Modeling the structure of amorphous tetrahedrally coordinated semiconductors. I *

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(Received 15 January 1974)

A continuous random network (CRN) consisting of 238 tetrahedrally coordinated atoms has been
constructed so as to contain only even-membered rings. The structural properties of the model (density,
bond-length distribution, bond-angle distribution, dihedral-angle distribution, radial distribution function)
are in satisfactory agreement with experimental results for amorphous Ge, Si, and the III-V compounds.
The present model eliminates the conflict between the Polk CRN model, which contains approximately
50% of odd-membered rings, and experimental photoemission, optical, and heat-of-crystallization results
for the amorphous III-V's, which indicate the absence of a significant number of such rings.
Comparison of the CRN models suggests that a determination of the experimental dihedral-angle
distribution of each material is very important for a unique definition of its structure.

The problem of modeling the structure of amorphous Si and Ge has been discussed in several re-
cent papers. 1,2 It was shown that the continuous random network (CRN) built by Polk 3 and adjusted
to reduce bond-length variations has a radial dist-
tribution function (RDF) that compares satisfac-
tory with experiments on Si and Ge, thus confirm-
ing the earlier but less conclusive work of Polk 3
and Shevchik and Paul. 4 An important and charac-
teristic part of the Polk model is the considerable
number of odd-membered rings, which for binary
compounds would necessarily lead to the existence
of “wrong bonds.” Experimentally, Shevchik and Paul showed that the RDF’s of all of the III-V com-
 pounds that they measured were very similar to
those of Si and Ge, reflecting tetrahedral bonding,
and that some of them had a wider distribution of
nearest-neighbor distances. 5 They therefore sug-
gested that these latter data were generally con-
sistent with wrong bonds in the proportion found in
the Polk model. Such numbers of them, however,
are expected to produce observable effects in the
electronic density of states of both the valence-band
and core levels and in the heat of crystallization,
but such effects have not been seen. 6–8 Other ex-
perimental observations favoring the existence
of wrong bonds in the III-V’s are the measured en-
ergy gaps and the energy-gap pressure and tempera-
ture coefficients, 9 which, in contrast to Si and Ge, are
very different from those for the crystal; however,
only a small fraction of wrong bonds is required to
explain these experiments. This article describes
a tetrahedrally coordinated CRN that has no odd-
membered rings and no wrong bonds when the
atoms of a binary compound are assigned to lattice
positions so as to avoid such bonds. Its structural
parameters provide new insights into the question
of the uniqueness of the amorphous structure and
suggest what experimental tests could establish
the existence of odd-membered rings, or at least
their relative frequency of occurrence in different
materials.

A roughly spherical model was constructed from
238 plastic tetrahedra interconnected by aluminum
rods. Noncrystallinity was achieved through vari-
ations in the tetrahedral angle and through the re-

tative rotation of adjoining tetrahedra into configu-

A50s that the staggered or eclipsed. The
model had no broken bonds and no odd-membered
rings. It appeared that whenever a surface config-
uration occurred that could lead to a fivefold or
sevenfold ring, a reorganization of the adjacent
surface atoms would eliminate it. Later, it will
be seen that this type of reorganization apparently
minimizes the number of eclipsed configurations in
the network, an important criterion in the growth
of a real system. 10

The coordinates of each atom were measured and
the distances to the coordinating atoms determined.
A computer program was then used to reposition
the atoms so that the variance of the bond lengths
was equal to that due to static distortion measured
experimentally in amorphous Ge. 11 The new co-
ordinates, which will be published elsewhere, were
then used to determine the structural parameters
of the model.

The density was determined as a function of dis-

tance from the center of mass, and the RDF of the
model, J mod( r), was calculated. The RDF of an in-
finite model was then obtained by dividing J mod( r)
by the spherical characteristic function 12
\[ \gamma_0(r/2a) = 1 - 1.5(r/2a) + 0.5(r/2a)^3 \]

where a = 4.47r₁ is the effective radius of our approximately spherical model and r₁ is the bond length. \( \gamma_0(r/2a) \) is the probability that a point at a distance r in an arbitrary direction from a given point in a sphere of radius a will itself also be in the sphere. 12 The corrected RDF was then broadened, using experi-
mentally determined thermal broadening param-
eters, 11 to give the final RDF, J( r). Partial RDF’s,
that is, the first-, second-, and third-bond neighbor distributions, \( J_1(r) \), \( J_2(r) \), and \( J_3(r) \), respectively, were similarly determined. Finally, the bond-angle and dihedral-angle distributions were obtained. In the remainder of this paper, the average nearest-neighbor distance has been scaled to 2.47 Å, the value for amorphous Ge, and the discussion will be focused on this material.

The density \( \rho_0(r) \) is shown in Fig. 1 for a range of \( r \) in which atoms are fully coordinated. The density of diamond Ge, with a nearest-neighbor distance of 2.47 Å, is also plotted. It is evident that the density of the model is within about 1% of this value, as is the density of the Polk model. It is therefore unlikely that future CRN models with intermediate-ring statistics will have vastly different densities. Conversely, density cannot be used to link a model to experiment in a unique way. Further, it would seem that the gross changes in density, observed experimentally, are a result of defects rather than of different CRN’s.

The RDF is shown in Fig. 2. For comparison, the RDF’s of amorphous Ge and the Polk model are also shown. The prominent experimental features are present to some degree in both models. Both models reproduce the experimental nearest-neighbor distribution excellently. In the Polk model, the peaks at 4 and 6 Å are narrower than in experiment, and the one near 6 Å is shifted to lower \( r \). On the other hand, the present model describes the 4 Å peak reasonably well, but near 6 Å, the structure is broadened and shifted to higher \( r \). Be-
yond about 7.5 Å, the RDF of a 238-atom model is increasingly dominated by partially coordinated atoms, and the relaxation procedure is thus not subject to the same number of constraints at these large \( r \). The sharpness of the structure near 8 Å in the RDF is therefore unreliable and would likely be absent or greatly reduced in a larger model.

Figure 3 shows a breakdown of \( J(r) \) into the \( J_n(r) \) for \( n = 1, 2, \) and 3. A surprising result is the relatively large height of \( J_3(r) \) near \( r = 4.0 \) Å, the second-neighbor distance, arising from opposite atoms in distorted "boat-like" six-membered rings. In fact, a weak shoulder in \( J_3(r) \) is evident in this vicinity. Previous analyses of experimental \( J(r) \) curves to determine the experimental bond-angle distortion \( \Delta \theta_a \) have assumed \( J_3(r) \) to be zero at 4.0 Å and obtained \( \Delta \theta_a = 10^\circ \). For the \( J_3(r) \) of Fig. 3, a \( \Delta \theta_a = 12^\circ \) would be a better fit to experiment. Similarly, the height of \( J_3(r) \) for \( r < 4.0 \) Å would explain the experimental result of more than six atoms in the \( r < 4.0 \)-Å half of the second-neighbor peak. In contrast, \( J_3(r) = 0 \) below 4.0 Å in the Polk model as a result of the "shorting out" of boatlike rings by five-membered rings.

The numbers of \( n \)-bond neighbors, \( N_n \), determined from \( J_n(r) \) for \( n = 1, 2, \) and 3 are \( N_1 = 4.03, N_2 = 11.36, \) and \( N_3 = 23.78 \) atoms, in good agreement with the diamond and wurtzite structures. The width of \( J_3(r) \) corresponds to a \( \Delta \theta_a = 10.7^\circ \). \( J_3(r) \) is a two-peaked function, having maxima at 4.85 and 6.05 Å. These maxima correlate with, and could be predicted from, the shape of the dihedral-angle distribution, shown in Fig. 4.  

(The dihedral angle \( \theta_d \) is \( 0^\circ \) for tetrahedra in the eclipsed configuration and \( 60^\circ \) for tetrahedra in the staggered configuration.)

The staggered configuration is approximately four times more probable than the eclipsed configuration. In the Polk model, however, the eclipsed configuration is relatively more probable, as is indicated in Fig. 4, and, as noted by Steinhardt et al., essentially all of this difference is associated with fivefold rings. It would therefore seem that an experimental determination of the dihedral-angle distribution is crucial to establish the proportion of odd-membered rings in a particular material.

Steinhardt et al. constructed a 201-atom model in which each adatom was placed in its position of minimum energy under bond-stretching and bond-bending forces alone. The model so constructed had a dihedral-angle distribution and ring statistics that were similar to those of the Polk model. Pauling, however, indicates that an additional term resulting from the overlap of the two sets of bond orbitals that originate on nearest-neighbor atoms and proportional to \( \cos \theta_a \) should be included in a calculation of the position of minimum energy. We therefore argue that the effect of its inclusion on the structure would be a reduction in the number of eclipsed configurations and fivefold rings. The possibility then arises that different materials, which have similar RDF's, could have very different dihedral-angle distributions and ring statistics, depending on the relative importance of the dihedral-angle term in the energy minimization. However, if the ring statistics and dihedral-angle distribution are to be obtained from the experimental RDF's, further structural modeling is needed to understand the variation of the RDF with these distributions.

Neither the RDF of the present model nor the Polk model fits the experimental RDF of amorphous Ge within experimental error. However, it would seem that the structure of amorphous Ge might, in fact, be intermediate between these models, since an average of the two agrees better with experiment than either alone. On the other hand, the experimental RDF's of the amorphous III-V's indicate that they have a somewhat larger bond-angle distortion than amorphous Ge and agree better with the present model than that of Polk. We therefore conclude that it is entirely possible that there is only a small fraction of wrong bonds in these compounds. The present model thus allows a successful reconciliation of the experimental photoemission, optical, and heat-of-crystallization data mentioned earlier, with a CRN structure with no wrong bonds.

We thank Warren Warren, Albert Boudreaux, and David MacLeod for their diligence in measuring the coordinates of the model. We especially thank William Paul for many helpful suggestions and comments.

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