Tight-binding studies of crystalline $Si_{1-x}Ge_x$ alloys

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Abstract. Lattice constants and bond lengths in crystalline Si$_{1-x}$Ge$_x$ alloys are calculated by the bond orbital model and radial force model. The results are compared with theoretical results obtained by the valence force-field model calculation and experimental results obtained by x-ray diffraction and extendeded x-ray absorption fine-structure measurements, and are found to be in good agreement with experiments. The trends in elastic constants and electronic band structure as functions of composition x are obtained in the simple virtual-crystal approximation.

1. Introduction

The atomic structure of an alloy is important for understanding its properties, in which bond-length relaxation and the lattice constant are the key parameters. Theories of bond-length relaxation and the lattice constant in alloys were put forward by Pauling and Vergard a long time ago. Pauling [1] noted that the bond lengths in an alloy are the sum of their constituent-element atomic radii, i.e. the bond lengths are independent of the alloy composition. Vegard [2] discovered that the lattice constant is approximately equal to the composition-weighted average of the lattice constants of the pure materials, i.e. the lattice constant is dependent on the alloy composition.

Crystalline silicon–germanium (c-Si$_{1-x}$Ge$_x$) alloy is one of the important semiconductor materials, and is known to form solid solutions over the entire composition range. Its local structures have been determined by x-ray diffraction and extend x-ray absorption fine-structure (EXAFS) experiments [3]. These have indicated that the Ge–Ge and Ge–Si bond lengths are close to the sum of their constituent-element atomic radii, i.e. nearly follow the Pauli limit, but the lattice constant varies monotonically and exhibits a small, negative deviation from Vegard's law. Its atomic structures have also been studied theoretically. For the lattice constant of c-Si$_{1-x}$Ge$_x$ alloys, de Gironcoli *et al* [4] obtained a positive deviation from Vegard's law, and Mousseau and Thorpe [5] obtained the exact Vegard's law from their theoretical study. These results are not consistent with the result of the x-ray diffraction measurement [3]. Using a valence force-field (VFF) model, Ichimura *et al* [6] have calculated the bond lengths in Si$_{1-x}$Ge$_x$ alloys. Their results are consistent with those of the earlier calculations [7], but they are inconsistent with the experimental results obtained by the EXAFS technique [3].

In this paper we illustrate how the lattice constant of Si$_{1-x}$Ge$_x$ alloys and the bond lengths $d_{\text{Ge–Ge}}$, $d_{\text{Ge–Si}}$, $d_{\text{Si–Ge}}$ and $d_{\text{Si–Si}}$ in the dilute limit can be simply predicted. Then

under the simple virtual-crystal approximation (VCA), the trends of elastic constants and the electronic band structure versus composition x are calculated. All of the results are compared with experimental and other theoretical results.

2. Theoretical formalism

2.1. Lattice constant

Using the tight-binding (TB) theory, we can obtain approximate but meaningful predictions of the bonding properties of solids. Following the ideas and methods proposed by Harrison [8], Baranowski [9] made a very simple modification of the overlap interaction, and gave a formula for the bond lengths of semiconductors. For all tetrahedral compounds, the bond length d_0 can be obtained from

$$d_0 = \frac{(-2\eta_0\hbar^2/m)^{1/2}}{(k^2\bar{\varepsilon}_h^2 - 4V_3^2)^{1/4}} \tag{1}$$

where for sp^3 bonds

$$\eta_\sigma = (1/4)\eta_{ss\sigma} - (2\sqrt{3}/4)\eta_{sp\sigma} - (3/4)\eta_{pp\sigma}$$

in which $\eta_{ss\sigma} = -1.4$, $\eta_{sp\sigma} = 1.84$ and $\eta_{pp\sigma} = 3.24$ are dimensionless Harrison universal parameters, and $\hbar^2/m = 7.62$ eV Å^2. The effective k parameter will be given by the following average:

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

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

$$\bar{\varepsilon}_h = \tfrac{1}{8}(n_c\varepsilon_h^c + n_a\varepsilon_h^a) \tag{3}$$

where n_c and n_a are the numbers of electrons associated with the cation and anion, respectively, which participate in the bonds. The terms ε_h^c and ε_h^a are the averages of the cation and anion hybrid energy respectively, the V_3 is the hybrid polar energy, which can be approximated in the following way:

$$V_3 = \tfrac{1}{2}(\varepsilon_h^c - \varepsilon_h^a). \tag{4}$$

Here, equation (1) is used to calculate the average bond length for Si$_{1-x}$Ge$_x$ alloys. On the basis of Vegard's picture, the lattice constant is given simply as $4d/\sqrt{3}$. According to the values of $k_3 = 1.45$, $k_4 = 1.33$ and $k_5 = 1.12$ for Si, Ge and Sn rows given by Baranowski [9], we have $k_4 \simeq (k_3 + k_5)/2 + (k_3 - k_5)/8$, i.e. k_4 is larger than the average of k_3 and k_5. So we can assume that the average value of the appropriate k parameters for Si$_{1-x}$Ge$_x$ alloys is linear, with a small positive correction. A relatively simple assumption that one can make is

$$k_i = k_j = (1-x)k_{Si} + xk_{Ge} + [x(1-x)]^{1/2}|k_{Si} - k_{Ge}|/4 \tag{5}$$

where k_{Si} and k_{Ge} are the k parameters for pure Si and Ge, which can be determined by using the bond length or lattice constant obtained by experiment [3]. The average hybrid energy is linearly interpolated as a function of x, i.e. [10]

$$\varepsilon_h^c = \varepsilon_h^a = (1-x)\varepsilon_h^{Si} + x\varepsilon_h^{Ge} \tag{6}$$

where ε_h^{Si} and ε_h^{Ge} stand for the average of the silicon and germanium hybrid energy, respectively,

$$\varepsilon_h^{Si} = \tfrac{1}{4}(\varepsilon_s^{Si} + 3\varepsilon_p^{Si}) \qquad \varepsilon_h^{Ge} = \tfrac{1}{4}(\varepsilon_s^{Ge} + 3\varepsilon_p^{Ge}) \tag{7}$$

and ε_s^{Si}, ε_p^{Si}, ε_s^{Ge} and ε_p^{Ge} are the free-atom energies for s and p states for silicon and germanium, respectively [11].

2.2. Bond-length relaxation

Harrison's bonding theory, the valence force field (VFF) and an elastic continuum have been combined in a study of the substitution energy and local bond lengths of isoelectronic impurities in semiconductors [12]. Several models based on VFF alone are also derived for comparison. Comparison among the models show that, while extending the boundary helps the relaxation, the inclusion of the bond-bending forces prevents it. The comparison of the theoretical results with the available experimental data indicates that some models are the least accurate, and some models have a smaller average absolute deviation. The most surprising results is that the simple spring model (radial force model [13]) has the smallest variance in bond length. The reason is that the simple spring model, which contains neither of these terms, evidently represents a delicate cancellation of these effects and predicts results close to those of the full perturbation theory and experiment.

In this section we consider two models based on Harrison's bonding theory and the valence force field, i.e. bond orbital model and radial force model.

2.2.1. Bond orbital model..
The approximate estimation of 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 Δd ($\Delta d > 0$ outward and $\Delta d < 0$ inward) can be calculated as follows:

$$\Delta E_b = \Delta E_b^1 + 3\Delta E_b^2 \tag{8}$$

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

$$\Delta E_b^1 = -2\{[V_2^2(d_0 + \Delta d) + V_3^2]^{1/2} - V_2^2(d_0 + \Delta d)/k|\bar{\varepsilon}_h| - [V_2^2(d_0) + V_3^2]^{1/2}$$
$$+ V_2^2(d_0)/k|\bar{\varepsilon}_h|\} \tag{9}$$

and

$$\Delta E_b^2 = -2\{[V_2'^2(d_0 + \Delta d') + V_3'^2]^{1/2} - V_2'^2(d_0 + \Delta d')/k'|\bar{\varepsilon}_h'| - [V_2'^2(d_0) + V_3'^2]^{1/2}$$
$$+ V_2'^2(d_0)/k'|\bar{\varepsilon}_h'|\} \tag{10}$$

where V_2 ($\equiv \eta_\sigma \hbar^2/md^{-2}$), V_3 and $k|\bar{\varepsilon}_h|$ refer to the covalent, polar and average hybrid energy of the impurity nearest-neighbour bond, respectively, and $\Delta d'$ is the change in the
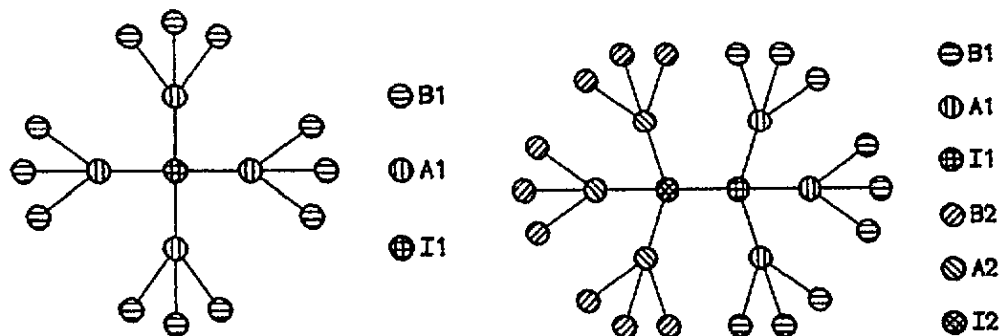
Figure 1. (a) An impurity atom I1 (Si or Ge) substitutes for a Ge or Si atom in a Ge or Si crystal; the tetrahedral symmetry is preserved at the impurity (I1) atom. (b) Two impurity atoms I1 and I2 substitute for two Ge or Si atoms in a Ge or Si crystal; the D_{3d} symmetry is preserved at the mid-point of the impurities I1 and I2.

bond length between the first and second nearest neighbours. If we hold the second nearest neighbours fixed, the following formula can be obtained:

$$\Delta d' = [d_0^2 - 2/3 d_0 \Delta d + (\Delta d)^2]^{1/2} - d_0.$$

Under the first-order approximation,

$$\Delta d' = -\Delta d / 3. \tag{11}$$

The terms V_2', V_3' and $k'|\bar{\varepsilon}_h'|$ are the covalent, polar and average hybrid energy of the host crystal [10], respectively.

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

When there is an impurity (I1, see figure 1(a)) Ge (or Si) atom in a Si (or Ge) crystal, its nearest-neighbour atoms would relax outward (or inward). According to the above method, the local relaxation Δd_A can be obtained at the minimum of the total energy ΔE_1, so the bond length between I1 and A1 is $d_{IA} = d_0 + \Delta d_A$ and the bond length between A1 and B1 is $d_{AB} = d_0 + \Delta d_A'$.

Then, assume that another impurity I2 substitutes one of the nearest-neighbour atoms of impurity I1 (see figure 1(b)). Suppose that the symmetry of the relaxation is held. Let us call Δd_I the outward relaxation displacement of the two impurity atoms, and Δd_A the outward relaxation displacement of the six A atoms, which are the nearest-neighbour atoms of the two impurity atoms. The energy associated with the distortion is

$$\Delta E_b = \Delta E_b^1 + 3\Delta E_b^2 + 9\Delta E_b^3 \tag{12}$$

where ΔE_b^1, ΔE_b^2 and ΔE_b^3 are, respectively, the changes in the energy of the bonds caused by distortion in the impurity–impurity, impurity–host and host–host systems. These are given by

$$\Delta E_b^1 = -2\{[V_2''^2(d_0 + 2\Delta d_I) + V_3''^2]^{1/2} - V_2''^2(d_0 + 2\Delta d_I)/k''|\bar{\varepsilon}_h''|$$
$$- [V_2''^2(d_0) + V_3''^2]^{1/2} + V_2''^2(d_0)/k''|\bar{\varepsilon}_h''|\} \tag{13}$$

$$\Delta E_b^2 = -2\{[V_2^2(d_0 + \Delta d_A + \Delta d_I') + V_3^2]^{1/2} - V_2^2(d_0 + \Delta d_A + \Delta d_I')/k|\bar{\varepsilon}_h|$$
$$- [V_2^2(d_0) + V_3^2]^{1/2} + V_2^2(d_0)/k|\bar{\varepsilon}_h|\} \tag{14}$$

and

$$\Delta E_b^3 = -2\{[V_2'^2(d_0 + \Delta d_A') + V_3'^2]^{1/2} - V_2'^2(d_0 + \Delta d_A')/k'|\bar{\varepsilon}_h'|$$
$$- [V_2'^2(d_0) + V_3'^2]^{1/2} + V_2'^2(d_0)/k'|\bar{\varepsilon}_h'|\}. \tag{15}$$

Within this approximation, the minimum of the total energy predicts the impurity–impurity relaxation, the bond length of impurity–impurity $d_{II} = d_0 + 2\Delta d_I$, the bond length of impurity–host $d_{IA} = d_0 + \Delta d_A + \Delta d_I'$ and the bond length of host–host $d_{AB} = d_0 + \Delta d_A'$.

2.2.2. Radial force model.. The nearest-neighbour bond length in a pseudobinary alloy is explained by a simple radial force-constant model (RFM) [12, 13] in which the weak angular forces are neglected. Here, we will show the bond lengths of the nearest-neighbour impurities in a binary alloy.

Consider a crystal of element A (e.g. semiconductor Si) in which *one* of the A atoms is replaced by an impurity I (e.g. Ge) atom. This configuration represents the dilute limit of I–A in an A host. In this configuration, four I–A bonds are identical and the tetrahedral symmetry (T_d) is preserved at the I atom. Let us call k the stretching force constant for the host A and Δd_A the outward relaxation displacement of the A atoms. Then Δd_{IA}, the amount by which the final I–A bond length deviates from d_{IA}^0 (where d_{IA}^0 is the bond length of the zincblende structure IA, which is approximately equal to the average of the bond lengths of I and A crystals) is $d_A^0 + \Delta d_A - d_{IA}^0$. The bond lengths of the neighbouring A–B bonds are decreased $-\Delta d_A/3$. The energy associated with the distortion is

$$E = 4[(k/2)(d_A^0 + \Delta d_A - d_{IA}^0)^2 + 3(k/2)(\Delta d_A/3)^2]. \tag{16}$$

By minimizing the energy with respect to Δd_A we obtain

$$\Delta d_A = \tfrac{3}{4}(d_{IA}^0 - d_A^0) \tag{17}$$

or the deviation of the I–A bond length

$$\Delta d_{IA} = \tfrac{1}{4}(d_A^0 - d_{IA}^0). \tag{18}$$

Now, consider a crystal A in which *two* nearest-neighbour A atoms are replaced by two I atoms. This configuration represents the dilute limit of I–I in an A host. In this configuration, six I–A bonds are identical and the D_{3d} symmetry is preserved at the mid-point between the two I atoms. Let us call Δd_I the outward relaxation displacement of the two I atoms and Δd_A the outward relaxation displacement of the six A atoms, which are the nearest-neighbour atoms of the two I atoms. The energy associated with the distortion is

$$E = (k/2)(d_A^0 + 2\Delta d_I - d_I^0)^2 + 6(k/2)(d_A^0 - \Delta d_I/3 - d_{IA}^0 + \Delta d_A)^2$$
$$+ 18(k/2)(\Delta d_A/3)^2. \tag{19}$$

By minimizing the energy with respect to Δd_A and Δd_I we obtain the analytic expressions for the bond-length deviations of the solution in the dilute limit:

$$\Delta d_I = \tfrac{1}{25}(12d_I^0 - 3d_{IA}^0 - 9d_A^0) = \tfrac{21}{25}(d_{IA}^0 - d_A^0)$$

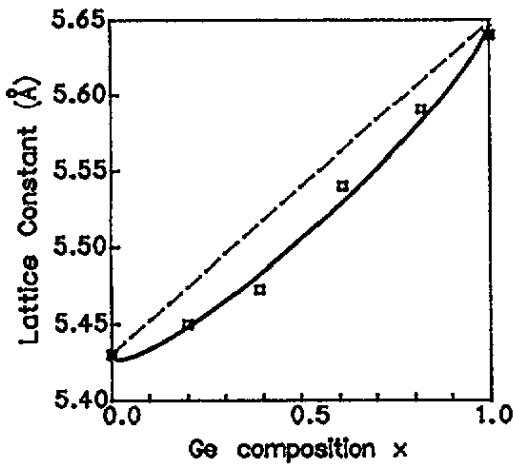$$\Delta d_A = \tfrac{1}{25}(3d_I^0 + 18d_{IA}^0 - 21d_A^0) = \tfrac{24}{25}(d_{IA}^0 - d_A^0). \tag{20}$$

Figure 2. Changes in lattice constant with Ge concentration x in crystalline $Se_{1-x}Ge_x$ alloys. The full curve presents our BOM results. The open squares are determined by x-ray diffraction measurement [3]. The broken line presents Vegard's law.
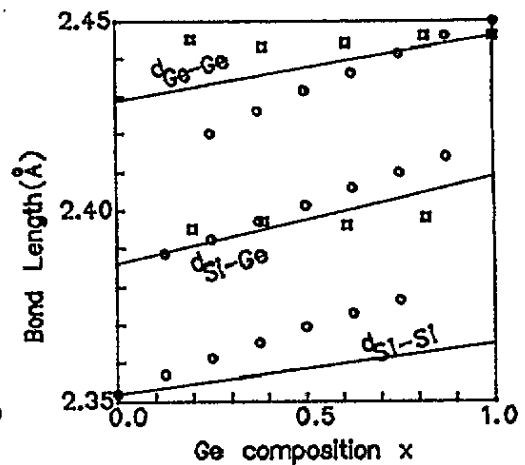
Figure 3. Ge–Ge, Ge–Si and Si–Si bond lengths, as a function of Ge concentration x in crystalline $Si_{1-x}Ge_x$ alloys. The full lines present our BOM results. The open squares present the EXAFS measurement results [3]. The open circles present VFF results [6].

3. Results and discussion

In this section we present the results of our tight-binding bond orbital model (BOM) calculations for the lattice constant in $Si_{1-x}Ge_x$ alloys and the results of BOM and RFM for the relaxation of the nearest-neighbour atoms around isovalent impurities Ge in Si and Si in Ge. The trends in elastic constants and the electronic band structure as the function of composition x are given in this section.

3.1. Lattice constant

Prediction of the lattice constant for $Si_{1-x}Ge_x$ is given in figure 2 by the full curve. The dependence of the lattice constant on Ge composition obtained by x-ray diffraction experiment [3] is shown by the open squares; the lattice constant deviates (downward bowing) slightly from Vegard's law (shown by the broken line). From figure 2, it is clear that our results are in excellent agreement with the experimental data [3]. In fact, if the last term in equation (5) is neglected, the exact Vegard's law will be obtained, so the definition of equation (5) is very important for the lattice. In the framework of pseudopotential *ab initio* calculations, de Gironcoli *et al* [4] obtained an upward bowing, i.e. lattice constant with a small positive deviation from Vegard's law. Mousseau and Thorpe [5] obtained the exact Vegard's law from their theoretical study. Very recently, Xu [14] has calculated the bond lengths and lattice constant in $Si_{1-x}Ge_x$ alloys by use of the empirical tight-binding force method; the results show that the lattice constant generally obeys Vegard's rule. According to our calculation, the largest negative deviation is about -0.58% at $x \simeq 0.5$. This deviation is probably caused by a difference in the relaxation of the impurity (see table 1, the results of BOM), i.e. a small impurity (Si in Ge crystal) has a larger relaxation than that of a larger impurity (Ge in Si crystal). The lattice constant of zincblende Si_1/Ge_1 superlattice has been calculated by use of the local-density approximation (LDA) [15] method; the result shows that the lattice constant of Si_1/Ge_1 superlattice is about 0.2% smaller than that of the average of bulk Si and Ge.

Table 1. Predictions of the impurity bond lengths for four systems (Si:Ge, Si:GeGe, Ge:Si and Ge:SiSi). All the bond lengths and their changes are in ångströms; ξ is the dimensionless relaxation parameter.

System	d_0	Δd_A	d_{1A}	d_{AB}	ξ	Method
Si:Ge	2.352	0.0343	2.386	2.340	0.73	BOM
	2.352	0.0353	2.387	2.340	0.75	RFM
Ge:Si	2.446	−0.0364	2.409	2.458	0.77	BOM
	2.446	−0.0353	2.411	2.458	0.75	RFM

System	Δd_1	Δd_A	d_{11}	d_{1A}	d_{AB}	ξ	Method
Si:GeGe	0.0386	0.0439	2.429	2.383	2.337	0.82	BOM
	0.0396	0.0452	2.432	2.384	2.337	0.84	RFM
Ge:SiSi	−0.0405	−0.0468	2.365	2.413	2.461	0.86	BOM
	−0.0396	−0.0452	2.366	2.414	2.461	0.84	RFM

3.2. Bond lengths

Predictions of the bond lengths around the impurity for four systems (Si:Ge, Si:GeGe, Ge:Si and Ge:SiSi) are given in table 1. It can be seen from table 1 that the local atomic structures for a single impurity and double impurities are nearly the same. According to the results obtained from BOM, for Si:Ge and Ge:Si systems, the lattice relaxations (Δd_A) are 0.0343 and −0.0364 Å, respectively. The bond length of Ge–Si is in the range of 2.386 to 2.409 Å. For the Si:GeGe and Ge:SiSi systems, Δd_1 are about 0.0386 and −0.0405 Å, respectively, so the small impurities have large relaxation. The cause of this small effect is that the bond-stretching force constant α of Si is larger than that of Ge [16]. We also find from table 1 that the bond lengths (2.429 and 2.365 Å) of Ge–Ge in Si and Si–Si in Ge are approximately equal to the bond lengths (2.446 and 2.353 Å) of crystal Ge and Si, and that the bond length of Ge–Si is in the range 2.383 to 2.413 Å. For dilute alloy systems, the probabilities of Si:Ge and Ge:Si are larger than Si:GeGe and Ge:SiSi, respectively, so the bond length of Ge–Si is mainly in the range of 2.386 to 2.409 Å. The results obtained by using the radial force model (RFM) [12, 13] are also given in table 1. It is clear that the results obtained from simple RFM are consistent with the results from BOM. However, RFM cannot give the difference between the dimensionless relaxation parameters of Si:Ge and Ge:Si, because the difference of elastic constants of Si and Ge is neglected.

Ichimura *et al* [6] have recently calculated the bond lengths in crystalline $Si_{1-x}Ge_x$ alloys by a VFF model. The dimensionless relaxation parameters ξ for Ge–Ge, Si–Si and Si–Ge bonds are about 0.6, which is consistent with the results (0.58 for Si:Ge, 0.63 for Ge:Si) obtained by Martins and Zunger [7]. However, a serious discrepancy exists between the VFF calculation and the EXAFS analysis [3]. According to our calculation, the ξ values for Ge–Ge and Si–Si are about 0.84, and for Si–Ge and Ge–Si about 0.75, respectively. Our results are closer to the results obtained by the EXAFS experiment [3]. But the difference between our results and EXAFS experimental results is also significant. In view of Mousseau and Thorpe [17], the EXAFS experimental results, i.e. ξ values for Ge–Ge and Ge–Si close to 1.0, are caused by the existence of hydrogen in the samples, and EXAFS measurements on $Si_{1-x}Ge_x$ samples are not containing hydrogen are required.

Using the fact that the long-range order is maintained, as confirmed by x-ray diffraction, the weighted-average bond length over d_{Si-Si}, d_{Ge-Ge} and d_{Si-Ge} must follow the average bond length i.e.

$$(1-x)^2 d_{Si-Si} + x^2 d_{Ge-Ge} + 2(1-x)x d_{Si-Ge} = d_0.$$

Because d_0 has a small negative deviation from Vegard's law, the bond lengths d_{Si-Si}, d_{Ge-Ge} and d_{Si-Ge} will also have small negative deviations from a linear average.

It is clear from EXAFS experiments that the relationship between the bond length d_{Ge-Ge} and the composition is nearly linear (it has a negative deviation, but it is very small). So our model for the dilute alloy can be extended to the whole range of composition by a linear interpolation of the data of the end-point materials. Our BOM results of the Si–Si, Ge–Si and Ge–Ge bond lengths in crystalline $Si_{1-x}Ge_x$ alloys are shown in figure 3 along with the experimental results obtained by the EXAFS technique [3] and the results calculated by the VFF model [6]. Our results show that the Ge–Ge, Ge–Si and Si–Si bond lengths tend to maintain their respective values: nearly 2.446 Å for the Ge–Ge bond, 2.397 Å for the Ge–Si bond and 2.352 Å for the Si–Si bond. It is clear that our results are better than that of the VFF model, and are in good agreement with the EXAFS experiment [3]. However, the Si–Si bond length in the alloy has not been investigated in the EXAFS experiment [3]. According to our results, the Si–Si bond length is in the range of 2.352 to 2.365 Å, which is close to the sum of the Si atomic radii.

From figure 3, it is clear that the three full lines are not parallel. The reason for this is that the dimensionless relaxation parameters for the four systems (Si:Ge, Si:GeGe, Ge:Si and Ge:SiSi) are different (as can be seen from table 1). This is a significant feature of our results in comparison to others [4–7, 16].

3.3. Elastic constants

The elastic constants of a Si/Ge superlattice have been calculated by use of the local-density approximation (LDA) [15] method. However, to the best of our knowledge, the elastic constants of crystalline $Si_{1-x}Ge_x$ alloys have never been measured nor calculated. Because the polarity of crystalline $Si_{1-x}Ge_x$ alloys is independent of composition x and because the average bond length d_0 changes with composition x, according to our previous work [16] under the virtual-crystal approximation (VCA), i.e. the bond length of crystalline $Si_{1-x}Ge_x$ alloys is taken as the average bond length d_0, the elastic constants B, C_{11}, C_{12} and C_{44} will vary directly as d_0^{-5}, and α and β will vary directly as d_0^{-4}. When the average bond length follows Vegard's law exactly, the trends in elastic constants as a function of composition x have a very small negative deviation from the linear average, as shown by the dotted line in figure 4. In fact, because the average bond length has a negative deviation from Vegard's law, the trends in elastic constants as a function of composition x have a positive deviation from the linear average, as shown by the full curve in figure 4. The largest deviations for elastic constants B, C_{11}, C_{12} and C_{44} are about 2.6%, and for α and β are about 2.2% at $x = 0.5$. The results for elastic constants B, C_{11}, C_{12} and C_{44} in Si_1/Ge_1 superlattice obtained by LDA are 1.15%, 2.7%, 0.9% and 3.4%, respectively. So our results are comparable with the LDA results. As we know, the LDA has proven to be an effective and useful method for studying both structural and electronic properties in many materials, and the results for elastic constants in Si and Ge crystals are in excellent agreement with the experimental results. So if we think the results for Si_1/Ge_1 superlattices are correct, our results for crystalline $Si_{1-x}Ge_x$ alloys are reasonable.

3.4. Electronic band structure

To calculate the energy band structure of crystalline $Si_{1-x}Ge_x$ alloys, we use the virtual-crystal approximation and define the Hamiltonian of the alloy in terms of the pure-crystal Hamiltonian [18]. Following Harrison [8], the weighted-average TB parameters for the alloy crystal including the on-site matrix elements, the second-neighbour and third-neighbour
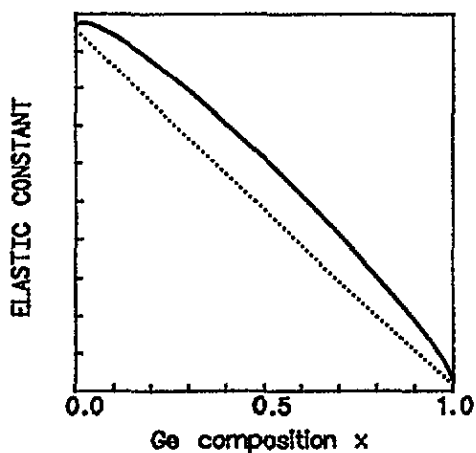
Figure 4. The trend in elastic constants as a function of composition *x*. The full curve presents our BOM result. The dotted line is the result for bond length of Vegard's law.
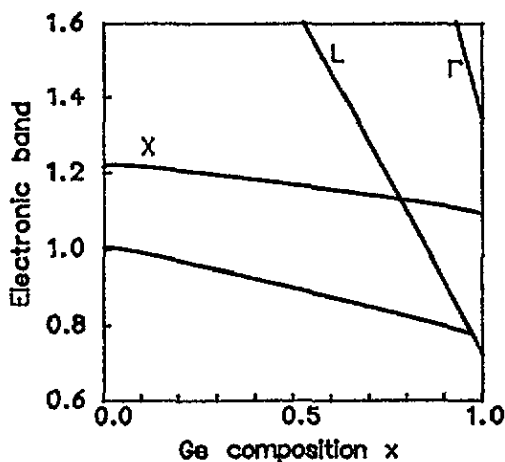
Figure 5. The conduction band edge as a function of composition *x*, where the zero of energy is taken to be the top of the valence band edge for all *x*. The crossover point occurs at $x = 0.97$.

parameters are linearly interpolated as a function of x, while the first-neighbour off-diagonal matrix elements P are interpolated assuming that Pd^2 is a constant [19]. Figure 5 reveals clearly the dependence of the minimum gap on x. We find that the crossover point from an indirect gap at L $(0.5, 0.5, 0.5)2\pi/a$ to $(0.81, 0, 0)2\pi/a$ near X $(1, 0, 0)2\pi/a$ occurs at $x = 0.97$; the bottom of the conduction band is at $(0.81, 0, 0)2\pi/a$ for $x = 0.97$ varying to $(0.85, 0, 0)2\pi/a$ for $x = 0$. Our result $x = 0.97$ is in reasonable agreement with experimental results [20], $x = 0.85$. Our results differ from those of Talwar *et al* [10], who obtain $x = 0.8$, and of Newman and Dow [21], who obtain $x = 0.75$. The small disparity of the x values is probably due to the choice of different TB schemes (the host band structure for Si and Ge is described with the TB parameters up to and including third, second [10] and first neighbours [21], respectively) and the methods adopted in evaluating the parameters by fitting different non-local pseudopotential data for the host band structures. It is nearly independent of the choice of the average bond length, i.e. using the Vegard's bond length or the bond length with a small negative deviation from Vegard's law. So although the change in bond length (i.e. small negative derivation from Vegard's law) has an effect on the structure of the energy band, the effect is very small.

4. Conclusions

The bond orbital model is used to predict the lattice constant and Si–Si, Ge–Si and Ge–Ge bond lengths in crystalline $Si_{1-x}Ge_x$ alloys. The results are compared to other theoretical and experimental results, and are found to be in good agreement with x-ray diffraction and EXAFS experiments. The lattice constant varies monotonically, and has a small negative deviation from Vegard's law. The Ge–Ge, Ge–Si and Si–Si bond lengths are close to the Pauling limit, but are composition-dependent; they also have small negative deviations from linear averages. The trends in elastic constants as a function of composition x have a positive deviation from the linear average. The bottom position of the conduction band is

changed with the variation of x. The effect of change in average bone length on electronic band structure is very small.

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