[3]M. A. Maidique, A. von Hippel, and W. B. Westphal, J. Chem. Phys. 54, 134, 150 (1971).
[4]N. Bjerrum, Kgl. Dan. Vidensk. Selsk., Mat-Fys. Medd. 27, 32, 41 (1951).
[5]H. Granicher, Z. Krist. 110, 432 (1958), and Phys. Kondens. Mater. 1, 1 (1963).
[6]C. Jaccard, Helv. Phys. Acta 32, 89 (1959), and Phys. Kondens. Mater. 3, 99 (1964), and Ann. N.Y. Acad. Sci. 125, 391 (1965).
[7]L. Friedman and T. Holstein, Phys. Rev. 165, 1019 (1968).
[8]W. F. Brinkman and T. M. Rice, Phys. Rev. B 4, 1566 (1971).
[9]R. Kubo, Can. J. Phys. 34, 1274 (1956).
[10]A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinski, *Method of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Englewood Cliffs, N.J., 1963), p. 104.
[11]W. F. Brinkman and T. M. Rice, Phys. Rev. B 2, 1324 (1970).
[12]A. von Hippel, J. Chem. Phys. 54, 145 (1971).
[13]The reason for this is that interchanging J_x and J_y in Eq. (4) reverses the direction in which each path is traversed, thus reversing the sign at the phase factors in Eq. (1). Thus, when the sum of these phase factors is zero, we see from Eq. (2) that the Hall mobility is zero.
[14]B. Bullemer and N. Riehl, Phys. Lett. 22, 411 (1966).
[15]T. Minagawa, unpublished.
[16]L. Onsager, J. F. Nagle, and J. C. Bonner, to be published.

Tetrahedrally Coordinated Random-Network Structure

D. E. Polk and D. S. Boudreaux
Materials Research Center, Allied Chemical Corporation, Morristown, New Jersey 07960
(Received 23 May 1973)

A computer study of a tetrahedrally coordinated random-network structure is reported as a model for amorphous Si or Ge. A previous model is refined to produce equal near-neighbor distances; it is more carefully statistically characterized and the coordinates of each individual atom are now known. The radial distribution function has been obtained to greater precision and to a greater radial distance; it compares well with experiment.

The structures and properties of amorphous silicon and germanium have been the subject of many studies and much controversy over the last several years. Moss and Adler[1] have provided a critical review of previous work on the structure of these materials.

A tetrahedrally coordinated random-network structure had been constructed[2] as an idealized model of the structure of amorphous Si or Ge, based on the concepts of Zachariasen.[3] In such a structure, each atom has four neighbors in an approximately tetrahedral arrangement; non-crystallinity is achieved through variations in the tetrahedral angle and through the relative rotation of adjoining tetrahedra into configurations other than the staggered or eclipsed configurations found in the diamond cubic and wurtzite structures.

Since the coordinates of the atomic positions in the structure were not obtained, the properties of the structure such as its diffraction behavior, electronic energy levels, and vibrational spectra could not be calculated. Further, statistical data for the structure were incomplete and difficult to obtain. This note reports the obtaining of the refined atomic coordinates for the model and the improved statistical characterizations such coordinates make possible.

The model[2] was rigidly fastened to three thin vertical rods that extended through it. A laser was mounted on a horizontal platform which could be moved in an x-z plane or a y-z plane with the beam then being in the y or x direction, respectively. The coordinates of each "atom" were determined from those of the laser when its beam struck the center of the tetrahedral unit. Each atom was assigned an arbitrary number and both its coordinates and the numbers of its first neighbors were recorded.

Using these data, the distance of each surface atom (i.e., each atom having fewer than four first neighbors) from the centroid of the structure was calculated. The structure was then expanded from 440 atomic centers to 519 atomic centers so as both to increase the size of the model and to make it more nearly spherical. The coordinates of the added atoms and any surface atoms moved appreciably by the additions were then determined.

The physical characteristics of the tetrahedral units used to produce the model caused some of the first-neighbor distances to be lengthened when

the stresses due to the distortions were too great for the connectors to hold together. Some of these "bonds" also broke during handling of the model. These effects together with the uncertainties in the measurement of the central position produced original data with large fluctuations in the first-neighbor distances.

A model with no significant variation in the first-neighbor distances was desired. Hence, using a computer, all of the first-neighbor distances and their mean were calculated, and a program was written to seek the first-neighbor distance which differed most from the mean. The two atoms defining that distance were then each moved an equal distance along the line joining the two atoms so that the difference between that distance and the mean was reduced by 50%. The first-neighbor distances affected by the movement were then recalculated and the procedure was repeated until the standard deviation of the first-neighbor distance distribution was less than a predetermined value.

A program to compute the radial distribution function (RDF) was written. Given a selected central atom, the program would compute the distance to all atoms which could be reached by traversing less than a given number of bonds.

Additionally, statistical data such as the mean first-neighbor distance and its standard deviation, the mean tetrahedral bond angle and its standard deviation, and the density were determined. The distribution of the relative rotations of adjoining tetrahedra was also obtained; for each bond joining two four-coordinated atomic centers, the three other bonds associated with each of the two atoms were projected onto a plane perpendicular to the bond joining the two four-coordinated atomic centers being considered. Then, the smallest algebraic sum of the three angles between one set of projected bonds and the other set was computed. This sum varies from 0 for an eclipsed configuration to 180 for a staggered configuration.

All atomic centers within a radius of about 40 (arbitrary units) were found to be four-connected. The sphere so defined contains the atoms most representative of the model since it does not include partially unrestrained surface atoms. Data for atoms in the sphere are quoted below.

The data recorded from the physical model were found to have a mean first-neighbor distance of 7.9421 with a standard deviation of 0.599 (7.54%) and a mean bond angle of 109.2° with a standard deviation of 9.1° within the sphere of radius 40. Further, the atoms within a radius of 15 were found to have a mean first-neighbor distance somewhat more than 2% greater than those within a radius of 40.

Using the move program, iterations reduced the standard deviation of the first-neighbor distance, very rapidly at first and then more slowly, until the mean throughout the model approached the same value. It appears that the standard deviation of the first-neighbor distance can be reduced to as small a value as is desired. For the present purposes, 12 000 iterations gave sufficient refinement of the model.

Within the radius of 40, the mean bond length of the refined model was 7.9403 with a standard deviation of 0.0133 (0.168%). The mean bond angle was 109.2° with a standard deviation of 9.1°, essentially unchanged from the unrefined data. The bond-angle distortions as measured by the standard deviation of the bond angle are, within statistical uncertainty, constant throughout the model.

The density was determined by counting the number of atomic centers within spheres of radius 35, 36, ..., 40 having the centroid as their center. Based on a first-neighbor distance of 1, these speres have volume/atom values of 1.5513, 1.5539, 1.5574, 1.5402, 1.5526, and 1.5749, respectively. The mean value of the preceding is 1.5550, versus 1.5396 for the diamond cubic lattice with a first-neighbor distance of 1. Thus this model random-network structure is 1.0% less dense than a diamond cubic structure with a near-neighbor distance equal to the mean of that of the random network.

Figure 1 is the RDF, $4\pi r^2\rho(r)$, computed from the refined coordinates by using as central atoms

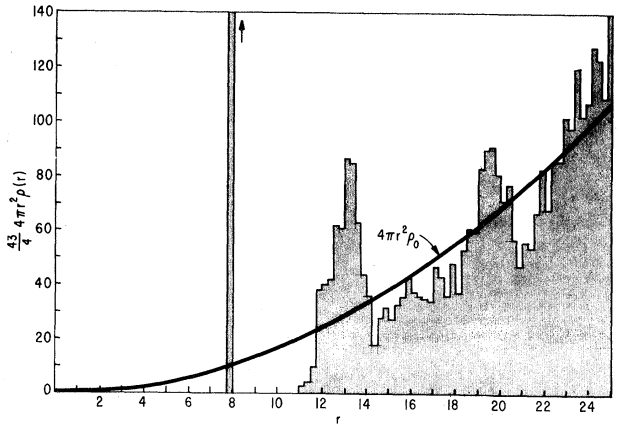

FIG. 1. The RDF of the refined model and the parabola representing the average density.

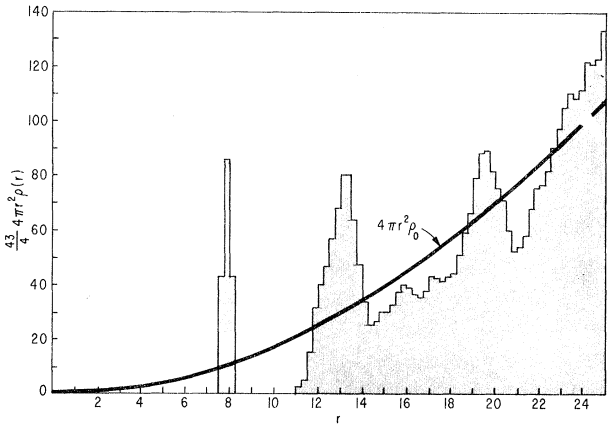

FIG. 2. The RDF of Fig. 1 broadened to reduce statistical fluctuations.

the 43 atoms within a radius of 20 from the centroid. The upper limit of $r = 25$ is chosen so as to remain within the model. Also shown is $4\pi r^2\rho_0$, where ρ_0 is the average density.

Figure 2 is derived from Fig. 1 by broadening Fig. 1 so as to reduce statistical fluctuations. Each bar in the histogram of Fig. 1 was broadened to a set of three bars of weight 0.25, 0.50, and 0.25.

Figure 3 shows $G(r) = 4\pi r[\rho(r) - \rho_0]$ for the model as derived from the $4\pi r^2\rho(r)$ of Fig. 2. Also shown is the experimental $G(r)$ obtained by Moss and Graczyk[4] for amorphous Si.

Figure 4 represents the distribution of the relative rotation of adjoining tetrahedra within the model. The eclipsed configuration ($\theta = 0$) is seen to be about one-half as likely as the staggered configuration ($\theta = 180$), and the distribution has no relative minimum between the staggered and eclisped configurations.

It has been demonstrated that it is possible to construct a tetrahedrally coordinated random-network structure in which all first-neighbor distances are equal and the bond distortions do not increase as the structure is made larger. Further, the coordinates of one such structure have been determined. For equal mean first-neighbor distances, the model random-network structure has a density 1.0% less than the diamond cubic structure, to be compared with the (3 ± 2)% previously reported.[2] The standard deviation of the bond angle is found to be 9.1°, compared to the 10° previously estimated. It appears that the bond-angle distribution of the random network structure is primarily a function of the topology since refinement of the first-neighbor distance distribution did not change its variance.

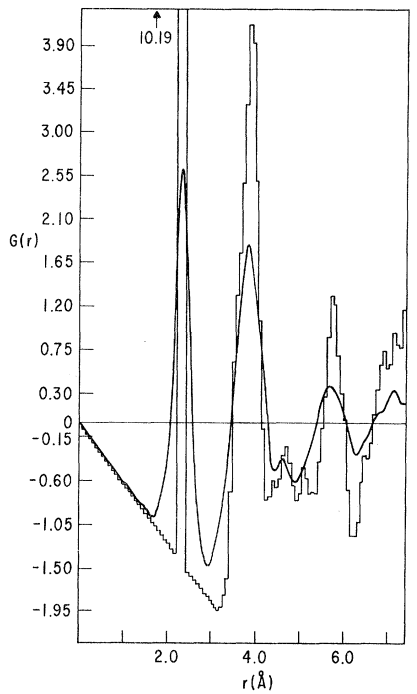

FIG. 3. $G(r) = 4\pi r[\rho(r) - \rho_0]$ as derived from Fig. 2 for the model (histogram) and for amorphous Si as obtained by Moss and Graczyk (Ref. 4).

The RDF of the model has been obtained with greater precision and to a greater radial distance than the one previously reported. The third peak at $r = 19.5$ is seen to be sharp and well defined though qualitative considerations of the characteristics of the random network might suggest that, because of the relative rotations of tetrahedra and bond bending, all relative maxima in the RDF after the second peak should be quite broad. Further, it is clear that a fourth peak in the RDF occurs for the model.

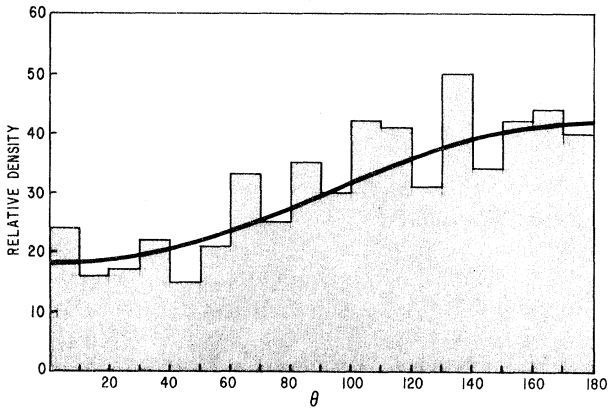

FIG. 4. The distribution of the relative rotation of adjoining tetrahedra within the model.

As noted previously,[2] the RDF of the random network gives good agreement with those obtained for amorphous Si or Ge. As is the case, the peaks in $G(r)$ for the model (Fig. 3) are expected to be sharper than those shown for amorphous Si since the experimental $G(r)$ for Si includes broadening due to thermal, experimental, and mathematical effects. Significantly, the widths of the second peaks, which depend on bond-angle distortions, are similar when thermal and other broadening effects are removed.[2,4]

That region of the RDF of the model between the second and third major peaks is of special interest since the Si RDF of Moss and Graczyk[4] shows a small relative maximum at an r about twice the value of the maximum of the first peak. Because of the limited size of the model, the statistical fluctuations which are readily evident in Fig. 1 make it difficult to determine whether the model exhibits this behavior. Figure 2, however, suggests that the model may have a similar behavior while the $G(r)$ of Fig. 3, since it includes the term $[\rho(r) - \rho_0]$, magnifies the statistical fluctuations. From Fig. 2 it is clear, however, that the dip between the second and third major maxima will be different than that between the first and second or between the third and fourth.

The coordinates and identification of the first neighbors of the atomic positions comprising the model are available on an individual basis from the authors.

[1]S. C. Moss and D. Adler, Comments Solid State Phys. 5, 47 (1973).

[2]D. E. Polk, J. Non-Cryst. Solids 5, 365 (1971).

[3]W. H. Zachariasen, J. Amer. Chem. Soc. 54, 3841 (1932).

[4]S. C. Moss and J. F. Graczyk, in *Proceedings of the Tenth International Conference on the Physics of Semiconductors, Cambridge, Massachusetts, 1970,* edited by S. P. Keller, J. C. Hensel, and F. Stern, CONF-700801 (U.S. AEC Division of Technical Information, Springfield, Va., 1970), p. 658.

Elastic Constants in Singlet Ground-State Systems: PrSb and Pr†

B. Lüthi and M. E. Mullen
Physics Department, Rutgers University, New Brunswick, New Jersey 08903

and

E. Bucher
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

(Received 9 May 1973)

The effect of crystal-field levels on the elastic constants has been measured for the singlet ground-state system PrSb. The results can be accounted for quantitatively. Elastic-constant measurements in double-hexagonal close-packed Pr reveal also strong crystal-field effects.

In rare-earth compounds the ground-state multiplet of the rare-earth ion is split typically of the order of several hundred wave numbers by the crystal field. The effect of these split levels on thermal, magnetic, and electric properties is well documented.[1] In this communication we would like to show the effect of these crystal-field levels on the elastic constants for the case where the lowest level is a singlet state. We show experimental results for two representative samples: PrSb, where the crystal-field effects dominate exchange effects, and double-hexagonal close-packed (dhcp) Pr, where the exchange is not negligible. This is the first time the effect of the crystal-field levels on the elasticity alone has been observed, neglecting complications due to exchange and quadrupole-quadrupole interaction, which can result in magnetic and structural transitions.

A study of this simple situation is worthwhile for the proper understanding of more complicated cases: (1) In cases where the ground-state level is orbitally degenerate, there occurs often a structural transition (the cooperative Jahn-Teller effect) which is accompanied by a softening of a symmetry elastic constant. This effect has been observed now in several cases (e.g., $DyVO_4$, $TbVO_4$, $NiCr_2O_4$).[2] In some cases (DySb, TmCd),

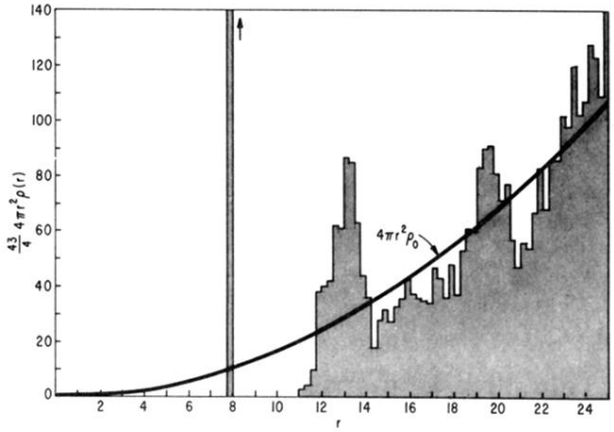

FIG. 1. The RDF of the refined model and the parabola representing the average density.

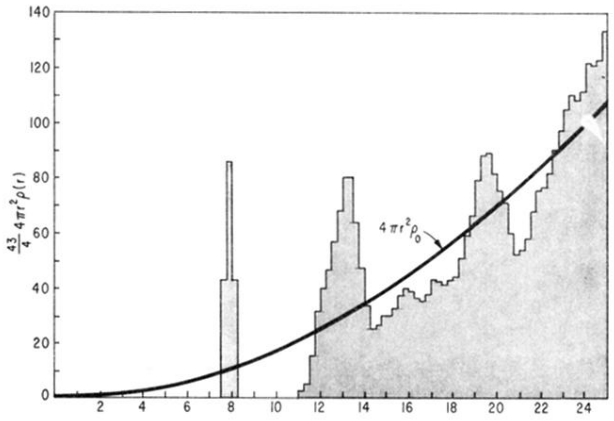

FIG. 2. The RDF of Fig. 1 broadened to reduce statistical fluctuations.

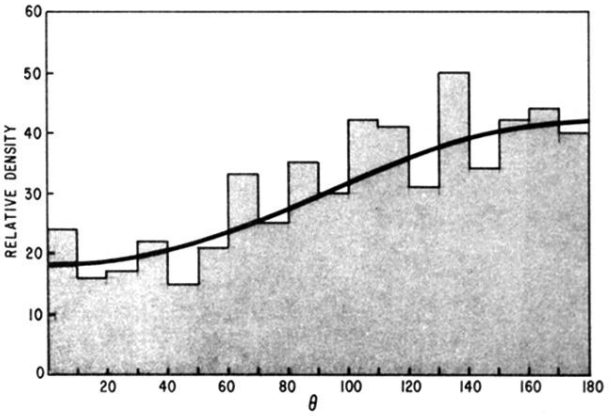

FIG. 4. The distribution of the relative rotation of adjoining tetrahedra within the model.