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PERIODIC STRUCTURAL MODELS AND RADIAL DISTRIBUTION FUNCTIONS OF SiO_x: x=0. to 2.*

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Abstract

A series of random network structural models with periodic boundary conditions for SiO_x for x range from 0. (pure amorphous Si) to 2. (pure vitreous silica) within the context of microscopic random bond mixing model have been constructed. A Keating type of potential is used in the computer relaxation process. These cubic models which have 54 Si atoms and variable number of O atoms have no internal voids or dangling bonds. Each O atom binds to two Si atoms in a non-linear bridging position while each Si atom binds to four other atoms (Si or O) in a tetrahedral configuration. The densities, radial distribution functions (RDF) and partial RDF are studied as a function of x and are compared with available x-ray scattering data. It is found that for cases of $x \neq 0.$ or 2., the Si-Si bond lengths tend to be larger and Si-O bond lengths tend to be shorter than their respective crystalline bond lengths. Utilization of these structural models in the electronic and vibrational calculations is also discussed.

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Introduction

In the past few years, the continuous random network (CRN) theory[1] has been generally accepted as the appropriate theory to describe the structure of glasses, amorphous semiconductors and other covalently bonded non-crystalline solids. Cluster models (CM) of CRN which contain no internal voids or dangling bonds has been constructed for vitreous silica or amorphous SiO_2 (a-SiO_2) as early as mid-sixties.[2] Later, many tetrahedrally bonded network models were also constructed for amorphous silicon (a-Si).[3,4] These physical models enable us to calculate theoretical radial distribution functions (RDF) and compare with the RDF deduced from scattering experiments. Since the RDF is only an average property of a bulk solid, the agreement in RDF with experimentally measured one is a necessary but not sufficient condition of being a good model. A more stringent test is to calculate the electronic[5,6] or vibrational properties[7] of the material based on the atomic coordinates of the model structure. It is expedient to have a CRN with periodic boundary conditions (PBC). Since then, the mathematical formulism of electronic or vibrational calculations will be similar to the crystalline cases with perhaps an enormous increase in the complexity of the calculation because of the large number of atoms in the quasi unit cell. The first of such quasi-periodic model (QPM) has been constructed by D. Henderson for a-Si.[8] In contrast to the CM which always associate itself with a finite surface, the QPM represents a truely infinite array of network from which the density of the material can be accurately determined and no surface effect will present. Of course, the unit cell should be sufficiently large such that the residual long range order of quasi-crystallinity is negligible. The only drawback of QPM is that the constraint of PBC make the construction of model much more difficult.

In this paper, I present the first QPM for vitreous silica which has a RDF and density in excellent agreement with experiment. Similar models are also constructed for SiO_x with x = 1.5, 1.0, and 0.5 within the context of microscopic random bond mixing model.[9] These models should be very useful in elucidating the atomic structures of SiO_x films and $Si-SiO_2$ interfacial regions and provide a means of deeper microscopic understanding about the interfacial electronic states.

Model Construction

The construction of QPM of CRN for amorphous solid is a rather difficult and extremely time consuming process. Fortunately, reasonably good QPM for a-Si is already in existance and can be utilized to construct QPM for a-SiO_2 and SiO_x. We start with the QPM originally constructed by Guttman,[6] which has 54 Si-atoms in a cubic cell and insert O atoms between each pair of Si atoms. We then rescale the size of the cell such that the density of the model is equal to 2.2 gm/c.c. for vitreous silica. A two dimensional illustration of the process is shown in Figure 1. From this initial configuration in which the topology of the network and the bond pattern is determined, a computer relaxation process[4] is applied which reduce the overall elastic energy of the network by successively moving each atom to the position of zero force under a Keating[10] type of potential.

$$V = \Sigma_\ell V_\ell^{S_i} + \sum_n V_n^O$$

$$V_\ell^{S_i} = \frac{3}{16}\frac{\alpha}{d^2}\sum_{i=1}^{4}(\vec{r}_{\ell,i}\cdot\vec{r}_{\ell,i} - d^2)^2 + \frac{3}{8}\frac{\beta_1}{d^2}\sum_{(i,i')}^{6}(\vec{r}_{\ell,i}\cdot\vec{r}_{\ell,i'} - d^2\cos^{-1}\phi)^2$$

$$V_n^O = \frac{3}{16}\frac{\alpha}{d^2}\sum_{j=1}^{2}(\vec{r}_{n,j}\cdot\vec{r}_{n,j} - d^2) + \frac{3}{8}\frac{\beta_2}{d^2}(\vec{r}_{n,j}\cdot\vec{r}_{n,j'} - d^2\cos^{-1}\theta)^2$$

where $\vec{r}_{\ell,i}$ is the radius vector from atom ℓ to its nearest neighbor atom i; ϕ is the ideal O-Si-O angle (109° 28'); θ is the average Si-O-Si angle (147.° in this work) and d is the Si-O or Si-Si bond length as the case

may be. The first term in the above expressions sums over nearest neighbors, while the second term sums over the nearest neighbor pairs.
The ratio of bond bending to bend streching force constants are set to be $\beta_1/\alpha = 0.17$,[8] $\beta_2 = 1/3\ \beta_1$. The model structure is found to be rather insensitive to a reasonable range of choice of the constants α, β_1, β_2.

If only a random fraction of the available O sites in the above described process is occupied, we have the initial configuration of a random bond mixing model of SiO_x.[9] Each O atom binds to two Si atoms and each Si atom binds to four atoms which may be O or Si, depends on the random statistics. The unit cell sizes are rescaled appropriately according to x. The densities are found to be 2.45, 2.50, 2.44 gm/c.c. for $x = 1.5$, 1.0, 0.5, respectively. The structures are then relaxed as before where we assumed the bond streching constant α for Si-Si and for Si-O are the same, so are the bond bending constants β_1 for Si-Si-Si, Si-Si-O and O-Si-O angles. For each value of x three inequivalent models with different random statistics were constructed.

Result

In Figure 2 (a) and (b) we present the calculated RDF of a-SiO_2 for x-ray and neutron scattering respectively. The atomic scattering factors used for x-ray (neutron) scattering are F_{Si}^{x} = 14.75 electrons (f_{Si}^{n}= 0.4210 x 10^{-12} cm) and f_{O}^{x} = 7.625 electrons (f_{O}^{n} = 0.577 x 10^{-12} cm) respectively.[12] The corresponding experimental curves as presented in Ref. 12 are also shown as dotted lines. It is apparent that the agreement is very good up to a radial distance of 8 Å. Not only the position of the major peaks are in match, but also the smaller structures are quite well reproduced. The resolved Si-Si, O-Si and O-O partial RDF are shown in Fig. 3 (a) to (c). These results are also in good agreement with those from CM of a-SiO_2 by Bell and Dean.[12] The only difference being the absence of a shoulder at 3.7 Å which is attributed to Si-O pairs in four membered rings. The present model, being derived from a model for a-Si[6] does not contain four membered rings. The distributions of Si-O bond lenths R, the O-Si-O angles ϕ and the Si-O-Si angle θ are shown in Figure 4 (a) to (c). The average value is indicated by an arrow. It is obvious that the distortion of SiO_4 units from a perfect tetrahedron is very small. The root mean square deviations of R and ϕ are only 0.017 Å and 4.8° respectively. The distribution of θ is non-symmetric and ranges from 116° to 180° with an average value $\bar{\theta}$ = 147°. This is to be compared with the value of $\bar{\theta}$ = 153° in the model of Bell and Dean[12] and also $\bar{\theta}$ = 144° in α-quartz crystal.

The RDF for x-ray scattering of SiO_x for x from 2.0 (vitreous silica) to 0. (a-Si) are shown in Figure 5 (a) to (e). For x = 1.5, 1.0 and 0.5, the curves represent the average of three statistically inequavalent models. Going from x = 2.0 to 0. the Si-O peak diminishing and the Si-Si peak growing and moving from 3.12 Å in a-SiO_2 to 2.33 Å in a-Si. The interpretations of other peaks above 2.5 Å is less straight forward because in the microscopic random bond mixing model, all types of atomic pairs contribute. It was found that for x not equal to 2.0 or not equal to 0. the Si-O (Si-Si) bond distances tend to be slightly shorter (longer) than the corresponding crystalline bond length. This is a consequence of additional short range disorder present in the cares of x ≠ 2.0 or 0. in contrast to the presence of short range order in vitreous silica or a-Si.

Experimental x-ray RDF for the specific x values of 1.5, 1.0 and 0.5 are not aware to us at this time. The closest is the x = 1.08 measurement of Yasaitis and Kaplan.[13] The RDF below 5 Å have four prominent peaks and agrees quite well with the calculated RDF for x = 1.0 of Figure 5 (c).

Discussion

We have successfully constructed QPMS which represent an infinite array of random network structure for a-SiO_2 and SiO_x. The calculated RDF is in good agreement with experimental measurement and that of earlier CM. Because of limitation of size of the present paper, detailed analysis of these models with respect to the ring topology, random bond statistics, partial RDF, effects of presence of four member rings, effects of varying relaxation parameters etc., will be presented elsewhere. It should be pointed out that the flexibility of Si-O-Si angle plays an important role in model construction. This accounts for the fact that the distortion of SiO_4 tetrahedral coordination in the case of a-SiO_2 is much smaller than the corresponding distortion in a-Si case.[6]

The models for SiO_x should be of particular interest because they yield microscopic information about atomic scale structures of Si-SiO_2 interfacial regions. At present there are two competing models for the structure of SiO_x: (1) the microscopic random bond mixing model,[9] base on which the present models are constructed and (2) the randomly dispersed mixture of tetrahedrally bonded a-Si and a-SiO_2 model[13] in which the domain of Si-like or SiO_2-like regions are of few tetrahedral units. Although the present result based on the idea of first model is not inconsistent with experiment, we should be able to construct similar QPMS based on second model and make critical comparisons. Similar models with specific bonding configurations of defects can also be constructed. Using the atomic positions of the QPM constructed, one should be able to attempt realistic quantum mechanical calculations of electronic and vibrational states of SiO_x for various values of x. In conjunction with photoemission or vibrational spectroscopy data, we are then in position to discriminate between competing models for SiO_x and achieve a deeper understanding about the microscopic origin and nature of interfacial states. Work in this direction is in progress and will be reported in future publication.

Figure Captions

Figure 1. Two dimensional illustration for obtaining initial atomic configurations of a periodic model of a-SiO_2 from periodic model of a-Si. ○ Si atom; ◍ O atom.

Figure 2. RDF of vitreous silica for: (a) x-ray scattering, (b) neutron scattering. Solid line, computed from the present model; dotted line, experimental curve as presented in Ref. 12.

Figure 3. Partial RDF of vitreous silica from present model: (a) Si-Si, (b) Si-O, (c) O-O.

Figure 4. Distribution of (a) Si-O bond lengths, (b) O-Si-O bond angles, (c) Si-O-Si bond angles in the present model. The average value is indicated by an arrow.

Figure 5. Calculated x-ray scattering RDF for SiO_x, (a) $x = 2.0$ (vitreous silica), (b) $x = 1.5$, (c) $x = 1.0$, (d) $x = 0.5$, (e) $x = 0.$ (amorphous Si).

References

1. R. J. Bell and P. Dean, Physics Chem. Glasses, 9, 125, 1968.
2. F. Ordway, Science, 143, 800 (1964);
   D. L. Evans and S. V. King, Nature, Lond., 212, 1353 (1966);
   R. J. Bell and P. Dean, Nature, Lond., 212, 1354 (1966).
3. D. E. Pock, J. Non-Crystalline Solids, 5, 365 (1971);
   D. E. Polk and D. S. Bondreaux, Phys. Rev. Lett., 31, 92 (1973);
   G. A. N. Connell and R. J. Temkin, Phys. Rev. B, 9, 5323 (1974).
4. P. Steinhardt, R. Alben and D. Weaire, J. Non-Crystalline Solids, 15, 199 (1974).
5. W. Y. Ching, C. C. Lin, Phys. Rev. Lett., 34, 1223 (1975).
   W. Y. Ching, C. C. Lin and D. L. Huber, Phys. Rev. B, 14, 620 (1976).
   W. Y. Ching, C. C. Lin, Phys. Rev. B, 18, 6829 (1978).
6. W. Y. Ching, C. C. Lin, L. Guttman, Phys. Rev. B, 16, 5488 (1977).
7. P. Dean, Review of Modern Physics, 44, 127 (1972).
8. D. Henderson, J. Non-Crystalline Solids, 16, 317 (1974).
9. H. R. Phillips, J. Non-Crystalline Solids, 8-10, 627 (1972).
10. P. N. Keating, Phys. Rev., 145, 637 (1966).
11. F. L. Galeener, Phys. Rev. B, 19, 4292 (1979).
12. R. J. Bell and P. Dean, Phil. Mag., 25, 1381 (1972).
13. J. A. Yasaitis and R. Kaplow, J. Appl. Phys., 43, 995 (1972).
14. R. J. Temkin, J. of Non-Crystalline Solids, 17, 215 (1975).

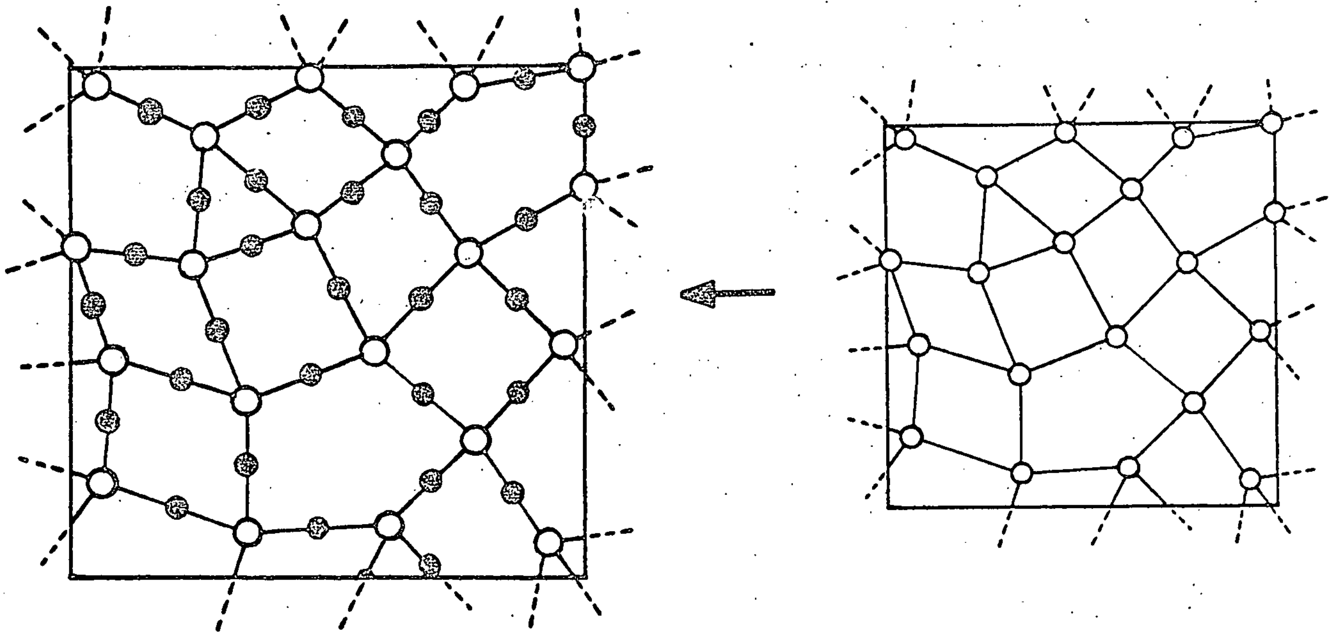

Figure 1

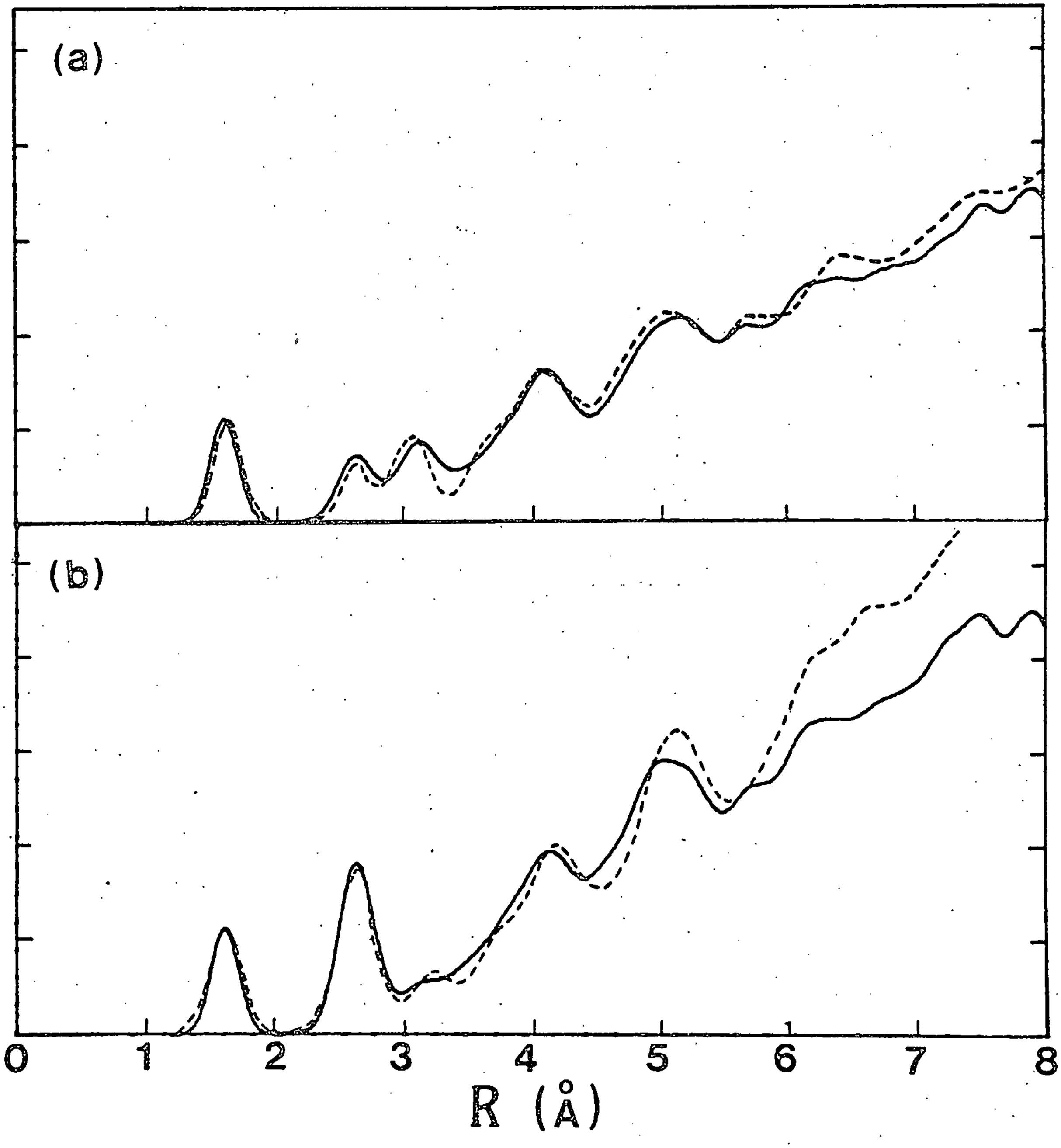

Figure 2

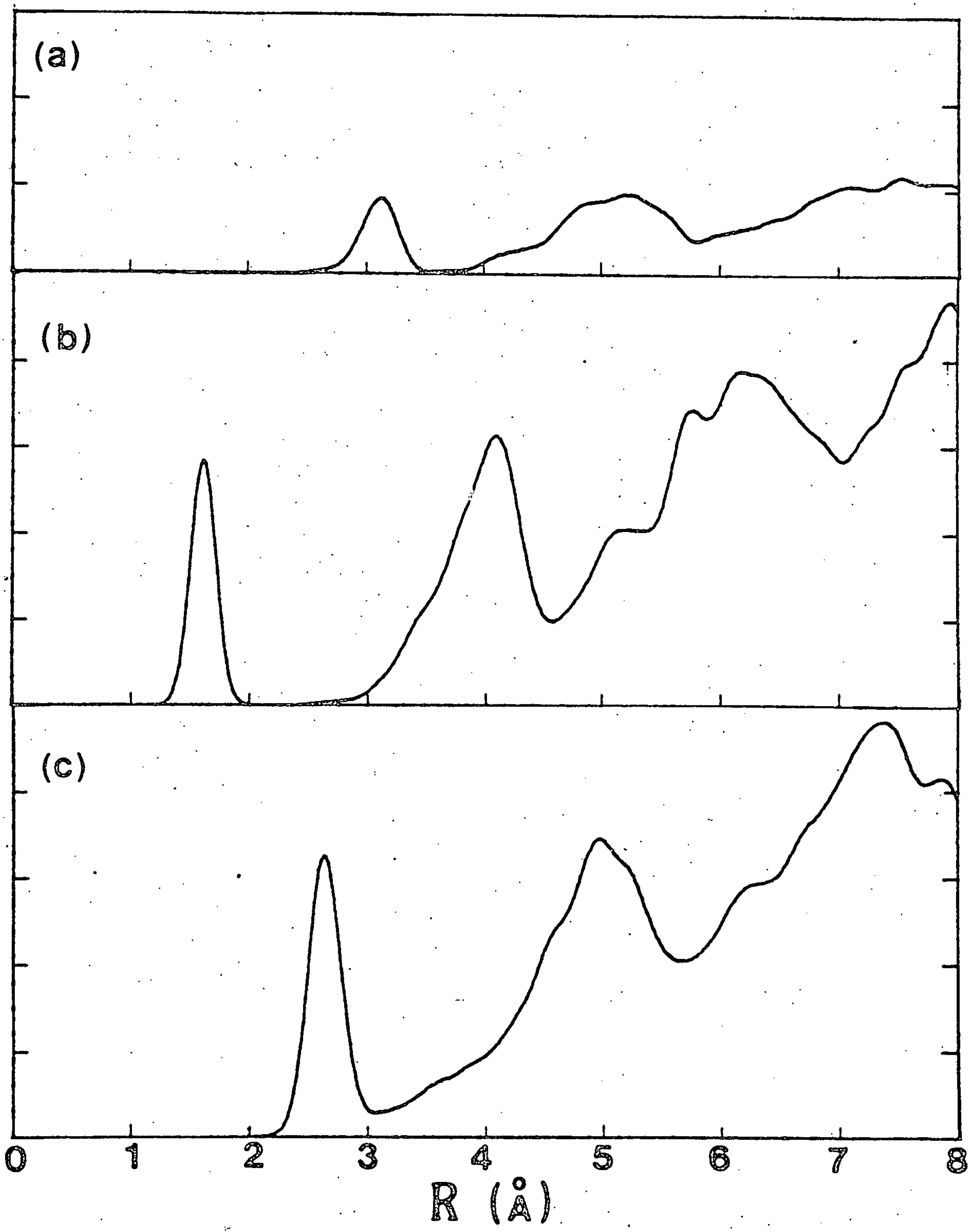

Figure 3

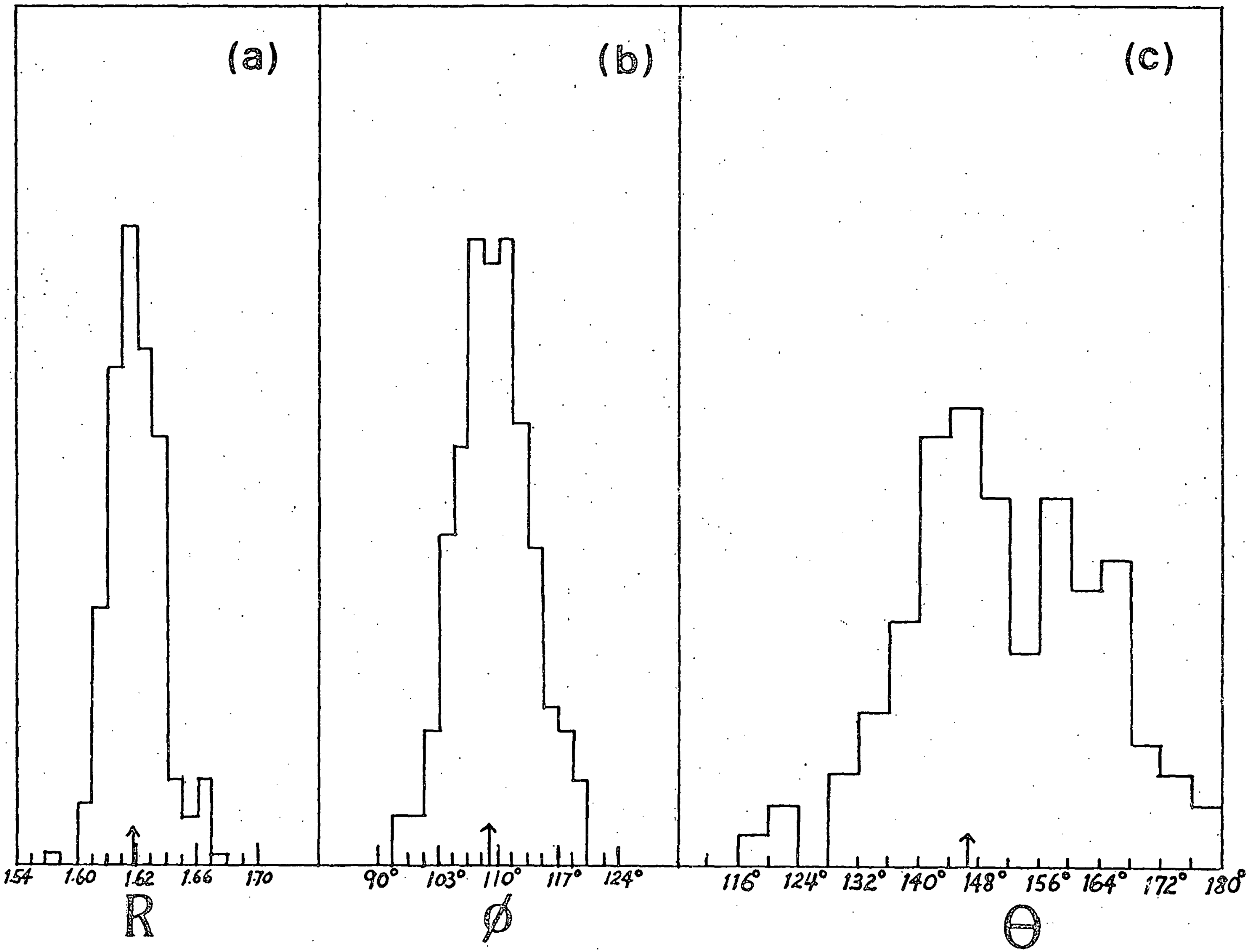
(a)
(b)
(c)
1.54
1.60
1.62
1.66
1.70
R
90°
103°
110°
117°
124°
ϕ
116°
124°
132°
140°
148°
156°
164°
172°
180°
Θ

Figure 4

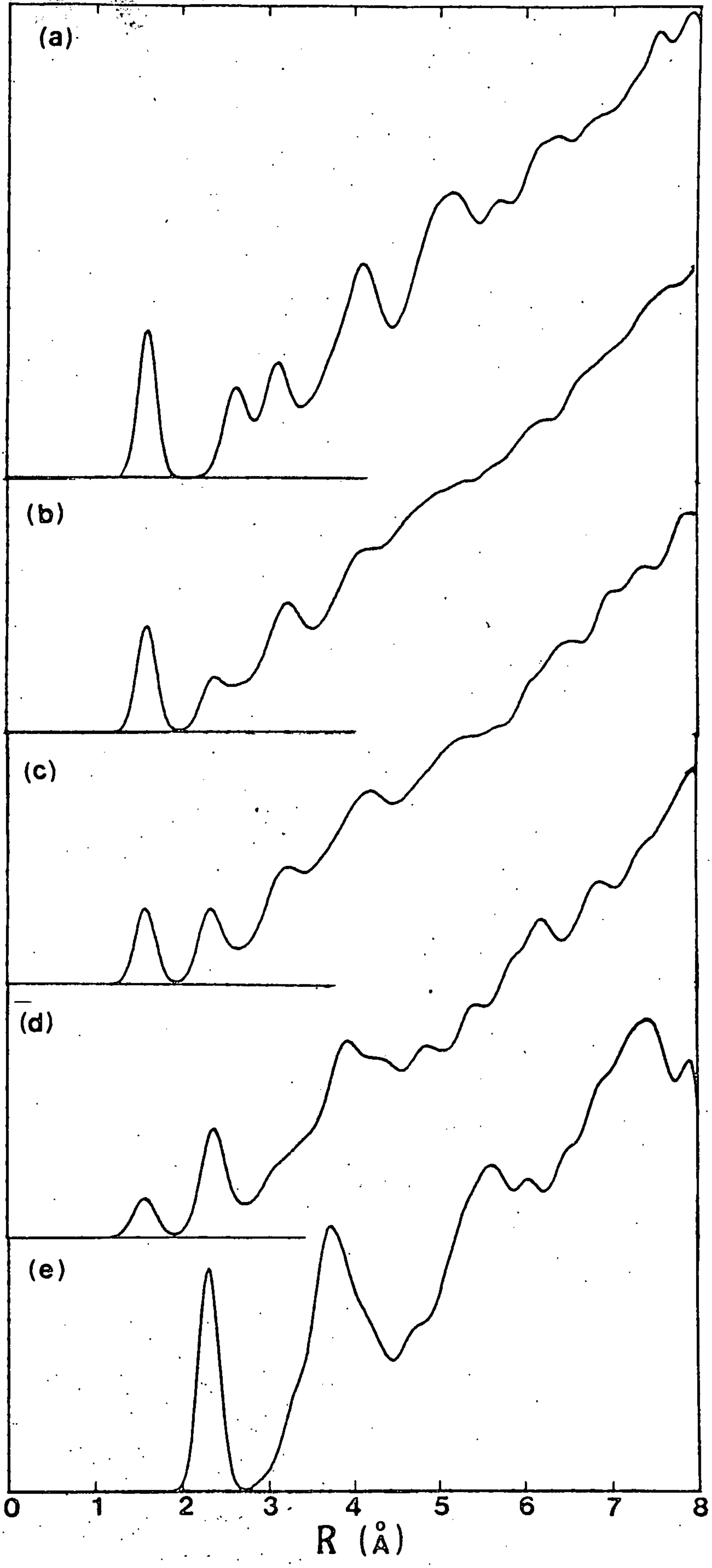

Figure 5