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Structural and vibrational properties of a threefold-coordinated two-dimensional random lattice

J. Y. Chen* and J. F. Vetelino†
Department of Electrical Engineering, University of Maine, Orono, Maine 04473

S. S. Mitra
Department of Electrical Engineering, University of Rhode Island, Kingston, Rhode Island 02881

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A two-dimensional amorphous lattice has been constructed using the generalized random-walk technique. The bond lengths and angles were obtained from the random-number-generation functions. The lattice sites were assumed to have a coordination number of 3 and were connected to form closed polygons. The lattice and the associated structural properties, such as polygon types, radial distribution function, density, bond length, and bond-angle distribution are calculated. The lattice dynamics is then performed using this network as a two-dimensional amorphous structural representation. A simple harmonic force field with central and noncentral near-neighbor interactions which vary from site to site is utilized for the present lattice-dynamical calculation. The explicit vibrational spectra are obtained for the random network and the corresponding threefold-coordinated honeycomb lattice. The implication and extension of the present construction technique to a real amorphous system are discussed.

I. INTRODUCTION

The random-network concept was first introduced by Zachariasen[1] in the description of a two-dimensional lattice for a glass. Using this concept Ordway,[2] Evans and King,[3] and Bell and Dean[4] have constructed random models for vitreous silica. In the last few years, this concept has been extensively studied in the modelling of an amorphous structure. Kaplow *et al.*[5] simulated a model for amorphous selenium by perturbating the atomic positions in the corresponding crystalline lattice. Although the resulting model radial distribution function (RDF) matched well with the experimental one, the original crystalline topology did not change appreciably. Therefore, the model would not be considered to be truly amorphous in structure.[6,7] Polk[8] hand built a 440-atom tetrahedrally bonded random network with no broken bonds and a rather large-bond length variation (≈ 6%).[8,9] This model was then expanded to 519 atoms and refined to reduce the bond-length variation by Polk and Boudreaux.[9] Shevchik and Paul[10] computer-modeled a 1000-atom model using a procedure very similar to the actual deposition process. This model, however, was characterized by a large number of broken bonds. Henderson and Herman[11] obtained a 64-atom model by perturbing the atoms in a distorted diamond lattice. Even though the variations of the bond lengths and angles were found to be rather large,[7,12] the small number of atoms made the model convenient for the calculation of various physical properties.[12,13] Energy minimization methods employing Keating's expression[14] have recently been carried out by Steinhardt *et al.*[15] and also by Duffy *et al.*[7] The relaxation procedure, which implies that the amorphous atomic arrangements are in a metastable equilibrium system, is a physically realizable approach. However, Keating's expression for the energy cannot be defined exactly because of the uncertainty of the force constants.[6] Random-network models have also been built for the nontetrahedrally bonded amorphous materials such as carbon and arsenic. Kakinoki *et al.*[16] have constructed a model for amorphous carbon using a mixture of diamondlike and graphitelike basic units. Greaves and Davis[17] have modeled amorphous arsenic based on the structural units derived from the double layers of the corresponding crystalline material.

Most of the previous models are either perturbations of crystalline structures or rough hand-built models consisting of tetrahedral units. The tetrahedral units were distorted in order to achieve the connectivities. However, the randomness and the statistics of the bond lengths and bond angles were not considered in the connecting process. Further adjustments were therefore necessary to make the model RDF match well with the experimental one. The adjusting procedure obviously improves the model geometry but does not change the topological structure.[6] The nonrandomness introduced by using crystalline structural units as a starting point may still exist after adjustments. It might be more realistic to use random numbers with a certain distribution rather than any perturbated structural interconnections for the random model construction. This certainly will cause more difficulty in the construction process in order to satisfy the randomness and the statistics of bond lengths and bond angles as well as to achieve perfect connectivities. However, the resulting model should have real amorphous topology and geometry, hence further adjustment is no longer needed.

The purpose of this paper is to present an approach which utilizes the random-walk concept to construct a truly random network. The interatomic bonds in the amorphous material are compared to the random steps of a drunkard. As an example to illustrate the application of the random-walk technique, a two-dimensional random network with coordination number 3 was constructed in this work. The assumption of a constant coordination number complies with the short-range-order (SRO) characteristic of amorphous materials.[6,18] The corresponding crystalline lattice exhibits the honeycomb structure. This kind of amorphous network might serve as a two-dimensional analogy for certain planes in three-dimensional diamond, zinc-blende, or wurzite structures. It can also be used as a basis to develop the random models for graphitelike or layerlike amorphous materials such as amorphous graphite, amorphous arsenic, and chalcogenide glasses.

In the present approach, random numbers for bond lengths and bond angles are first generated from a random-number-generation function. A two-dimensional amorphous lattice is then drawn by using these random numbers under the constraint of a coordination number of 3. The model structural properties are examined and compare well with the input data.

The present random model is also employed for lattice-dynamical calculations. The vibrational properties of the structurally disordered solids such as glasses or amorphous systems have been extensively studied in recent years. Dean[19] has first computed the vibrational spectra for glasslike disordered chains. The disorder was introduced by the continuously distributed force constants through different interatomic distances. The authors[20] have also calculated the phonon density of states of a 40 000-atom disordered chain with SRO. The various lattice spacings were determined by a sequence of random numbers with Gaussian distribution. In the above one-dimensional systems, the geometrical disorder not only smeared out the spectral singularity but extended the frequency range of the corresponding ordered chain. Bell[21] has obtained the vibrational spectrum of a topologically disordered chain by assuming the force constants were equal but the neighbor interactions were randomly selected. The resulting spectrum is essentially a smoothed-over version of the corresponding ordered-chain spectrum.

Two- and three-dimensional work are much more difficult. Bell *et al.*[22] have examined the frequency spectra in a two-dimensional glass-forming model. The effect of topological disorder and that of geometrical disorder were discussed separately. Bell's recent paper[23] also indicated the influence of topological disorder on the vibrations of three-dimensional lattices. It was pointed out[22,23] that, in glasses, topological disorder mainly changes the detailed spectral characteristic, whereas geometrical disorder extended the frequency range. Very recently, Alben and Weaire[24] have extensively reviewed the vibrational properties of amorphous Si and Ge. The vibrational density of states has been calculated using various kinds of physical models for the amorphous solids. These models, however, consist of only 90 atoms because of the computational complexity involved. In addition, the geometrical disorder incorporated with force-constant variations was not considered in the paper.

A majority of the work mentioned above simply shows the effects of some sort of structural disorder on the vibrational spectra rather than an explicit calculation of the lattice dynamics using a physical model which is truly random and has a significantly large size. Additionally, either topological disorder or geometrical disorder does not, in general, appear isolated but always combines with the other to form amorphicity in actual amorphous materials.[23] Recently, the authors[25] have introduced a statistical approach to calculate the phonon distribution function in amorphous silicon and germanium. However, this approach makes use of the amorphous structural properties. In this paper, the 272-atom truly random network is used for the lattice-dynamical calculation. Both geometrical disorder caused by bond length and angle variations and topological disorder inherent in the structural connectivity are included in the present calculation. The vibrational spectra are obtained for both the random lattice and the corresponding perfect honeycomb lattice.

II. MODEL CONSTRUCTION

The construction of the model basically consists of two steps. First, the random numbers associated with the bond lengths and bond angles were generated by a random number generation computer program.[20] Second, a two-dimensional random lattice was manually drawn using these numbers.

Experimentally, it is known from the RDF of amorphous materials,[10,26,27] that the bond lengths, i.e., nearest-neighbor distances, have a Gaussian distribution with a static standard deviation about a mean corresponding to the crystalline value. The bond-angle distribution is also suggested to have a shape similar to a Gaussian form[7,8] with a mean at the perfect tetrahedral angle, a standard deviation and a cutoff angle. In the present work, experimental data appropriate to amorphous silicon was used for the bond length.[27] The data used for the bond angle spread and cutoff was according to the RDF analysis of amorphous germanium[10] and silicon.[26] The random numbers for bond lengths were generated from a random number generation function having a Gaussian distribution with a mean at 2.35 Å and a standard deviation of 0.09 Å. Since there are only two linearly independent angles associated with one lattice site, two sequences of Gaussian distributed random numbers were generated having a 120° mean and 10° standard deviation. In order to obtain a cut off angle of 20° from the mean angle, only those angles between 100° and 140° were retained. Also, a pair of angles whose sum was outside the interval of 220°–260° was rejected to ensure that the third angle had a cutoff of ± 20° from the mean.

In the second step, a two-dimensional amorphous lattice, was drawn using the random numbers generated for the bond lengths and bond angles, respectively. The assumption of three nearest neighbors for each lattice site implies that no interior broken bonds exist and no bonds cross each other. In other words, the lattice sites when connected form closed polygons. In the process of connecting the last two bonds on a polygon, two random bond lengths and one random bond angle were chosen simultaneously. In order to achieve perfect connectivity in the polygon, the random bond lengths and angles were allowed to vary up to a few percent about the value given by the random-number generation procedure. The bond-angle variation usually was higher than the bond-length variation. This is due to the fact that the bond lengths should maintain a Gaussian form, whereas the bond-angle distribution is not necessarily an exact Gaussian. As indicated in Polk's paper,[8] the bond angles might form a shape similar to a Gaussian distribution because of the Gaussian distribution for the second-nearest-neighbor distances along with the small change for the nearest neighbor distances. The small but nonzero static standard deviation of bond lengths indicate that the bond-angle distribution is at best a distorted Gaussian. The individual polygon construction was time consuming in that if a polygon could not be closed, the bonds had to be erased and new bonds drawn to attempt to close the polygon. Finally, a lattice consisting of 233 interior atoms and 39 boundary atoms was obtained. A total of 369 random numbers have been used for the bond lengths and 699 for the bond angles. From the coordinates of all the sites, the corresponding lattice was redrawn by the computer to ensure that the coordinates are correct and to reduce the model size. Figure 1 presents the resulting two-dimensional random lattice. No crystallinity appears in the lattice, however, SRO does exist in the immediate neighborhood of each lattice site. Every bulk atom has three nearest neighbors and six next-nearest neighbors.

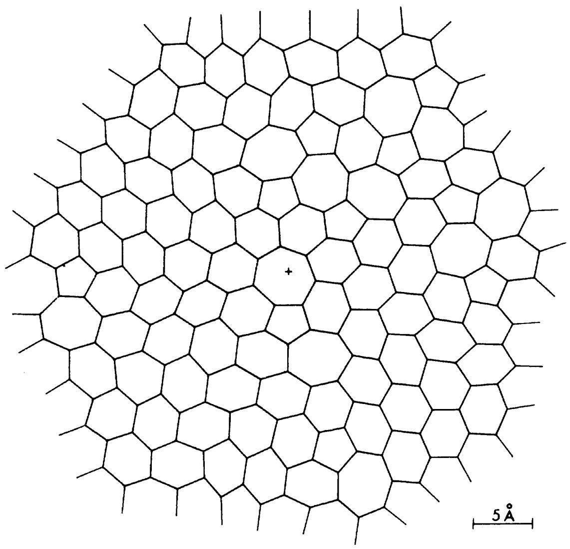

FIG. 1. Two-dimensional random network of coordination number 3.

III. STRUCTURAL PROPERTIES

A. Polygon types

The number of sides in the polygon can be expressed as

$$n = 360°/(180° - \bar{\theta}) . \tag{1}$$

n is the number of polygon sides and $\bar{\theta}$ is the average internal angles of the polygon. Since $\bar{\theta}$ lies between 100° and 140°, the polygon could have only 5, 6, 7, 8, or 9 sides. By referring to the angular distribution, it can be seen that the probability of having a nine- or eight-sided polygon with average internal angles of 140° and 135°, respectively is quite low. Among the 98 polygons in the random lattice, there are 10 pentagons, 11 septagons, and the remaining 77 are all hexagons. The average number of polygon sides is 6.0102. This result agrees well with Euler's theorem,[28] which states that in an infinite two-dimensional lattice with a coordination number of 3, the average number of polygon sides is exactly six. Another interesting fact is that the pentagons and septagons in the lattice always locate together. The reason for this is that for any random two-dimensionally connected array, the distortion of the internal angle inside a polygon has to be compensated by the variation of a corresponding external angle. A relation between the number of sides (n) in a polygon and the average number of sides (m) of the neighboring polygons was originally proposed by Aboav[29] and then modified by Weaire[30] as

$$m \approx 5 + 6/n . \tag{2}$$

Equation (2) has served as an independent check

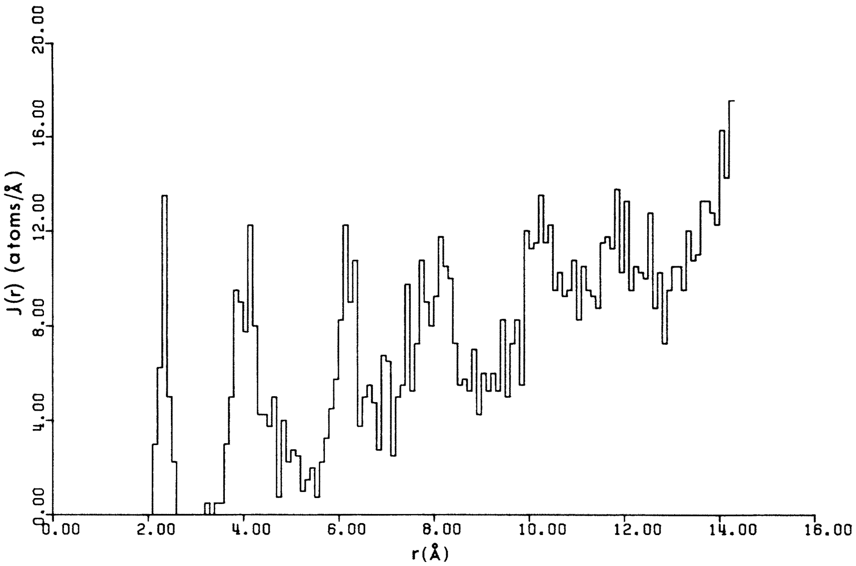

FIG. 2. Radial distribution function $J(r)$ of the model. The histogram is calculated with radius intervals $\Delta r = 0.1$ Å.

for the present lattice and the agreement is very good.

B. Radial distribution function

Figure 2 presents the RDF of this model. The calculations were based on the method described in Polk and Boudreaux's paper[9] for a finite-size model. The 40 atoms around the lattice centroid (Fig. 1) were selected as central atoms. The preservation of SRO in this lattice produces the distinct first and second peak under which the area is exactly 3 and approximately 6, respectively. As a consequence of the two-dimensional model, the RDF increases linearly with distance instead of the parabolic variation observed in three dimensions.[8]

The density of this lattice is shown in Fig. 3. The average density within $r = 6.4$ Å was used for the first point on the density curve; the other points represent the local density in the ring between r and $r + \Delta r$. Since our density plot corresponds to the local density for different circular rings the density fluctuations are larger than that of other density calculations in which the average density was calculated within the total circle. The density of the entire lattice is 0.1401 atoms/Å^2. This value is close to the density of the perfect honeycomb lattice which is 0.1394 atoms/Å^2. This result along with the other density investigations[9,15] concludes that the density of a fully coordinated

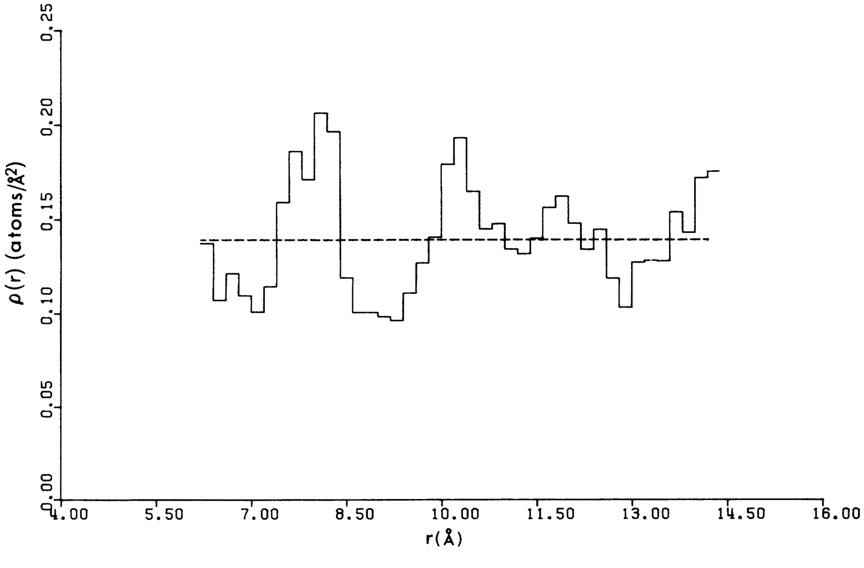

FIG. 3. Density distribution $\rho(r)$ of the model. The histogram is calculated with radius intervals $\Delta r = 0.2$ Å. The dashed line represents the density of the corresponding perfect-lattice honeycomb.

amorphous model is approximately the same as that of the corresponding crystal.

C. Bond-length and bond-angle distribution

The values of all the bond lengths and angles were calculated using the measured coordinates as input data. The bond-length distribution shown in Fig. 4 simulates a Gaussian shape fairly well, whereas the angle distribution in Fig. 5 is a distorted Gaussian. The reason for this has been discussed previously. The quantitative data, such as the means, the standard deviations, and the cutoff angle has also been calculated. The bond length was found to have a mean 2.35 Å with a standard deviation of 0.12 Å. The large standard deviation of ±5% about the mean is mainly due to the fact that in the laborious connecting process, a few distorted bond lengths were allowed. It is very difficult if not impossible to obtain a perfect connection using only the generated random numbers without any exceptions.[3] This 5% value, is lower than other unrefined random network calculations.[8,9,11,12] All the calculated statistical values for bond angles fit fairly well to the data used in this paper. The mean bond angle is 120° with a standard deviation of 11° and a cutoff at ±23°.

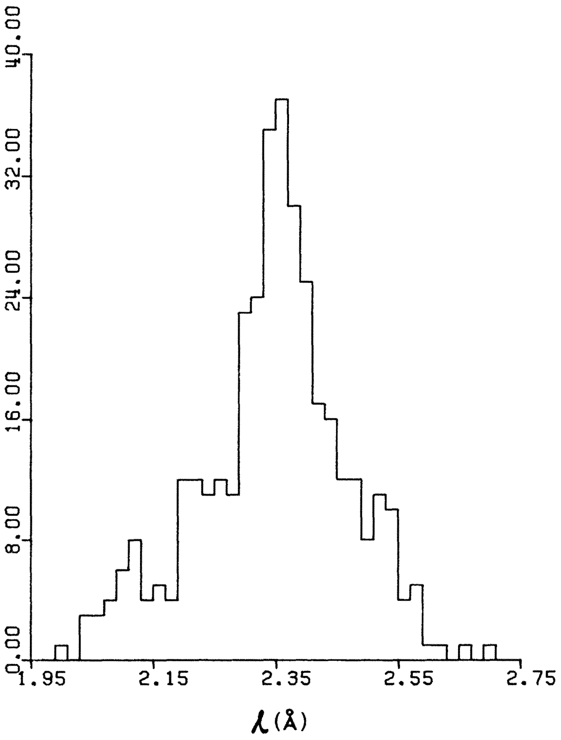

FIG. 4. Bond-length distribution of the model. The histogram is calculated with a length interval $\Delta l = 0.02$ Å.

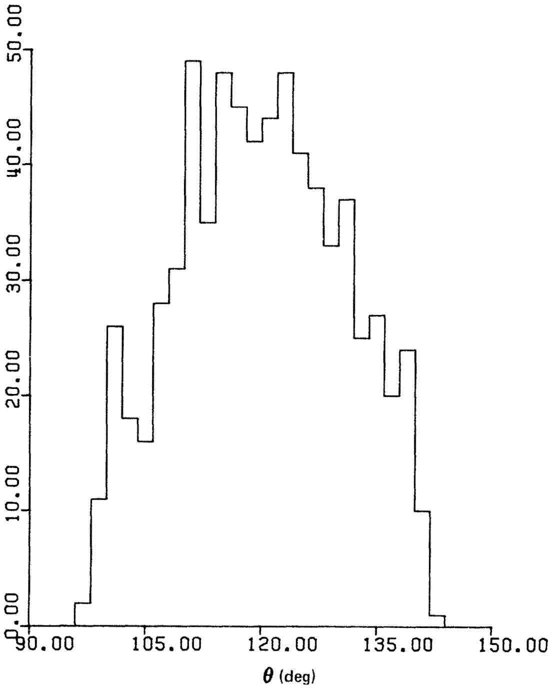

FIG. 5. Bond-angle distribution of the model. The histogram is calculated with an angle interval of $\Delta\theta = 2°$.

IV. VIBRATIONAL PROPERTIES

The 272-atom random network shown in Fig. 1 is employed in the present lattice-dynamical calculation. Each atom was assumed to be subject to a simple force field[31] with central and noncentral nearest-neighbor interactions. The equation for the eigenfrequency ω for an interior atom i in the lattice can be written

$$-m\omega^2\vec{u}_i = \sum_j \left[\alpha_{ij}(r_{ij})\hat{r}_{ij}\cdot\hat{r}_{ij} + \beta_{ij}(r_{ij})(\underline{1} - \hat{r}_{ij}\cdot\hat{r}_{ij})\right]\cdot(\vec{u}_j - \vec{u}_i)\ , \quad (3)$$

where $\alpha_{ij}(r_{ij})$ is the nearest-neighbor central force constant, $\beta_{ij}(r_{ij})$ is the nearest-neighbor noncentral force constant, r_{ij} is the bond length between atom i and atom j at equilibrium, $\hat{r}_{ij}$ is the unit vector from atom i to atom j at equilibrium, $\vec{u}_i$ is the displacement vector of atom i, m is the particle mass, and $\underline{1}$ is a 2×2 unit dyadic. The summation is restricted to the three nearest neighbors.

The free-end boundary conditions which are physically realistic for the actual solid surface[31] are imposed on the lattice boundaries. The equation of motion for a boundary atom is the same as Eq. (3) except there is no summation sign because there is only one nearest neighbor for each boundary atom.

The secular equation for eigenfrequencies for the entire 272-atom lattice then becomes

$$(\underline{D} - \omega^2 \underline{I})\vec{u} = 0 \; . \qquad (4)$$

The dynamical matrix $\underline{D}$ is a real 544×544 symmetric matrix.

Since only nearest-neighbor interactions are considered, there are no more than eight nonzero elements in each row of the matrix. The neighbor atoms were labeled so closely that these nonzero elements only appear near the main diagonal submatrix. The resultant 544×544 $\underline{D}$ matrix is therefore of band[32] form which means all the nonzero elements are within an interval around the main diagonal with a half-bandwidth of 80. Those nonzero elements are placed according to the neighbor relationships. Their positions were not regular because of the topological disorder in the lattice. The matrix elements, which are a function of force constants, hence the bond length and bond angle (θ_{ij}) are different due to the geometrical disorder associated with the variation of bond lengths and angles.

The force constants are determined by relating them to the pressure dependences of the elastic constants and the optical-mode frequency. In the perfect threefold coordinated honeycomb lattice, the relationship between the physical observables and force constants may be written[20]

$$C_{11} = \frac{1}{r_{ij}} \, \frac{\alpha_{ij}(\alpha_{ij} + 3\beta_{ij})}{\alpha_{ij} + \beta_{ij}} \; ,$$

$$C_{12} = \frac{1}{r_{ij}} \, \frac{\alpha_{ij}^2 - 3\alpha_{ij}\beta_{ij} - 2\beta_{ij}^2}{\alpha_{ij} + \beta_{ij}} \; , \qquad (5)$$

$$C_{66} = \frac{1}{2r_{ij}} \, \frac{\beta_{ij}(\beta_{ij} + 3\alpha_{ij})}{\alpha_{ij} + \beta_{ij}} \; ,$$

and

$$\omega_0 = [3(\alpha_{ij} + \beta_{ij})/m]^{1/2} \; .$$

A pressure may be associated with the bond length by the use of Murngahan's equation

$$P = \left[\left(\frac{r_0}{r_{ij}} \right)^{3(dB/dp)} - 1 \right] \frac{B_0}{dB/dp} \; , \qquad (6)$$

where

$$B = \tfrac{1}{3}(C_{11} + 2C_{12})$$

and r_0 is the crystalline bond length. This approximation enables one to determine an appropriate pressure given a lattice spacing r_{ij}. The physical observable associated with that pressure is then used in Eq. (5) to calculate the appropriate force constants in a least-squares sense. In order to obtain numerical results the elastic constant data[33] and Raman frequency[34,35] appropriate to silicon was used.

The distribution of the near-neighbor central and noncentral force constants is presented in Fig. 6. There are a total of 369 values for each of the force constants which correspond to the 369 bond lengths. The arrow in each figure corresponds to the force constant value associated with the perfect honeycomb lattice. The high values for some of the force constants is due to the fact that a few distorted bond lengths were allowed in the laborious connecting process.

After the location and value of each nonzero matrix element is specified, the $\underline{D}$ matrix is stored in a 544×80 computer array. Dean and Bacon's method[32] based on the negative eigenvalue theorem[36] is then used to find the frequency distribution associated with $\underline{D}$. Both the computer storage and execution time are enormously reduced[32] since the $\underline{D}$ matrix is symmetric and of band form.

A simple force field with nearest-neighbor central and noncentral force constants is used for the perfect honeycomb lattice. The details of this calculation may be found elsewhere.[20] The phonon density of states for the perfect honeycomb lattice

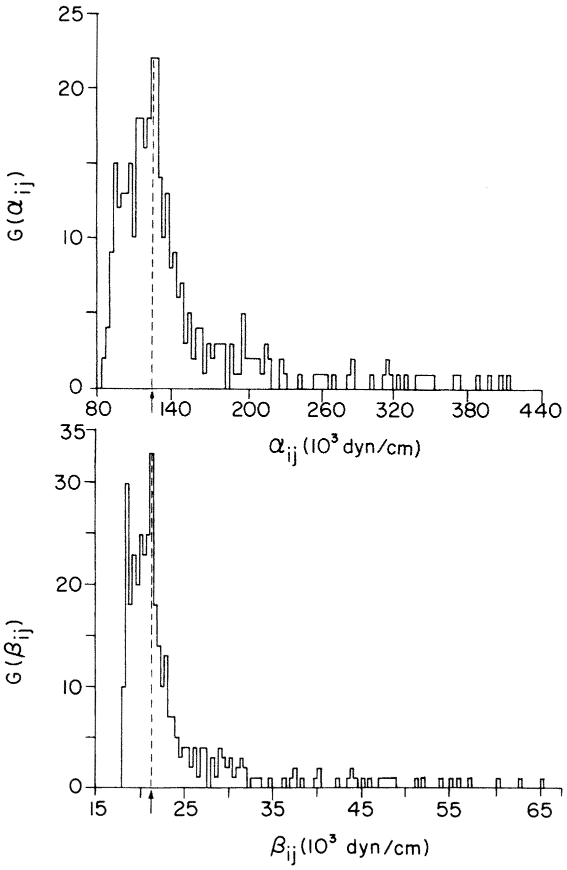

FIG. 6. Force-constant distribution for the central force constant α_{ij} and the noncentral force constant β_{ij}. The arrows in each figure indicate the appropriate values for the perfect-honeycomb lattice.

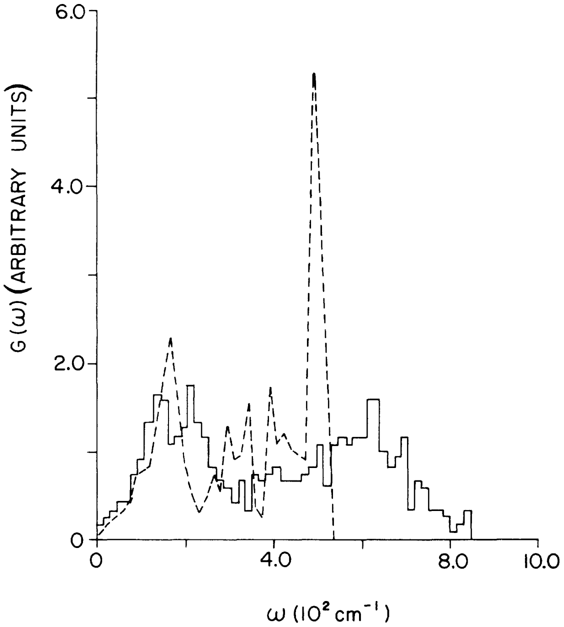

FIG. 7. Vibrational spectrum. Solid line, the random-network lattice; dashed line, the perfect-honeycomb lattice.

is calculated for 91 independent k vectors equally distributed over the irreducible $\frac{1}{12}$th of the first Brillouin zone.

The resulting phonon density of states of both the perfect honeycomb and the random lattice is presented in Fig. 7. In the amorphous material the phonon spectrum becomes broader due to the amorphous disorder in the lattice. The geometric disorder induced by force constant variations extends the spectrum to a higher-frequency range, hence reducing the height of the high-frequency peak. The finite size of our model, although quite large as far as computer storage and time is concerned, may not be large enough to produce a very smooth vibrational spectral profile (Fig. 7).

V. CONCLUSIONS

In the present work, a two-dimensional random lattice has been constructed using the random-walk technique. The bond-length and bond-angle random number statistics were obtained from the experimental data. The only topological constraint in the connection process was the assumption of a coordination number of 3. No other constraint was introduced which might have caused any degree of periodicity in the lattice. The resulting lattice is a truly random network having amorphous properties which agree well with the input data. A lattice of this type can also be utilized for the calculation of electronic and vibrational properties since there is no broken bond inside the model. Two-dimensional random networks of higher coordination numbers, e.g., four (quadratic) and six (triangular) can also be constructed using this technique. An extension of this random-walk technique to a three-dimensional tetrahedrally bonded lattice is under consideration. Such a model is expected to be a better simulation of amorphous Ge, Si, and the III-V compounds than any of the restricted models so far presented.

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*Present address: Dept. of Electrical Engineering and Computer Sciences and the Electronics Research Laboratories, University of California at Berkeley, Berkeley, Calif. 94720.

†On leave at Max-Planck-Institut für Festkörperforschung, Stuttgart, Federal Republic of Germany.

[1] W. H. Zachariasen, J. Am. Chem. Soc. 54, 3841 (1932).

[2] F. Ordway, Science 143, 800 (1964).

[3] D. L. Evans and S. V. King, Nature 212, 1353 (1966).

[4] R. J. Bell and P. Dean, Nature 212, 1354 (1966).

[5] R. Kaplow, T. A. Rowe, and B. L. Averbach, Phys. Rev. 168, 1068 (1968).

[6] W. Paul, in *Proceedings of the NATO Advanced Study Institute on Physics of Structurally Disordered Solids, Kingston, R. I.*, 1974, edited by S. S. Mitra (Plenum, New York, to be published).

[7] M. G. Duffy, D. S. Boudreaux, and D. E. Polk, J. Non-Cryst. Solids 15, 435 (1974).

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

[9] D. E. Polk and D. S. Boudreaux, Phys. Rev. Lett. 31, 92 (1973).

[10] N. J. Shevchik and W. Paul, J. Non-Cryst. Solids 8–10, 381 (1972).

[11] D. Henderson and F. Herman, J. Non-Cryst. Solids 8–10, 359 (1972); D. Henderson, in *Computational Solid State Physics*, edited by F. Herman (Plenum, New York, 1972), p. 175.

[12] D. Henderson, J. Non-Cryst. Solids 6, 317 (1974).

[13] R. Alben, J. E. Smith, Jr., M. H. Brodsky, and D. Weaire, Phys. Rev. Lett. 30, 1141 (1973).

[14] P. W. Keating, Phys. Rev. 145, 637 (1966).

[15] P. Steinhardt, R. Alben, and D. Weaire, J. Non-Cryst. Solids 15, 199 (1974).

[16] J. Kakinoki, K. Katada, T. Kanawa, and T. Ino, Acta. Crystallogr. 13, 171 (1960).

[17] N. Greaves and A. Davis, Philos. Mag. 29, 1201 (1974).

[18] J. D. Axe, in Ref. 6.

[19] P. Dean, Proc. Phys. Soc. Lond. 84, 727 (1964).

[20] J. Y. Chen, M. S. thesis (University of Maine at Orono, 1975) (unpublished).

[21] R. J. Bell, J. Phys. C 5, L315 (1972).

[22] R. J. Bell, N. F. Bird, and P. Dean, J. Phys. C 7, 2457 (1974).

[23] R. J. Bell, J. Phys. C 7, L265 (1974).

[24] R. Alben and D. Weaire, Phys. Rev. B 11, 2271 (1975).

[25] J. Y. Chen, J. F. Vetelino, and S. S. Mitra, Solid State Commun. 16, 1313 (1975).

[26] N. J. Shevchik and W. Paul, J. Non-Cryst. Solids 3, 1 (1973/74).

[27] S. Moss and J. Graczyk, in *Proceedings of the Tenth International Conference on the Physics of Semiconductors, Cambridge, Mass.*, 1970, edited by S. P. Keller *et al.*, Conf. No. 700801 (USAEC Div. of Technical Information, Springfield, Va., 1970), p. 658.

[28] C. S. Smith, Rev. Mod. Phys. 36, 524 (1964).

[29] D. A. Aboav, Metallogr. 4, 425 (1971).

[30] D. Weaire, Metallogr. (to be published).

[31] R. J. Bell and P. Dean, J. Inst. Maths. Appl. 4, 375 (1968).

[32] P. Dean and M. D. Bacon, Proc. R. Soc. A 283, 64 (1965).

[33] M. S. McSkimin and P. Andreatch, Jr., J. Appl. Phys. 35, 2161 (1964).

[34] S. S. Mitra, in *Optical Properties of Solids*, edited by S. Nudelman and S. S. Mitra (Plenum, New York, 1969), p. 333.

[35] E. Anastassakis, A. Pinczuk, E. Burstein, F. H. Pollak, and M. Cardona, Solid State Commun. 8, 133 (1970).

[36] P. Dean and J. L. Martin, Proc. R. Soc. A 259, 404 (1960).