RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 39, NUMBER 8 15 MARCH 1989-I

Modeling solid-state chemistry: Interatomic potentials for multicomponent systems

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(Received 31 October 1988)

A general form is proposed for an empirical interatomic potential for multicomponent systems. This form interpolates between potentials for the respective elements to treat heteronuclear bonds. The approach is applied to C-Si and Si-Ge systems. In particular, the properties of SiC and its defects are well described.

Intense interest has recently developed in modeling the energetics of covalent systems with classical interatomic potentials. While less accurate than *ab initio* methods, such potentials are invaluable for the treatment of complex systems or performance of extended simulations.

To date, most such work has focused on silicon, and at least nine independent groups have proposed potentials for silicon in the last 4 years.[1] A potential for carbon has also been reported.[2] However, pure elemental systems are rare. Most problems involve more than one type of atom, whether in compounds, impurities, alloys, or interfaces. While a few potentials for specific mixed systems have been presented,[3] no systematic approach to multicomponent systems has yet been proposed.

Here, a previous approach for the modeling of elemental systems is extended to multicomponent systems. First, potentials for C, Si, and Ge are *independently* determined by our fitting a *single* parametrized potential to the respective elemental data. The use of accurate potentials for the respective elements is a central feature here. Then, by the introduction of a *single* additional parameter for each pair of elements, the potential is generalized to treat mixtures of these elements.

This new approach is tested by applications to SiC and its defects, where results of quantum-mechanical calculations within the local-density approximation (LDA) for correlation and exchange have recently become available.[4,5] Carbon and silicon differ sufficiently in their properties to make this a rather stringent test. In view of the fact that only a single parameter is included to characterize the heteronuclear interaction, the accuracy of the results is remarkable. Even greater accuracy is obtained for Si-Ge systems, where the difference between the atoms is much smaller.

The form proposed here to model the interatomic forces is a direct generalization of that used earlier[6,7] for elemental systems. The energy is modeled as a sum of pairlike interactions, where, however, the coefficient of the attractive term in the pairlike potential (which plays the role of a bond order) depends on the local environment, giving a many-body potential.

The energy E, as a function of the atomic coordinates, is taken to be

$$E=\sum_i E_i=\tfrac{1}{2}\sum_{i\neq j}V_{ij}\,,\quad V_{ij}=f_C(r_{ij})[f_R(r_{ij})+b_{ij}f_A(r_{ij})]\,; \tag{1a}$$

$$f_R(r_{ij})=A_{ij}\exp(-\lambda_{ij}r_{ij})\,,\quad f_A(r_{ij})=-B_{ij}\exp(-\mu_{ij}r_{ij})\,; \tag{1b}$$

$$f_C(r_{ij})=\begin{cases}1, & r_{ij}<R_{ij}\\ \tfrac{1}{2}+\tfrac{1}{2}\cos[\pi(r_{ij}-R_{ij})/(S_{ij}-R_{ij})], & R_{ij}<r_{ij}<S_{ij},\\ 0, & r_{ij}>S_{ij}\,;\end{cases} \tag{1c}$$

$$b_{ij}=\chi_{ij}(1+\beta_i^{n_i}\zeta_{ij}^{n_i})^{-1/2n_i}\,,\quad \zeta_{ij}=\sum_{k\neq i,j}f_C(r_{ik})\omega_{ik}g(\theta_{ijk})\,,\quad g(\theta_{ijk})=1+c_i^2/d_i^2-c_i^2/[d_i^2+(h_i-\cos\theta_{ijk})^2]\,; \tag{1d}$$

$$\lambda_{ij}=(\lambda_i+\lambda_j)/2\,,\quad \mu_{ij}=(\mu_i+\mu_j)/2\,,\quad A_{ij}=(A_iA_j)^{1/2}\,,\quad B_{ij}=(B_iB_j)^{1/2}\,,\quad R_{ij}=(R_iR_j)^{1/2}\,,\quad S_{ij}=(S_iS_j)^{1/2}\,. \tag{1e}$$

Here i, j, and k label the atoms of the system, r_{ij} is the length of the ij bond, and θ_{ijk} is the bond angle between bonds ij and ik. Singly subscripted parameters, such as λ_i and n_i, depend only on the type of atom (C, Si, or Ge).

For a single component, Eq. (1) reduces to the potential of Ref. 6; the physical motivation and interpretation of the respective terms are discussed there. Note, however, that some terms have been rewritten relative to Ref. 6 to simplify the notation for the multicomponent case. Also, the parameters α and λ_3 of Ref. 6 have been set to zero, simplifying the form of the potential.

The only new parameter used here is χ, which strengthens or weakens the heteropolar bonds, relative to the value obtained by simple interpolation. Thus any "chemistry" is included in this parameter, or in the choice of the interpolation formula. Here $\chi_{ii}=1$, and $\chi_{ij}=\chi_{ij}$, so there is one independent parameter per pair of atom types. In addition, parameters ω_{ij} (where $\omega_{ii}=1$) are available

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for possible future use, to permit greater flexibility when dealing with more drastically different types of atoms. However, here ω is not used, i.e., all $\omega_{ij}=1$.

Table I gives the suggested parameters for C, Si, and Ge. These parameters for C and Si have been presented and discussed in detail elsewhere.[2,7] Note that two sets of parameters have been proposed for Si with this potential.[6,7] The more recent[7] is used here because, while it is apparently inferior in treating surfaces, it is better at describing strain, which is crucial for C-Si systems because of the very different atomic sizes. Note also that, because of the short range of the potential, there is no difference in energy between cubic and hexagonal polytypes, which have identical first-neighbor arrangements. Only cubic SiC is considered here.

The parameters for Ge are new, and are fitted to polytype energies[8] etc., much as for C and Si, although the available data for Ge are more limited. As before,[6] the parameters R and S in f_c are not systematically optimized, but are chosen rather arbitrarily. The abruptness of the cutoff f_c is awkward in molecular-dynamics simulations, so substitution of a smoother cutoff may prove desirable.

Table I also gives the crucial new parameters, $\chi_{\text{C-Si}}$ and $\chi_{\text{Si-Ge}}$ which are chosen to give correctly the heat of formation of the zinc-blende-structure compound. For Si-Ge, only a theoretical value is available for this hypothetical phase.[9] The necessary data for the determination of $\chi_{\text{C-Ge}}$ do not appear to be available at present, although this combination is not of particular interest in any case. The resulting cohesive energies, in eV per atom, are 6.165 for SiC and 4.231 for SiGe to be compared with 7.37, 4.63, and 3.85 for C, Si, and Ge, respectively.

The success of the present approach relies on a relatively good interpolation scheme as a starting point, with the additional parameter χ providing fine tuning. It is therefore interesting to note that, even if χ is omitted, the potential correctly predicts that compound formation is exothermic for SiC but endothermic for SiGe. Moreover, the final value of χ is reassuringly close to unity in both cases.

Results for SiC are now presented, as a test of the accuracy of this new approach. These results are summarized in Tables II and III. The parameters of Table I, fitted only to the heat of formation and to the properties of the respective elements, give a lattice constant for cubic SiC of $a=4.32$ Å, in excellent agreement with the experimental value of 4.36 Å. Note that the lattice constant is given with an accuracy of 1%, much better than the 3% accuracy of Vegard's law (arithmetic mean of constituent values), which would predict 4.50 Å. The bulk modulus and elastic constants for this model are given in Table II, along with experimental values.[10] (The origin and accuracy of the experimental elastic constants is, however, unclear.) Except for c_{44} being rather too large, the agreement is quite good. Even c_{44} is much more accurate than a simple average of C and Si values would be.

One of the most stringent tests for an empirical potential is its ability to predict energies of point defects. Although the available data for SiC are much less extensive than for Si, Bernholc *et al.*[4] have recently performed LDA calculations of several point defects in SiC. Their results for relaxed defect energies are compared with those of the present model in Table III. Here V_{C} denotes a vacancy at a C site, C_{Si} denotes a carbon on a Si site, $\text{C}_{T\text{Si}}$ denotes a carbon interstitial at the tetrahedral site surrounded by four silicons, etc. Note that only combinations of defects which preserve stoichiometry are given, since other energies are not well defined unless the chemical potentials are fixed. For the four interstitials reported,[4] there are three independent numbers characterizing stoichiometric pairs, and all three are given in Table III.

The accuracy is quite impressive, especially given the complex interplay of strain and rebonding in these defects. In fact, only for the vacancies is the discrepancy significant on the scale of the expected accuracy of the LDA calculations. Even there, the discrepancy can be attributed to the small vacancy formation energy for the elemental carbon potential,[2] and so does not reflect a shortcoming of the scheme for the treatment of heteropolar bonds here.

Some properties of SiC have also been calculated for the rocksalt structure.[5] Since, in this structure, the bonding has considerable ionic character, the potential might be expected to fail drastically. However, it actually does reasonably well, although the accuracy is certainly less than for more covalent bonding.

The rocksalt-structure lattice constant is 4.25 Å here, compared with an LDA result of 4.03 Å by Chang and Cohen,[5] a discrepancy of 5%. The equilibrium energy of

TABLE I. Parameters for carbon, silicon, and germanium to be used in Eq. (1). R and S were not systematically optimized.

	C	Si	Ge
A (eV)	1.3936×10^{3}	1.8308×10^{3}	1.769×10^{3}
B (eV)	3.467×10^{2}	4.7118×10^{2}	4.1923×10^{2}
λ (Å^{-1})	3.4879	2.4799	2.4451
μ (Å^{-1})	2.2119	1.7322	1.7047
β	1.5724×10^{-7}	1.1000×10^{-6}	9.0166×10^{-7}
n	7.2751×10^{-1}	7.8734×10^{-1}	7.5627×10^{-1}
c	3.8049×10^{4}	1.0039×10^{5}	1.0643×10^{5}
d	4.384×10^{0}	1.6217×10^{1}	1.5652×10^{1}
h	-5.7058×10^{-1}	-5.9825×10^{-1}	-4.3884×10^{-1}
R (Å)	1.8	2.7	2.8
S (Å)	2.1	3.0	3.1
	$\chi_{\text{C-Si}}=0.9776$		$\chi_{\text{Si-Ge}}=1.00061$

TABLE II. Calculated lattice constant a (Å) and elastic constants (Mbar) of cubic SiC, compared with experiment (Ref. 10).

	Theory	Experiment
a	4.32	4.36
B	2.2	2.2
c_{11}	4.2	3.6
c_{12}	1.2	1.5
c_{44}	2.6	1.5

TABLE III. Calculated energies of stoichiometric defect combinations in cubic SiC, in eV, and results of previous LDA calculations (Ref. 4).

Defect	Theory	LDA
$V_{Si}+V_C$	7.4	12.7
$C_{Si}+Si_C$	7.2	8.4
$Si_{TC}+C_{TSi}$	22.6	23.3
$Si_{TSi}+C_{TC}$	23.2	26.0
$C_{TC}-C_{TSi}$	3.0	2.4

the rocksalt phase is 1.5 eV/atom higher than the zinc blende here, compared with 0.7 for LDA. This represents a 12% error in the cohesive energy.

Both the energy and lattice constant indicate an underestimation of the binding for the rocksalt structure, consistent with the omission of any explicit ionic behavior in the present potential. Since such ionic configurations do not generally occur without huge applied pressure, this does not seem to be an important shortcoming.

Si-Ge systems are much easier to treat than C-Si, since the two types of atoms are so similar. Because of the current interest in semiconductor superlattices and alloys, a general potential for these systems is highly desirable. Such a potential has been constructed here just as for SiC.

For a hypothetical zinc-blende phase of SiGe, both the lattice constant and bulk modulus are found to be very close to an average of the respective elemental values, in agreement with LDA calculations of Martins and Zunger.[9] An alternative hexagonal phase with *AB-BA* stacking is found to have an energy 2 meV/atom lower than zinc blende, again in good agreement with LDA.[9] The enthalpy of mixing for a random 50-50 alloy at 0 K is found to be 7 meV/atom, in reasonable agreement with the value of 11 meV/atom obtained by Qteish and Resta[11] from LDA calculations. Because the present potential describes strain, heteronuclear bonding, and defects reasonably accurately, it should be particularly appropriate for studies of the stability of strained-layer superlattices.

In conclusion, this generalization to multiple types of atoms immensely increases the number and variety of systems which can be treated with accurate empirical potentials. The approach has been successfully applied to SiC and its defects, a stringent test because of the severe mismatch of the two components. A potential for Si-Ge systems has also been presented, and is expected to be about as accurate as the elemental Si potential.

This work was supported in part by ONR Contract No. N00014-84-C-0396.

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