PHYSICAL REVIEW B VOLUME 54, NUMBER 7 15 AUGUST 1996-I

Tight-binding models for compounds: Application to SiC

James L. Mercer
Sandia National Laboratories, Albuquerque, New Mexico 87185-1421

(Received 11 January 1996; revised manuscript received 29 March 1996)

A simple method for combining single element, tight-binding models into models for compounds is investigated. Using parameters fitted to silicon, carbon, indium, and phosphorous band structures, test cases for SiC and InP band structures show excellent results, especially when on-site energy shifts are included through the use of intra-atomic matrix elements. Two long-ranged silicon and carbon models are developed and combined to test total energy results for silicon carbide. Total energies and band structures for the compound system are in very good agreement with first-principles results, indicating that models for compound systems may be readily produced from properly developed single element models. [S0163-1829(96)06631-3]

I. INTRODUCTION

Tight-binding (TB) models have proven to be very useful for the study of both semiconductor and metallic systems, especially in systems which are too large to study via *ab initio* techniques. A number of surface relaxations, clusters, and bulk defects have been accurately analyzed via parametrized, two-centered, tight-binding (P2CTB) models.[1–6] Despite the successes of TB techniques, the method has some notable limitations. One of the more important of these limitations is the treatment of compound or multielemental systems. Since most TB models are developed for systems composed of a single element, there is no specific path for using these models in compound systems. In fact it appears unknown as to how much information is transferable from a single element (SE) model to a model for a compound system. Do SE models have only limited utility in making compound models or can models for compound systems be developed directly from SE models? How transferable would such models be? These questions need to be addressed if TB models are to be developed and used as successfully in the compound environment as they have been in single element systems.

We present here a simple method of using models developed for SE systems to produce models for compound systems. By making accurate SE models which incorporate intra-atomic or crystal field parameters,[7–15] a simple averaging of band structure parameters and repulsive energy terms results in a reasonable band structure and total energy model for a compound system. While the most important interaction terms are the interatomic parameters, the intra-atomic terms provide a fine tuning mechanism to help describe shifts in on-site energies, due to the location and element type of the neighboring atoms. This fine tuning by the intra-atomic terms has been shown to be important in SiO_2 band structure studies[13] and in silicon total energies,[15] but has not previously been used in total energy models for compound systems or for development of such models from SE models.

Previous attempts at modeling compound systems (within P2CTB) generally fall into two categories. The first category[16] relies almost completely on the interatomic parameters to provide different values for interactions between like and unlike atoms. Using SiC as an example, the separate inter-atomic parameters would describe interactions between Si-Si, Si-C, and C-C. Additionally, the repulsive potential, which together with the electronic band structure energy gives the total energy, will likely also change depending on whether the interaction is between Si-Si, Si-C, or C-C. The on-site energies are held constant, presumably at some level which would reflect the correct energies for a particular arrangement of neighboring atoms.

Holding the on-site energies constant presents a drawback to the models. First, the on-site energies, while often referred to as atomic energies, are actually a combination of atomic energies and terms which depend on the arrangement and type of neighboring atoms. As such, the on-site energies could change noticeably with only moderate changes in the neighboring atoms, and failing to make allowances for this fact can present a significant limitation to transferability.[17,18,15] Even for a single element model, the effect of allowing the on-site energies to vary with changes in the neighboring atom locations is very noticeable.[15] For the more complex compound system, not only can the intra-atomic terms be important, but in some cases such as SiO_2 band structures can be crucial to the understanding of the origins of various band shifts.[13]

The other common approach to compound tight-binding models allows for changes in the on-site energies, usually as a function of charge transfer, but sometimes as a function of the system strain.[19,20,14,4] Since the on-site energies have a large affect on charge flow, they represent a straightforward way of controlling charge flow or of being determined from charge flow constraints. In these charge dependent models, the charge distribution must be solved in a self-consistent manner. Some of these charge flow models are, therefore, referred to as self-consistent tight binding models (SCTB). the A drawback to these models is that the repeated diagonalizations (or equivalent technique) needed to determine the charge density can seriously reduce the time advantage that tight binding has over *ab initio* methods. More importantly, the SCTB models do not parametrize the on-site interactions with respect to atomic position and atomic type, but instead use charge flow criteria to effectively solve for the shifts in the on-site energies. Yet, P2CTB has had much success with parameterizing the interatomic interactions based on atomic positions and then transferring these interaction parameters

© 1996 The American Physical Society

to systems of interest. Therefore, it would seem equally valid to parametrize the shifts in the on-site energies in terms of the intra-atomic interactions and then use these parameters, rather than self-consistently ''solve'' for them.

The following section outlines the basic TB framework to be used here and suggests a simple method for describing compound interactions based on single element information. This method is then used to show that compound band structures for SiC and InP can easily be reproduced from parameters found by fits to individual band structures of silicon, carbon, indium, and phosphorus. Finally, the silicon and carbon band structure fits are developed into total energy models for each element, and the models are combined to study SiC. It will be shown that the band structures and total energies for SiC are in good agreement with *ab initio* data, and indicate that compound models can be developed almost directly from single element models.

II. METHOD

The cohesive energy E_c in a two centered TB model as used here is

$$E_c = E_{\mathrm{bs}} + E_{\mathrm{rep}} - E_0, \tag{1}$$

where E_0 is the energy of an isolated atom. E_{bs} treats the electron-electron and electron-ion interactions and E_{rep} is a repulsive potential that accounts for the ion-ion interaction and for the overcounting of the electron-electron interaction. E_{rep} is usually written as

$$(E_{\mathrm{rep}})_i = \sum_j \Phi(r_{ij}). \tag{2}$$

Here, Φ is a two-body potential.

The value of E_{bs} is found from summing over the occupied eigenvalues of the system,

$$E_{\mathrm{bs}} = \Sigma \varepsilon, \tag{3}$$

where the states of the system are a linear combination of the atomic orbitals,

$$|\Psi_n\rangle = \Sigma_{i\alpha} a_{n,i\alpha} |i\alpha\rangle. \tag{4}$$

Here the notation $i\alpha$ refers to atom i's α orbital.

The Hamiltonian matrix elements are given by

$$\langle i\alpha|H|j\beta\rangle, \tag{5}$$

with

$$H = T + \Sigma_i V_i. \tag{6}$$

T is the kinetic energy operator and V_i is the core potential from atom i. In the two center approximation, the number of unique centers in $\langle i\alpha|$, $|j\beta\rangle$, and H is limited to two. The interatomic interactions are

$$H_{i\alpha,j\beta} = \langle i\alpha|T + V_i + V_j|j\beta\rangle. \tag{7}$$

These terms are frequently parametrized by fitting to empirical or first-principles data according to interaction type and distance, while the angular contributions are taken from Slater and Koster.[21] In an orthogonal sp^3 basis for example, we would have $H_{ss\sigma}(r_{ij})$, $H_{sp\sigma}(r_{ij})$, $H_{pp\sigma}(r_{ij})$, and $H_{pp\pi}(r_{ij})$.

Additional terms relating to the free, neutral atom are written as

$$\alpha\beta_0 = \langle i\alpha|T + V_i|i\beta\rangle. \tag{8}$$

Since these terms have no dependence on neighboring atoms, they are constant with respect to changes in the neighboring atoms. For a sp^3 basis, $\alpha\beta_0$ reduce to s_0 and p_0, since the atomic orbitals are orthogonal to each other.

The third set of parameters, the intra-atomic terms, are written as

$$I_{i\alpha,i\beta;j} = \langle i\alpha|V_j|i\beta\rangle. \tag{9}$$

As with the interatomic terms these are parametrized as a function of interaction type and distance, $I_{ss\sigma}(r_{ij})$, $I_{sp\sigma}(r_{ij})$, $I_{pp\sigma}(r_{ij})$, and $I_{pp\pi}(r_{ij})$. Chadi has shown that the angular dependence for these terms is the same as for the interatomic terms.[12]

The s on-site energy E_s is, then,

$$(E_s)_i = s_0 + \sum_j I_{ss\sigma}(r_{ij}) \tag{10}$$

and the p_x on-site energy E_{p_x} is written as

$$(E_{p_x})_i = p_0 + \sum_j [l_{ij}^2 I_{pp\sigma}(r_{ij}) + (1 - l_{ij}^2) I_{pp\pi}(r_{ij})], \tag{11}$$

where l_{ij} is the direction cosine to the x axis. For E_{p_y} or E_{p_z}, the direction cosine m_{ij} or n_{ij} is substituted for l_{ij} in the above formula. Being to some extent embedding terms, these parameters represent the effect of the ionic field of the crystal on the orbitals of atom i and are sometimes referred to as crystal field terms. These terms have been shown to be important in understanding the origins of band shifts in SiO_2 (Ref. 13) and in developing a simplified, transferable, total energy model for silicon.[15] By not explicitly including the intra-atomic terms in a parameterization, we force the interactions they represent to be included in the remaining terms. By treating these interactions separately, transferability both within the polytypes of an element crystal and from single element to compound systems should increase.

Once a parameterization for the H, I, s_0, and p_0 terms has been obtained, a model can be applied to systems of interest. However, many systems of interest are multielemental systems which require parameterizations for like element interactions as well as unlike element interactions. The like element interactions could be taken from SE models. The remaining problem then is to describe the interatomic and intra-atomic terms, such as

$$\langle i\alpha^A|V_j^B|j\beta^B\rangle \tag{12}$$

and

$$\langle i\alpha^A|V_j^B|i\beta^A\rangle, \tag{13}$$

where the superscript refers to the element type of atom *i* and *j*.

Here, we will test a simple way of approximating these terms by averaging the single element terms, i.e.,

$$\langle i\alpha^A|V_j^B|j\beta^B\rangle=(\langle i\alpha^A|V_j^A|j\beta^A\rangle+\langle i\alpha^B|V_j^B|j\beta^B\rangle)/2. \quad (14)$$

Similarly, the intra-atomic terms could be approximated from

$$\langle i\alpha^A|V_j^B|i\beta^A\rangle=(\langle i\alpha^A|V_j^A|i\beta^A\rangle+\langle i\alpha^B|V_j^B|i\beta^B\rangle)/2. \quad (15)$$

The repulsive term used for the compound interaction will also be an average of the single element repulsive terms.

This simple approximation can be motivated from a couple of considerations. First, we can consider the overlap of the orbitals that gives rise to the interactions that are parametrized. For a system such as tetrahedral silicon, the orbital overlap is equally balanced between the two orbitals. In a simple two-dimensional picture of this system, the orbitals (especially *s* orbitals) can be viewed as overlapping circles of equal size. If we replace some of the silicon atoms with carbon atoms, then we have the overlap of two differing sized orbitals which would be like the overlap of two differing sized circles, say circle *A* and circle *B*. If the circles are close to the same size (differ by about 20%), the amount of overlap *AB* is very close to the average of the overlaps of equal circles, i.e., $(AA+BB)/2$. As the difference in the size of the circles increases, the error in the averaged overlap versus the actual overlap increases. Thus, for the overlap of spherical *s* orbitals which differ only moderately in size, this approximation is likely to be very good. For *p* and *d* orbitals, being more ellipsoidal, the approximation is likely to be valid only for smaller differences in size. However, charge transfer would likely improve the approximation because smaller orbitals are generally associated with more electronegative elements. As the smaller orbitals draw a charge from the other atom's orbitals, they will likely increase in size while the other atom's orbitals decrease in size, thereby making the differing orbitals more similar in size. Thus, the approximation would actually remain effective for larger differences in orbital size provided there was also a charge flow that tended to make the differing orbitals more similar in size.

Finally, recent work has shown that single element, TB-LMTO parameters can readily be combined for the study of compound systems.[18] This fact, the authors noted, was in contrast to ordinary SE P2CTB band structure parameters, which failed to reproduce certain compound interactions such as densities of states. An empirical shift of the SE P2CTB on-site parameters resulted in a much improved density of states. The work presented here removes the need for an empirical shift by including the intra-atomic interactions.

III. RESULTS AND DISCUSSION

A. SiC and InP band structures

In order to make an initial evaluation of the above method, two simple band structure test cases were performed, one for SiC and the other for InP, both in the zinc-blende structure. First, TB parameters for Si, C, In, and P were fitted to *ab initio* band structures of these elements in the cubic diamond phase at the SiC or InP lattice constant. These single element parameters were then used to construct the band structures for the compounds using the above averaging technique. The *ab initio* data were obtained from density functional theory, local density approximation, pseudopotential calculations.[22–25] For silicon and carbon, 27 *k* points were fitted. These *k* points are Γ, X, L; the ten special *k* points needed for a well converged band energy (in diamond); and fourteen *k* points which give a reasonable description of the band structure. For indium and phosphorus, only the last fourteen *k* points were used (see Fig. 1).

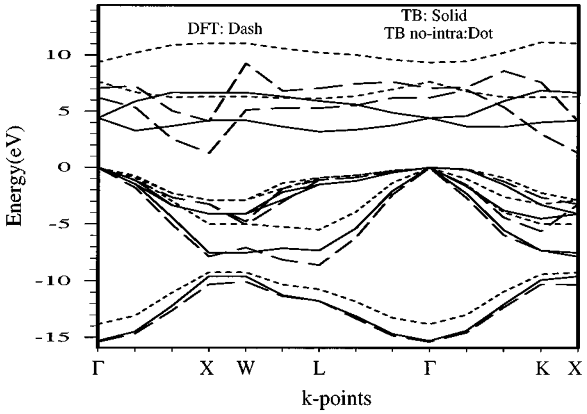

FIG. 1. A comparison of tight binding and *ab initio* band structures for SiC. The tight-binding parameters for the SiC interactions were obtained from averaging the Si-Si and C-C interaction parameters. For one TB calculation (solid), the intra-atomic terms were included while for the other TB calculation (dotted), the intra-atomic terms were left out, thereby freezing the on-site terms.

The fits were for one volume or lattice constant and included four valence bands and the lowest conduction band. Each fit, being limited to first nearest neighbor (nn) orthogonal interactions and *s* and *p* orbitals, involves the parameters $H_{ss\sigma}$, $H_{sp\sigma}$, $H_{pp\sigma}$, $H_{pp\pi}$, E_s, and E_p. The intra-atomic parameters ($I_{\alpha\beta\gamma}$), and atomic values (s_0 and p_0) are embedded in E_s and E_p. Estimates of s_0 and p_0 for each element were loosely based on the atomic eigenvalues created during the pseudopotential generation. $I_{pp\pi}$ was assumed to be $\frac{1}{2}$ of $I_{pp\sigma}$ (as had been found previously to be acceptable for silicon[15]) in order to break down E_p into p_0, $I_{pp\sigma}$, and $I_{pp\pi}$. Due to symmetry, the sum of the angular prefactors for $I_{sp\sigma}$ is zero in both the single element and compound cases. All of the parameters are listed in Table I. It should be noted that the large values for the intra-atomic elements is possibly due to kinetic energy contributions from overlapping orbitals.[26–28] Since no overlap parameters are included, some of their effect could be manifested in the intra-atomic terms. This assumption is supported by the fact that the intra-atomic parameters tend to rise very rapidly as the lattice constant decreases.

With all of the parameters determined, the band structures of SiC and InP were then calculated and compared to *ab initio* band structures. The results, as seen in Figs. 2 and 1, are quite good. The valence bands are extremely well described with much of the error actually coming from the fits to the individual elements rather than from the simple combination of parameters. For example, the individual element

TABLE I. First nn parameters (in eV) for Si, C, In, and P. The first six parameters were fitted, while the remaining six were derived from E_s and E_p (see text).

	Si	C	In	P
E_s	7.1	−1.8	2.7	−4.0
E_p	15.1	5.7	9.1	3.4
$H_{ss\sigma}$	−2.71	−2.17	−2.06	−1.20
$H_{sp\sigma}$	2.29	2.57	2.08	1.70
$H_{pp\sigma}$	3.10	2.85	2.88	1.82
$H_{pp\pi}$	−1.92	−1.0	−1.38	−.59
s_0	−5.0	−9.0	−5.4	−11.2
p_0	1.4	−3.0	0.0	−4.0
$I_{ss\sigma}$	3.02	1.80	2.02	1.80
$I_{sp\sigma}$	0.00	0.00	0.00	0.00
$I_{pp\sigma}$	5.14	3.26	3.41	2.78
$I_{pp\pi}$	2.57	1.63	1.71	1.39

fits at the k- point X contained an error similar to that shown in Figs. 2 and 1. Additionally, from X to W the TB bands are seen to be flat, while the *ab initio* bands show some curvature. This flatness, however, is due to a first nn model and is therefore present from the initial fittings and will continue to be present as long as the models remain first nn's only.[29] The conduction bands are not as well described as the valence bands, because only one conduction band versus four valence bands were fitted. Improvement in the conduction bands should come with an improvement in the basis used. Good results were also obtained for the ten special k points showing that k points which are not along high symmetry directions are also well described. For comparison, the plot for SiC also has a band structure which used averaged interatomic values, but which froze the intra-atomic terms at their single element value. The poor quality of this third band structure illustrates the importance of shifting the on-site energies.

It would be instructive to fit SiC and InP as compounds, using only one set of $H_{\alpha\beta\gamma}$, but allowing each element to have its own E_s and E_p. For the InP compound fit, $H_{ss\sigma}$, $H_{sp\sigma}$, $H_{pp\sigma}$, and $H_{pp\pi}$ are -1.56, 1.89, 2.32, and -1.06 eV, respectively. Comparing these to the averaged values -1.63, 1.89, 2.34, and -0.98 eV, we see that the averaging is actually quite good. As for the intra-atomic values, the comparison is more difficult since many assumptions can go into determining these parameters. However, comparing the InP (E_s,E_p) fitted values, In:(1.98,8.63), P:(-3.27,4.39), to those in Table I, it can be seen that phosphorus tended to decrease indium's E_s and E_p; while indium did the opposite for phosphorus. These shifts are similar to those given by the intra-atomic terms from the single element fits.

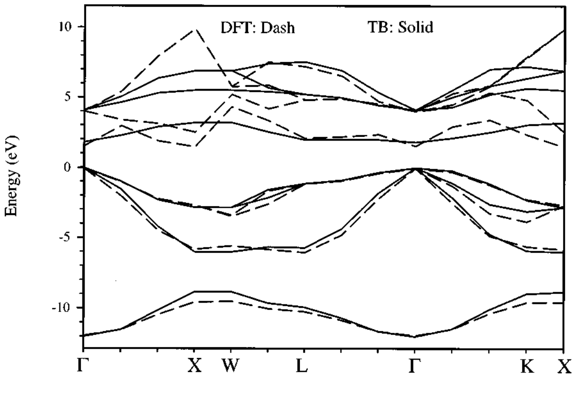

FIG. 2. A comparison of tight-binding and *ab initio* band structures for InP. The tight-binding parameters for the InP interactions were obtained from averaging the In-In and P-P interaction parameters.

Taking the averaged values for H and allowing the E's to be fit produces a fitting error only slightly larger than the above fit, indicating that the set of averaged values are virtually as good as fitted values. If now the E's are held at their atomic values, effectively setting all I parameters to zero, and only the H's are allowed to be fit, the H values are -1.50, 1.84, 1.78, and -0.98 eV, respectively. With the exception of $H_{pp\sigma}$ these values are similar to the compound fit; however, the error for this fit has increased by more than 30% over the compound fit. This rise in error indicates that shifts in the on-site energies, as could be determined by intra-atomic parameters, provide a useful fine tuning to the modeling.

For the SiC compound fit, $H_{ss\sigma}$, $H_{sp\sigma}$, $H_{pp\sigma}$, and $H_{pp\pi}$ are -2.72, 2.65, 3.02, and -1.87 eV, respectively. While the E's followed the same trends as were seen in InP, the averaged values of H, -2.44, 2.43, 2.98, and -1.46 eV, do not agree with the compound fit nearly as well. This deviation could, perhaps, be expected since the difference in size between the silicon and carbon orbitals ideal range (as indicated by the difference in silicon and carbon lattice constants) is quite large. In order to determine the error from using these values, the E values were fitted while the H values were held at the averaged values. For this fit, the error was less than 10% more than the fitting error in the compound fit, indicating that the averaged values of H are actually a reasonable set of parameters.

Next, the values for E were set to the atomic values (again, equivalent to setting the I parameters to zero) and the H values were fitted to SiC. The values for $H_{ss\sigma}$, $H_{sp\sigma}$, $H_{pp\sigma}$, and $H_{pp\pi}$ that resulted were -2.44, 2.25, 1.20, and -0.68 eV. The deviations from the values for the compound fit have increased greatly and the error for this fit has now doubled. This increased error indicates not only that the averaged values are very good by comparison, but also that for SiC shifts in the on-site energies are more important than they were in the InP case.

B. C and Si Models

This section details two orthogonal, SE P2CTB models for silicon and carbon. These models will be necessary to make a more thorough test of the SE to compound method. As above, the models were fit to *ab initio* band structures and total energies for each element in the diamond structure at a number of volumes. For Si, 20 volumes (45% – 190% of the ideal tetrahedral volume, corresponding to first nn distances of 1.8 to 2.9 Å) were used, while for carbon 31 volumes (45% – 250% of the ideal tetrahedral volume, corresponding to first nn distances from 1.2 to 2.1 Å) were used.

Once again, a fit to the four valence bands and the lowest conduction band for the 27 k points (mentioned above) was performed at each volume. The basis is still limited to s and p orbitals making the fitted matrix parameters $H_{ss\sigma}$, $H_{sp\sigma}$, $H_{pp\sigma}$, $H_{pp\pi}$, E_s and E_p. Initially, first and second nearest neighbor interactions were allowed. Once an approximate distance dependence had been worked out from these parameters, it was generalized to cover all interactions within the specified cutoff region (< 4.5 Å). The fitting was then performed again until reasonable results were obtained. A similar fitting process was performed for Φ and the $I_{\alpha\beta\gamma}$ parameters. The assumptions mentioned in the previous subsection were used to help separate the $I_{\alpha\beta\gamma}$, s_0, and p_0 parameters from E_s and E_p.

Due to the wide range of volumes, a few compromises had to be made in the development of the parameters. Additionally, for carbon, the desire to reproduce the graphite band structure required further compromises. The origin of most of the compromises was due to a three-body or, more specifically, a shell effect on the parameters. For example, beyond the first nn shell the $ss\sigma$ and $sp\sigma$ interactions were nearly zero. Similarly, beyond the second nn shell, $pp\sigma$ and $pp\pi$ were roughly zero. However, since the bond lengths and thus the distance to the shells were changed so much, neighboring shells overlapped (for silicon, first nn shell: 1.8 – 2.9 Å; second nn shell: 2.9 – 4.8 Å; and third nn shell: 3.4 – 5.6 Å) and created regions where parameters would be both zero and nonzero depending on the shell. Some sort of three-body cutoff function or fully three centered terms could have been used, but it was best to stay completely within the two-center approximation for now. Also, while it has been shown before that a fit to diamond data alone is nearly sufficient to make a model for a number of structures,[15] it was considered expedient and judicious to make use of suggestions about the relative strengths and distance dependence of parameters obtained from fits to other polytypes of silicon or carbon.

The resulting band structures of carbon and silicon for all of the volumes are reasonably well described. Since they are fitted and monoelemental, the carbon and silicon band structures are better than the band structures shown in Figs. 1 and 2. The largest error in the fit tended to be in the conduction band, which is to be expected since only one conduction band, versus four valence bands, was fit. Despite this error, the low points in the conduction band are reasonably close to those of the *ab initio* bands. The graphite band structure was also reasonably well described although less accurately than the diamond band structure. The main improvement in the graphite band structure over a first nn carbon model[5] is due to the inclusion of interplanar interactions, which splits the each of the degenerate lower bands into separate bands.

A plot of the fitted parameters is shown in Figs. 3 and 4, while the Appendix discusses the formula and lists the parameters. Although not shown, E_s and E_p had very large slopes.[15] As mentioned above, some of this slope could be due to kinetic energy terms from overlapping orbitals.[26–28] Since the slope of the E_s term is based on a two-body interaction and is somewhat arbitrary from a tight-binding point of view, it can be removed and put into the repulsive term. However, this can only be done provided an equal amount is removed from E_p, thus maintaining the $E_p - E_s$ separation, and provided the correct (or at least reasonable) contribution from the intra-atomic parameters is left in both E_s and E_p.

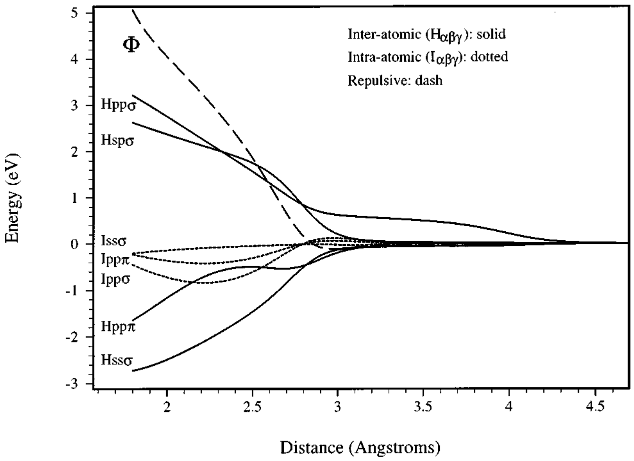

FIG. 3. The silicon parameters used in the models are plotted versus interatomic spacing.

Figure 5 shows a comparison of Si total energies obtained with the present model and from first-principles calculations.[30–33] Overall the results are very good, especially for the lower energy, lower coordinated structures. One notable feature is the energy of the relaxed[34] clathrate structure, which is about a 0.013 eV/atom above that of the diamond structure. This energy difference is only about half of the difference of *ab initio* calculations.[35] However, this result is quite good for an orthogonal model making it agree, in this instance, more with a nonorthogonal model[3] than with other orthogonal models that give an incorrect ordering of diamond and clathrate.[36,37]

The more highly coordinated structures tend to show increasing amounts of error. While the cubic metals (sc, bcc, and fcc) have the correct ordering, they are all too low in energy. Also, the volume per atom for these structures is too high and becomes worse as the nearest neighbors move outward (or as the coordination increases). These errors of energy and volume, while noticeable, are less than or comparable to the results of other TB models[4,15,3,38] and could be corrected (were it important) with small changes in the repulsive and electronic parameters. In the future, these structures could be included in the fitting of all of the parameters.

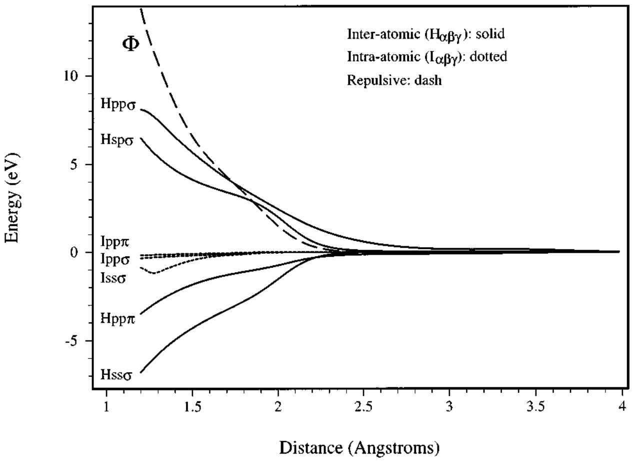

FIG. 4. The carbon parameters used in the models are plotted versus interatomic spacing.

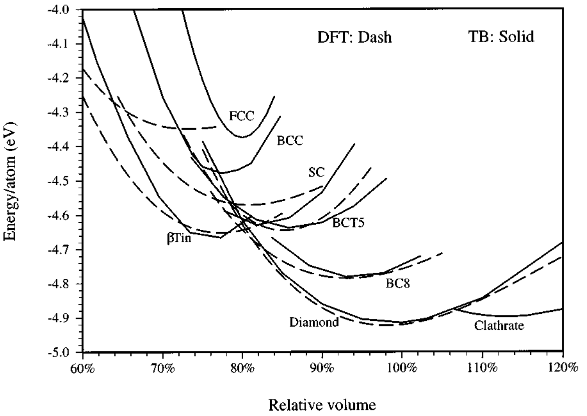

FIG. 5. A comparison of tight-binding and *ab initio* total energies for a number of silicon polytypes.

The dimer Si_2, unfortunately, was not well described, having a bond length that came out too short [2.01 versus 2.23 Å (Ref. 39)]. In fact, the Si_2 total energy is very flat in this region. For the diamond structure, this same region (2.0–2.2 Å) for the first nn shell corresponds to the third nn shell crossing from nearly zero to nonzero values. Thus, this error is a reflection of a small error in the description (for diamond) of this first nn region and made worse in Si_2, because it is the only interaction. Results for the zone edge phonons were more reasonable with LTO(Γ), TA(X), TO(X), and LAO(X) being 16.3, 4.0, 15.0, and 12.2 THz, respectively, as compared to the *ab initio* values[40] of 15.2, 4.45, 13.5, and 12.2 THz, respectively. The result for the shear modulus $c_{11}-c_{12}$, 0.64×10^{12} erg/cm^3, is low compared to an *ab initio* value of 0.98×10^{12} erg/cm^3.[41] This low shear modulus value is common among orthogonal tight-binding models which have reasonable phonon frequencies.[42]

The carbon model, Fig. 6, gives reasonable values for the linear chain, graphite, diamond, and BC8 structures.[43,5] The results for the more highly coordinated forms of carbon are acceptable although like silicon they have some error mostly in the minimum volume, but also in the minimum energy. The carbon clathrate structure is about a 0.01 eV/atom higher in energy than the diamond structure. As for silicon, this result is much smaller than the result predicted by *ab initio* tight-binding calculations,[36] but still represents an improvement since at least one other orthogonal tight-binding model[5] gives an incorrect ordering.[36] The carbon dimer bond length of 1.28 Å is close to the first-principles value of 1.24 Å.[44] Additionally, the relaxed fullerene (C60) agreed well with *ab initio* calculations.[45] Also in agreement with first-principles calculations, the fullerene dimer (C_{60}-C_{60}) is predicted to be bound, but the binding energy of 0.15 eV/dimer is only a fraction of the *ab initio* value of 1.2 eV/dimer.[45] The center to center distance for this dimer is roughly 9.5 Å compared to the *ab initio* value of 9.1 Å.

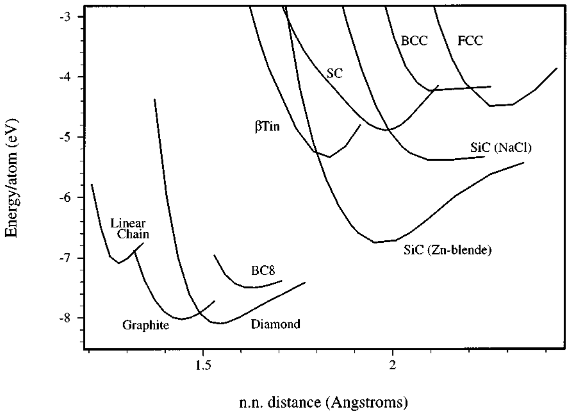

FIG. 6. Tight-binding total energies for a number of carbon and SiC polytypes. All structures are for carbon unless otherwise noted.

The lattice dynamical properties for carbon were generally good. The $c_{11}-c_{12}$ shear modulus for diamond was 8.8×10^{12} erg/cm^3, in very good agreement with the *ab initio* value.[46] The phonons LTO(Γ), TA(X), TO(X), and LAO(X) were 34.2, 25.6, 30.9, and 39.3 THz, respectively. These phonon frequencies are in reasonable agreement with the corresponding *ab initio* values.[47]

Despite a few shortcomings, the silicon and carbon models are quite reasonable. For the present purposes, modeling SiC, the models should be quite sufficient. The noted limitations stem primarily from the requirement of fitting such a large range of volumes. Additionally for the carbon model, the requirement that the graphite band structure be described (to some extent) was achieved although this is likely the reason for the low dynamical values.

C. The SiC model

The models for silicon and carbon are now combined to simulate SiC. As in the earlier test cases, zinc-blende SiC should represent a good test of the method since the first nn shell of each atom is replaced with atoms of the other type. However, one remaining adjustment, the relative position of the atomic energies s_0 and p_0 for the two elements, is needed. A small shift of silicon atomic values relative to the carbon atomic values makes only a small difference in the band structure. From a fitting viewpoint, a number of values are equally valid. However, the SiC total energy (shown in Fig. 6) depends strongly on the relative atomic values and from this total energy information it is possible to determine the correct relative shift. Using these values, the models were then used to obtain the energy of SiC in the NaCl structure. The energies for the two SiC structures are well described although the NaCl form is about 0.3 eV/atom higher in energy than the first-principles results indicate.[48] While this energy difference is noticeable, it is a significant improvement over a SiC SCTB model[20] which could not reproduce, within a 1.5 eV/atom, the energies of both the zinc-blende and NaCl structures.

The bulk modulus is 2.4 Mbar, in close agreement with the theoretical value of roughly 2.24 Mbar.[49,50] The phonons are also reasonably described as TO(Γ), TA(X), TO(X), and LAO(X), being 21.7, 7.0, 21.7, and 21.0 THz also in good agreement with *ab initio* calculations.[49,50] The shear modulus ($c_{11}-c_{12}$) is 1.1 Mbar for a distortion of $\epsilon = -0.0004$. This value is low compared with the first-principles result[50] of 2.56 Mbar and given the good bulk modulus it indicates that c_{12} is very close in value to c_{11}. Unlike the silicon and carbon values, the shear modulus for SiC changes values more readily with different strain amounts; for somewhat larger strains the value drops, while for strains greater than $|\epsilon| = 0.01$ the modulus increases. Further investigation suggests that the possible origin of this behavior is the silicon model, which could be improved by allowing for three center and overlap induced effects.

Figure 7 shows the TB band structure compared to the *ab initio* band structure for zinc-blende SiC (with a nn distance of 1.92 Å). The band structure is quite reasonable although it is not as good as in Fig. 2. These differences between the two TB band structures (Figs. 2 and 7) are, in part, indicative of the compromises made in developing the single element, total energy models. It should be noted that the present band structure is still much better than the band structure (in Fig. 2) which used frozen on-site terms. Had the present model also held the on-site terms constant, its band structure would be significantly worse.

The ionicity of the model can be calculated using Phillips' ionicity measure.[51] This method compares the size of the gaps from the single element (completely covalent) and compound (partially ionic) band structures. The present TB models produce an ionicity of 0.15 for zinc-blende SiC in reasonable agreement with 0.18 reported by Phillips and Van Vechten.[51] The Mulliken charge[52] flow given by the model is roughly 1.7 electrons from the silicon to the carbon atoms. This charge flow appears quite large, especially compared to the SCTB value of 0.45 electrons.[20] However, a recent calculation which projected an *ab initio* plane-wave basis onto an atomic orbital basis also showed a charge transfer of 1.7 electrons.[53] Similarly, a Hartree-Fock calculation gave the charge transfer in zinc-blende SiC as 1.8 electrons.[54]

As a final test, the energy of the the zinc-blende (3C) structure was compared to the relaxed wurtzite (2H) structure. The present model found zinc-blende to be 9 meV lower in energy than wurtzite. *Ab initio* values give the zinc blende to be lower by 2–5 meV.[48,55,50] While the present result is roughly twice the *ab initio* values it is better than the SCTB model, which predicts wurtzite to be lower than zinc-blende SiC by about 1 meV.[20]

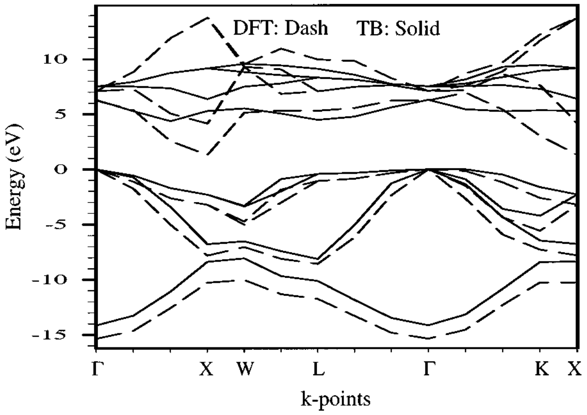

FIG. 7. A comparison of tight-binding and *ab initio* band structures for SiC. The tight-binding parameters were taken from the silicon and carbon models. Again, compound interactions were an average of single element interactions.

IV. CONCLUSION

A simple method is presented, which allows for the development of compound tight-binding models from single element models. This method makes use of the fact that the interatomic parameters for a compound (unlike-atom) interaction are close to the average of the parameters for the corresponding like-atom interactions. Use of intra-atomic terms tends to make the averaging even better by properly separating interactions typically forced into the interatomic parameters and by allowing for shifts in the on-site energies. Simple trial band structures indicate that single element parameters when properly developed can be as effective as parameters which are fitted specifically to one particular compound system. Total energy calculations for SiC, based almost solely on single element models developed for silicon and carbon, give good results for the zinc-blende, NaCl, and wurtzite energies. These total energy results indicate that these models can be even more accurate than previous mod-

TABLE II. Constants for the interatomic terms.

		Si				C		
	$ss\sigma$	$sp\sigma$	$pp\sigma$	$pp\pi$	$ss\sigma$	$sp\sigma$	$pp\sigma$	$pp\pi$
x_1	9.08663	−1.42384	−7.40396	61.3467	−0.639531	8.27429	−17.7028	8.19099
x_2	−17.0701	4.39884	12.7754	−69.7544	1.26939	−14.4521	49.6836	−6.82122
x_3	6.26870	−1.06212	−4.30467	20.6038	−4.72901	10.03216	−34.8750	−0.873676
x_4	0	0	0	−2.34284	0	0	0	−0.845502
x_5	0	0	0	0	0	0	8.29007	0
x_6	0	0	0.542991	−0.579387	0	0	−32.3941	−0.167200
x_7	−0.124956	0.0695169	0.330383	0.767627	0.030560	0.110718	32.2915	−0.00827222
b_1	0	0	0	0	0	0	−1.0	0
b_2	0	0	0	0	0	0	−10.0	0
b_3	0	0	0	0	0	0	1.2	0
		Si				C		
$f_1:a_1$		10.0				10.0		
$f_1:a_2$		2.8				2.05		
$f_2:a_1$		7.0				7.0		
$f_2:a_2$		4.0				3.5		

TABLE III. Constants for the intra-atomic terms.

	Si			C		
	$ss\sigma$	$pp\sigma$	$pp\pi$	$ss\sigma$	$pp\sigma$	$pp\pi$
x_1	−1.0	−76.6971	−38.4387	−17.833	−0.5	−0.25
x_2	−2.0	111.9801	56.0059	22.7058	0	0
x_3	1.0	1.96321	1.59764	−8.3577	0	0
x_4	8.25	−0.725929	−1.32833	0.667	0	0
x_5	2.8	14.0004	7.01702	−0.3334	0	0
x_6	−0.03	−246.407	−123.231	1.0	0	0
x_7	−40.0	223.536	112.314	50.0	0	0
x_8	3.1	8.23	8.23	1.23	0	0
x_9	0	2.31	2.31	0	0	0
a_1	0	0	0	−2.0	−2.0	−2.0
a_2	0	0	0	1.0	1.0	1.0
b_1	0	0	0	20.0	20.0	20.0
b_2	0	0	0	1.8	1.8	1.8

els fitted directly to SiC. Finally, the band structure results and total energy results indicate that compound models may be readily produced from models developed only for single element systems.

ACKNOWLEDGMENTS

I would like to thank Dr. M.Y. Chou, Dr. D.J. Chadi, Dr. S. Wei, Dr. E.B. Stechel, Dr. M. Menon, and Dr. A.A. Quong for their invaluable help and comments. I would also like to thank Dr. D.R. Jennison and Dr. J.D. Kress not only for a critical reading of this paper, but also for their helpful comments. This work was supported DOE under Contract No. DE-AC04-94AL8500 and in part by the Office of Basic Energy Sciences, DOE.

APPENDIX

This appendix lists the constants and the formulas for the silicon and carbon total energy models. As mentioned above, a number of factors led to compromises having to be made. The emphasis in formulating the parameters was on the accurate reproduction of band structures, rather than making simple formulas. As such, some of the formula are quite lengthy. Relaxing any of the numerous criteria enforced in the fitting could lead to a noticeable simplification of the formula.

The atomic energies are ${}^{\mathrm{Si}}s_0=-5.0$, ${}^{\mathrm{Si}}p_0=1.4$, ${}^{\mathrm{C}}s_0=-9.0$, and ${}^{\mathrm{C}}p_0=-3.0$.

The interatomic terms for silicon and carbon follow the same formula:

$$H_{\alpha\beta\gamma}(r)=\left\{\left[x_1+x_2\left(\frac{r_0}{r}\right)+x_3\left(\frac{r_0}{r}\right)^2+x_4r^2\right]\Big/ f_1(r)+x_5+x_6\left(\frac{r_0}{r}\right)+x_7\left(\frac{r_0}{r}\right)^2\right\}\Big/ f_2(r)+b_1\exp[b_2(r-b_3)]. \tag{A1}$$

The functions $f_1(r)$ and $f_2(r)$ are

$$f_{1,2}(r)=1+\exp[a_1(r-a_2)]. \tag{A2}$$

For silicon, r_0 is 2.35 Å and for carbon, 1.5445 Å, while the remaining constants are found in Table II.

The formula for the intra-atomic terms vary considerably: for Si we have

$$ss\sigma=\{(x_1\exp[x_2(r-x_3)]\}/\{1+\exp[x_4(r-x_5)]\}+x_6\exp[x_7(r-x_8)^2], \tag{A3}$$

while $sp\sigma$ is 0. $pp\sigma$ and $pp\pi$ have the same form

$$(x_1+x_2r+x_3/r+x_4/r^2+x_5/r^3+x_6/r^4+x_7/r^5)/\{1+\exp[x_8(r-x_9)]\}. \tag{A4}$$

For carbon the formulas are

$$ss\sigma=(x_1+x_2r+x_3r^2+x_4r^3+x_5f_1)/f_2+x_6/\{1+\exp[x_7(r-x_8)]\}. \tag{A5}$$

Again $sp\sigma$ is 0. $pp\sigma$ and $pp\pi$ are

$$x_1f_1/f_2, \tag{A6}$$

where

$$f_1=\exp[a_1(r-a_2)], \tag{A7}$$

TABLE IV. Constants for the repulsive terms.

	Si	C		
	Φ_a	Φ_a	Φ_b	P
x_1	−71.9534	−6.59675	−2.56056	−0.1
x_2	432.806	−6.71808	−2.45038	−-20.
x_3	-855.024	4.57941	4.79027	1.85
x_4	587.287	44.9380	0	0
x_5	0	7.09646	2.44182	0
x_6	0	−1.86826	−1.24899	0
x_7	0	0.70027	1.16622	0
x_8	10	7.59196	22.3862	0
x_9	2.80	1.95272	1.24115	0

$$f_2 = 1 + \exp[b_1(r - b_2)]. \tag{A8}$$

The values for the constants in the intra-atomic formula are in Table III.

The repulsive formula are

$$\Phi_a(r) = \phi_a(r)/f_a(r), \tag{A9}$$

$$\phi_a(r) = x_1 + x_2/r + x_3/r^2 + x_4/r^3 + x_5\sin(x_6 r - x_7), \tag{A10}$$

$$f_a(r) = 1 + \exp[x_8(r - x_9)]. \tag{A11}$$

For silicon, the total repulsive potential is $\Phi(r) = \Phi_a(r)$ while for carbon it is

$$\Phi(r) = \Phi_a(r) + \Phi_b(r) + P(r), \tag{A12}$$

where

$$P(r) = x_1\exp[x_2(r - x_3)^2]. \tag{A13}$$

The values for the parameters are in Table IV. The more complicated repulsive form for carbon can be viewed as the price paid for carbon's simpler intra-atomic terms. In general, fitting of long-ranged parameters, which tended in some cases to be zero and nonzero in the same region depending on the shell (for example $ss\sigma$ being roughly zero beyond the first nn region), was a difficult task. Added to this, the fitting was made more diffcult by polynomials for which a small change in the value of one parameter can lead to large changes throughout the length of the curve. In the future, the use of Hermite polynomials or similar piecewise functions for much of the fitting might prove to be very helpful.

---

[1] G.X. Qian and D.J. Chadi, Phys. Rev. B **35**, 1288 (1987).

[2] J.L. Mercer and M.Y. Chou, Phys. Rev. B **48**, 5374 (1993), and many of the references listed there.

[3] M. Menon and K.R. Subbaswamy, Phys. Rev. B **50**, 11 577 (1994).

[4] L. Goodwin, A.J. Skinner, and D.G. Pettifor, Europhys. Lett. **9**, 701 (1989).

[5] C.H. Xu, C.Z. Wang, C.T. Chan, and K.M. Ho, J. Phys. Condens. Matter **4**, 6047 (1992).

[6] R.E. Cohen, M.J. Mehl, and D.A. Papaconstantopoulos, Phys. Rev. B **50**, 14 694 (1994).

[7] D.W. Bullet, J. Phys. C **8**, 2695 (1975); *Solid State Physics: Advances in Research and Applications*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic Press, New York, 1980), Vol. 35.

[8] V. Heine, in *Solid State Physics: Advances in Research and Applications*, (Ref. 7).

[9] P.W. Anderson, Phys. Rev. **181**, 25 (1969).

[10] J.K. Rudra and W. Beall Fowler, Phys. Rev. B **28**, 1056 (1983).

[11] W.M.C. Foulkes, Phys. Rev. B **48**, 14 216 (1993).

[12] D.J. Chadi, in *Atomistic Simulation of Materials Beyond Pair Potentials*, edited by V. Vitek and D. Srolovitz (Plenum Press, New York, 1989).

[13] J.K. Rudra and W. Beall Fowler, Phys. Rev. B **28**, 1061 (1983).

[14] A.P. Sutton, M.W. Finnis, D.G. Pettifor, and Y. Ohta, J. Phys. C **21**, 35 (1988).

[15] J.L. Mercer and M.Y. Chou, Phys. Rev. B **49**, 8506 (1994).

[16] A. Kobayashi, O.F. Sankey, and J.D. Dow, Phys. Rev. B **25**, 6367 (1982); E.P. O'Reilly and J. Robertson, *ibid.* **34**, 8684 (1986); M. Menon and R.E. Allan, *ibid.* **38**, 6196 (1988); K. Nath and A.B. Anderson, *ibid.* **41**, 5652 (1990); D.W. Jenkins, J.D. Dow, and M-H. Tsai, J. Appl. Phys. **72**, 4130 (1992); D.A. Contreras-Solorio, V.R. Velasco, and F. Garcia-Moliner, Phys. Rev. B **47**, 4651 (1993); M. Sugawara, *ibid.* **47**, 7588 (1993); G. Lengel, R. Wilkins, G. Brown, M. Weimer, J. Gryko, and R.E. Allan, Phys. Rev. Lett. **72**, 836 (1994); C. Molteni, L. Colombo, and L. Miglio, Phys. Rev. B **50**, 4371 (1994); J. Phys. Condens. Matter **6**, 5243 (1994); K. Sieranski, J. Szatkowski, and K. Misiewicz, Phys. Rev. B **50**, 7331 (1994); H. Seong and L.J. Lewis, *ibid.* **52**, 5675 (1995).

[17] L. Brey, C. Tejedor, and J.A. Verges, Phys. Rev. B **29**, 6840 (1984); M. Rosenbauer and H.J.F. Jansen, *ibid.* **47**, 16 148 (1993).

[18] M.H.F. Sluiter and P.P. Singh, Phys. Rev. B **49**, 10 918 (1994).

[19] F. Guinea, J. Sanchez-Dehesa, and F. Flores, J. Phys. C **16**, 6499 (1983); J. Sanchez-Dehesa, F. Flores, and F. Guinea, *ibid.* **17**, 2039 (1984); R. Strehlow, M. Hanke, and W. Kuhn, Phys. Status Solidi B **131**, 631 (1985); J.P. Bourdin, M.C. Desjonqueres, D. Spanjaard, and J. Friedel, Surf. Sci. **157**, L345 (1985), and references therein; J. Tersoff and W.A. Harrison, Phys. Rev. Lett. **58**, 2367 (1987); L. Brey and C. Tejedor, *ibid.* **59**, 1022 (1987); J.A. Majewski and P. Vogl, Phys. Rev. B **35**, 9666 (1987); C. Priester, G. Allan, and M. Lannoo, *ibid.* **38**, 9870 (1988); J. Ortega, J. Sanchez-Dehesa, and F. Flores, *ibid.* **37**, 8516 (1988); C. Priester, G. Allan, and M. Lannoo, *ibid.* **37**, 8519 (1988); C. Priester, G. Allan, and M. Lannoo, J. Vac. Sci. Technol. B **6**, 1290 (1988); H. Xu and U. Lindefelt, Phys. Rev. B **41**, 5979 (1990); Ch. Huasleitner and J. Hafner, J. Phys. Condens. Matter **2**, 6651 (1990); D. Bertho, D. Boiron, A. Simon, C. Jouanin and C. Priester, Phys. Rev. B **44**, 6118 (1991); C. Tserbak, H.M. Polatoglou, and G. Theodorou, *ibid.* **47**, 7104 (1993); F. Liu, *ibid.* **52**, 10 677 (1995).

[20] M. Kohyama, S. Kose, M. Kinoshita, and R. Yamamoto, J. Phys. Condens. Matter **2**, 7791 (1990).

[21] J.C. Slater and G.F. Koster, Phys. Rev. **94**, 1498 (1954).

[22] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[23] J.P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[24] D.R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

[25] N. Troullier and J.L. Martins, Phys. Rev. B **43**, 1993 (1991).

[26] W.A. Harrison, Phys. Rev. B **27**, 3592 (1983).

[27] J. Dorantes-Davila, A. Vega, and G.M. Pastor, Phys. Rev. B **47**, 12 995 (1993).

[28] O.K. Anderson (private communication).

[29] D. Papaconstantopoulos, (private communication).

[30] J.L. Mercer and M.Y. Chou, Phys. Rev. B **47**, 9366 (1993).

[31] M.T. Yin and M.L. Cohen, Phys. Rev. B **26**, 5668 (1982).

[32] M.T. Yin, Phys. Rev. B **30**, 1773 (1984).

[33] L.L. Boyer, E. Kaxiras, J.L. Feldman, J.Q. Broughton, and M.J. Mehl, Phys. Rev. Lett. **67**, 715 (1991).

[34] Using Hellman-Feynman forces. See R.P. Feynman, Phys. Rev. **56**, 340 (1939).

[35] G.B. Adams, M. O'Keefe, A.A. Demkov, O.F. Sankey, and Y.-M. Huang, Phys. Rev. B **49**, 8048 (1994).

[36] A.A. Demkov, O.F. Sankey, K.E. Schmidt, G.B. Adams, and M. O'Keeffe, Phys. Rev. B **50**, 17 001 (1994); the orthogonal models tested by this group were for silicon Goodwin, *et al.* (Ref. 4) and for carbon Xu, *et al.* (Ref. 5).

[37] I tested the model from Ref. 30.

[38] O.F. Sankey and D.J. Niklewski, Phys. Rev. B **40**, 3979 (1989).

[39] K. Raghavachari, J. Chem. Phys. **35**, 3520 (1985); K. Raghavachari and V. Logovinsky, Phys. Rev. Lett. **55**, 2853 (1985).

[40] M.T. Yin and M.L. Cohen, Phys. Rev. B **26**, 3259 (1982).

[41] O.H. Nielsen and R.M. Martin, Phys. Rev. B **32**, 3792 (1985).

[42] R. Biswas (private communications).

[43] S. Fahy and S.G. Louie, Phys. Rev. B **36**, 3373 (1987).

[44] K. Raghavachari and J.S. Binkley, J. Chem. Phys. **87**, 2191 (1987).

[45] M.R. Pederson and A.A. Quong, Phys. Rev. Lett. **74**, 2319 (1995). The coordinates to make C_{60} and C_{60}-C_{60} were provided by A.A. Quong.

[46] A rough *ab initio* calculation gives a result of 9.14×10^{12} erg/cm^3.

[47] P. Pavone, K. Karch, O. Schütt, W. Windl, D. Strauch, P. Giannozzi, and S. Baroni, Phys. Rev. B **48**, 3156 (1993).

[48] K.J. Chang and M.L. Cohen, Phys. Rev. B **35**, 8196 (1987).

[49] N. Churcher, K. Kunc, and V. Heine, J. Phys. C **19**, 4413 (1986).

[50] K. Karch, P. Pavone, W. Windl, O. Schütt, and D. Strauch, Phys. Rev. B **50**, 17 054 (1994).

[51] J.C. Phillips, *Bonds and Bands in Semiconductors* (Academic Press, New York, 1973); J.C. Phillips and J.A. Van Vechten, Phys. Rev. Lett. **23**, 1115 (1969).

[52] R.S. Mulliken, J. Chem. Phys. **23**, 1833 (1955).

[53] D. Sanchez-Portal, E. Artacho, and J.M. Soler, Solid State Commun. **95**, 685 (1995).

[54] R. Orlando, R. Dovesi, C. Roetti, and V.R. Saunders, J. Phys. Condens. Matter **2**, 7769 (1990).

[55] P. Käckell, B. Wenzien, and F. Bechstedt, Phys. Rev. B **50**, 17 037 (1994).