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Structural model for crystalline and amorphous Si-Ge alloys

Normand Mousseau and M.F. Thorpe

Department of Physics and Astronomy and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan 48824

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There are serious contradictions between extended x-ray-absorption fine structure (EXAFS) measurements of the Si-Ge and Ge-Ge bond lengths in both crystalline and amorphous silicon-germanium alloys, and in the theoretical and simulation predictions. In particular, results from EXAFS experiments show that the Si-Ge and Ge-Ge bond lengths are *independent* of the alloy composition, indicating that there is no *topological rigidity* in the lattice. These EXAFS results on Si-Ge alloys are in sharp disagreement with all previous EXAFS results on III-V and II-VI semiconductor alloys. We discuss the implications of the EXAFS results regarding the local and global structure of the alloys. We also propose a structural model to serve as a focus for further experiments. In order to satisfy the overall floppiness of the network, we suggest that the Si-Ge samples may contain a large density of planar cracks, lined with hydrogen, and separated by $\sim$ 10 Å. Some measurements that could confirm (or discredit) this model are suggested.

I. INTRODUCTION

With the development of extended x-ray-absorption fine-structure (EXAFS) techniques, there has been a renewed interest on the part of experimentalists to examine the local structure of disordered materials. Some of the most exciting work in the past decade has been on crystalline semiconductor alloys;[1,2] both III-V and II-VI compounds. Many different materials have been examined at various compositions and a very consistent picture emerges. The mean bond length of chemically specific pairs, for example, Ga-As bonds in $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{As}$, is composition dependent but much less strongly so than the *overall* mean bond length. The overall mean bond length, or unit cell size, can be obtained independently from x-ray diffraction experiments, and is always found to be close to linear (Végard's law) (Ref. 3) in agreement with the result expected if a weighted average of the different bond lengths is found using the EXAFS results. The weaker composition dependence of the chemically specific mean bond lengths is due to the soft nature of the zinc-blende lattice.

The situation is very different for binary semiconductor alloys made from the group-IV elements Si, Ge, and Sn. Recent experimental EXAFS results involving the alloy $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ have shown that the Ge-Ge and Ge-Si mean bonds lengths are *independent* of the composition x, for *both* crystalline and amorphous alloys. Similar composition independent bond lengths results have also been reported for Si-C and Ge-Sn alloys, but these systems are more complex because of the likelihood of some local graphitic bonding of the C in Si-C, and the possibility of local metallic bonding associated with the Sn in Ge-Sn. We therefore concentrate in this paper on the Si-Ge alloys.

II. SUMMARY OF THEORY

In order to understand the EXAFS and x-ray experiments in detail, a theoretical model for the structural distortions in the zinc-blende lattice must be used. Because there are static concentration waves with *all* wavelengths present, the precise nature of the model used is probably not too important. Almost all work[1,2,4–10] has been focused around simple rigid ion models like the Keating model[11] and/or the Kirkwood model.[12] Both of these models have strong nearest-neighbor central forces and weaker angular forces, which are determined by fairly gross overall fits to the elastic constants and/or the optic phonons of the pure materials. The zinc-blende structure is unstable under nearest-neighbor central forces, so that small angular forces are required for stability. Good qualitative and quantitative agreement is found between theory and experiment in for *all* III-IV and II-VI semiconductors. It has recently been pointed out by Cai and Thorpe (CT) (Ref. 7) that the theory describing the nearest-neighbor (and also second neighbor) EXAFS results can be expressed in terms of a single quantity, the *topological rigidity parameter* a^{**}. For small angular forces, the Kirkwood model[12] gives

$$a^{**} = \frac{1 + 1.25(\beta/\alpha)}{1 + 3.60(\beta/\alpha) + 1.17(\beta/\alpha)^2}, \tag{1}$$

where α is the strength of the nearest-neighbor central force and β is the strength of the angular force, involving two adjacent nearest-neighbor bonds as given below in Eq. (2). By fitting to elastic and/or optic mode measurements in the pure materials ($x = 0$ or $x = 1$), we can say that $0.1 \leq \beta/\alpha \leq 0.2$ for all semiconductors, with β/α being rather smaller for the II-VI alloys than for the III-V alloys.[7] Using Eq. (1), this leads to a topological rigidity parameter a^{**} lying between 0.7 and

0.8. If $a^{**} = 1$, then the network is *floppy* and each bond can achieve its own natural length. On the other hand if $a^{**} = 0$, the network becomes *rigid* and all ions lie on the sites of a perfect crystal; that is all nearest-neighbor bonds have the same length. This rigid limit is not obtainable, but close packed metallic alloys come close.[13] Analytic work and numerical simulations are in good agreement with experimental results for this type of approach[2,7–9] in the many III-V and II-VI semiconductor alloys studied to date. Most of the experimental work has concentrated on pseudobinary semiconductors ($\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{As}$, $\mathrm{Zn}_x\mathrm{Cd}_{1-x}\mathrm{Te}$, etc.) where a correct understanding of the internal strains can lead to a better production of layered materials. The situation is dramatically different in Si-Ge alloys where the mean Ge-Ge and Si-Ge bond lengths from EXAFS are found to be composition *independent*.[14–17] This immediately, and without invoking any particular theoretical approach, suggests that these networks are much less rigid (i.e., floppier) than the III-V and II-VI alloys. However it is useful to continue the present discussion by using an extension of the CT model that was successful and transparent in the III-V and II-VI alloys.[9]

III. THEORY FOR GROUP-IV ALLOYS

We have extended the theoretical description of the local structure of crystalline, and with minor changes, amorphous binaries[9] to group-IV alloys. Recent EXAFS measurements on *a*-Si-Ge and *c*-Si-Ge compounds[14–16] have shown quite severe disagreement with both CT theory and simulation predictions. The goal of this paper is to examine these discrepancies between experimental EXAFS work on one side and theoretical and simulation work on the other, as well as to propose a structural model that may resolve these discrepancies.

We use a harmonic potential with angular forces of the Kirkwood type,[12]

$$V = \frac{\alpha}{2}\sum_{\langle ij\rangle}\left(L_{ij} - L^0_{ij}\right) + \frac{\beta}{8}\langle L\rangle^2 \sum_{\langle ijk\rangle}\left(\cos\theta_{ijk} + \tfrac{1}{3}\right)^2, \quad (2)$$

where α and β are considered constant for all interactions, Si-Si, Si-Ge, and Ge-Ge, etc. The variation in the force constants is $\sim 20\%$ in Si-Ge alloys and this can only produce effects of $\sim 2\%$ in deviations from straight line behavior in the alloy[9] which is much too small to account for the observed discrepancies. For this potential and using

$$L^0_{\mathrm{SiGe}} = \frac{1}{2}\left(L^0_{\mathrm{SiSi}} + L^0_{\mathrm{GeGe}}\right), \quad (3)$$

the CT approach[9] gives the following behavior for the partial and total lengths:

$$\begin{aligned}
\langle L\rangle &= (1-x)L^0_{\mathrm{SiSi}} + xL^0_{\mathrm{GeGe}},\\
\langle L_{\mathrm{SiSi}}\rangle &= \langle L\rangle - xa^{**}(L^0_{\mathrm{GeGe}} - L^0_{\mathrm{SiSi}}),\\
\langle L_{\mathrm{GeGe}}\rangle &= \langle L\rangle + (1-x)a^{**}(L^0_{\mathrm{GeGe}} - L^0_{\mathrm{SiSi}}),\\
\langle L_{\mathrm{SiGe}}\rangle &= \frac{1}{2}(\langle L_{\mathrm{SiSi}}\rangle + \langle L_{\mathrm{GeGe}}\rangle),
\end{aligned} \quad (4)$$

where a^{**} is the topological rigidity constant which depends on the ratio β/α as given in (1). Two assumptions have been made to obtain the preceding results (4).

(a) The elastic constants are the same for all interactions. The topological rigidity parameter a^{**} is not very sensitive to changes in the local force constants,[8] and the elastic constants for the pure Si and Ge differ by about 20%, which will only produce a hardly perceptible bowing of the Z plots to be discussed later.

(b) The length L^0_{SiGe} is the arithmetic average of the two other partial lengths [see Eq. (3)]. The additivity of atomic radii is found to hold generally in the case of semiconductors.[7–9,18]

IV. COMPARISON OF THEORY AND EXPERIMENT

From Eq. (4) we see that this theory predicts an average length following Vegard's law, and the three parallel partial lengths varying linearly with the concentration x. As we have commented earlier, similar straight line behavior is predicted and has been seen experimentally in ternary III-V and II-VI compounds.[1] For the binaries, we find a few experimental papers on Si-Ge alloys, using either x-ray measurements or EXAFS on the Ge atoms. Kajiyama *et al.*[14] measured the mean Ge-Ge and Ge-Si bond lengths in bulk *c*-Si-Ge alloys; Incoccia *et al.*[15] and Nishino *et al.*[16] in bulk *a*-Si-Ge alloys; and Matsuura, Tonnerre, and Cargill[17] measured these lengths in Si-Ge/Si(100) films. There has also been some work on *a*-Ge-Sn and *a*-Si-C alloys; both by the same group.[19,20] However, since Sn and C can have variable bonding (Sn can have local metallic bonding and C can have local graphitic bondings), conclusions in these cases are more difficult to draw and will not be directly addressed here. Moreover, because the CT theory applies only to the bulk, we will concentrate on the three first papers.[14–16] Nevertheless we note that *all* these experiments cited above on Si-Ge, Si-C, and Ge-Sn alloys are consistent with the result that there is *no composition dependence of the chemically specific bond lengths*, for *both* crystalline and amorphous samples. In the three papers on Si-Ge,[14–16] both the Ge-Ge and the Ge-Si mean nearest-neighbor bond lengths have been measured using Ge EXAFS, but *not* the Si-Si bond length. All of these experiments agree on the fact that the measured mean bond lengths do *not* vary with composition. The exact bond length varies only slightly and within a 0.02 Å range from one paper to the other, but the conclusions are the same: the Ge-Ge and Si-Ge nearest-neighbor distances are independent of concentration.

Looking at Eq. (4), we see that the only way to obtain flat curves for Ge-Ge and Ge-Si bond lengths is for the network to be *floppy*, i.e., to have a^{**} very close to 1. Even relaxing the condition where we have used the same force constants for the three different kinds of pair interactions, we find in the low concentration (single defect) limit,[21]

$$\langle L_{\mathrm{SiGe}}\rangle = L^0_{\mathrm{SiSi}} + x\left[\frac{(1-a^{**})\alpha_{\mathrm{SiGe}}}{(1-a^{**})\alpha_{\mathrm{SiSi}} + a^{**}\alpha_{\mathrm{SiGe}}}\right] \times \left(L^0_{\mathrm{SiGe}} - L^0_{\mathrm{SiSi}}\right), \qquad (5)$$

where we have introduced different central force constants α_{SiSi} and α_{SiGe} for the Si-Si and Si-Ge bonds. Different angular force constants can be incorporated by adjusting a^{**} as in Ref. 8. We have also *not* assumed that $L^0_{\mathrm{SiGe}} = (L^0_{\mathrm{SiSi}} + L^0_{\mathrm{GeGe}})/2$. So, independently of the values of the force constants, we can only obtain a flat EXAFS curve (i.e., independent of composition x) with $a^{**} = 1$. The first way to achieve this result is to affect the value of a^{**} by varying the ratio β/α. From Eq. (1), we have the behavior of a^{**} as a function of the ratio of the angular force β to the bond stretching force α from CT. To obtain $a^{**} = 1$, we need a ratio β/α that is essentially zero, and certainly much smaller than the usual range 0.1–0.2. In order to explain their results, Kajiyama *et al.*[14] suggested that the angular term β is anomalously small compared to the stretching term α but for this explanation to be valid would require a ratio β/α of less than 0.05 which would lead to a much weakened shear modulus. Direct measurements of the elastic constants in Si-Ge solid solutions grown by evaporation in the absence of hydrogen show no such weakening.[22] It would be interesting to repeat these experiments on hydrogenated samples. Also indirect measurements like Raman spectra can be well reproduced theoretically using the same force constants for all bonds and taking into account only the mass differences.[23] The Raman peak at about 470 cm^{-1} in pure silicon can be rescaled using only the appropriate reduced mass to the Ge peak at 280 cm^{-1} and to the additional Si-Ge peak centered at about 380 cm^{-1}, all to within 5%, confirming that the force constants are close for the three kinds of bonds. The samples used for the Raman scattering were polycrystalline and should not contain hydrogen. It is therefore very unlikely that any appreciable change in the ratio β/α occurs, and we dismiss this possibility. We do however expect a softening of the elastic constants in hydrogenated samples—not due to the weakened angular forces—but due to the mechanical degradation of the network caused by the presence of large amounts of hydrogen.

In their paper on c-Si-Ge alloys, Kajiyama *et al.*[14] measured the lattice constant as a function of the composition x using x-ray diffraction. It is worth mentioning that previous measurements showed a small deviation from Végard's law of less that 4% (Ref. 24) compared with the the much larger 16% presented in Kajiyama's paper. Using the (exact) sum rule

$$\langle L\rangle = (1-x)^2\langle L_{\mathrm{SiSi}}\rangle + 2x(1-x)\langle L_{\mathrm{SiGe}}\rangle + x^2\langle L_{\mathrm{GeGe}}\rangle, \qquad (6)$$

and the values for $\langle L_{\mathrm{SiGe}}\rangle$ and $\langle L_{\mathrm{GeGe}}\rangle$ obtained by EXAFS, it is possible to predict the expected value of $\langle L_{\mathrm{SiSi}}\rangle$. If Végard's law is exactly obeyed, then (6) gives $\langle L_{\mathrm{SiSi}}\rangle = L^0_{\mathrm{SiSi}}$ which is also concentration independent. However, the measured x-ray diffraction data[14] can be fit with

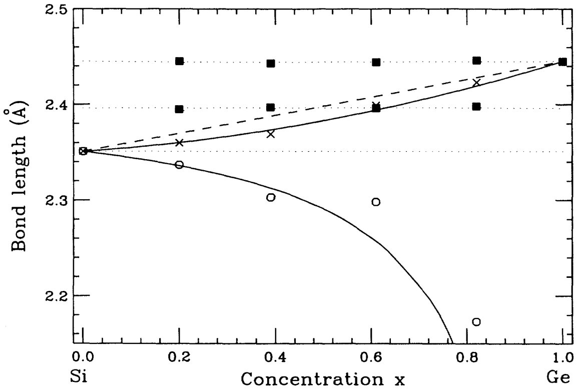

FIG. 1. A Z plot from the experiments of Kajiyama *et al.* (Ref. 14). The Ge-Ge and Si-Ge bond lengths measured by EXAFS are shown by full squares and the average length obtained by x-ray diffraction, by crosses and the dashed line is Végard's law. The Si-Si bond length (empty circles) was deduced using Eq. (6). The solid lines are obtained from Eqs. (7) and (8) using $\theta = 0.06$ Å.

$$\langle L\rangle = (1-x)L^0_{\mathrm{SiSi}} + xL^0_{\mathrm{GeGe}} - \theta x(1-x), \qquad (7)$$

where θ is the *bowing* parameter. From (6)

$$\langle L_{\mathrm{SiSi}}\rangle = L^0_{\mathrm{SiSi}} - \theta\frac{x}{1-x} \qquad (8)$$

showing that the composition dependence of $\langle L_{\mathrm{SiSi}}\rangle$ will become large as the Ge composition $(1-x)$ increases, as shown in Fig. 1. We emphasize that the result (8) is independent of any model. It would be useful to have EXAFS experiments on the Si available so that this quantity would be available to provide an important internal consistency check. It would be quite unusual if the length of the Si-Si bond decreased upon the introduction of the larger Ge. Theoretically this behavior has been predicted in some metallic alloys (e.g., Au-Ag) where it is attributed to the effects of charge transfer.[13] However, we cannot use the same argument here since Si and Ge are in the same column of the Periodic Table and charge transfer effects are negligible. It is difficult to justify the Ge-Ge and Si-Ge bond lengths remaining so constant compared with such a marked change in Si-Si bond length, although such an occurrence would not violate any geometrical constraints.

Another way to increase floppiness in the alloy would be to *decrease* the average coordination number of the atoms. This is a likely explanation since in all three experiments,[14–16] the sample preparation took place in the presence of *hydrogen.* Hydrogen is a network terminator, and attaches itself to one (or more) of the four bonds formed by the Si and Ge ions. As a consequence its main effect on the network is to decrease the effective coordination and hence the rigidity of the network.

V. STRUCTURAL MODEL

We have examined the effect of the inclusion of hydrogen on the topological rigidity of the network. Hydrogen is a terminator that makes a single bond to either Si or Ge, both of which remain fourfold coordinated. Hydrogen that goes in interstitially or as molecular hydrogen is irrelevant to the mechanical properties of the network and will be ignored here. The method we use gives an estimate for the variation of a^{**} with the degree of hydrogenation. The numerical method used is the same as the one presented in Ref. 9 where the Kirkwood potential is used and the static relaxation is accomplished using a conjugate-gradient algorithm. We have introduced hydrogen into the network by cutting a bond and inserting *two* hydrogens. This is an unphysical procedure as the Si-H and Ge-H bonds lengths are too large (about 1.5 Å) compared with 2.35 and 2.43 Å for Si-Si and Ge-Ge bonds, respectively, for this to occur. Nevertheless, since we consider the hydrogenated bond as absent, this procedure does encompass the main effects of hydrogen which is to act as a terminator and hence lower the mean coordination of the network.[25] In our simulations, we just randomly remove bonds,[25] but never attach more than than two hydrogens to a Si or Ge atom. This procedure can be accomplished with equal computational facility for both the crystalline and amorphous networks.

It is possible to obtain the limits of a^{**} analytically, i.e., the fully coordinated and the floppy limit when the rigidity vanishes. In between these two limits, we have to resort to computer simulations. The fourfold-coordination limit of a^{**} is found from Eq. (1) to be 0.707 for a ratio $\beta/\alpha = 0.20$. The floppy limit is obtained by looking at the rigidity percolation transition, using a mean field approach. This has been used elsewhere[26] and has been shown to be very accurate. The network becomes floppy when F, the number of zero frequency modes, is greater than zero.[26] The number of zero frequency modes is equal to the number of degrees of freedom minus the number of constraints. Because we do not allow more than two hydrogens per Si or Ge, the whole network remains fully connected. Counting 4/2 central force and five angular constraints per Si and/or Ge, and 1/2 central force constraint for each H in $\mathrm{Si}_{1-x}\mathrm{Ge}_x$:$\mathrm{H}_y$, we get

$$F = 3N(1+y) - N[2+5] - Ny\left[\frac{1}{2}\right] = N(\tfrac{5}{2}y - 4). \tag{9}$$

For $F = 0$ we find

$$y_p = \tfrac{8}{5} = 1.6 \tag{10}$$

which corresponds to a $y_p/(1+y_p) = 8/13 = 62$ at.% fraction of hydrogen.

The essential idea is that each hydrogen atom terminates a bond and has no other interactions. Since hydrogen does not participate in connecting the network together, being a terminal bond, we can consider it as being absent for most purposes. Our simulation procedure consists then in removing bonds at random in *c*-Si-Ge or *a*-Si-Ge solid solutions to obtain the topological rigidity parameter a^{**} associated with a certain concentration x and y. This is done by computing the various mean distances, as in Fig. 2, and fitting the resulting straight line Z plot found with the single unknown parameter a^{**}. This is a somewhat indirect procedure, but appropriate in the present context. Indeed it is probably the best way to obtain the topological rigidity parameter in amorphous networks. The quantity of hydrogen needed to take the topological rigidity a^{**} of the lattice to unity (i.e., the floppy limit) would be extremely large (62 at.%) and it is difficult to imagine such amounts of hydrogen distributed evenly throughout the sample.

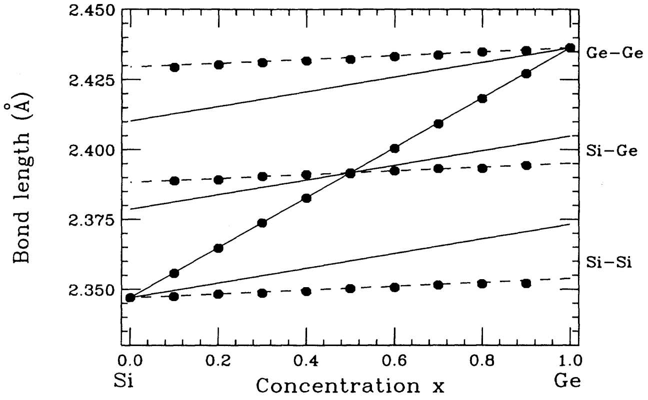

FIG. 2. A Z plot for a-$\mathrm{Si}_x\mathrm{Ge}_{1-x}$:$\mathrm{H}_y$ from a computer relaxation of a crystalline alloy. The solid lines correspond to a topological rigidity parameter $a^{**} = 0.707$ and the dashed lines are a fit to the simulation results (shown by solid circles) where $y = 1.0$ and $a^{**} = 0.923$. The fraction of hydrogen is determined by assigning two hydrogens to each removed bond.

The bulk calculations for Fig. 3 have been made for randomly removed bonds in crystalline as well as amorphous cells of $2^{15} = 32\,768$ atoms with periodic bound-

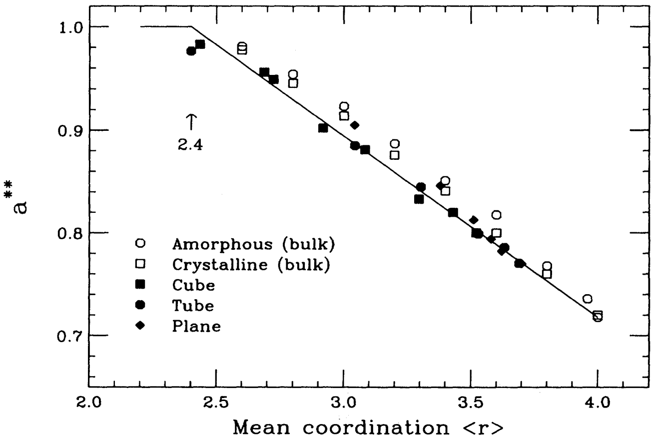

FIG. 3. The variation of the topological rigidity parameter a^{**} with the mean coordination $\langle r\rangle$ in Si-Ge alloys. The open symbols are for simulations with periodic boundary conditions (bulk) and the solid symbols for (clusters) with free boundary conditions. The solid line is a linear interpolation between the floppy limit $a^{**} = 1$ and the $a^{**} = 0.707$ for the perfect network, given in Eq.(11).

ary conditions, constructed by Wooten[27] following the algorithm by Wooten, Winer, and Weaire.[28] The Wooten sample contained $2^{12} = 4096$ atoms but we replicated it eight times to form a larger cube. We then decorated the full lattice randomly with Si and Ge atoms following the procedures described in Ref. 9. In our previous work we have shown, using computer simulations, that since the connectivity is the same in the crystalline and *perfect* amorphous Si structure, the topological rigidity a^{**} is identical in both systems.[9] Moreover, as the strain due to alloying is about two orders of magnitude smaller than the strain due to amorphization, we can treat the former as a perturbation and use the CT theory developed for crystalline alloys. The results for all the partial lengths in both the amorphous and crystalline structures are always the expected set of three parallel straight lines that can be fit with the single parameter a^{**} using Eqs. (4). From our computer simulations, we find that the topological rigidity parameter a^{**} is linear in the mean coordination $\langle r\rangle$ of the network and so can be written

$$a^{**} = \tfrac{5}{8}[(4-\langle r\rangle) + a_0^{**}(\langle r\rangle - 2.4)], \qquad (11)$$

where $\langle r\rangle = 4-y$ is the mean coordination of the network (ignoring the hydrogen) and the topological rigidity parameter $a^{**} = a_0^{**} = 0.707$ when no hydrogen is present.

The precise way in which the hydrogen is distributed in the network is irrelevant as far as the topological rigidity is concerned, as long as it is homogeneous on some reasonable length scale. It is therefore possible to think of a physically more plausible model that could result in the same amount of floppiness in the network. We have studied the topological rigidity for *finite* pieces of crystalline $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloys of different sizes and shapes with free surfaces. The three shapes we used were cubic ($l \times l \times l$), tubular ($l \times l \times L$), and planar ($l \times L \times L$), where l is a variable and L was fixed at 54 Å which we can regard as infinite (Fig. 4). There is no hydrogen implanted in these pieces. A physical realization of this situation would be that all the dangling bonds at the surface of these pieces are saturated with hydrogen. Again the topological rigidity parameter is extracted from the computer simulations by fitting the three parrallel lines in the Z plot like that in Fig. 2 with the single unknown parameter a^{**}. We do indeed always obtain simple straight line Z plots from the simulations on cubes, tubes, and planes. Our results in Fig. 3 shows that the *geometry* of the defects is almost irrelevant to the topological rigidity a^{**}; the mean coordination of the system uniquely determines its topological rigidity.

For these structures shown in Fig. (3), the open surfaces are saturated with hydrogen. We are therefore free to choose any geometry, for a given concentration of dangling bonds, without affecting the mechanical rigidity of the network. A probable structural model would be one with a high density of thin planar cracks with a typical size of the two regions between cracks being about 10 Å as deduced from Fig. 5. A sketch of this model is presented in Fig. 6. These cracks will be filled with hydrogen saturating the dangling bounds of the surfaces. Such a structure would be almost completely free of strain due to the alloying, resulting in an almost flat Z plot, and would also respect the random proportion of Si-Ge to Ge-Ge bonds found experimentally from EXAFS.[14–16]

From this model, it is also possible to find the softening of the elastic constants. This is done by applying an external strain to the model and then again minimizing the energy as before. The difference in the relaxed energy leads to the elastic moduli.[25] Figure 7 shows how the bulk modulus varies with the effective coordination $\langle r\rangle$, in a bulk *c*-Si where *planar cracks* were introduced. These cracks were created the following way: in a crystalline cell of $2^{15} = 32\,768$ Si atoms, the position and direction of a plane were chosen at random; all the bonds that crossed the plane in a square area of side two unit cells around the origin of the plane were removed. We compare these results with an expression found by He and Thorpe[25] for removing bonds at random. This expression is valid around the rigidity threshold, but is probably not critical behavior,

$$B = 0.328\,(\langle r\rangle - 2.4)^{1.5} \qquad (12)$$

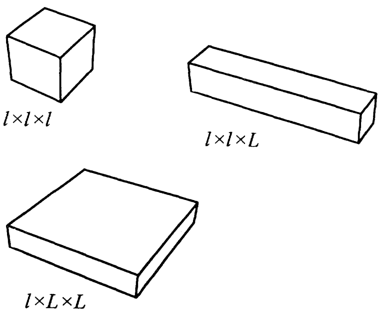

FIG. 4. A sketch of the cube, tube, and plane, where the long dimension $L = 54$ Å and the short dimension can be varied. The results obtained were not sensitive to the length L which can be regarded as infinite.

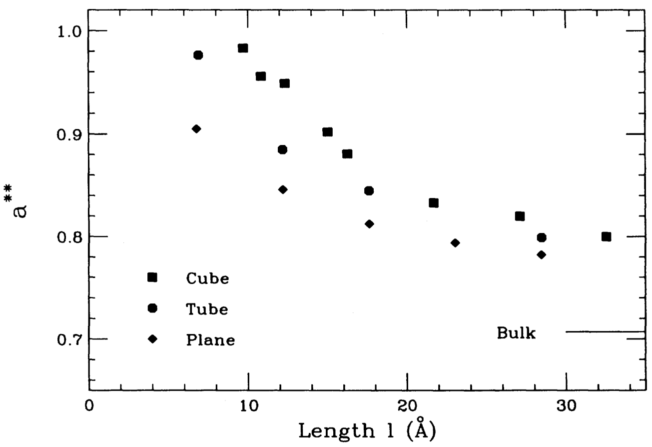

FIG. 5. The variation of the topological rigidity parameter a^{**} with the length scale l for the cubes, tubes, and planes shown in Fig. 4. Here the large dimension $L = 54$ Å can be regarded as infinite.

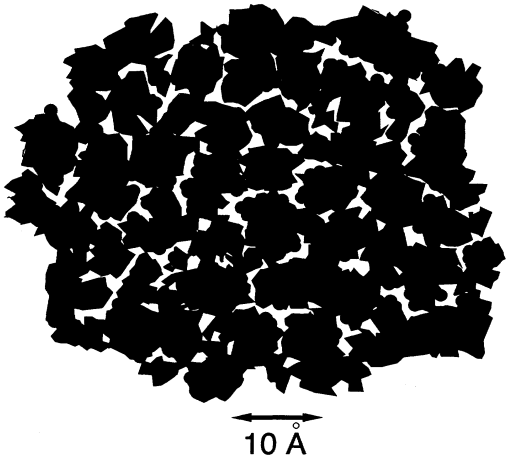

FIG. 6. A sketch of the proposed structural model for Si-Ge alloys. The dark region is network and the open cracks are saturated with hydrogen to tie off the dangling bonds.

in units where the bulk modulus is 1 at full coordination ($\langle r \rangle = 4$). Within the numerical accuracy, we see than the *distribution* of the hydrogen does not effect the bulk modulus either. We see once again that the mean coordination is much more important than the detailed geometry in determining the mechanical/elastic properties of the system. For hydrogenated samples near the rigidity threshold, which are required to explain the EXAFS results, the elastic constants should be an order of magnitude lower than in Si-Ge alloys that do not contain hydrogen. Sample annealing, allowing for the removal of cracks and hydrogen, would increase the rigidity of the lattice, and hence produce more composition dependence of the EXAFS results and larger elastic moduli.[9]

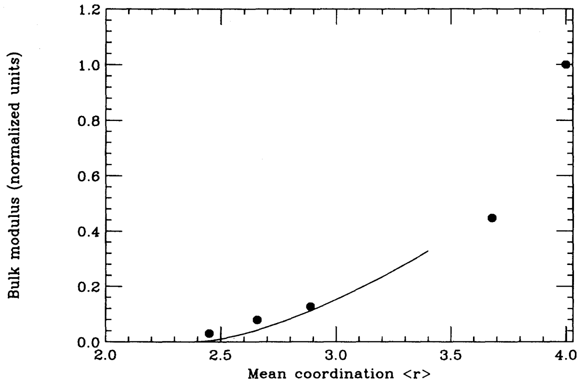

FIG. 7. The variation of the bulk modulus B as a function of the mean coordination $\langle r \rangle$ in c-Si-Ge:H. The solid symbols are from a simulation on a sample with planar planar cracks like that shown in Fig. 6 and the solid line is Eq. (12).

VI. DISCUSSION

How do we account for these fundamental disagreements between theory and experiment in crystalline and amorphous alloys? It is possible that the angular forces β become anomalously small in the alloy: much smaller than in pure Si or Ge. This could be due to some complicated charge transfer effects of the kind that are known to occur in metals.[13] However no such effects have been seen in any III-IV or II-VI compounds and so this possibility has to be regarded as extremely unlikely. It is possible that the presence of hydrogen might substantially weaken the angular force β, but no evidence of such a phenomenon has been seen in hydrogenated amorphous silicon. For example, Maley and Lannin[29] showed with Raman scattering that the *position* of the peaks remains the same in a-Si with or without hydrogen.

A second possibility is that the EXAFS data has been incorrectly interpreted. While some theory is necessary to extract the number and distance associated with the various nearest-neighbor pairs, the EXAFS technique has been successful in other semiconducting alloys for nearest-neighbor distances and it is difficult to see why it would fail here. However, although these results are all consistent with a flat curve, we must not forget that the error bars on the measurements are around 0.02 Å. It is true that the size mismatch between Si and Ge is only 5% but this is comparable with the 8% bond length mismatch for Ga-As and In-As bonds, $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{As}$, for example. We should also note that all the experiments cited agree that Si-Ge forms a good random solid solution, as evidenced by the relative weights in the EXAFS components. It is true that if the Si and Ge were phase separated, this would account for the observed composition independence of the Ge-Ge and Si-Ge bond lengths. However, this would lead to very little weight in the Si-Ge component, as these bonds would only occur along the interfaces between the two phases.

Finally we have the possibility that there is a very large fraction, between 45 at. % and 65 at. %, of hydrogen. Although this is a huge amount, we can find proportions of hydrogen in a-Si and *technological* a-Si that contain typically between 10 and 30 at. % H.[30] Such material would be mechanically weakened and show very soft elastic behavior, when compared with crystalline Si and Ge (see Fig. 7). We have been unable to find any measurements of the elastic constants for hydrogenated material. Maley and Lannin[29] also pointed to a marked sharpening of the TO peak associated with hydrogen and due the improvement of the local structure in a-Si-Ge:H alloys with up to 40 at. % H.

Also the same results are obtained experimentally for both crystalline and amorphous Si-Ge alloys and it is even harder to envisage how so much hydrogen could be incorporated uniformly into the crystalline alloys. However, the presence of planar cracks on a very short length scale can apply to both crystalline and amorphous alloys and is compatible with the preparation method used to obtain these samples.

VII. CONCLUSION

EXAFS is a very powerful technique that has opened up a field of measurements, i.e., the local structure of disordered systems. However, because this technique is an indirect one, one has to remain very careful in interpreting the results. The curious results for Si-Ge alloys open up many questions which will require more experiments to sort out. In particular, we would suggest EXAFS measurements on Si-Ge samples not containing hydrogen.

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