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Bond lengths around isovalent impurities and in semiconductor solid solutions

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Abstract. Using a bond orbital model, we calculate the bond length and polarity of semiconductors, the symmetric relaxations around isovalent impurities in semiconductor–impurity systems, and the bond-length variations in solid solutions $A_{1-x}B_xC$ of semiconductor alloys. We find that small impurities have a large relaxation, but the variations in bond energy are smaller than those of large impurities. The results are compared with other theoretical and experimental results and are found to be in excellent agreement with experiments.

1. Introduction

Nonlinear variation in the band gaps of solid solutions $A_{1-x}B_xC$ of binary AC and BC semiconductors have long been known to be associated with changes in the microscopic atomic structure of the alloy. How atoms form a crystal in a specific structure is a fundamental question in solid state physics. Considering the x dependence of the two bond lengths $R_{AC}(x)$ and $R_{BC}(x)$ in an alloy (figure 1), two limiting possibilities were recognized quite early [1–3]. First, Bragg's [1] and Pauling's [2] ideas are that atomic radii are approximately conserved quantities (and hence are transferable) in different chemical environments and will equal their ideal values R_{AC}^0 and R_{BC}^0 , respectively, of the pure end-point materials (denoted as $R_{AC}^P(x)$ and $R_{BC}^P(x)$ in figure 1). Hence, the dimensionless relaxation parameter

$$\epsilon = (R_{BC}[AC:B] - R_{AC}^0)/(R_{BC}^0 - R_{AC}^0) \quad (1)$$

where $R_{BC}[AC:B]$ is the BC bond length around the B impurity in the AC host crystal, which equals unity in this limit (complete relaxation), and the alloy is thought of as sustaining two chemically distinct bonds (bond alternation). On the other hand, Vegard [3] discovered that the alloy lattice constant $a(x)$ equals approximately the concentration-weighted average of the lattice constants a_{AC} and a_{BC} of the end-point materials ($a(x) \simeq (1-x)a_{AC} + xa_{BC}$). This has led many workers in the field to assume that, since the bond length R_{AC}^0 of the pure solid is a simple linear function of its lattice constant (e.g. in zinc blende systems $R_{AC}^0 = \sqrt{3}a_{AC}/4$), $R_{AC}(x)$ and $R_{BC}(x)$ in the alloy will also display such a linear averaging $R_{AC}(x) = R_{BC}(x) = \sqrt{3}a(x)/4$. In this limit, $\epsilon = 0$ (no relaxation), and the alloy is thought of as sustaining a single (average) chemical bond (i.e. no bond alternation). This is

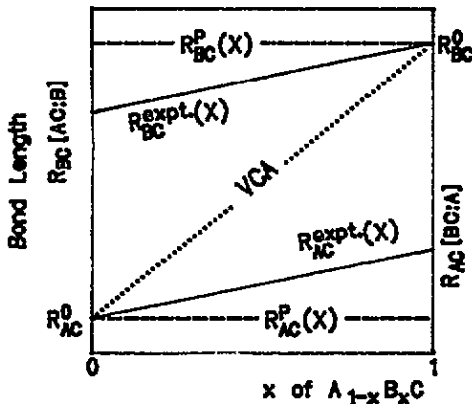


Figure 1. Schematic variation in the bond lengths $R_{AC}(x)$ and $R_{BC}(x)$ in an $A_{1-x}B_xC$ alloy with x depicting the predictions of the VCA, Pauling's model ($R_{AC}^P(x)$ and $R_{BC}^P(x)$) and experiment ($R_{AC}^{expt}(x)$ and $R_{BC}^{expt}(x)$). Here, R_{AC}^0 and R_{BC}^0 denote the bond lengths of the pure end-point compounds.

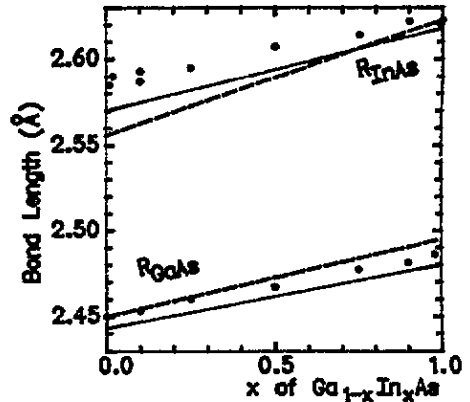


Figure 2. Schematic variation in the bond lengths $R_{InAs}(x)$ and $R_{GaAs}(x)$ in a $Ga_{1-x}In_xAs$ alloy with x : ●, EXAFS measuremental results [4]; —, our BO model results; ---, VFF results [6].

the underlying premise of the virtual-crystal approximation (VCA) that has been invoked to explain optical bowing in terms of the band structure of such an equal-bond-length material.

Recent extended x-ray absorption fine-structure (EXAFS) experiments [4,5] on $In_{1-x}Ga_xAs$ and $GaAs_{1-x}P_x$ alloys have indicated that reality ($R_{AC}^{expt}(x)$ and $R_{BC}^{expt}(x)$ in figure 1) is intermediate between these two limits but is considerably closer to the Pauling limit ($\epsilon = 1$) than to the VCA limit ($\epsilon = 0$). Theoretical studies, using a valence force field (VFF) theory [6], also support distinct bond lengths in alloys.

In this work, using a simple bond orbital (BO) model, we show

- (i) how the bond lengths R_{AC} and R_{BC} and the bond polarity can be simply predicted for all semiconductors,
- (ii) how the bond lengths $R_{AC}[BC:A]$ and $R_{BC}[AC:B]$ (and hence ϵ) in the dilute limit can be simply predicted for all isovalent impurities (results are given for 66 systems) and
- (iii) that the concentration dependences $R_{AC}(x)$ and $R_{BC}(x)$ in the alloy are to a good approximation, merely linear interpolations between these values and R_{AC}^0 and R_{BC}^0 , respectively. The simple BO model requires only knowledge of the Herman-Skillman atomic term value [7] ϵ_s and ϵ_p , the Harrison [8] universal parameters and the parameters k [9] for the rows of the periodic table.

2. Theoretical formalism

2.1. Bond length and polarity of the compounds

Tight-binding theory has been able to obtain approximate but meaningful predictions of the bonding properties of solids. In order to improve the description of the bond energy, Baranowski [9] made a very simple modification of the overlap interaction, on the basis of the idea and methods proposed by Harrison [8], and gave a formula for the bond length of

a semiconductor. For all tetrahedral compounds, the bond length R^0 is

$$R^0 = \frac{(-2\eta_\sigma \hbar^2/m)^{1/2}}{(k^2 \bar{\epsilon}_h^2 - 4V_3^2)^{1/4}} \quad (2)$$

where, for sp^3 bonds, $\eta_\sigma = \frac{1}{4}\eta_{ss\sigma} - (\sqrt{3}/2)\eta_{sp\sigma} - \frac{3}{4}\eta_{pp\sigma}$, in which $\eta_{ss\sigma} = -1.4$, $\eta_{sp\sigma} = 1.84$ and $\eta_{pp\sigma} = 3.24$ are dimensionless Harrison universal parameters and $\hbar^2/m = 7.62 \text{ eV \AA}^2$. The effective parameter k will be given by the following average:

$$k = (k_i k_j)^{1/2} \quad (3)$$

where k_i and k_j are connected with rows i and j , respectively, of the periodic table. The cation–anion average hybrid energy $\bar{\epsilon}_h$ is the weighted average

$$\bar{\epsilon}_h = \frac{1}{3}(n_c \epsilon_h^c + n_a \epsilon_h^a) \quad (4)$$

where n_c and n_a are the numbers of electrons associated with the cation and anion, respectively, which participate in the bonds. ϵ_h^c and ϵ_h^a are the averages of the cation and anion hybrid energies respectively:

$$\begin{aligned} \epsilon_h^c &= \frac{1}{4}(\epsilon_s^c + 3\epsilon_p^c) \\ \epsilon_h^a &= \frac{1}{4}(\epsilon_s^a + 3\epsilon_p^a) \end{aligned} \quad (5)$$

in which ϵ_s^c , ϵ_p^c , ϵ_s^a and ϵ_p^a are the free-atom energies for s and p states for the cation and anion, respectively [7], V_3 is the hybrid polar energy, which can be approximated in the following way:

$$V_3 = \frac{1}{2}(\epsilon_h^c - \epsilon_h^a). \quad (6)$$

The bond polarity of the compound can be obtained from

$$\alpha_p = \frac{V_3}{(V_2^2 + V_3^2)^{1/2}} \quad (7)$$

where V_2 is the hybrid covalent energy, which can be approximated in the following way:

$$V_2 = -\eta_\sigma \frac{\hbar^2}{m(R^0)^2}. \quad (8)$$

2.2. Lattice relaxation

An approximate estimation of the impurity–host relaxation in semiconductors has been suggested by Baranowski [9]. In the notation of Harrison [8], the gain in the impurity–host bond energy per bond connected with a distortion ΔR ($\Delta R > 0$ outwards and $\Delta R < 0$ inwards) can be calculated as

$$\Delta E_b = \Delta E_b^1 + \Delta E_b^2 \quad (9)$$

where ΔE_b^1 and ΔE_b^2 are the changes in the energy of the bonds caused by distortion in the nearest-neighbour and second-nearest-neighbour atom positions respectively. These are given by

$$\Delta E_b^1 = -2\{[V_2^2(R^0 + \Delta R) + V_3^2]^{1/2} - V_2^2(R^0 + \Delta R)/k|\bar{\epsilon}_h| - [V_2^2(R^0) + V_3^2]^{1/2} + V_2^2(R^0)/k|\bar{\epsilon}_h|\} \quad (10)$$

and

$$\Delta E_b^2 = -6\{[V_2^2(R^0 + \Delta R') + V_3^2]^{1/2} - V_2^2(R^0 + \Delta R')/k'|\bar{\epsilon}'_h| - [V_2^2(R^0) + V_3^2]^{1/2} + V_2^2(R^0)/k'|\bar{\epsilon}'_h|\} \quad (11)$$

in which $V_2(= \zeta R^{-2})$, V_3 and $k|\bar{\epsilon}_h|$ refer to the covalent energy, the polar energy and the average hybrid energy of the impurity nearest-neighbour bond, respectively; $\Delta R'$ is the change in the bond length between the first- and second-nearest neighbours which is considered to be approximately equal to $-\frac{1}{3}\Delta R$ [9]. Here, we hold the second neighbours fixed; then the following formula is obtained:

$$\Delta R' = [(R^0)^2 - \frac{2}{3}R^0\Delta R + (\Delta R)^2]^{1/2} - R^0. \quad (12)$$

Its first-order approximation is $-\frac{1}{3}\Delta R$. The terms V_2' , V_3' and $k'|\bar{\epsilon}'_h|$ are the covalent energy, the polar energy and the average hybrid energy of the host crystal, respectively.

Within this approximation the minimum of the total energy predicts the impurity-host relaxation.

3. Results and discussion

In this section we present the results of our tight-binding BO model calculations for the bond length and bond polarity of semiconductors and the relaxation of the nearest-neighbour atoms around the isovalent impurity in semiconductors.

(i) The results for the bond length and polarity for semiconductors are given in table 1 together with the experimental values [10, 11]. From table 1 it is clear that our results are in good agreement with the experimental data [10, 11]. For the bond length of alloy, the Pauling and VCA predictions can be directly obtained from table 1.

(ii) Predictions of the impurity bond length for 66 systems are given in tables 2 and 3 together with the relaxation energy ΔE and relaxation parameter ϵ ; the results on the bond length and ϵ taken from [6], which are calculated from the VFF model, are also given in table 3 for comparison.

It is clear from table 2 that small impurities have a large relaxation, but the variations in bond energy are smaller than those of large impurities. For example, in the case of GaAs:In and InAs:Ga, the natural atomic radius of Ga is smaller than that of In, and the value of the relaxation of Ga in InAs is 0.138 Å, which is larger than that (0.127 Å) of In in GaAs; the variation in the bond energy of Ga in InAs is 0.060 eV, which is smaller than that (0.064 eV) of In in GaAs. The fact that the bond-stretching force constant α of GaAs is larger than that of InAs causes this small effect. This means that the amount of lattice relaxation is small for a bond with a large bond-stretching force constant α (for the bond of the material with a large bulk modulus B).

From table 3, we find the following.

Table 1. Predicted bond lengths and polarities of semiconductors. The experimental bond lengths and bond polarities are taken from [10] and [11], respectively.

Compound	R (Å)		α_p	
	BO	Experimental	BO	Experimental
C	1.615	1.544	0	0
Si	2.357	2.352	0	0
Ge	2.448	2.449	0	0
α -Sn	2.802	2.810	0	0
SiC	1.953	1.887	0.160	0.096
AlP	2.343	2.367	0.337	0.326
AlAs	2.417	2.442	0.338	0.314
AlSb	2.610	2.657	0.289	0.297
GaP	2.370	2.358	0.320	0.310
GaAs	2.443	2.448	0.318	0.300
GaSb	2.635	2.639	0.263	0.287
InP	2.538	2.541	0.397	0.317
InAs	2.618	2.623	0.398	0.302
InSb	2.820	2.805	0.345	0.289
ZnS	2.302	2.341	0.549	0.605
ZnSe	2.413	2.455	0.553	0.586
ZnTe	2.658	2.642	0.542	0.569
CdTe	2.865	2.805	0.611	0.581
β -HgS	2.468	2.543	0.608	
HgSe	2.589	2.635	0.612	
HgTe	2.851	2.797	0.603	0.533
γ -CuCl	2.122	2.345	0.639	0.826
γ -CuBr	2.268	2.464	0.652	0.822
γ -CuI	2.576	2.622	0.677	0.802

(i) According to the VFF model, ϵ is in the range 0.6–0.8 for most semiconductors; in our BO model, ϵ is in the range 0.7–0.8, which is closer to the result of the simple radial force constant model [12] ($\epsilon = 0.75$) and considerably closer to the Pauling limit ($\epsilon = 1$) than to the VCA limit ($\epsilon = 0$). Hence, the VCA model and its application to optical bowing appears to be substantially in error.

(ii) Small impurities have larger relaxation parameters than large impurities do.

(iii) In the VFF model, ionic host systems have larger relaxation parameters than covalent hosts do, but in the BO model one cannot draw this conclusion. In fact, according to the EXAFS experimental results [4, 5] the covalent host system has a larger relaxation parameter (for $\text{Si}_{1-x}\text{Ge}_x$, ϵ is close to unity) than ionic hosts do (for $\text{In}_{1-x}\text{Ga}_x\text{As}$, $\epsilon \simeq 0.77$ and, for InP:Ga and InP:As , $\epsilon \simeq 0.72$).

There are some quantum-mechanical calculations of relaxation parameters for C:Si available for comparison. The results of the VFF model for C:Si is $R = 1.665$ Å (or $\epsilon = 0.35$); the semi-empirical cluster complete-neglect-of-differential-overlap (CNDO) calculation of Mainwood [13] yields $R = 1.93$ Å (or $\epsilon = 0.52$); the result of our BO model is $R = 1.873$ Å (or $\epsilon = 0.76$). The difference between these results is large, but our result is normal; $R (= 1.873$ Å) is in excellent agreement with the EXAFS [14] result of the Si–C average bond length (about 1.86 ± 0.015 Å) in hydrogenated amorphous silicon–carbon alloy films, and $\epsilon (= 0.76)$ is approximately equal to the result of simple radial force constant model [12] ($\epsilon = 0.75$).

Experimental results are available for a limited number of systems. The errors in the Pauling limit, VCA limit, VFF model and BO model with respect to the experimental results

Table 2. Predicted variation in the BC bond length $R = R_{BC}^{AC:B}$ for an isovalent B-atom impurity in an AC host crystal and the variation ΔE in bond energy.

System	ΔR (Å)	ΔE (eV)	System	ΔR (Å)	ΔE (eV)
AlP:In	0.142	-0.093	InP:Al	-0.153	-0.081
GaP:In	0.122	-0.067	InP:Ga	-0.132	-0.062
AlAs:In	0.147	-0.088	InAs:Al	-0.158	-0.077
GaAs:In	0.127	-0.064	InAs:Ga	-0.138	-0.060
AlSb:In	0.154	-0.075	InSb:Al	-0.164	-0.065
GaSb:In	0.134	-0.056	InSb:Ga	-0.145	-0.052
AlP:As	0.055	-0.015	AlAs:P	-0.055	-0.013
AlP:Sb	0.201	-0.198	AlSb:P	-0.205	-0.133
AlAs:Sb	0.145	-0.094	AlSb:As	-0.147	-0.069
GaP:As	0.054	-0.014	GaAs:P	-0.055	-0.013
GaP:Sb	0.200	-0.192	GaSb:P	-0.204	-0.130
GaAs:Sb	0.145	-0.091	GaSb:As	-0.146	-0.067
InP:As	0.060	-0.012	InAs:P	-0.061	-0.011
InP:Sb	0.213	-0.153	InSb:P	-0.216	-0.099
InAs:Sb	0.152	-0.070	InSb:As	-0.152	-0.050
ZnS:Se	0.082	-0.025	ZnSe:S	-0.084	-0.021
ZnS:Te	0.268	-0.268	ZnTe:S	-0.281	-0.148
ZnSe:Te	0.183	-0.106	ZnTe:Se	-0.189	-0.069
β -HgS:Se	0.089	-0.019	HgSe:S	-0.092	-0.016
β -HgS:Te	0.289	-0.206	HgTe:S	-0.303	-0.108
HgSe:Te	0.196	-0.080	HgTe:Se	-0.202	-0.050
ZnS:Hg	0.118	-0.048	β -HgS:Zn	-0.132	-0.045
ZnSe:Hg	0.125	-0.044	HgSe:Zn	-0.141	-0.042
ZnTe:Cd	0.146	-0.042	CdTe:Zn	-0.166	-0.040
ZnTe:Hg	0.138	-0.037	HgTe:Zn	-0.154	-0.035
γ -CuCl:Br	0.107	-0.047	γ -CuBr:Cl	-0.133	-0.037
γ -CuCl:I	0.339	-0.430	γ -CuI:Cl	-0.382	-0.215
γ -CuBr:I	0.225	-0.148	γ -CuI:Br	-0.248	-0.093
C:Si	0.258	-1.448	Si:C	-0.324	-0.587
Si:Ge	0.034	-0.007	Ge:Si	-0.035	-0.006
Si:Sn	0.159	-0.140	Sn:Si	-0.178	-0.092
Ge:Sn	0.129	-0.079	Sn:Ge	-0.138	-0.055
SiC:Si	0.313	-1.010	SiC:C	-0.277	-0.945

R are given in table 4. It is clear that the errors in the VCA are the largest, the errors in the Pauling limit are the second largest and the errors in the VFF model and BO model are the smallest. However, all the knowledge that the VFF model required, such as the lattice constants, bulk moduli and ionicities of the pure end-point compounds, can be obtained in the simple BO model.

The variations $R_{AC}(x)$ and $R_{BC}(x)$ with composition for an $A_{1-x}B_xC$ alloy (figure 1) can be obtained by linear interpolation between $(R_{AC}^0, R_{AC}[BC:A])$ and $(R_{BC}^0, R_{BC}[AC:B])$, using the data in tables 1 and 3. Our model for the dilute alloy can be extended to the whole range of compositions by interpolation of the data for the end-point materials. If we consider each individual A or B atom as an isovalent impurity system in the average alloy, the alloy bond lengths are

$$R_{AC}(x) = R_{AC}^0 + x(1 - \epsilon_{[BC:A]})(R_{BC}^0 - R_{AC}^0) \quad (13a)$$

and

$$R_{BC}(x) = R_{BC}^0 - (1 - x)(1 - \epsilon_{[AC:B]})(R_{BC}^0 - R_{AC}^0). \quad (13b)$$

Table 3. Predicted impurity BC bond length $R = R_{BC}^{AC:B}$ for an isovalent B-atom impurity in an AC host crystal and the relaxation parameter ϵ . The result of the VFF model [6] are also shown in this table for comparison.

System	R (Å)		ϵ		System	R (Å)		ϵ	
	BO	VFF	BO	VFF		BO	VFF	BO	VFF
AlP:In	2.485	2.480	0.73	0.65	InP:Al	2.385	2.414	0.79	0.73
GaP:In	2.492	2.472	0.73	0.63	InP:Ga	2.406	2.409	0.79	0.73
AlAs:In	2.564	2.553	0.73	0.60	InAs:Al	2.460	2.495	0.79	0.74
GaAs:In	2.570	2.556	0.73	0.62	InAs:Ga	2.480	2.495	0.79	0.73
AlSb:In	2.764	2.746	0.73	0.61	InSb:Al	2.656	2.693	0.78	0.75
GaSb:In	2.769	2.739	0.72	0.60	InSb:Ga	2.675	2.683	0.78	0.74
AlP:As	2.398	2.422	0.74	0.65	AlAs:P	2.362	2.395	0.74	0.67
AlP:Sb	2.544	2.542	0.75	0.61	AlSb:P	2.405	2.444	0.77	0.73
AlAs:Sb	2.562	2.574	0.75	0.60	AlSb:As	2.463	2.510	0.76	0.71
GaP:As	2.424	2.414	0.74	0.62	GaAs:P	2.388	2.387	0.75	0.68
GaP:Sb	2.570	2.519	0.76	0.57	GaSb:P	2.431	2.436	0.77	0.73
GaAs:Sb	2.588	2.564	0.76	0.60	GaSb:As	2.489	2.505	0.76	0.70
InP:As	2.598	2.595	0.75	0.67	InAs:P	2.557	2.562	0.76	0.74
InP:Sb	2.751	2.700	0.76	0.60	InSb:P	2.604	2.597	0.77	0.79
InAs:Sb	2.770	2.739	0.75	0.64	InSb:As	2.668	2.667	0.75	0.75
ZnS:Se	2.384	2.420	0.74	0.70	ZnSe:S	2.329	2.367	0.76	0.78
ZnS:Te	2.570	2.539	0.75	0.67	ZnTe:S	2.377	2.407	0.79	0.78
ZnSe:Te	2.596	2.584	0.75	0.71	ZnTe:Se	2.469	2.502	0.77	0.74
β -HgS:Se	2.557	2.611	0.74	0.76	HgSe:S	2.497	2.553	0.76	0.80
β -HgS:Te	2.757	2.716	0.76	0.71	HgTe:S	2.548	2.579	0.79	0.82
HgSe:Te	2.785	2.748	0.75	0.74	HgTe:Se	2.649	2.665	0.77	0.80
ZnS:Hg	2.420	2.482	0.71	0.73	β -HgS:Zn	2.336	2.380	0.80	0.80
ZnSe:Hg	2.538	2.587	0.71	0.74	HgSe:Zn	2.448	2.494	0.80	0.78
ZnTe:Cd	2.804	2.755	0.71	0.70	CdTe:Zn	2.699	2.674	0.80	0.78
ZnTe:Hg	2.796	2.748	0.72	0.69	HgTe:Zn	2.697	2.673	0.80	0.78
γ -CuCl:Br	2.229	2.440	0.73	0.81	γ -CuBr:Cl	2.155	2.367	0.77	0.79
γ -CuCl:I	2.461	2.563	0.75	0.80	γ -CuI:Cl	2.194	2.407	0.84	0.76
γ -CuBr:I	2.493	2.585	0.73	0.79	γ -CuI:Br	2.328	2.500	0.80	0.76
C:Si	1.873	1.665	0.76	0.35	Si:C	2.033	2.009	0.80	0.74
Si:Ge	2.391	2.380	0.76	0.58	Ge:Si	2.413	2.419	0.76	0.63
Si:Sn	2.516	2.473	0.75	0.53	Sn:Si	2.624	2.645	0.77	0.70
Ge:Sn	2.577	2.549	0.75	0.55	Sn:Ge	2.664	2.688	0.76	0.67
SiC:Si	2.266		0.77		SiC:C	1.676		0.82	

Table 4. The errors in the Pauling limit, VCA limit, VFF model [6] and our BO model with respect to the experimental results [4-6] for seven systems.

System	$R^{\text{expt}} - R^{\text{P}}$ (Å)	$R^{\text{expt}} - R^{\text{VCA}}$ (Å)	$R^{\text{expt}} - R^{\text{VFF}}$ (Å)	$R^{\text{expt}} - R^{\text{BO}}$ (Å)
InP:Ga	0.050	-0.130	0.001	0.004
InP:As	-0.023	0.070	0.005	0.002
GaAs:In	-0.035	0.139	0.031	0.017
InAs:Ga	0.040	-0.134	-0.007	0.008
ZnSe:Te	-0.042	0.142	0.011	0.001
ZnTe:Se	0.043	-0.141	-0.006	0.027
GaP:As	-0.036	0.052	-0.002	-0.012
Si:Ge		0.051	-0.021	-0.015
Ge:Si		-0.043	0.015	0.004

The results for $\text{Ga}_{1-x}\text{In}_x\text{As}$ are shown in figure 2. EXAFS data and the results of the first-principles pseudopotential (FPP) method [15] are available for several systems (table 5). The results of our model are in excellent agreement with EXAFS experiments [4, 5] and FPP theoretical results [15].

Table 5. The bond length R of the EXAFS experimental results [4, 5], the BO model, the FPP method [15], the VFF model [6], the Pauling limit and the VCA limit for five systems.

System	Bond length	R^{expt} (Å)	R^{BO} (Å)	R^{FPP} (Å)	R^{VFF} (Å)	R^{P} (Å)	R^{VCA} (Å)
$\text{Ga}_{0.5}\text{In}_{0.5}\text{As}$	Ga-As	2.46	2.462	2.464	2.472	2.443	2.533
$\text{Ga}_{0.5}\text{In}_{0.5}\text{As}$	In-As	2.608	2.594	2.602	2.589	2.623	2.533
$\text{GaAs}_{0.5}\text{P}_{0.5}$	Ga-As	2.43	2.434	2.434	2.431	2.443	2.401
$\text{GaAs}_{0.5}\text{P}_{0.5}$	Ga-P	2.38	2.379	2.373	2.374	2.358	2.401
$\text{Si}_{0.5}\text{Ge}_{0.5}$	Si-Ge	2.397	2.402		2.400		2.401

4. Conclusions

The BO model is used to calculate the bond length, the bond polarity of compounds and the symmetric distortions around isovalent impurities in semiconductor-impurity and semiconductor solid solution systems. We find that small impurities have a large relaxation, but the variations in bond energy are smaller than those of large impurities. The results are compared with other theoretical and experimental results and are found to be in excellent agreement with experiments.

References

- [1] Bragg W L 1920 *Phil. Mag.* **40** 169
- [2] Pauling L 1967 *The Nature of the Chemical Bond* (Ithaca, NY: Cornell University Press)
- [3] Vegard L 1921 *Z. Phys.* **5** 17
- [4] Mikkelsen J C and Boyce J B 1982 *Phys. Rev. Lett.* **49** 1412; 1983 *Phys. Rev. B* **28** 7130
- [5] Sakai T, Onda T, Ito R and Ogasawara N 1986 *Japan. J. Appl. Phys.* **25** 231
Oyanagi H, Takeda Y, Matsushita T, Ishiguro T, Yao T and Sasaki A 1988 *Solid State Commun.* **67** 453
Kajiyama H, Muramatsu S, Shimada T and Nishino Y 1992 *Phys. Rev. B* **45** 14 005
- [6] Martins J L and Zunger A 1984 *Phys. Rev. B* **40** 6217
- [7] Herman F and Skillman S 1963 *Atomic Structure Calculations* (Englewood Cliffs, NJ: Prentice-Hall)
- [8] Harrison W A 1980 *Electronic Structure and the Properties of Solids* (San Francisco, CA: Freeman)
- [9] Baranowski J M 1984 *J. Phys. C: Solid State Phys.* **17** 6287
- [10] Mitra S S and Massa N E 1982 *Handbook on Semiconductors* vol 1, ed W Paul (Amsterdam: North-Holland) p 81
- [11] Falter C, Ludwig W, Selmeke M and Zierau W 1984 *Phys. Lett. A* **105** 139
- [12] Shih C K, Spicer W E, Harrison W A and Sher A 1985 *Phys. Rev. B* **31** 1139
- [13] Mainwood A 1979 *J. Phys. C: Solid State Phys.* **12** 2543
- [14] Pascarelli S, Boscherini F, Mobilio S and Evangelisti F 1992 *Phys. Rev. B* **45** 1650
- [15] Magri R, Froyen S and Zunger A 1991 *Phys. Rev. B* **44** 7947