-0.039	0.595	-0.49	C ^a	-4.38	-0.108	1.785	-0.87
Si ^a	-2.87	0.167	-3.018	0.60	Si ^a	-2.64	0.077	-1.478	0.22
Ge ^a	-2.75	0.187	-3.983	0.66	Ge ^a	-2.54	0.093	-2.069	0.28
Sn ^a	-2.33	0.268	-5.784	0.86	Sn ^a	-2.15	0.166	-3.738	0.48
Pb ^a	-1.82	0.401	-23.557	0.92	Pb ^a	-1.70	0.281	-13.818	0.54
N ^a	-5.90	-0.110	2.336	-0.99	N ^a	-5.43	-0.173	3.902	-1.37
As ^a	-3.48	0.083	-2.683	0.37	As ^a	-3.21	0.000	0.000	-0.01
Sb ^a	-3.25	0.112	-4.334	0.44	Sb ^a	-3.01	0.025	-0.932	0.06
Bi ^a	-2.70	0.195	-8.216	0.70	Bi ^a	-2.50	0.100	-4.047	0.32
O ^a	-7.14	-0.169	68.761	0.77	O ^a	-1.98	0.205	***	0.39
S ^a	-4.13	0.014	4.776	-1.49	S ^a	-6.57	-0.226	6.728	-1.87
Se ^a	-3.77	0.050	-1.011	0.14	Se ^a	-3.81	-0.062	3.987	-0.24
Te ^a	-3.09	0.134	-4.505	0.22	Te ^a	-3.48	-0.030	2.315	-0.1
Po ^a	-2.42	0.249	-16.295	0.54	Po ^a	-2.86	0.045	-4.142	0.16
F ^a	-8.48	-0.217	12.723	-	F ^a	-2.25	0.146	11.574	-
Cl ^a	-4.80	-0.041	8.145	-1.99	Cl ^a	-7.81	-0.269	10.414	-2.37
I ^a	-3.47	0.084	18.621	-0.09	I ^a	-4.43	-0.112	22.940	-0.47
At ^a	-2.71	0.194	21.285	0.38	At ^a	-3.96	-0.075	24.870	-0.38
			6.222	-		0.98	0.098	4.236	-

^c-cationic substitution; ^a-anionic substitution; ps: present study; †: Talwar *et al* [1]

host-impurity bondlengths of isovalent impurities estimated based on the present UPTB theory is in good agreement with those of Martins and Zunger [12].

For heterovalent systems which are common to the present work and that of Talwar *et al* [1], the estimates of bondlength distortion are in good agreement with each other. Also the inward movement of P atom towards Ge impurity replacing Ga in GaP by 3% obtained in the present study is consistent with the 3.5% reported by the self-consistent calculations of Scheffler [9].

Though the EXAFS measurements are more reliable to provide accurate measures of local lattice distortion due to atomic substitutions, they are rather sparse. EXAFS measurements [23] of Sb in Si give an outward distortion of $+0.176 \text{ \AA}$. The lattice distortion estimated in the present work also reveals the same trend of outward distortion with a magnitude equal to 0.095 \AA which is quantitatively better than the theoretical prediction of 0.05 \AA by Talwar *et al* [1]. However, in the case of As in Si the EXAFS measurement [24] gives an outward distortion of 0.06 \AA whereas the present study predicts an inward distortion of 0.04 \AA as also the case with Talwar *et al* [1].

4. Conclusion

In conclusion, the UPTB scheme used in the present work has also been proved to be another simple and effective method for the study of bondlength distortion. A systematic behaviour of the bondlength distortion of impurities in semiconductors with respect to the covalent energy of the host-impurity bond, the difference in electronegativity between the host and that of the impurity atom, and the change in covalency of the bond when the impurity replaces the host is observed. This seems to suggest that when an impurity enters a semiconductor substitutionally, the resulting bondlength distortion is a function of the above mentioned parameters and not just decided by the difference in size between the impurity and host atoms.

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