Computer restructuring of continuous random tetrahedral networks

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A procedure is described for the gradual modification by computer of the topology of hand-built models of tetrahedrally coordinated amorphous semiconductors. Starting from a model which had no odd-membered rings, we generated a series of structures with increasing numbers of five-membered rings, and increasing distortion in bond angle. The best fit to the experimentally determined radial distribution function of amorphous germanium was obtained with a model having an average of 0.336 five-membered rings per atom and an rms bond angle distortion of 11.6° .

I. INTRODUCTION

In attempts to determine the structure of certain amorphous semiconductors, several methods have been used to construct models of random configurations of tetrahedrally coordinated atoms, where every interior atom is bonded to four others to satisfy its valence. Some of these have had considerable success at matching the radial distribution function (RDF) obtained from x-ray diffraction data of amorphous Ge samples. Still, one would not say that a completely satisfactory model has been found nor that much can yet be concluded on the basis of these models about the internal structure of the semiconductors. This is especially evident when one considers two of the most successful models, respectively, by Connell and Temkin, ¹ and by Steinhardt, Alben, and Weaire.² While both have RDF's which are fairly close to the experimental, there are significant differences between the structures, particularly in the ring statistics. Thus the range of structures which are possible candidates for an accurate model is yet quite wide.

A more thorough investigation is needed to further limit the possible structures. One needs to examine many more models, searching for correlations between internal parameters and the resulting RDF's, in order to determine the structural parameters characterizing the actual substance. Of particular interest might be models which are structurally midrange between the two mentioned. A possible explanation of having two very different models being close matches to experiment but not close enough is that they both differ from the actual structure only in being too far to one side or the other from an optimum model in the middle. This is suggested by Connell and Temkin, who note that the average of the two model RDF's gives a better match than either. The most obvious way of carrying out this investigation is simply to build many models independently one after another and compare their characteristics and RDF's. The main difficulty here, aside from the lack of control over

the properties of the completed model during construction so that only some of the models will be in the region of particular interest, is in knowing just how to make meaningful comparisons. Since there are so many parameters which can be used to characterize a structure, it is quite a complex matter to organize the data by somehow ordering or arranging the models with respect to each other. That is, it is not at all clear how one determines how similar or different in structure two models are. Thus, the investigation most likely degenerates into a hit-or-miss attempt at finding a model with an RDF more like the experimental one.

We have chosen a more systematic approach to the problem whereby a single model is changed little by little to give a whole series of models of gradually varying characteristics. Starting from a model with an RDF close to experiment, a small amount of topological disorder is introduced; that is, a few of the bonding assignments are changed. After relaxing to a strain energy minimum, we have a new structure which is very similar to the original one. It may then be used as a new starting point and the procedure repeated. By studying the trends in variation of the characteristics of the obtained series of models and comparing with the RDF's, one can begin to understand what internal parameters a model must have which will match the experimental RDF. If one is selective in creating this series by accepting only some of the produced models as new starting points and rejecting others to go back to the previous starting point, then one can have a considerable amount of control over the general direction of the change from one model to the next. The change can possibly be guided so that the RDF comes gradually closer to experiment. Thus our method has great potential for systematically finding models whose RDF's are improved from those of previous models, while remaining within the limitations of any number of restrictions imposed to insure physical reasonableness. Here, we have already had some success. Starting from the Connell and Temkin model and in-

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vestigating those structures in the range between it and the Steinhardt *et al.* model, we have produced a new model whose RDF is closer to experiment than either of the two previous ones.

II. PROCEDURE

Our computer program modifies a given model to give a similar model by means of a randomization of its coordinates, a "topology search" which finds a consistent assignment of bonding neighbors and a relaxation to a local strain energy minimum. The topology search is the crucial step in defining the new structure and requires some explanation here. The problem here is to assign a topology to a given set of atomic coordinates by specifying the locations of the bonds. In doing this, one takes into account the relative distances between atoms so that each atom tends to bond to those nearest to it, although it is not in general a simple matter of bonding each to the four closest neighbors. This care must be taken in the assignment to avoid getting a structure with unreasonable distortion after it is relaxed. Once the topology is assigned, the final atomic coordinates are completely and uniquely defined (disregarding translations and rotations of the entire model) for a specific choice of relaxation procedure. Thus, the influence of the initial model on the final one occurs exclusively through its effect on the topology search. This approach was first used by Henderson and Herman,³ involving initial coordinates which were randomly distributed. Guttman⁴ used a search involving a probabilistic weighting of bonding to first or second neighbors in a diamond lattice. Neither of these attemps gave very good models, but we have found the approach useful for our method. In our method, the initial coordinates are given by any continuous tetrahedral network. To avoid always finding the same topology as that of the initial structure, each coordinate is displaced a random distance in a random direction. The maximum displacement (about 0.22 crystal-bond lengths) is chosen to be as small as possible without repeatedly finding the previous topology. Several restrictions are placed on the topology search: Exactly four bonding neighbors must be chosen for each atom, excepting surface atoms. The new topology must be self-consistent, so that each atom is a bonding neighbor of each of its bonding neighbors. No three- or four-membered rings are permitted, since these inevitably produce too much distortion in the final structure. Bonds are not allowed between atoms too far apart (about 1.5 crystal-bond lengths). The limitations placed on the formation of a bond by these restrictions depend on what bonds have been previously assigned. Thus the order in which bonds are assigned is significant. We ordered the atoms in increasing distance from the centroid of the model,

so that the bond formation "grows" outward from a spherical cluster. The atoms are then taken in order and each assigned bonds to the closest atoms possible within the restrictions. If at any point the restrictions cannot all be obeyed, we return to the initial structure and try a new randomization of the coordinates. Unless periodic boundary conditions are employed, the model will contain many surface atoms having fewer than four bonding neighbors. These atoms are required to have the same number of bonds they had in the initial structure. The bonds between surface atoms are fixed so that the topology search will not change these. The result of the search is an assignment of bonding neighbors which differs from the previous assignment in only a few of the bonds. We go to so much trouble for such a small topological change in order to insure a minimal increase of distortion in the new structure.

At this point, the numbers of five-, six-, and sevenmembered rings are counted and compared with the count for the initial model. If a specific type of change is desired in these statistics but is not obtained, the topology is rejected and we return to the initial structure with a new randomization. Otherwise we continue with a crude preliminary relaxation by a method used by Henderson and Herman, and then a fine relaxation to a metastable state using sufficient Monte Carlo iterations minimizing the Keating expression for the strain energy⁵ until no further change is observed in the RDF. The relaxed structure may then be rejected if it is found to have excessive distortion in the bond lengths or angles, or if nonbonded neighbors are too close, or if any specific desired change from the initial structure is not obtained. If, however, the structure is accepted, it is then used as a new initial structure and the entire process is repeated. After several repetitions, one has a series of physically reasonable models with only slight changes from one to the next. This change is easily directed to be monotonic through the series in some desired respect. There is a limitation, however, in how long a series may be created in this way. This is due to the tendency for distortion to accumulate in the model and to the restraint imposed by the boundary conditions. Thus our method cannot produce models with RDF's much different from that of the starting model of the series. For this reason, a crystalline structure whose RDF is so different from that of the amorphous structure is a poor choice for a starting model, as we have found from trials with both the diamond and BC-8 structures. A random model built by hand or computer and having an RDF already close to experiment is the best choice.

There have been, in previous models, some discrepancies in details of the calculation of the RDF's presented for these models. These details can make a significant difference, particularly when comparing RDF's which are all very close to the experimental one. For our method, where changes are very small from one cycle to the next, details in the RDF become especially important in comparisons within a series of models. Thus, there is a definite need at this point to establish a consistent most reasonable method of calculation. We consider here two points of discrepancy which need clearing up: relaxation of the structure and correction for finite size. In some models, ^{2,6} the Keating energy expression has been used to relax the structure before calculating the RDF. Although this expression does not agree well with experiment for numerical values of the strain energy,⁷ there is reason to believe that it is still sufficiently accurate for defining the atomic positions which give an energy minimum. In any case, it is certainly preferable to the alternative of letting the positions be determined by the particular elastic characteristics of the pieces used in a hand-built model or by some arbitrary relaxation algorithm. For a realistic RDF, the model must be relaxed to a metastable state. In the case of models with periodic boundary conditions, it is also necessary in the relaxation to allow the density to vary. For defining an energy minimum, only a single parameter in the Keating expression need be specified: the ratio of bond-bending to bond-stretching force constants, β/α . Experimental data⁸ only put this parameter in the approximate range of 0.1 to 0.3. The particular choice of β/α within this range does not have an especially large effect on the RDF. We chose a value of 0.14 on the basis of results obtained from relaxing by computer a BC-8 crystal, which has bond distortions of the approximate magnitude that one would expect exist in amorphous germanium. Since this crystal structure exists in nature and so must be metastable, relaxation using an ideal energy expression should have no effect on the RDF. Relaxing BC-8 using the Keating expression has a minimal effect on the RDF when $\beta/\alpha = 0.14$. The effect in this case is so small that it suggests that the Keating expression is quite satisfactory for purposes of relaxation.

Another discrepancy involves the finite-size correction to be made in measuring the RDF of a cluster-type model without periodic boundary conditions. Most of the interatomic distances can still be used in averaging the RDF, thereby getting greater statistical weight, if the distances are properly weighted to account for the effect of a limited model. Each distance r is weighted by the reciprocal of the function

$$P(r) = 1 - \frac{3}{4} (r/a_0) + \frac{1}{16} (r/a_0)^3 , \qquad (1)$$

where a_0 is a specified parameter. The proper

choice of a_0 becomes clear when one considers the derivation of Eq. (1). We suppose that a sphere S of radius R is inscribed within a model of infinite extent and that the RDF of this model is to be calculated by using the positions of *only* those atoms which are inside S. In measuring the distribution about one particular atom in S a distance d from its center, one counts the number of atoms in S distant from it by an amount between r and $r + \delta r$. This, however, is only a fraction of the *total* number of atoms in the model within this distance range. This fraction is given by

$$P(r,d) = \begin{cases} 1, & \text{if } r+d \leq R\\ [R^2 - (r-d)^2]/4rd, & \text{if } r+d > R \end{cases}.$$
(2)

The distribution count should be weighted by the reciprocal of this function to account for the atoms outside S. If S contains a large number of atoms, then calculations may be simplified by averaging P(r, d) over the entire sphere S in order to eliminate its dependence on d. This results in the function P(r) given by Eq. (1) if one makes the identification $a_0 = R$. We have found that when S contains about 150 atoms or more, there is scarcely any difference in the RDF whether Eq. (1) or Eq. (2) is used for weighting.

This technique will apply in exactly the same way to a model of finite size, provided the model appears no different within the inscribed sphere S than if it were of infinite extent. This is assured by placing S in the interior of the model and making it small enough not to include surface effects. That is, one uses for calculations a spherical sample which is representative of the model's bulk structure. It is also advantageous to make S as large as possible for statistical weight, but it must not be excessively large. Only when S is sufficiently small to be a representative sample, when only atoms within S are used in the calculation, and when a_0 is set to the radius of S, will Eq. (1) be appropriate for use in weighting. In our calculations, we took the center of S to be at the centroid of the model and took its radius to be 0.5 bond lengths greater than the distance from the centroid to the nearest atom with less than four bonding neighbors. For the Connell-Temkin model, this resulted in only 127 of the 238 atoms being used to calculate the RDF. This eliminated most surface effects and, in particular, assured that S did not extend past the extent of the model by including empty space which would contain atoms if the model were to be extended. Both Steinhardt et al. and Connell and Temkin use Eq. (1) in their calculations. However, their choices for the parameter a_0 , based on quite different reasoning from that which is consistent with the derivation of Eq. (1), along with their use of all atoms in the model in their RDF calculations, result in RDF's which differ from those which we have obtained using their atomic coordinates. These differences are significantly greater than the statistical variations due to our use of a smaller sphere. Although the smaller a_0 makes the RDF's obtained more sensitive to the nature of the initial "seed" of atoms from which hand-built models are constructed, we feel that the criterion given here represents the compromise giving the RDF most typical of a bulk material.

III. RESULTS

We present here a specific application of our method to a case where a particular topological change was of interest. For our initial structure used in generating the series, we used a 238-atom random tetrahedral network model hand built by Connell and Temkin.¹ This model was constructed to be free of any odd-membered rings, so that it might model amorphous binary III-V compounds, in which such a ring would require a "wrong bond," i.e., a bond between like atoms. It is supposed that the structure of these compounds is similar to that of amorphous IV elements. However, heat-ofcrystallization data shows that such compounds may have a small percentage of wrong bonds, although a maximum is set at about 7%.⁹ Also, the structure of the elements may differ from that of the compounds in that the former has more would-be wrong bonds since no additional energy is associated with such bonds, as in the compounds. We thus thought it would be of interest to observe the effect of restructuring this model to introduce an increasing number of odd-membered rings. Starting from the Connell-Temkin model, and placing the restriction that the number of five-membered rings increase with each cycle, we produce a series of gradually varying models. Characteristics of six of these are summarized in Table I (models H1-H6). The model by Steinhardt et al. (model Y) is also included for comparison. All of these models were first relaxed as described earlier. From model H1 (a relaxed version of the Connell-Temkin model) to model H6 (with the largest number of five-

TABLE I. Structural parameters of the models. The strain energy E_s is in arbitrary units.

Model	5	Rings/ atom 6	7	$\Delta \theta_b$ (deg)	$\frac{\Delta r_1}{r_1}$	Wrong bonds (%)	Es
H1	0.000	2,432	0,000	9.1	0.013	0.0	0.0092
H2	0.059	2.270	0.156	10.2	0.014	1.4	0.0112
H3	0,158	2,090	0.313	10.6	0.014	3.0	0.0120
H4	0.198	1,955	0.469	10.8	0.015	4.2	0.0126
H_{5}	0,336	1,506	0.808	11.6	0.015	7.0	0.0143
H6	0.398	1,287	1,008	13.3	0.015	8.4	0.0173
Y	0.430	0.889	0,989	6.8	0.007	9.9	0.0053



FIG. 1. Radial distribution functions $J(R/R_0)$ of model H1 (crosses, relaxed Connell-Temkin model), model H5 (full circles), and model Y (dashed line, Ref. 2) compared to experiment (solid line, Ref. 10). R_0 is the crystalline-Ge nearest-neighbor distance 2.47 Å.

membered rings), there is a steady increase in the (static) bond-length spread $\Delta r_1/r_1$, bond-angle spread $\Delta \theta_b$, and strain energy E_s . These are all considerably greater than in the Steinhardt et al. model. In the calculation of the ring statistics presented here, atoms on the surface were not included, since the boundary conditions described earlier place an arbitrary restriction on the rings passing through these atoms. This accounts for the discrepancy with the values published by Steinhardt et al. These statistics were corrected for the finite model size by using equations derived by Steinhardt et al. The wrong bond percentage applies if the atoms of a III-V compound are assigned to lattice postions in such a manner as to minimize the number of bonds between like atoms.

The RDF's of the models in this series approached closer and closer the experimental RDF for amorphous Ge (Ref. 10), coming closest when the number of five-membered rings per atom reached 0.336, and then getting farther away as the number increased beyond that. Figure 1 compares the RDF of our "best" model, H5, (RDF closest to experiment) with the experimental RDF and with the RDF's for the relaxed Connell-Temkin and Steinhardt *et al.* models. All of these model RDF's were made with relaxation and finite-size correction, as described above.

Thermal and termination broadening are ac-



FIG. 2. Dihedral angle distribution $P(\theta_d)$ for models H1 (solid line), H5 (full circles), and Y (dashed line). $P(\theta_d)$ is normalized to given the percentage of angles falling in the two-degree interval centered on θ_d .

counted for by a Gaussian convolution, using standard deviations of 0.049 equilibrium bond lengths for the first peak and 0.057 lengths beyond that. These parameters are taken from experimental data for crystalline Ge (Ref. 10). It is seen here that the increase in bond-length spread of our model does not ruin the fit to the experimental first peak and that the increase in bond-angle spread improves the fit to the experimental second peak. From this we would conclude that the bond-angle spread of a model characterizing amorphous Ge should be around 11 or 12° .

The dihedral angle distribution of models H1, H5, and Y is shown in Fig. 2. As is the case with the RDF's shown in Fig. 1, any discrepancies between these data and those given in Refs. 1 and 2 are accounted for by the different relaxation parameter β/α and the smaller size of the sampling sphere S. As one might expect from the intermediate number of five-membered rings, model H5 has a dihedral angle distribution intermediate between

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that of the Connell-Temkin topology and the Steinhardt *et al.* topology.

IV. CONCLUSION

Our results indicate that the suggestion made by Connell and Temkin, that an ideal model would contain a wrong-bond percentage and odd-membered ring counts intermediate between their model and other proposed models, is quite reasonable. Indeed, we have found one such intermediate model which shows an improved match to experiment over previous models. We would be pleased to supply the coordinates of this model to those interested in using it as a basis for calculations of electronic and vibrational properties. No attempt has been made to compare the RDF's of our restructured models with experimental RDF's of amorphous III-V compounds, which may have slight variations from those of IV elements.¹¹ On the other hand, it is noteworthy that model H5 has 7% wrong bonds, which is within the limits suggested by Ref. 9. As the models presented here are all based on successive permutations of one model (H1), it is not vet possible to make any definite conclusions about the topological structure of amorphous tetrahedrally bonded semiconductors based on the results obtained thus far. Certainly more investigation would be required for this, using other hand-built models as starting points. We propose that the method we have described here may be a useful tool in reaching this goal.

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