# Theory of bond-length variations in relaxed, strained, and amorphous silicon-germanium alloys

C. Tzoumanekas and P. C. Kelires
*Physics Department, University of Crete, P.O. Box 2208, 710 03 Heraclion, Crete, Greece*
*and Foundation for Research and Technology-Hellas (FORTH), P.O. Box 1527, 711 10 Heraclion, Crete, Greece*
(Received 14 June 2002; published 13 November 2002)

We present a theoretical study of bond-length and angle variations in relaxed, epitaxially strained, and amorphous $Si_{1-x}Ge_x$ alloys. Our approach is based on Monte Carlo simulations, within the semigrand-canonical ensemble utilizing Ising-like identity flips, and in conjuction with energies calculated using the empirical potential of Tersoff [Phys. Rev. B **39**, 5566 (1989)]. The method offers great statistical precision enabling us to extract clear variations through the whole composition range and for all types of bonds. Our simulations show that in relaxed crystalline alloys, where the lattice constant takes its natural value, bond lengths depend on composition $x$ and that these variations are type specific, in agreement with recent experimental studies. Similar type-specific variations are found for the angles and the second-nearest-neighbor distances. This analysis also reveals that the negative deviation of the lattice constant from Vegard's law is mainly due to radial, and not angular, relaxations. In the epitaxially strained alloys, bond lengths decrease with $x$ due to the two-dimensional confinement in the growth layers, in good agreement with predictions based on the macroscopic theory of elasticity. The dimer bond lengths at the $(100)$-$(2\times1)$-reconstructed alloy surface remain nearly constant, and they are elongated with respect to the bulk values. In the amorphous alloys, we unravel a remarkable behavior of bond lengths at the dilute low-$x$ alloy limit, characterized by strong relaxations and elongation. Furthermore, the bond lengths decrease with increasing Ge content. We offer an explanation of this effect based on the analysis of the enthalpy of formation of the amorphous alloy.

DOI: 10.1103/PhysRevB.66.195209 PACS number(s): 61.43.Dq, 61.43.Bn, 68.35.Bs

## I. INTRODUCTION

There has been considerable discussion in the last ten years about bond-length variations in SiGe alloys, instigated by both practical and fundamental reasons. Crystalline $Si_{1-x}Ge_x$ alloys and heterostructures have by now been established as an important semiconducting system, integrated on Si technology, with band-gap engineering capabilities, as a high-speed component in electronic devices, and with promising optoelectronic properties.[1] The advent of multistacked, self-aligned quantum nanostructures (dots) with a strong photoemission signal adds further to this interest. The knowledge of the local structure is essential to elucidate the above properties. The question of how the bond lengths vary with alloy composition is probably the best probe of changes in the microstructure, and can be directly studied with experimental techniques. For similar reasons, amorphous $Si_{1-x}Ge_x$ alloys, widely used in solar cell applications because the optical gap can be easily tuned, need to be studied in this respect.

The subject is of fundamental interest too. In general, the local structure of an alloy, as a function of the composition, is controlled by the interplay between the strain, due to the size mismatch of the constituents, and the chemical energy that favors one type of bond over the others.[2,3] In the case of large size mismatch and strong heteropolar bonds, this interplay dictates chemical ordering; the fraction of heteropolar bonds is maximized and consequently strain is minimized. This is the zinc-blende (ZB), strain-free case of SiC and GaAs. In the case of small size mismatch and weak heteropolar bonds, all possible types of bonds are present, in general, with a tendency for randomness, and strain is accomodated through bond-length and- angle distortions. This is the case that interests us here. These principles hold for both crystalline and amorphous alloys. However, since the latter are less rigid, they accomodate strain due to size mismatch more efficiently, and so local relaxation effects might become more pronounced.

It is well known that the $c$-$Si_{1-x}Ge_x$ mixture is a thermodynamically stable random alloy at room temperature, at all compositions, obeying regular solution theory very closely. As shown by theoretical simulations,[4–6] this mixture phase separates (unmixes) into Si-rich and Ge-rich phases below a critical temperature $T_c \simeq 170$–$200$ K, because it has a small but positive enthalpy of formation ($\sim 7$ meV/atom for the 50%-50% composition).[4,7] In practice, phase separation is hindered due to the negligible diffusion at such low temperatures. Regarding the amorphous $Si_{1-x}Ge_x$ alloys, we have found recently[8] that the topological disorder of the amorphous network totally suppresses the unmixing behavior (long-range segregation). Yet, some remnants of this tendency are manifested through local clustering of homopolar bonds, even at elevated temperatures, rather easily accomodated in the less rigid amorphous network, but not seen in the stiffer crystalline environment because clustering induces large local strains. Evidence for such deviation from chemical randomness in the amorphous alloys is provided by recent experimental work.[9]

Much of the discussion about the composition dependence of bond lengths in SiGe alloys, and the related changes in the local microstucture, has been concentrated on the relaxed crystalline case. In the theory of alloys, conventionally two extreme competing limits are considered to describe the behavior of bond lengths and angles.

(i) The Pauling limit[10] in which the bond length between a given atom pair is the sum of the constituent-element atomic radii and thus is fixed, independent of composition. In this case, bond bending is energetically favored over bond

 

stretching, and so strain is accomodated by bond angle changes.

(ii) If bond stretching is favored, the alloy reaches the Vegard limit,[11] in which all bond lengths have the same value and vary linearly as a function of composition, accomodating the strain, while bond angles are fixed.

Intensive work over the years has made it possible to get a rather clear picture about relaxed *c*-SiGe alloys. It is beyond any doubt that the lattice constant as a function of composition does not follow an exact linear relation as Vegard's law demands, but has a slight negative deviation. This was first pointed out experimentally by Dismukes *et al.*[12] and confirmed by further experimental work.[13–15] From the theoretical point of view, negative deviations have been found by the empirical calculations of Kelires and collaborators,[16] and more recently by *ab initio* calculations.[17,18] The work of de Gironcoli *et al.*[5], instead, found positive deviations from Vegard's law. Regarding bond-length variations, while some earlier experimental x-ray-absorption fine-structure (XAFS) investigations[19–21] suggested that bonding is at the Pauling limit, more recent refined XAFS studies[15,22–24] showed definite signs of non-Pauling behavior. The work of Aubry *et al.*[15] is the most detailed of these studies. The important outcome of this investigation is not only that bond lengths depend on composition, though rather weakly, but also that the variations are type-dependent, i.e., the slopes of the linear fits to the Si-Si, Si-Ge, and Ge-Ge bond lengths as a function of composition are dinstinctly different. A similar, but less firm, type-dependent variation for the Ge-Ge and Si-Ge first-shell distances was reported by Ridgway *et al.*,[24] and for the Ge-Ge distance by Aldrich *et al.*[23]

A number of theoretical studies have been devoted to this subject. Earlier work at the empirical or semiempirical level[5,6,25,26] found compositional dependence of all three types of bonds, in the form of three equally spaced, parallel lines. In a significant contribution to the problem, Thorpe and co-workers[27–29] set up the theoretical framework and offered a quantitative analytical treatment of the bond-length variations, supplemented by simulations with the Kirkwood harmonic interatomic potential.[30] The central ingredients of this theory are embodied in a single parameter $a^{**}$, the *topological rigidity parameter*, which represents the response of a certain lattice to a radial displacement (expansion or contraction) from a central atom, and is an indication of its rigidity. This theory assumes that all the force constants are the same. The values of $a^{**}$ could range from 0 to 1. When $a^{**}=1$, the lattice is flexible, so every bond adjusts to its natural length, and we have the Pauling limit. When $a^{**}=0$, the lattice is perfectly rigid, so all bonds adjust their lengths to a common value to fit within the unit cell determined by a given lattice constant, and we are at the Vegard limit. Mixed behavior is indicated by intermediate values. Within this theory, it was proposed that $a^{**}=0.707$ for SiGe alloys,[28,31] showing a partial Vegard-like character which is independent of the type of the bond, in agreement with the other calculations[5,6,25,26] but in contrast to the latest experimental results.

Two recent *ab initio* calculations[17,18] have reported results about type-specific bond-length variations, in qualitative agreement with experiment.[15,24] Venezuela *et al.*[17] calculated $a_{ij}^{**}$'s that vary with the type of bond, but less than what has been found experimentally.[15] They've also quantified the negative deviation of the lattice constant from Vegard's law. Yu *et al.*[18] claimed to have found type-dependent variations too, but no effort has been made to fit the variations and extract rigidity parameters, and their conclusions are not so convincing. Summarizing, we could say that in relaxed *c*-SiGe alloys, bond-length variations are likely to have a partial Vegard-like character and be type specific, but this issue is not yet fully understood.

Less understood are amorphous and epitaxially strained SiGe alloys. Thin films of *c*-SiGe grown pseudomorphically on Si substrates, i.e., grown below the critical thickness for relaxation and introduction of misfit dislocations, are confined to have laterally the Si lattice constant and so they are in a metastable strained state. They have important applications in SiGe devices as quantum wells and it is essential to understand how strain is accomodated. Woicik *et al.*[22] performed extended XAFS (EXAFS) experiments on a strained $Si_{0.79}Ge_{0.21}$ alloy, and found that Ge-Ge and Ge-Si bond lengths might be even shorter (within the error bars) than in the unstrained dilute $x=0$ limit. It is extremely interesting to examine whether such behavior, that is, shrinkage of bond lengths upon increase of Ge content in epitaxially strained alloys, persists over the whole composition range, and also to study the Si-Si variation. Such an investigation, either experimental or theoretical, is lacking.

Regarding amorphous alloys, EXAFS experiments reported composition-independent bond lengths for both hydrogenated[32–34] and nonhydrogenated[35] samples. One might argue that a Pauling-limit behavior would be the result of the less rigid character of the amorphous network that permits larger bond-angle variations, keeping the bond lengths fixed at their natural values. However, Mousseau and Thorpe, in the only theoretical work on this, pointed out[28] that a rigidity parameter $a^{**}=1$ requires a completely flexible network, and this can only happen through the introduction of excessive amounts of hydrogen, much more than seen experimentally. The argument does not apply to the nonhydrogenated[35] samples anyway. Instead, their model[28] predicts composition-dependent bond lengths, but not type specific, with the same $a^{**}=0.707$ as they predict for the crystal. This implies the same local rigidity in the amorphous alloy as in the crystal. In view of recent calculations of local rigidity in our group[36,37] we think that this issue requires reexamination. The more recent experimental work of Ridgway *et al.*[24] claims composition-dependent bond lengths, but the trends are not so clear because of the huge error bars. Also, a very recent experimental work by Chapman *et al.*[38] on samples grown with glow discharge and studied with EXAFS claims composition-independent lengths, but the reported curves seem to indicate a different behavior, as we discuss below.

We present in this paper a detailed theoretical/simulational study of bond-length composition dependence in all three categories of SiGe alloys discussed above: relaxed, epitaxially strained, and amorphous. We performed Monte Carlo simulations, offering great statistical precision,

within the empirical potential approach. For the relaxed crystal, we confirm that bond lengths depend on composition and are slightly type specific, extracting the relevant rigidity parameters. For the strained and amorphous alloys, we unravel in both cases an inverse composition-dependent behavior, characterized by a *decrease* of bond lengths with increasing Ge content. We also calculated in the strained case the dimer bond lengths at the SiGe surface, a controversial issue, and compared them with previous experimental and theoretical results. The paper is organized as follows. In Sec. II, we outline our simulational methodology. In Sec. III, we give the results of our simulations and discuss their implications. We start with the relaxed alloys, then study the strained alloys and the surface-dimer problem, and finally investigate the amorphous alloys. In Sec. IV, we give our conclusions.

## II. METHODOLOGY

The key element in the theoretical discussion of SiGe alloys is the proper statistical equilibration of the system. Statistical accuracy is even more important for the present problem, characterized by a narrow window within which bond lengths are expected to vary ($\sim 0.03$ Å), and given the large error bars reported in the experimental papers. It is thus desirable to minimize as much as possible the fluctuations in the theoretical work in order to arrive at consistent results, clear trends, and firm conclusions.

We achieve this goal by equilibrating the binary system with Monte Carlo (MC) simulations. The appropriate statistical ensemble underlying the simulations is the *semigrand canonical* (SGC) ensemble, used previously with success in simulations of both crystalline[4,6,39,40] and amorphous[8] SiGe alloys. In this ensemble, denoted as $(\Delta\mu,N,P,T)$, and for a general multicomponent system, the total number of atoms $N$, the pressure $P$, and the temperature $T$ remain fixed, but the number of atoms of each species is allowed to fluctuate through Ising-type identity flips, which convert with equal probability the identity of a randomly chosen atom into one of the other identities of the system. These flips are driven by the appropriate chemical-potential differences ($\Delta\mu=\mu_{\mathrm{Si}}-\mu_{\mathrm{Ge}}$, in the present case), and lead in the ergodic limit (several $10^6$ moves) to compositional equilibration. In addition, we have exchanges of volume with the heat bath (volume moves), as well as the traditional MC moves involving random atomic displacements. Thus, the SGC ensemble can be considered as a combination of the grand-canonical and the more familiar isobaric-isothermal $N$-$P$-$T$ ensemble. Within this framework the MC simulations account fully in a unified way for positional and configurational contributions to the free energy.

For the implementation of the SGC ensemble we use the Metropolis algorithm.[41] The traditional random atomic moves ($s^N \rightarrow s'^N$) and the volume changes $V \rightarrow V'$ are accepted with a probability

$$P_{\mathrm{acc}} = \mathrm{Min}[1, \exp(-\beta \Delta W)], \tag{1}$$

where

$$\Delta W = \Delta U_{\mathrm{displ}}(s^N \rightarrow s'^N) + P(V'-V) - N k_B T \ln(V'/V). \tag{2}$$

The notation $s^N$ denotes the $3N$ scaled atomic coordinates in the cell. $\Delta U_{\mathrm{displ}}(s^N \rightarrow s'^N)$ is the change in the potential energy of the alloy due to the atomic displacements. The trial identity moves are accepted with a probability

$$P_{\mathrm{acc}}^{\mathrm{iden}}(i \rightarrow i') = \mathrm{Min}\left[1, \frac{\lambda_{i'}}{\lambda_i} \exp[-\beta \Delta U(s^N)]\right] \sim e^{\beta \Delta\mu} e^{-\beta \Delta U(s^N)}. \tag{3}$$

$\Delta U(s^N)$ denotes the change in the potential energy due to the identity $(i \rightarrow i')$ flip, and $\lambda_i = e^{\mu_i / k_B T}$ are the fugacities in the system. We start with chemical potentials $\mu_{\mathrm{Si}} = -4.63$ eV and $\mu_{\mathrm{Ge}} = -3.85$ eV (the cohesive energies of the respective bulk crystals), and so $\Delta\mu = -0.78$ eV. This yields $\sim 50\%$-$50\%$ composition. We then vary $\Delta\mu$ in either direction to achieve the desired composition.

In certain cases, it is preferable to work with a fixed alloy composition. In that case we start with the SGC ensemble in order to achieve the desired compositions. We then switch to the $N$-$P$-$T$ ensemble which, however, still includes identity flips but in the form of *mutual particle interchanges* (from Ge to Si at a randomly chosen site and *vice versa* at another site), so that the composition is kept constant.

The large number of MC moves involved in the simulations makes it computationally impractical to equilibrate the SGC ensemble using *ab initio* or tight-binding energies. We therefore model the energetics of the binary alloy using the empirical potential approach. We use the model potential of Tersoff (TF) for Si-Ge systems,[42] extensively tested and applied with success in similar contexts.[4,8,40] Its form is a direct generalization of that for the elemental systems Si and Ge. The potential is fitted so as to reproduce the enthalpy of formation ($\Delta H = 8.9$ meV/atom) of the ZB SiGe alloy, as calculated by Martins and Zunger.[2] The 50%-50% random alloy comes out to have a $\Delta H = 7.3$ meV/atom, compared to the experimental value of 6.5 meV/atom.[7] The recent *ab initio*, plane-wave based, work of Venezuela *et al.*[17] reported 4.8 meV/atom for this, while the *ab initio* molecular-dynamics work, with a local orbital basis, of Yu *et al.*[18] did not report any value.

The potential describes strain effects and heteronuclear bonding reasonably accurately.[4,40,43] In particular, it predicts a negative deviation from Vegard's law for the lattice constant. This is a crucial test that a theoretical method has to withstand when applied to the present problem. The deviation from linear behavior is usually quantified in terms of a bowing parameter $\theta$: a parabolic dependence of the lattice constant on concentration is incorporated by adding the term $\theta x(1-x)$ to Vegard's law,

$$a_0(x) = (1-x)a_{\mathrm{Si}} + x a_{\mathrm{Ge}} + \theta x(1-x) = a_{\mathrm{Si}} + (a_{\mathrm{Ge}} - a_{\mathrm{Si}} + \theta)x - \theta x^2. \tag{4}$$

The variation of the lattice constant with $x$ can be fitted with a second-order polynomial and then be compared with the above equation. As found previously,[16] this yields a bowing

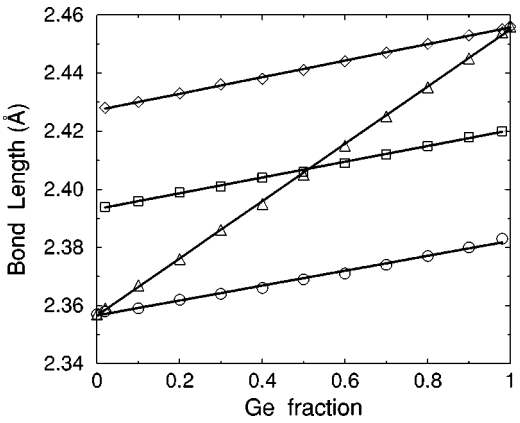


FIG. 1. Variations of bond lengths with Ge fraction in relaxed $c$-$Si_{1-x}Ge_x$ alloys at 300 K. Circles denote $R_{\text{Si-Si}}$, squares $R_{\text{Si-Ge}}$, diamonds $R_{\text{Ge-Ge}}$, and triangles the mean bond length. Lines are fits to the points.

parameter $\theta = -0.01$ Å, for the TF potential. Although this is lower than the experimental value of $-0.027$ Å,[7] the trend is clearly followed.

To perform the simulations, we use supercells subjected to periodic boundary conditions. The cells are either cubic, with 4096 atoms, when simulating the relaxed crystalline alloys and the amorphous alloys (the system is allowed to take its natural dimensions), or tetragonal, with 4032 atoms, when simulating the strained epitaxial alloys which are constrained to match the lattice constant of the Si substrate. To simulate the amorphous network, we use cells obtained by relaxing with the TF potential the atom positions and volume of the Wooten-Winer-Weaire[44] (WWW) models as constructed by Djordjević *et al.*[45] This kind of cells is proven to be an accurate representation of the structural properties of amorphous semiconductors. They do not contain coordination defects, which are present in the TF amorphous models formed by quenching from the liquid, and so the calculated bond properties are not blurred by the presence of defects.

## III. RESULTS AND DISCUSSION

### A. Relaxed crystalline alloys

We first present our investigation of the relaxed crystalline alloys. Figure 1 shows the variation of bond lengths as a function of Ge content, calculated at 300 K. The bond lengths are calculated by averaging over thousands of configurations, leading to smooth and well-defined variations. They are extracted from the partial pair distribution functions $g_{\text{Si-Si}}(r)$, $g_{\text{Si-Ge}}(r)$, and $g_{\text{Ge-Ge}}(r)$ (not shown here). For a given pair $AB$, the bond length is defined by

$$R_{AB} = \frac{\int_0^{R_{cut}} r g_{AB}(r) dr}{\int_0^{R_{cut}} g_{AB}(r) dr}, \tag{5}$$

where $A(B)$ denotes the type of atom, and $R_{cut}$ is the cutoff radius that limits the search for nearest neighbors, taken as the first minimum in the respective $g_{AB}(r)$. For all three correlations and for the TF potential, this minimum lies in the region 2.7–2.8 Å. Extending $R_{cut}$ to 3.0 Å has a negligible effect on the results. Alternatively, one can extract the bond lengths from the most probable values in the $g(r)$, i.e., from the peak positions, instead of the average values defined above. This alternative way gives somewhat less smooth variations than the first method, but the overall results are practically the same.

It is evident from Fig. 1 that there is a partial Vegard-like character in all three bond-length variations, signifying composition dependence, but overall the bonding is rather close to the Pauling limit. To quantify this and check whether there is any type-specific dependence, we extracted the topological rigidity parameters $a_{ij}^{**}$ for the three types of bonds. Following Venezuela *et al.*,[17] one can simply define these parameters as

$$a_{ij}^{**} = 1 - \frac{\theta_{ij}}{(R_{\text{Ge}}^0 - R_{\text{Si}}^0)}, \tag{6}$$

where $\theta_{ij}$ is the slope of the curve for a given type of bond, and $R_{\text{Si}}^0$ and $R_{\text{Ge}}^0$ are the equilibrium bond lengths for pure bulk Si and Ge, respectively, also calculated at 300 K. This definition is equivalent to Thorpe's, which does not however differentiate between different bond types because of the use of the same force constants. We find a slight type-specific dependence of bond lengths, with all $a_{ij}^{**}$'s being close to the value of Mousseau and Thorpe ($a^{**} = 0.707$). Specifically, we find $a_{\text{SiSi}}^{**} = 0.741$, $a_{\text{SiGe}}^{**} = 0.726$, and $a_{\text{GeGe}}^{**} = 0.712$. Compared to experiment, our value for the Ge-Ge bond is in very good agreement with both the values reported by Aubry *et al.* (0.70) and Ridgway *et al.* (0.72). For the Si-Ge and Si-Si bonds our values are lower than the experimental ones (Aubry found 0.84 and 0.94, respectively), indicating more Vegard-like behavior. This is more evident for the Si-Si bond, which Aubry *et al.* found nearly insensitive to composition.

Our results are quite close to the *ab initio* values of Venezuela *et al.* (0.73, 0.69, and 0.65 for the Si-Si, Si-Ge, and Ge-Ge bonds, respectively). These authors pointed out that the large error bars in the experimental results, especially for the Si-Si and Si-Ge bonds, might have put some uncertainty in the respective $a_{ij}^{**}$'s. The *ab initio* molecular-dynamics work of Yu *et al.*, while claiming type-dependent variations, did not extract the $a_{ij}^{**}$'s from them, so it is hard to compare. From a visual inspection of their curves, it looks like the Ge-Ge bond has more Pauling character than the Si-Si bond, something quite unexpected. The trend in our results as well as in the results reported by Venezuela *et al.* and Aubry *et al.*, despite the quantitative differences, is clear: the most sensitive bond to the changing alloy environment is the Ge-Ge bond, while the Si-Si bond is the least sensitive. This behavior can be explained in terms of the weaker and less stiff character of the Ge-Ge bond compared to Si-Si and Si-Ge bonds.

To quantify this notion, we refer to the elastic moduli of the elemental Si and Ge crystals and of the hypothetical ZB SiGe alloy,[43] which reflect the stiffness of the Si-Si, Ge-Ge,

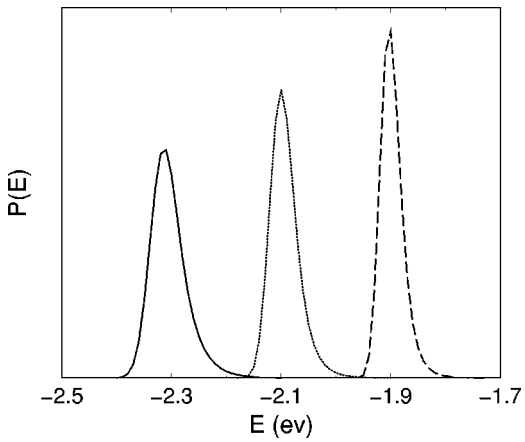


FIG. 2. Bond-energy probability distributions in relaxed $c$-$Si_{0.5}Ge_{0.5}$ alloys at 300 K. The solid line denotes $E^{bond}_{SiSi}$, the dashed line $E^{bond}_{GeGe}$, and the dotted line $E^{bond}_{SiGe}$.

and Si-Ge bond, respectively. All elastic constants, and the bulk modulus, were found to decrease in the same order as the $a^{**}_{ij}$'s do. An alternative way, which is more appropriate for the environment of the random alloy where all kinds of bonds are present in different proportions, is to extract the *bond energies* that reflect the strength of each bond in the random matrix. Bond energetics are readily defined within the empirical formalism we use, by decomposing the total cohesive energy of the alloy into bond contributions. Bond energies depend on the local environment and thus a distribution arises. We show in Fig. 2 the probability distributions for bond energies at 300 K, for $x=0.5$. Integrating over the distributions, or from the peaks, yields the average values: $E^{bond}_{SiSi}=-2.3$ eV, $E^{bond}_{SiGe}=-2.1$ eV, $E^{bond}_{GeGe}=-1.9$ eV. We see that the $a^{**}_{ij}$'s decrease in the order of descending bond strength.

It is also interesting to calculate and analyze the variations of the next-nearest-neighbor (NNN) distances as a function of composition. The only theoretical work on this comes from Mousseau and Thorpe,[28] while there are no experimental data on these quantities. Our results at 300 K are plotted in Fig. 3. Each distance is associated with a triplet of atoms.

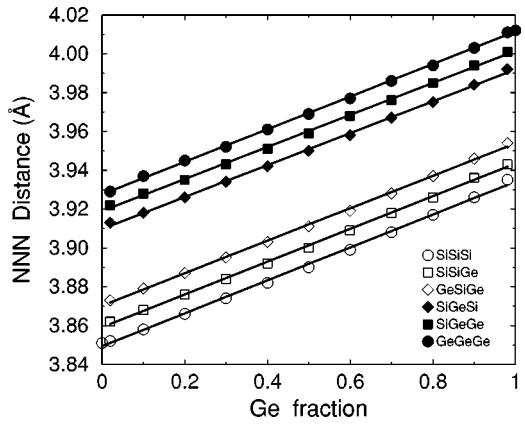


FIG. 3. Variations of next-nearest-neighbor distances with Ge fraction in relaxed $c$-$Si_{1-x}Ge_x$ alloys at 300 K. Lines are fits to the points.

The type of atom in the middle shows the vertex atom. End atoms define the pair of NNN atoms whose distance is calculated. There are six possible curves which get divided into two well-separated groups corresponding to the type of atom at the vertex. There is clear composition dependence of all curves. Their ordering is in perfect agreement with the results of Mousseau and Thorpe. However, while the theory of these authors assumed the same slope for all six curves, a close inspection of our results shows a slightly different slope for each curve. This indicates a type dependence of the NNN distances on composition. It is weaker than the corresponding one for the bond lengths, but well defined and systematic. It can be quantified using corresponding rigidity parameters $a^{**}_{ijk}$ for the NNN distances. These are defined in a way similar to the $a^{**}_{ij}$'s as

$$a^{**}_{ijk}=1-\frac{\theta_{ijk}}{(R^0_{GeGeGe}-R^0_{SiSiSi})}, \tag{7}$$

where $\theta_{ijk}$ is the slope of the curve for a given triplet and $R^0_{SiSiSi}$ and $R^0_{GeGeGe}$ are the equilibrium NNN distances in bulk Si and Ge, respectively. The values of the $a^{**}_{ijk}$'s range from 0.47 for the Si-Si-Si distance to 0.49 for the Ge-Ge-Ge distance, with the other correlations taking intermediate values. We thus observe a reversal of the behavior seen in the bond-length variation case: The Si-Si-Si NNN distance has more Vegard character than the Ge-Ge-Ge distance. This can be explained by considering that the former triplet involves two Si-Si bonds. Since these bonds have more Pauling character, they relax more by bond bending rather than by bond stretching. Bond bending is reflected in changes in the angle subtended by the two bonds. Both modes of relaxation (bending and stretching) affect the NNN distance, but it turns out that bond bending is slightly the dominant factor, making the Si-Si-Si distance more sensitive, on the average, to the changing environment than the GeGeGe distance. The latter is associated with two Ge-Ge bonds which have more Vegard character than the Si-Si bonds, relax more by bond stretching, and so the NNN distance acquires more Pauling character.

Further insight is gained by looking at the variations of bond angles with composition. These are shown in Fig. 4 for all six triplets. Similarly to the bond lengths, the bond angles $\Theta_{\alpha\beta\gamma}$ are mean values extracted from the partial bond-angle distribution functions $g_{\alpha\beta\gamma}(\theta)$, not shown here, using the expression

$$\Theta_{\alpha\beta\gamma}=\frac{\int \theta g_{\alpha\beta\gamma}(\theta)d\theta}{\int g_{\alpha\beta\gamma}(\theta)d\theta}. \tag{8}$$

The bond-angle variations get divided into three well-separated groups, characterized by a certain trend in the deviations from the tetrahedral angle: the deviations of $\Theta_{SiSiSi}$ and $\Theta_{SiGeSi}$ are always positive, while those of $\Theta_{GeGeGe}$ and $\Theta_{GeSiGe}$ are always negative. The $\Theta_{SiSiGe}$ and $\Theta_{SiGeGe}$ variations have a mixed behavior, with both negative and positive deviations, the crossover taking place at $x=0.5$.

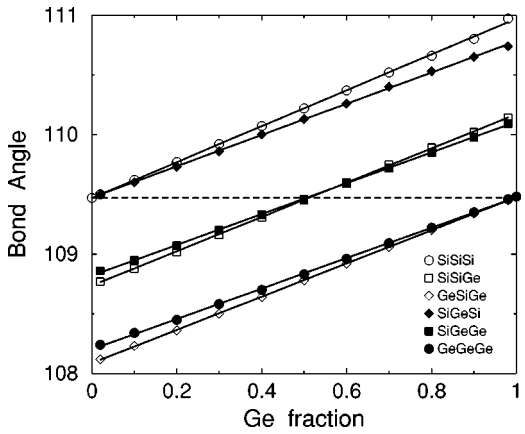


FIG. 4. Bond-angle variations with Ge fraction in relaxed $c$-$Si_{1-x}Ge_x$ alloys at 300 K. Lines are fits to the points.

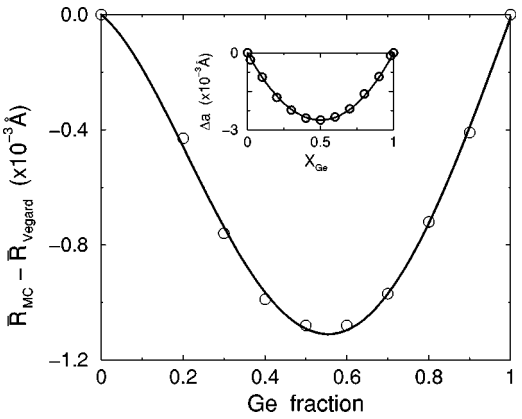


FIG. 5. Mean bond-length difference from the Vegard value as a function of composition. The inset shows the negative deviation of the lattice constant from the Vegard value. Lines are fits to the points.

The same overall trends have been found by Yu *et al.*,[18] but there is an important difference which becomes transparent at $x=0.5$. At this composition, we find that the positive deviations overwhelm the negative deviations ($\Delta\Theta_{\mathrm{SiSiSi}}=0.75°$, $\Delta\Theta_{\mathrm{SiGeSi}}=0.66°$, while $\Delta\Theta_{\mathrm{GeGeGe}}=-0.65°$ and $\Delta\Theta_{\mathrm{GeSiGe}}=-0.69°$). This confirms our above notion that triplets involving Si-Si bonds are subject to more bond bending than triplets involving Ge-Ge bonds. However, Yu *et al.* found that the negative deviations outweigh the positive ones. This difference leads to a different interpretation of the origin of the negative deviation from Vegard's law in the lattice constant. There are two possible contributions to this: (a) the negative deviations of angles from the tetrahedral value, and (b) the negative deviation of the mean bond length from the mean Vegard length. Our investigations show, on the average, positive angle deviations, so the effect is determined by the overwhelming negative deviation of the mean bond length. On the contrary, Yu *et al.* attributed the effect to a net negative angular deviation, while their average bond length presumably shows no deviation from the Vegard value.

We can demonstrate that factor (b) is the dominant mechanism for the reduction of the lattice constant in the following way. We show in Fig. 5 the mean bond-length difference from the Vegard value as a function of composition, and in the inset the negative deviation of the lattice constant. The two are correlated through the relation between bond length and lattice constant in the diamond lattice, $\Delta R=(\sqrt{3}/4)\Delta a_0$. At $x=0.5$, where the deviations are maximized, $\Delta R=-0.0011$ Å. This yields a $\Delta a_0=-0.0026$ Å, a value very close to what we have calculated directly (see inset). Thus, we conclude that indeed the radial relaxation is responsible for the negative deviation in the lattice constant.

### B. Pseudomorphically strained alloys

Contrary to the relaxed alloys, strained epitaxial alloys are not so well studied or understood. This is partly because pseudomorphically strained films, which are grown below the critical thickness for relaxation and introduction of misfit dislocations, present problems for EXAFS measurements due to the limited thickness.[15] Thus, a full range experimental study of the composition dependence of bond lengths is very hard to achieve. However, some EXAFS studies[19,22] have reported Si-Ge and Ge-Ge bond lengths in thin films with low Ge content ($x\leqslant 0.3$). Woicik *et al.*[22] indicated that bond lengths are as small if not smaller than in the unstrained dilute $x=0$ limit. An explanation of this effect was given using simple arguments based on elasticity theory.[22] On the other hand, a direct theoretical study of the compositional dependence of bond lengths in thin strained SiGe films is lacking.

We have carried out a detailed study of epitaxially strained SiGe alloys, following the methodology applied for the relaxed alloys, which covers the whole composition range and all types of bonds. The computational cells are strained on Si(100). They are tetragonally distorted, i.e., biaxially compressed in the (100) plane, forced to take the Si lattice constant, and uniaxially expanded in the [100] direction to accomodate the strain due to the lattice mismatch. We use periodic boundary conditions in all directions. The bond lengths extracted this way are appropriate for the bulk portions of a thin film. (Surface effects are considered below).

The results of our investigations, at 300 K, are summarized in Fig. 6. All bond lengths *decrease* monotonically, as Ge is added, from their dilute $x=0$ limit values through the whole concentration range. Analysis of the individual slopes of the curves shows that practically, within the limits of our calculations, there is hardly any type-specific variation, as in the case of the relaxed alloys. Epitaxial strain seems to supress this subtle effect. The amount of contraction of all bond lengths, from the values at $x=0$ to the values at $x=1$, is $\sim 0.01$ Å. It is quite small compared to $\sim 0.025$ Å for the relaxed alloys. This explains why it is difficult to detect such variation by EXAFS, and why it has been assumed that the bond lengths are independent of Ge concentration.[19] Nevertheless, the effect is clearly revealed by our simulations: there is compositional dependence, it is systematic for all types of bonds, and persists over the whole range. On the other hand, the average bond length in the strained cells smoothly increases, as expected, reflecting the expanding normal lattice constant.

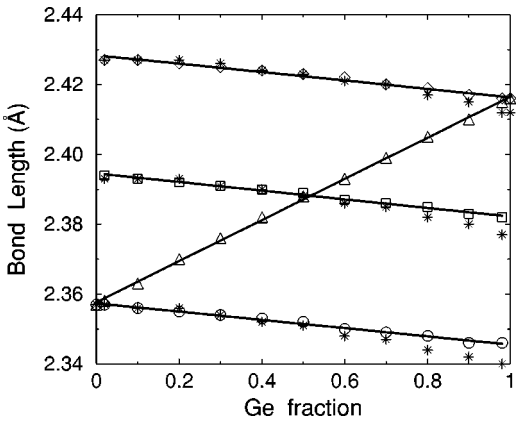


FIG. 6. Variations of bond lengths with Ge fraction in strained $c$-$Si_{1-x}Ge_x$ alloys at 300 K. Circles denote $R_{\text{Si-Si}}$, squares $R_{\text{Si-Ge}}$, diamonds $R_{\text{Ge-Ge}}$, and triangles the mean bond length. Lines are fits to the points. Stars show the MTE predictions (see text).

This picture confirms the experimental result of Woicik *et al.*[22] about contracted Ge-Ge and Si-Ge bonds in a strained $Si_{0.79}Ge_{0.21}$ alloy, and generalizes it by including Si-Si bonds as well, and by extending it to the whole composition range. As shown nicely by Woicik *et al.*,[22,46] such bond-length contractions in strained films can be accounted for by the macroscopic theory of elasticity (MTE), which leads to the following expression for the contraction of a given bond $AB$:

$$\Delta r = r'_{AB} - r^0_{AB} = -\frac{2}{3}\left(1 - \frac{c_{12}}{c_{11}}\right)(r_{mean} - r^0_{Si}), \qquad (9)$$

where $r'_{AB}$ is the epitaxially strained bond-length, $r^0_{AB}$ is the relaxed bulk bond-length value, $r_{mean}$ is the mean bond-length value in the relaxed cell (slightly deviating from the Vegard value), $r^0_{\text{Si}}$ is the bulk Si bond length, and $c_{11}$ and $c_{12}$ are cubic elastic constants of the alloy (very close to a linear interpolation of the elemental elastic constants). This expression assumes the same contraction for all bonds, since the second term on the right-hand side is constant for a given $x$, a hypothesis validated by our results. Using this expression along with our calculated values for the relaxed bond lengths and the interpolated elastic constants (using the elemental values determined by the Tersoff potential) we can extract $r'_{AB}$. The results are shown in Fig. 6. The agreement of the simulational results with the analytical MTE values is excellent for most of the composition range, giving further support to the notion of contracted bonds in strained alloys. Only at high $x$ there is some deviation from the MC results, but this is towards even more contracted bonds.

In the tetragonally distorted epitaxial configurations, strain is accomodated not only by these small bond-length contractions but also by bond-angle changes. Actually, the latter are dominating. Analysis of bond-angle deviations from the tetrahedral value in our cells reveals that bond angles within the (100) planes (in-plane) decrease, while out-of-plane angles increase relative to the tetrahedral value. The ratio of in-plane to out-of-plane deviations is about 2 (a similar ratio is proposed also by Woicik). Thus, the out-of-plane opening of angles produces the expansion of the normal, while the overwhelming shrinkage of in-plane angles produces the small contraction of bond lengths.

Another related, and quite controversial, issue concerns the dimer bond lengths at the surface of strained SiGe alloys. In the case of a single monolayer of Ge on Si(100), x-ray standing-wave measurements[47] found asymmetric Ge dimers with a bond length of 2.60 Å, while EXAFS measurements[48] indicated symmetric dimers with a bond length of 2.51 Å. The finding of elongated dimers, with respect to the bulk crystalline Ge-Ge bond length, is in sharp contrast to the shortened dimer bond length at the clean Si(100)-$(2\times1)$ surface, borne out by the majority of experimental and theoretical work. On the other hand, calculations based on the local-density approximation[49–51] (LDA) for Ge:Si(100)-$(2\times1)$ found asymmetric Ge dimers with a shortened bond length of 2.39 Å. Note, however, that the consideration in this type of calculations of higher-order reconstructions gives longer bonds. For example, for a $c(2\times2)$ cell the bond length is found to be 2.48 Å,[52] and for a $p(2\times2)$ cell, 2.51 Å.[53]

We have investigated the more general issue of how the dimer bond lengths vary at the $Si_{1-x}Ge_x$:Si(100)-$(2\times1)$ surface, as a function of $x$. Calculations are done at 300 K. We used slab cells with $(2\times1)$-reconstructed surfaces. Dimers are symmetric. (At elevated temperatures dimers oscillate between opposite orientations giving rise to an average symmetric configuration.) For the clean Si(100)-$(2\times1)$ surface, the empirical potential used here gives, at 0 K, a dimer bond length of 2.34 Å, slightly shorter than the bulk value. Average site occupancies, which determine the type of dimers formed on the surface, and the resulting average dimer bond lengths are calculated during several $10^6$ of atom-identity flip moves.

The variations of the Ge-Ge and Ge-Si dimer bond lengths as a function of $x$ are shown in Fig. 7. Due to the limited thickness of the slab cells (14 layers from the center of the slab towards each surface), $x$ deviates from its bulk value. It rather refers to a near surface composition. So, even at low values of the so-defined $x$ the Ge population at the surface at this temperature is overwhelming.[4] Because of this, Ge-Ge dimers are much more abundant than Ge-Si dimers, and Si-Si dimers are practically absent. There are two important aspects of these results. First, we observe that both bond lengths are nearly independent of composition, contrary to bulk bond lengths that either increase with $x$ (relaxed alloys) or shrink (strained alloys). This can be explained by considering the less rigid surface environment that permits greater freedom in bond-angle relaxation, leading to Pauling behavior. Indeed, it was shown by Mousseau and Thorpe[54] that the topological rigidity parameter $a^{**}$ sharply increases, becoming very flexible, near and at the surface layer of SiGe(100). Although their result referred to a nondimerized surface, the effect is present at the more realistic dimerized situation as well.

The second important result of our calculations is that we find elongated dimers with respect to the bulk values, even in the $(2\times1)$ reconstructed surface. The Ge-Ge dimer is on the average $\sim$2.5 Å long, and the Si-Ge dimer bond length is

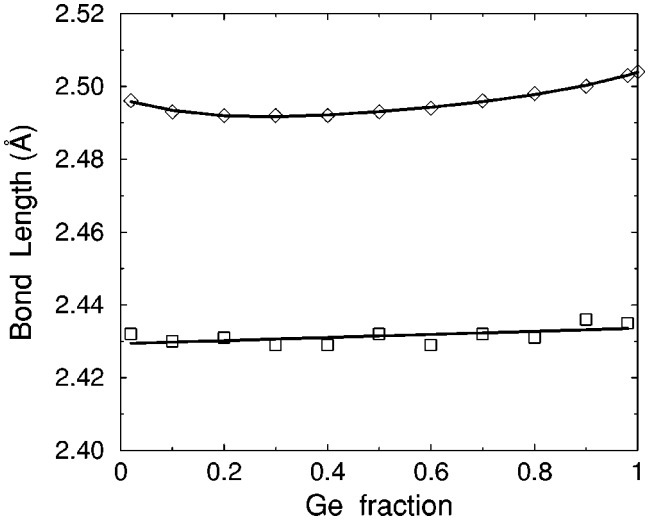


FIG. 7. Variations of dimer bond lengths with Ge fraction in strained $c$-$Si_{1-x}Ge_x$ alloys at 300 K. Diamonds denote $R_{\text{Ge-Ge}}$ and squares $R_{\text{Si-Ge}}$. Lines are fits to the points.

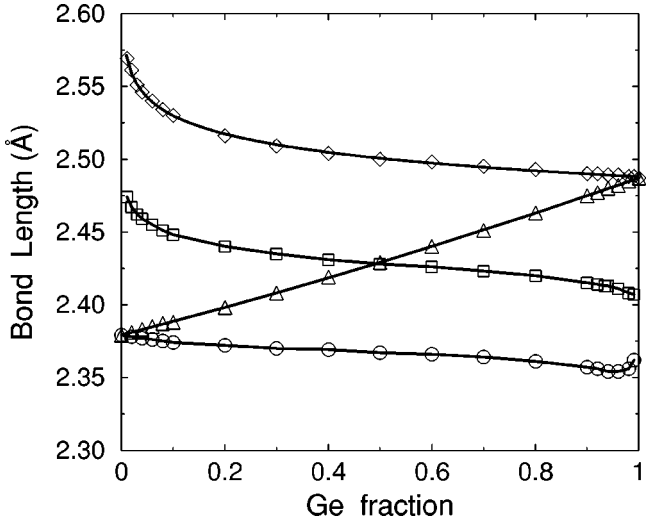


FIG. 8. Variations of bond lengths with Ge fraction in amorphous $Si_{1-x}Ge_x$ alloys at 300 K. Symbols stand as in Fig. 1. Lines are fits to the points.

$\sim$2.43 Å. (For the appropriate $x$ corresponding to 1 ML Ge coverage we actually find $d_{\text{Ge-Ge}}=2.49$ Å). These values are in excellent agreement with the experimental results of Oyanagi *et al.*[48] for $d_{\text{Ge-Ge}}$(2.51 Å), and of Chen *et al.*[55] for $d_{\text{Ge-Si}}$(2.43 Å). The latter work is for 0.1 ML Ge coverage. For this coverage we find $d_{\text{Ge-Si}}=2.433$ Å. Our finding of elongated dimers is also consistent with the experimental work of Fontes *et al.*,[47] and with a more recent x-ray-diffraction study[56] of $Si_{0.5}Ge_{0.5}$ alloys on Ge(100), reporting $d_{\text{Ge-Ge}}=2.69$ Å, but it seems that these two works overestimate the elongation of the Ge-Ge dimer. For the bond between a Ge atom belonging to a surface dimer and a Si atom in the second layer, we find a length of $\sim$2.4 Å, again in agreement with Oyanagi *et al.*

On the other hand, our results contradict those based on LDA calculations that predict the contraction of dimers in the $(2\times1)$ surface. The empirical formalism used here does not capture quantum-mechanical effects (charge transfer), as *ab initio* methods do, but it treats strain effects very well. Both effects are expected to influence the dimer bond lengths. In addition, our statistical method is superior in effectively sampling the alloyed surface. Also, the disagreement of LDA results on this subject with most experimental work is counterintuitive. Perhaps more accurate approximations of exchange and correlation, such as the generalized gradient approximation, are needed to address this problem from the *ab initio* point of view.

### C. Amorphous alloys

Finally, we consider bond-length variations in amorphous SiGe alloys. As we pointed out in the Introduction, the main debate in this case is whether bond lengths are compositionally independent or not. All early EXAFS experiments reported composition-independent bond lengths,[32–35] contrary to the theory of Mousseau and Thorpe[28] who proposed composition-dependent lengths with the same rigidity parameter as for the crystal. As far as we know, the only experimental work that proposes composition dependence comes from Ridgway *et al.*[24] This is a more recent EXAFS study but there are large error bars in the measured Ge-Ge and Ge-Si lengths, especially in the latter. The Si-Si bond length has not been studied.

The results of our simulations are given in Fig. 8. We remind the reader that the values are statistical averages over several $10^6$ of configurations generated by atom-identity flips in the amorphous (WWW) network, so the statistical accuracy is ensured. Our simulations unravel a quite unexpected composition-dependent variation of bond lengths. Instead of increasing, all bond lengths decrease from their dilute $x=0$ limits as the Ge content increases. Note that at low-$x$ values, the Ge-Si and Ge-Ge bond lengths become unusually long, indicating large relaxations not seen in the crystal. The downward trend of bond lengths persists through the whole composition range, yet all bond lengths remain longer than in the crystal. (Compare with values in Fig. 1). This reflects the lower density of the amorphous network. Also note that the mean bond length increases linearly, while the individual lengths contributing to it decrease (as is the case for the strained alloys as well). This is possible because the mean bond length is a weighted average reflecting the lattice constant of the material, which increases with $x$.

To get some insight into this effect, we need to analyze the thermodynamics of the alloy. The central quantity is the enthalpy of formation at zero pressure, defined as the total energy per atom taken with respect to the energies of equivalent amounts of its amorphous constituents

$$\Delta H(a\text{-}Si_{1-x}Ge_x)=E(a\text{-}Si_{1-x}Ge_x)-(1-x)E(a\text{-Si}) - xE(a\text{-Ge}). \quad (10)$$

For consistency, the energies of the alloy (generated with the SGC procedure) and of pure $a$-Si and $a$-Ge are calculated using the same network topology (the WWW model). As we

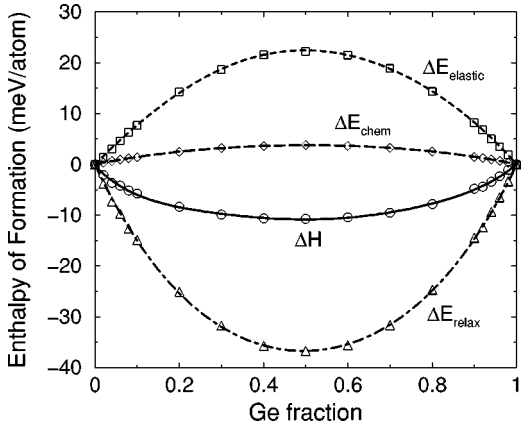


FIG. 9. Variation of the total enthalpy of formation and of the decomposed contributions with Ge fraction in $a$-$Si_{1-x}Ge_x$ alloys at 300 K. Lines are fits to the points.

have shown previously,[8] $\Delta H(a\text{-}Si_{1-x}Ge_x)$ takes *negative* values for all Ge contents, indicating the stabilization of the amorphous alloy with respect to phase separation into its amorphous constituents, at all compositions and temperatures. This is in contrast to the crystalline alloys that are predicted to phase separate under thermodynamic equilibrium at low $T$'s.[4–6] We proposed that the intrinsic strain associated with the local disorder in the amorphous network suppresses phase separation, as epitaxial strain suppresses separation in crystalline alloys.[2]

We can extract individual contributions to $\Delta H(a\text{-}Si_{1-x}Ge_x)$ following the procedure of Gironcoli, Giannozzi, and Baroni,[5] which was applied to the crystalline case. The formation of the amorphous alloy can be split into three steps taking place sequentially.

(i) For a given $x$, the ''sublattices'' of pure $a$-Si and $a$-Ge with the proper amount of Si and Ge atoms are isotropically deformed from their equilibrium atomic volumes $\Omega_{a\text{-Si}}$ and $\Omega_{a\text{-Ge}}$ to take the desired volume of the alloy $\Omega$. This costs an elastic energy

$$\Delta E_{elast}(x,\Omega) = x[E_{a\text{-Ge}}(\Omega) - E_{a\text{-Ge}}(\Omega_{a\text{-Ge}})] + (1-x) \times [E_{a\text{-Si}}(\Omega) - E_{a\text{-Si}}(\Omega_{a\text{-Si}})]. \quad (11)$$

(ii) The alloy with composition $x$ is formed by placing the appropriate numbers of Si and Ge atoms at the ideal (unrelaxed) positions $R$ of the amorphous WWW network with volume $\Omega$. An average distribution $\{\sigma_R\}$ in this unrelaxed network is obtained by generating thousands of configurations through Ising-type identity flips. This costs a chemical energy

$$\Delta E_{chem}(\{\sigma_R\}, \text{ideal}, \Omega) = \frac{N_a}{N}\delta, \quad (12)$$

where $N_a$ is the number of Si-Ge bonds in the cell, $N$ is the number of atoms in the cell, and $\delta$ is the excess Si-Ge bond energy. (iii) In the final step, the atoms are allowed to relax to their equilibrium positions, gaining a relaxation energy

$$\Delta E_{relax} = E(\{\sigma_R\}, \{u_R\}, \Omega) - E(\{\sigma_R\}, \text{ideal}, \Omega), \quad (13)$$

where $\{u_R\}$ is the displacement field of all atoms in the network due to relaxations, leading to bond-length and -angle changes. The sum of the elastic and relaxation terms is usually referred to as strain energy. The enthalpy of formation of the alloy $\Delta H(a\text{-}Si_{1-x}Ge_x)$ is the sum of these three contributions. Since we can calculate the total quantity using Eq. (10), then by calculating $\Delta E_{elast}$ [Eq. (11)] and $\Delta E_{chem}$ [Eq. (12)], we can extract $\Delta E_{relax}$ through Eq. (13).

Figure 9 shows the variation of the total $\Delta H(a\text{-}Si_{1-x}Ge_x)$, along with the decomposed contributions, as a function of the Ge content. The energies are calculated at 300 K. The elastic energy is a significant part of $\Delta H$ contributing $\sim$22 meV/atom at $x=0.5$. The chemical energy contributes less. For its calculation we took for $\delta$ (the excess bond energy) the value of $\sim$4.5 meV (to which the Tersoff potential was fitted). At $x=0.5$, $\Delta E_{chem} \simeq 3.8$ meV/atom, somewhat smaller than the value of 4.1 meV/atom calculated by Bernard and Zunger[3] for the crystalline random alloy at this composition using the method of cluster expansions and keeping the first two interaction energies. [Actually, Eq. (12) is equivalent to keeping only one term in the expansion, which converges very fast]. The difference between the crystal and the amorphous case has its origin in the relative ratio of Si-Ge bonds in the network. The crystal is random, and for the 50%-50% alloy, $N_a/N=1$. However, the amorphous alloy, as we showed previously,[8] exhibits a substantial clustering of homopolar bonds, with a maximum at intermediate compositions. So, $N_a/N$ is always less than 1 and $\Delta E_{chem}$ takes lower values.

The remarkable finding of this analysis is that the energy gained by relaxation is quite large, and so it compensates for the elastic and chemical energy costs, and leads to negative values for $\Delta H$ that stabilize the amorphous alloy. Compared to the crystalline random alloy having a strain energy $(\Delta E_{elast} + \Delta E_{relax})$ equal to 2.4 meV/atom at $x=0.5$,[3] the amorphous alloy has a strain energy of $-14.5$ meV/atom, overwhelmed by $\Delta E_{relax}$. This shows that contrary to the crystal, where the network is stiffer, the amorphous alloy easily accomodates large relaxations that lower its enthalpy of formation.

The large energy gain from relaxations explains the behavior of bond lengths at the dilute-alloy limit (low $x$). To make it transparent, we express $\Delta E_{relax}$ as the relaxation energy gain per formation of a heteropolar bond. In this way, the energy gain is properly weighted since heteropolar bonds exist in different proportions as $x$ varies. The network locally relaxes to accomodate the creation of a Si-Ge bond, and also Si-Si and Ge-Ge bonds are, by correlation, also affected. Figure 10 illustrates this analysis. $\Delta E_{relax}$ is plotted relative to the value at $x=0.5$. We clearly see large energy gains at low $x$ indicating that a significant relaxation of bond lengths and angles in this region sharply reduces the strain energy. (Bond-angle changes show similar behavior). The energy gain declines as $x$ increases and reaches a minimum at $x=0.5$; then it rises again, but it is considerably lower at the Ge-rich region, explaining the relatively small relaxations in the high-$x$ dilute-alloy limit.

The asymmetry occurs because it is easier for a Si-Ge bond, and consequently a Ge-Ge bond, to relax in a Si-rich

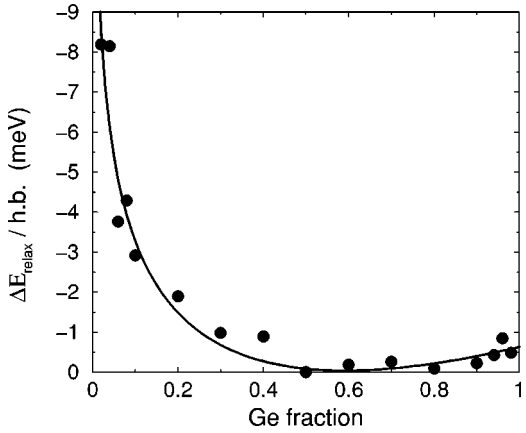


FIG. 10. Relaxation energy per heteropolar bond as a function of Ge fraction in $a$-$Si_{1-x}Ge_x$ alloys at 300 K, plotted relative to the value at $x=0.5$. Line is a fit to the points.

environment than at the other end. This comes from the consideration of the two terms at the right-hand side of Eq. (11). It costs more elastic energy to deform the $a$-Si sublattice, and thus the Si-Si and Si-Ge bonds, to alloy volumes characteristic of a Ge-rich host than to deform the $a$-Ge sublattice in a Si-rich host, as shown by the analysis of the elastic energy into the two contributions in Fig. 11. Also, the minimum in the energy gain due to relaxations at $x=0.5$ can be explained by an ''available-space'' argument: a lonely heteropolar bond can relax easier in the dilute-alloy limit rather than in the stoichiometric network with strong spatial correlations between heteropolar bonds.

The remarkable decrease of bond lengths with increasing $x$ predicted by our simulations needs to be verified by experimental work. A step toward this is made by the very recent work of Chapman *et al.*[38] who have grown samples with the rf glow discharge method and analyzed them with EXAFS. This method of growth is close to thermodynamic equilibrium, and so the results from the analyzed samples can be readily compared to our MC results. This experimental work

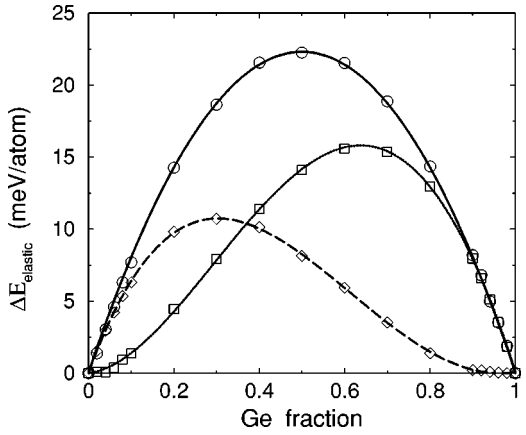


FIG. 11. Variation of the elastic energy and its decomposed contributions with Ge fraction in $a$-$Si_{1-x}Ge_x$ alloys at 300 K. Circles denote the total, diamonds $\Delta E_{a\text{-Ge}}$, and squares $\Delta E_{a\text{-Si}}$. Lines are fits to the points.

shows clearly that the Ge-Ge and Ge-Si, especially, bond lengths decrease with $x$, as we predict. These authors considered the variations as independent of composition within their statistical accuracy, but we believe that the trend is not accidental. In fact the reported slope of the Si-Ge curve agrees remarkably well with the slope of our curve. We hope that our work will instigate further experimental studies on this subject.

Regarding the elongated Ge-Ge bonds at the low-$x$ dilute-alloy limit, note that we have found elongated Ge-Ge dimer bonds at the strained $c$-SiGe(100) surface as well, and such bonds have been seen experimentally. Thus, such elongated bonds are not so odd and point to a similarity between the two cases. The less rigid the network the more extensive are the bond relaxations which relieve strain and lower the energy. The amorphous network is less rigid than the bulk crystal and can accomodate large relaxations to relieve the intrinsic strain. Similar less rigid situations occur at the surface of the strained alloy, and the Ge-Ge dimer bond length relaxes to values larger than the Pauling value because this relieves the epitaxial strain.

## IV. CONCLUSIONS

We have presented a comprehensive study of bond-length variations, and of related issues, in SiGe alloys. All three alloy systems of interest, i.e., relaxed, epitaxially strained, and amorphous were considered. Our theoretical approach was based on Monte Carlo simulations, within the semigrand-canonical ensemble utilizing Ising-like identity flips, and in conjuction with energies calculated using the empirical potential of Tersoff. The statistical accuracy of this methodology enabled us to extract clear variations through the whole composition range and for all types of bonds.

We found that in crystalline alloys, which relax to their natural lattice constant, bond lengths depend on composition $x$ in a way rather approaching the Pauling limit, and that this variation is type specific, in agreement with recent experimental studies. An analogous analysis is done for the second-nearest-neighbor distances and the angles. We found that the negative deviation of the lattice constant from Vegard's law is mainly due to radial, and not angular, relaxations.

In the epitaxial systems, bond lengths decrease with $x$ due to the two-dimensional confinement in the growth layers. Our simulational results are in good agreement with predictions based on the macroscopic theory of elasticity. The dimer bond lengths at the $(100)-(2\times1)$-reconstructed alloy surface remain nearly constant, which is consistent with the more flexible behavior of the surface environment, and they are elongated with respect to the bulk values. This is in agreement with most experimental results but in disagreement with LDA calculations.

In the amorphous alloys, we unraveled a remarkable behavior of bond lengths at the dilute-alloy limit, characterized by strong relaxations and elongation. An analysis of the thermodynamics of the alloy shows that this effect has to do with a complicated energetics compromise between the components of the enthalpy of formation of the alloy. The latter remains always negative, favoring stability, contrary to the

crystalline random alloys where it is positive. This is driven by the energy-gaining relaxations of bond lengths and angles, which overwhelm the costs due to the elastic and chemical energies of the alloy. Such extensive relaxations are not permitted in the stiffer network of the crystal.

**ACKNOWLEDGMENT**

This work was supported in part by a ΕΠΑΝ-M.4.3 grant (Α.Π.1819) from the Greek General Secretariat for Research and Technology.

[1] See *Properties of Silicon Germanium and SiGe: Carbon*, edited by E. Kasper and K. Lyutovich (INSPEC, London, 2000).
[2] J.L. Martins and A. Zunger, Phys. Rev. Lett. **56**, 1400 (1986).
[3] J.E. Bernard and A. Zunger, Phys. Rev. B **44**, 1663 (1991).
[4] P.C. Kelires and J. Tersoff, Phys. Rev. Lett. **63**, 1164 (1989).
[5] S. de Gironcoli, P. Giannozzi, and S. Baroni, Phys. Rev. Lett. **66**, 2116 (1991).
[6] M. Laradji, D.P. Landau, and B. Dünweg, Phys. Rev. B **51**, 4894 (1995).
[7] G.B. Stringfellow, J. Phys. Chem. Solids **34**, 1749 (1973).
[8] C. Tzoumanekas and P.C. Kelires, Phys. Rev. B **60**, 14 205 (1999).
[9] G. Goerigk and D.L. Williamson, Solid State Commun. **108**, 419 (1998); J. Non-Cryst. Solids **281**, 181 (2001).
[10] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, NY, 1967).
[11] L. Vegard, Z. Phys. **5**, 17 (1921).
[12] J.P. Dismukes, L. Ekstrom, and R.J. Paff, J. Phys. Chem. **68**, 3021 (1964).
[13] R.W. Olesinski and G.J. Abbaschian, Bull. Alloy Phase Diagrams **5**, 180 (1984).
[14] M.M. Rieger and P. Vogl, Phys. Rev. B **48**, 14 276 (1993).
[15] J.C. Aubry, T. Tyliszczak, A.P. Hitchcock, J.-M. Baribeau, and T.E. Jackman, Phys. Rev. B **59**, 12 872 (1999).
[16] G. Theodorou, P.C. Kelires, and C. Tserbak, Phys. Rev. B **50**, 18 355 (1994).
[17] P. Venezuela, G.M. Dalpian, A.J.R. da Silva, and A. Fazzio, Phys. Rev. B **64**, 193202 (2001).
[18] M. Yu, C.S. Jayanthi, D.A. Drabold, and S.Y. Wu, Phys. Rev. B **64**, 165205 (2001).
[19] M. Matsuura, J.M. Tonnerre, and G.S. Cargill, Phys. Rev. B **44**, 3842 (1991).
[20] J.C. Woicik, C.E. Bouldin, M.I. Bell, J.O. Cross, D.J. Tweet, B.D. Swanson, T.M. Zhang, L.B. Sorensen, C.A. King, J.L. Hoyt, P. Pianetta, and J.F. Gibbons, Phys. Rev. B **43**, 2419 (1991).
[21] H. Kajiyama, S. Muramatsu, T. Shimada, and Y. Nishino, Phys. Rev. B **45**, 14 005 (1992).
[22] J.C. Woicik, K.E. Miyano, C.A. King, R.W. Johnson, J.G. Pellegrino, T.-L. Lee, and Z.H. Lu, Phys. Rev. B **57**, 14 592 (1998).
[23] D.B. Aldrich, R.J. Nemanich, and D.E. Sayers, Phys. Rev. B **50**, 15 026 (1994).
[24] M.C. Ridgway, K.M. Yu, C.J. Glover, G.J. Foran, C. Clerc, J.L. Hansen, and A.N. Larsen, Phys. Rev. B **60**, 10 831 (1999).
[25] M.R. Weidmann and K.E. Newmann, Phys. Rev. B **45**, 8388 (1992).
[26] M. Ichimura, Y. Nishino, H. Kajiyama, and T. Wada, Jpn. J. Appl. Phys., Part 1 **29**, 842 (1990).
[27] Y. Cai and M.F. Thorpe, Phys. Rev. B **46**, 15 872 (1992).
[28] N. Mousseau and M.F. Thorpe, Phys. Rev. B **46**, 15 887 (1992).
[29] N. Mousseau and M.F. Thorpe, Phys. Rev. B **48**, 5172 (1993).
[30] J.G. Kirkwood, J. Chem. Phys. **7**, 506 (1939).
[31] Actually, Mousseau and Thorpe (Ref. 28) adjusted $a^{**}$ to the value 0.707 from the results of Gironcoli *et al.* (Ref. 5).
[32] L. Incoccia, S. Mobilio, M.G. Proietti, P. Fiorini, C. Giovanella, and F. Evangelisti, Phys. Rev. B **31**, 1028 (1985).
[33] A. Filipponi, P. Fiorini, F. Evangelisti, A. Balerna, and S. Mobilio, J. Phys. (Paris), Colloq. **8**, 357 (1986).
[34] Y. Nishino, S. Muramatsu, Y. Takano, and H. Kajiyama, Phys. Rev. B **38**, 1942 (1988).
[35] S. Minomura, K. Tsuji, M. Wakagi, T. Ishidate, K. Inoue, and M. Shibuya, J. Non-Cryst. Solids **59-60**, 541 (1983).
[36] P.C. Kelires, Phys. Rev. B **62**, 15 686 (2000).
[37] C. Mathioudakis and P.C. Kelires, J. Non-Cryst. Solids **266-269**, 161 (2000).
[38] B.D. Chapman, S.-W. Han, G.T. Seidler, E.A. Stern, J.D. Cohen, S. Guha, and J. Yang, J. Appl. Phys. **92**, 801 (2002).
[39] B. Dünweg and D.P. Landau, Phys. Rev. B **48**, 14 182 (1993).
[40] P.C. Kelires, Phys. Rev. Lett. **75**, 1114 (1995).
[41] N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller, and E. Teller, J. Chem. Phys. **21**, 1087 (1953).
[42] J. Tersoff, Phys. Rev. B **39**, 5566 (1989).
[43] P.C. Kelires, Phys. Rev. B **49**, 11 496 (1994).
[44] F. Wooten, K. Winer, and D. Weaire, Phys. Rev. Lett. **54**, 1392 (1985).
[45] B.R. Djordjević, M.F. Thorpe, and F. Wooten, Phys. Rev. B **52**, 5685 (1995).
[46] J.C. Woicik, J.G. Pellegrino, B. Steiner, K.E. Miyano, S.G. Bompadre, L.B. Sorensen, T.-L. Lee, and S. Khalid, Phys. Rev. Lett. **79**, 5026 (1997).
[47] E. Fontes, J.R. Patel, and F. Comin, Phys. Rev. Lett. **70**, 2790 (1993).
[48] H. Oyanagi, K. Sakamoto, R. Shioda, Y. Kuwahara, and K. Haga, Phys. Rev. B **52**, 5824 (1995).
[49] P. Krüger and J. Pollmann, Phys. Rev. Lett. **72**, 1130 (1994).
[50] J. Cho and M. Kang, Phys. Rev. B **49**, 13 670 (1994).
[51] S.C. Gay and G.P. Srivastava, Phys. Rev. B **60**, 1488 (1999).
[52] J. Jin and L.J. Lewis, Phys. Rev. B **49**, 2201 (1994).
[53] Y. Miyamoto, Phys. Rev. B **49**, 1947 (1994).
[54] N. Mousseau and M.F. Thorpe, Phys. Rev. B **52**, 2660 (1995).
[55] X. Chen, D.K. Saldin, E.L. Bullock, L. Patthey, L.S.O. Johansson, J. Tani, T. Abukawa, and S. Kono, Phys. Rev. B **55**, R7319 (1997).
[56] K.L. Whiteaker, I.K. Robinson, J.E. Van Nostrand, and D.G. Cahill, Phys. Rev. B **57**, 12 410 (1998).