

AN ANALYSIS OF THE RADIAL DISTRIBUTION FUNCTION OF SiO_x ¹

R.J. TEMKIN²

Gordon McKay Laboratory, Harvard University, Cambridge, Mass. 02138, USA

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A theory is presented for the short-range order (sro) in the SiO_x alloy system for $0 \leq x \leq 2$. The parameters of the sro are taken to be fixed by the properties of amorphous Si and SiO_2 , except that the probability of an Si atom having $(i-1)$ oxygen neighbors is left as a free parameter, $C_i(x)$, for $i = 1$ through 5. The areas of the first three peaks in the radial distribution function (RDF) of SiO_x are calculated as a function of x and $C_i(x)$. It is shown that the RDF can be used to differentiate between the two models proposed for the sro in SiO_x , namely the Si– SiO_2 mixture model and the random bonding model. In the case of SiO powder, a mixture model at the atomic level is found to be consistent with the RDF. It is suggested that accurate RDF's of SiO_x films, which are not currently available, would be useful in determining the sro of the alloy system. The present theory may be extended to analyze the GeO_x and SnO_x alloy systems.

1. Introduction

Several workers [1–4] have determined the radial distribution function (RDF) of samples of amorphous SiO (a-SiO). In three studies – those of Brady [1], Lin and Joshi [3] and Yasaitis and Kaplow (YK) [4], the sample was a commercial powder of SiO and the experimental technique employed was X-ray diffraction. The RDF's obtained in these studies are very similar, although the results of YK appear to have the highest resolution. The work of Coleman and Thomas [2] differs from that of the other investigators in that thin films of SiO were investigated by electron diffraction. However, the resolution obtained by the electron diffraction technique was significantly poorer than that obtained in the X-ray studies and, unfortunately, the RDF of Coleman and Thomas is not sufficiently accurate to allow a meaningful comparison with the X-ray diffraction results. Such a comparison would be of great

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² IBM Postdoctoral Fellow. Present address: Massachusetts Institute of Technology, Francis Bitter National Magnet Laboratory, 170 Albany Street, Cambridge, Massachusetts 02139, USA.

interest. Commercial SiO, on which the X-ray studies were performed, is usually prepared by heating in vacuum a mixture of Si and SiO₂ powders [5]. Thin films of SiO, on the other hand, are often prepared by heating the commercial SiO powder in vacuum. The resultant thin SiO film may be structurally quite different from the SiO starting material, and there is evidence that this is the case. Howson and Taylor [6] have found that thin films of SiO prepared by evaporation of SiO powder in high vacuum have an infra-red absorption maximum at a wavelength of about 10.3 μm . The SiO powder starting material had an infra-red absorption maximum near 9 μm , which is close to the absorption maximum of SiO₂.

The model proposed by YK and others to explain the RDF of commercial SiO powder is a mixture model in which a-SiO is taken to be a mixture of a-Si and a-SiO₂. Such a mixture is not believed to occur as a large scale phase separation. It is known, for example, that a-SiO is soluble in HF, while Si is not [5]. Consequently, a-SiO cannot be a gross mixture of a-Si and a-SiO₂, but rather the mixture must occur at the atomic level. The RDF results also support the concept of a mixture at the atomic level. The Si-Si separation in a-Si is 2.35 Å, while the O-O separation is 2.65 Å in a-SiO₂. YK have shown that these two peaks would be resolved in the RDF of SiO if SiO were a simple mixture of large volumes of phase-separated a-Si and a-SiO₂. The observed single peak at 2.45 Å in the RDF of a-SiO indicates that a phase separation into large regions of a-Si and a-SiO₂ is not a possible model. However, if the phase separation occurs in regions as small as 5 to 10 Å, a large fraction of the atoms will be at the interface between Si-like and SiO₂-like regions. These atoms will be under considerable strain. Consequently, the distribution of Si-Si and O-O bond lengths could each be considerably spread out and would overlap to form a single broad peak in the RDF of a-SiO.

Previous analysis of the RDF's of SiO has clearly established that a mixture model can explain the experimental results. However, it is of interest to determine whether other models of the structure of SiO might also be consistent with the experimental RDF's. Phillip [7] has proposed a structural model to explain his optical results on thin a-SiO films. In his model, each Si atom is tetrahedrally coordinated by n oxygen and $(4-n)$ silicon atoms, with the probability of n being 0, 1, 2, 3, or 4 being determined statistically based on the proportion of Si and O atoms present, that is, based on x . This random model differs from the mixture model because, in the mixture model, each Si atom must have either 4 Si or 4 O neighbors, that is $n = 0$ or 4 only.

Phillip has suggested that evidence against the mixture model may be found in two sets of experimental optical data [7]. The reflectance between 0 and 25 eV of a-SiO₂ and a-SiO_{1.5} shows a series of peaks between 10 and 20 eV that are characteristic of the Si-O₄ configuration. The peaks are not present in a-SiO. This result is expected in the random model because, in a-SiO, only a small fraction (0.0625) of the Si atoms are expected to have 4 oxygen neighbors, while in a-SiO₂, all Si atoms have 4 oxygen neighbors and in a-SiO_{1.5}, 0.3164 of the Si atoms are expected to have 4 oxygen neighbors. The result is unexpected in the mixture model because

one half of a-SiO is believed to be a-SiO₂. On the other hand, the same data and the same method of analysis as those used by Phillip may also be used to support the mixture model. At energies below 10 eV, the reflectance of a-SiO closely resembles that of a-Si. This result is expected in the mixture model, where a-SiO is expected to be one half a-Si. It is unexpected in the random model, where a-SiO is expected to contain only a very small fraction (0.0625) of Si atoms with 4 Si neighbors. Consequently, the reflectance data do not directly support either the random model or the mixture model, at least when the analysis is done on a simple basis of correspondence of peaks in the reflectance.

The other evidence which is offered by Phillip in support of the random model is the variation with x in the position of the optical absorption edge of SiO _{x} films. Near the onset of absorption, Phillip finds that a-SiO films are about 20 times less absorbing than a-Si films. This is consistent with the random model of a-SiO, if one assumes that the onset of absorption is determined by those Si atoms having four Si neighbors. If a-SiO has random bonding, then only one Si atom in 16 has four Si neighbors, with the factor 16 being in excellent agreement with the observed factor of 20. However, this sort of quantitative analysis is predicated on the assumption that the optical absorption edge only shifts in the SiO _{x} system when x varies. In fact, the position of the optical absorption edge of a-Si is known to vary quite considerably as a function of annealing temperature [8], and this variation obviously occurs at constant x ($x = 0$). Since a small variation in the position of the optical absorption edges of a-Si and a-SiO will drastically change the results of the analysis proposed by Phillip of the SiO bonding, the optical edges cannot be used as quantitative support for the random bonding model. The optical absorption edge in a-Si varies because of the annealing out of defects such as voids, and similar variations in edge position would be expected in a-SiO _{x} films. Furthermore, the position of the edge is in general determined by a very small number of electronic states which in turn may be associated with a small fraction of the atoms. Consequently, in the present case, it is impractical to draw conclusions about a bulk property, such as the bonding arrangement in the film, from the position of the optical absorption edge.

Thus, a review of the optical properties of evaporated a-SiO _{x} films does not appear to require a random bonding model for these materials. However, it does not appear to rule out such a model either. Similarly, the RDF of commercial a-SiO is consistent with a mixture model of a-Si and a-SiO₂. However, it has not been shown whether the same RDF might be consistent with other models, such as the random model. Recently, Hollinger et al. [9] have studied thin films of SiO by X-ray photoelectron spectroscopy. They find a doublet in the Si 2p core level spectrum which is inconsistent with both the simple mixture model and the random model. Consequently, no experimental results have yet been able to clearly define the structure of a-SiO.

In sect. 2 of this paper, we present a general theory for analyzing the RDF of an a-SiO _{x} film and in sect. 3 the results of the theory are applied to the RDF of a-SiO. Phillip has conjectured that the RDF cannot be used to differentiate between the

random and mixture models [7]. Using the theory of sect. 2, we prove that the RDF can indeed differentiate between the models and that the SiO RDF of YK is consistent with a mixture model at the atomic level and inconsistent with the random model.

2. Theory

We consider the system SiO_x, where $0 \leq x \leq 2$. The theory of the atomic arrangement in these solids is based on the following assumptions, which are taken to apply at all x :

- (1) Each Si atom is bonded to 4 other atoms.
- (2) Each O atom is bonded to 2 other atoms.
- (3) O atoms do not bond with one another.
- (4) The average Si—O bond length is approximately 1.62 Å.
- (5) The average Si—Si bond length is approximately 2.35 Å.
- (6) The average bond angle at an Si vertex is the tetrahedral value, 109.5°.
- (7) The average bond angle at an O vertex is approximately 144°.

All of the assumptions listed above are based on the properties of crystalline and amorphous Si [10] and SiO₂ [11], except for the 144° angle at an O vertex which only applies to a-SiO₂. As will be discussed in sect. 3, most of these assumptions can be verified directly in the case of the RDF of a-SiO. Furthermore, the assumed bond lengths could vary by about 10% and the bond angles by about 15% without significantly changing the theory. The first two assumptions are often referred to as the $(8 - N)$ rule.

The set of assumptions uniquely specifies the near neighbor environment of each O atom but not of each Si atom. This is shown schematically in fig. 1. There are five possible tetrahedral environments for each Si atom. The i th arrangement, denoted T_i , is taken to be an Si atom with $(i - 1)$ oxygen neighbors and $(5 - i)$ silicon neighbors, with the fraction of tetrahedra of type T_i denoted C_i . Since each Si must be tetrahedrally coordinated, we can normalize so that

$$\sum C_i = 1, \quad (1)$$

where

$$0 \leq C_i \leq 1 \quad (2)$$

and where all summation signs, unless otherwise specified, will denote a sum from $i = 1$ to $i = 5$.

In the ensuing calculations, we will be primarily interested in the distribution of first (one-bond) and second (two-bond) neighbors. The parameters of these distributions have already been established, with only the five C_i unspecified at a given x . If we were to calculate the distribution of n -bond neighbors for $n \geq 3$, it would be necessary to consider such additional features as the ring statistics and the angle of rotation of next neighbors about bonds. One method of investigation these features

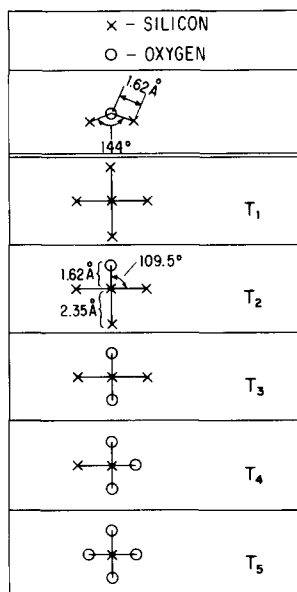


Fig. 1. Near neighbor configurations in a-SiO_x . Each O atom has 2 Si neighbors at 1.62 Å with a 144° bond angle. The five possible tetrahedral arrangements for Si are shown projected onto a plane. The Si-Si bond length is 2.35 Å and the tetrahedral bond angle is 109.5° . The fraction of tetrahedra with the i th arrangement is C_i .

is model building. It seems very likely that a continuous random network model (CRN) of a-SiO_x could be constructed for any x , and that a variety of models with different C_i or ring statistics could be built at each x . CRN's with different ring statistics have been constructed both for $x = 0$, a-Si [12–15] and for $x = 2$, a-SiO_2 [16–18]. Furthermore, it has been demonstrated that removing all of the O atoms from a model of a-SiO_2 produces a good model of a-Si [19]. It therefore seems reasonable that removing a fraction $\frac{1}{2}(2 - x)$ of the O atoms from a model of a-SiO_2 will yield a model of a-SiO_x . Of course, any two Si atoms from between which an intermediate O atoms has been removed would have to be moved closer together to form an Si-Si bond with the correct bond length. Previous experience with computer relaxation of atomic coordinates of models indicates that this can be done [13–15]. Finally, the removal of a fixed number of O atoms from an SiO_2 model to produce SiO_x can be done in a variety of ways, with each different way resulting in different values for the C_i . Of course, it would be of interest to verify that these models can be constructed. However, it will henceforth be assumed that the structures discussed can be built in the form of CRN's.

Using the assumptions about near neighbor bonding, it is possible to derive additional constraints on the C_i . Let the number of Si and O atoms be N_{Si} and N_{O} , re-

spectively. Then, for SiO_x , $N_{\text{O}} = xN_{\text{Si}}$. Since there are two O—Si bonds per O atom, the number of O—Si bonds is $2N_{\text{O}}$, which, since $N_{\text{O}} = xN_{\text{Si}}$, equals $2xN_{\text{Si}}$. Since the number of Si—O bonds must equal the number of O—Si bonds, the number of Si—O bonds is $2xN_{\text{Si}}$. The number of Si—O bonds may also be derived by considering the T_i . Each T_i contains $(i-1)$ Si—O bonds, so that:

$$\text{Number of Si—O bonds} = N_{\text{Si}} \sum (i-1) C_i = 2xN_{\text{Si}}. \quad (3)$$

Cancelling N_{Si} in eq. (3) and using eq. (1) leads to :

$$\sum i C_i = 2x + 1. \quad (4)$$

Eqs. (1) and (4) are two independent, linear equations for the C_i and obviously three additional independent, linear equations are needed to uniquely specify the C_i . These additional equations must come from experimental results and we will calculate below additional linear equations for the C_i using the experimental RDF results.

Further limits are imposed on the C_i by the condition $1 \geq C_i \geq 0$. For example, using eqs. (1) and (4), we have

$$\sum (i-2) C_i = 2x - 1 \quad (5)$$

or

$$2x - 1 + C_1 = C_3 + 2C_4 + 3C_5. \quad (6)$$

Since C_3, C_4 are each equal to or greater than zero, it follows that

$$C_1 \geq \begin{cases} 0 & \text{for } x \geq 0.5 \\ 1 - 2x & \text{for } x \leq 0.5. \end{cases} \quad (7)$$

Thus, C_1 cannot be zero when $x < 0.5$. This restriction can be easily understood. If $C_1 = 0$, all Si atoms have at least one O neighbor and the minimum number of Si—O bonds is N_{Si} . But the actual number of Si—O bonds is known and it is $2xN_{\text{Si}}$. Therefore, if $C_1 = 0$, $2xN_{\text{Si}}$ must exceed N_{Si} , or $x \geq 0.5$. Also, if C_1 is nonzero, ($C_1 > 0$), then it is necessary that $0.5 \leq x$. These results are consistent with eq. (7). Another constraint on C_1 is obtained from

$$5 \sum_{i=2}^5 C_i \geq \sum_{i=2}^5 i C_i. \quad (8)$$

Adding $5C_1$ and rearranging leads to

$$5 \sum C_i - \sum i C_i \geq 4C_1, \quad (9)$$

which reduces to

$$1 - 0.5x \geq C_1. \quad (10)$$

Thus, upper and lower bounds on C_1 exist at all x . Similar bounds exist for C_5 .

From

$$\sum (4-i) C_i = 3 - 2x$$

it can be shown that

$$C_5 \geq \begin{cases} 0 & \text{for } x \leq 1.5 \\ 2x-3 & \text{for } x \geq 1.5 \end{cases} \quad (11)$$

From

$$\sum (i-1) C_i \geq 4 C_5$$

it follows that

$$0.5x \geq C_5 \quad (12)$$

Note that the lower bound on C_1 changes abruptly near $x = 0.5$. Thus, $C_1 \geq 0$ at $x = 0.5$, but $C_1 \geq 0.4$ at $x = 0.3$. A similar result follows for C_5 near $x = 1.5$. Consequently, an accurate estimate of stoichiometry is important for SiO_x films for x near 0.5 and 1.5.

Before considering the experimental constraints on the C_i , it is of interest to calculate the expected value of C_i for several models of a-SiO_x . The total number of Si-O bonds is $2xN_{\text{Si}}$, so that on average each Si atom has $2x$ oxygen and $(4 - 2x)$ silicon neighbors. Therefore, the probability of an O neighbor, P_{O} , is $\frac{1}{2}x$ and P_{Si} is $\frac{1}{2}(2 - x)$. Furthermore, the number of ways of arranging the 4 near neighbor at-

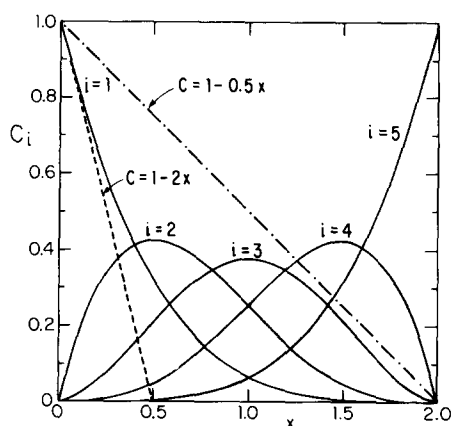


Fig. 2. The probability of the i th tetrahedral configuration, C_i , for $i = 1$ through 5, versus concentration x , in SiO_x , for the random model. The line $C = 1 - 0.5x$ (---) is an upper bound for C_1 and is also the value of C_1 in the mixture model. The line $C = 1 - 2x$ (---) is the lower bound for C_1 for $0.5 \geq x \geq 0$.

oms in T_i is 1, 4, 6, 4 and 1 for $i = 1$ through 5, respectively. Thus, in the random model, proposed by Phillip [7], we have

$$C_i(x) = \frac{4!}{(5-i)! (i-1)!} \left(\frac{1}{2}x\right)^{i-1} \left[\frac{1}{2}(2-x)\right]^{5-i}. \quad (13)$$

Note that

$$C_{6-i}(2-x) = C_i(x). \quad (14)$$

Fig. 2 shows the variation of $C_i(x)$ with x in the random model. Below $x = 0.3$, C_1 is not much larger than $1 - 2x$, which, according to eq. (7), is the lower limit for C_1 .

A second model for the C_i is the mixture model. If SiO_x is a mixture of a-Si and a- SiO_2 , then

$$C_1 = 1 - \frac{1}{2}x, \quad C_5 = \frac{1}{2}x, \quad C_2 = C_3 = C_4 = 0. \quad (15)$$

However, it is easy to show that it is not possible for C_2 , C_3 and C_4 to all be zero, if both C_1 and C_5 are non-zero. Consider two Si atoms, one with a T_1 configuration and the other with a T_5 configuration, such as atoms B and F, respectively, in fig. 3. Any atom which is bonded to B, such as C, cannot be T_5 since it already has at least one Si neighbor. Since C_2 , C_3 and C_4 are zero, atom C must be T_1 . This means that there are only T_1 tetrahedra in the solid, which contradicts the assumptions in eq. (15), except when $x = 0$. Thus, even if the material is a mixture of Si and SiO_2 , there must be connectivity regions between the T_1 or Si-like regions and the T_5 or SiO_2 -like regions. The Si atoms in the connectivity region can have T_2 , T_3 or T_4 arrangements. An example of such an atom is atom D in fig. 3. If the Si and SiO_2 regions are very large, then C_2 , C_3 and C_4 can become negligibly small or even zero for completely separated material. If is for this reason that the C_i values of eq. (15) are in fact consistent with the constraint equations, eqs. (1) and (4), even though they represent a non-physical atomic arrangement.

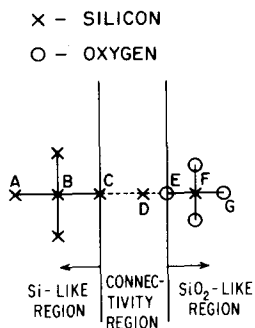


Fig. 3. In the mixture model, SiO_x is considered to consist of Si-like and SiO_2 -like regions. Where these regions meet, there must be Si atoms, like atom D, which are bonded to both Si and O atoms.

The mixture model was, in fact, not intended to define a network consisting of a large scale phase separation into Si- and SiO_2 -like regions: In a-SiO, for example, if the Si-like and SiO_2 -like regions are about 5–10 Å in diameter, the connectivity region is about equal in volume to the Si- and SiO_2 -like volumes. We might then expect for a-SiO

$$C_1 \approx C_5 \approx \frac{1}{3}, \quad C_2 + C_3 + C_4 \approx \frac{1}{3} \quad (16)$$

instead of $C_1 = C_5 = 0.5$, as in eq. (15). This model could be called a microscopic mixture model to differentiate it from the phase-separated or macroscopic mixture model defined by eq. (15).

Another possible model for the C_i is a uniform model in which $C_j = 1$ for some j , and therefore the $C_i = 0$ except for $i = j$. There are only five possible uniform models and these are $C_i = 1$ for $i = 1, 2, 3, 4$ or 5 when $x = 0, 0.5, 1.0, 1.5$ or 2.0 , respectively. The cases $C_1 = 1$ when $x = 0$ and $C_5 = 1$ when $x = 2$ are trivial cases because they represent the only solutions at those x values.

Finally, it is, of course, quite possible that the C_i values at a given x are not those determined by the random, mixture or uniform models. Some other factor, such as the relative strength of Si–Si versus Si–O bonds or the network topology, may be crucial. For this reason, the C_i should really be considered parameters to be determined experimentally. Atomic models and theoretical studies might also be relevant to understanding the C_i .

The short-range order in the RDF of a- SiO_x can be calculated in terms of the C_i . The $\text{RDF} = J(r) = 4\pi r^2 \rho(r)$ will be calculated using the notation of Kaplow et al. [20]. For a binary solid, $\rho(r)$ can be written

$$\rho(r) = \omega_{11}\rho_{11}(r) + 2\omega_{12}\rho_{12}(r) + \omega_{22}\rho_{22}(r), \quad (17)$$

where

$$\omega_{ij} = x_i K_{ij}(x) = \frac{x_i f_i(k) f_j(k)}{\langle f(k) \rangle^2}. \quad (18)$$

x_i is the atomic fraction of the i th element and $f_i(k)$ is its atomic scattering factor. The K_{ij} are assumed to be independent of k , which is reasonable for SiO_x . Let $i = 1$ and 2 refer to O and Si, respectively. YK have calculated for SiO: $K_{11} = 0.406$, $K_{12} = 0.858$ and $K_{22} = 1.876$. For SiO_x , $x_1 = x/(1+x)$ and $x_2 = 1/(1+x)$. Then

$$\omega_{11} = \frac{xK_{11}(x)}{1+x}, \quad \omega_{12} = \frac{xK_{12}(x)}{1+x}, \quad \omega_{22} = \frac{K_{22}(x)}{1+x}. \quad (19)$$

The RDF of an amorphous solid can be analyzed as a sum of n -bond neighbor distributions, where an n -bond neighbor of a given atom is one separated from that atom by a minimum of n bonds [21,22]. In the present calculation, only the 1-bond

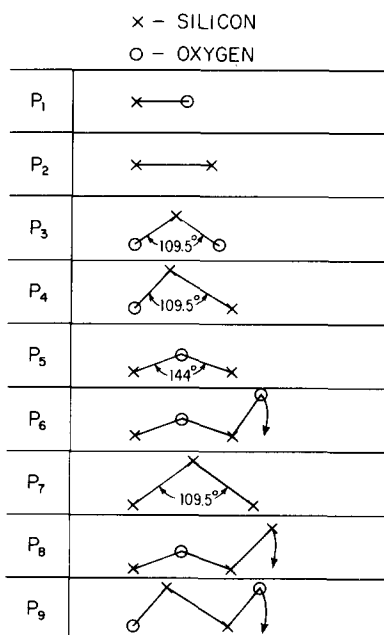


Fig. 4. The P_i are n -bond configurations of Si and O atoms. P_1 and P_2 are 1-bond configurations; P_3 , P_4 , P_5 and P_7 are 2-bond configurations; and P_6 , P_8 and P_9 are 3-bond configurations. In the 3-bond configurations, one atom is allowed to rotate about the adjoining bond, as indicated by an arrow.

and 2-bond distributions will be calculated. For $n \geq 3$, the n -bond distribution is difficult to calculate because the angle of rotation of atoms about bonds must be considered.

Fig. 4 illustrates some of the n -bond configurations of $\alpha\text{-SiO}_x$. P_1 and P_2 are the

Table 1
Peak areas in the RDF of SiO_x .

i	$r_i(\text{\AA})$	Pair	Number of atoms	A_i , Peak area (atoms)
1	1.62	O-Si	2	$4xK_{12}(x)/(1+x)$
2	2.35	Si-Si	$4-2x$	$2(2-x)K_{22}(x)/(1+x)$
3	2.65	O-O	$2(2x-1+C_1)$	$2x(2x-1+C_1)K_{11}(x)/(1+x)$
4	3.07	O-Si	$4(2-x-2C_1)$	$8x(2-x-2C_1)K_{12}(x)/(1+x)$
5	3.12	Si-Si	$2x$	$2xK_{22}(x)/(1+x)$
6	3.7	O-Si		
7	3.84	Si-Si		
8	3.9	Si-Si		
9	4.0	O-O		

two possible 1-bond configurations, P₃, P₄, P₅ and P₇ are all of the 2-bond configurations and P₆, P₈ and P₉ are 3 of the 5 possible 3-bond configurations. The two omitted 3-bond configurations are formed by bonding an Si or an O atom to P₇. The set of assumptions about bond lengths and angles uniquely defines the interatomic distances for 1-bond and 2-bond configurations, and these distances are listed in table 1. For a 3-bond configuration, there is an additional degree of freedom in that one atom may rotate about an adjoining bond.

The area of the peak in the RDF, A_i , contributed by the corresponding atomic configuration P_{*i*} is listed in table 1 for *i* = 1 through 5. The A_i are calculated as follows:

A_1 Each O atom has 2 Si neighbors, so that $N_{12} = 2$. Then, using eqs. (17) and (19),

$$A_1 = 2\omega_{12}N_{12} = 4xK_{12}(x)/(1+x). \quad (20)$$

A_2 Each Si atom has $(4 - 2x)$ Si neighbors on average, so $N_{22} = (4 - 2x)$. Therefore,

$$A_2 = \omega_{22}N_{22} = 2(2 - x)K_{22}(x)/(1+x). \quad (21)$$

A_3 An O atom, labeled A, has 2 Si neighbors labeled B and C. B and C cannot be T₁, but have a probability C_i of being T_{*i*} for *i* ≥ 2. We assume that the probability of B being T_{*k*} and C being T_{*p*} is just $C_k C_p$. That is, we assume that the tetrahedral arrangement of B does not influence the tetrahedral arrangement of C. This is a very reasonable assumption, but of course it might not be correct. Then the number of O neighbors of B (or C), not counting atom A, is zero for T₂, one for T₃, two for T₄ and three for T₅. Each of these O neighbors of B (or C) forms an O–O pair with atom A. Then

$$N_{11} = 2[C_3 + 2C_4 + 3C_5] = 2[2x - 1 + C_1] \quad (22)$$

and

$$A_3 = \omega_{11}N_{11} = 2x(2x - 1 + C_1)K_{11}(x)/(1+x). \quad (23)$$

A_4 The same atoms are considered as for A_3 , namely an O atom labeled A and Si atoms B and C. The number of Si neighbors of B is 3 for T₂, 2 for T₃, 1 for T₄ and zero for T₅.

Then

$$N_{12} = 2[3C_2 + 2C_3 + C_4] = 4[2 - x - 2C_1] \quad (24)$$

and

$$A_4 = 2\omega_{12}N_{12} = 8x(2 - x - 2C_1)K_{12}(x)/(1+x). \quad (25)$$

A_5 Each Si atom has $(i - 1)$ oxygen neighbors if it is type T_i . Each of these O neighbors has exactly one other Si neighbor. Therefore

$$N_{22} = \sum (i - 1)C_i = 2x \quad (26)$$

and

$$A_5 = \omega_{22}N_{22} = 2xK_{22}(x)/(1 + x). \quad (27)$$

Only the five peak areas at the lowest r values, which have been calculated above, can be easily compared to experiment. Unfortunately, these peak areas are a function of either x alone or of x and C_1 . Thus, only one new linear equation for the C_i is introduced, while three are needed to determine all of the C_i . However, this linear equation involves only C_1 and x and, since x is known, C_1 can be determined from the low r peak areas in the RDF. Since the random model and the mixture model predict quite different values for C_1 (cf. fig. 2), it is possible to differentiate between these models. By analyzing peaks at large r , it would be possible to obtain further equations for the C_i . For example, A_7 depends only on x and C_5 . However, such an analysis is beyond the scope of this paper.

3. Comparison of theory and experiment

The only accurate RDF's of a-SiO_x available are those obtained by X-ray diffraction from commercial powders of a-SiO [1,3,4]. The RDF obtained by YK [4] is shown in fig. 5. There are three peaks at $r < 3.5$ Å in the RDF and the location and area of each of these peaks, as estimated by YK, is listed in table 2. The first peak is

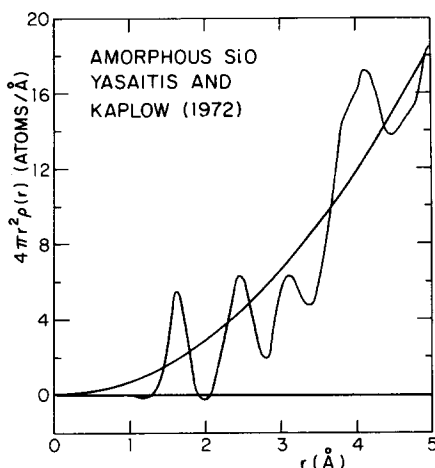


Fig. 5. The experimental radial distribution function of a commercial powder of SiO as determined by Yasaitis and Kaplow.

Table 2
Comparison of theoretical and experimental peak areas of SiO .

Peak	Location	Peak area (atoms)			
		Experiment (YK)	Mixture model	Random model	General theory
A_1	1.64 Å	1.75 ± 0.09	1.78	1.78	1.78
$A_2 + A_3$	2.45 Å	2.65 ± 0.27	2.61	2.19	$2.15 + C_1$
$A_4 + A_5$	3.11 Å	3.02 ± 0.60	1.95	4.91	$5.23 - 7.12 C_1$

associated with Si–O bonds, configuration P_1 in fig. 4. The second peak is the sum of contributions of Si–Si bonds, P_2 in fig. 4, and O–Si–O bonds, P_3 in fig. 4. The location of the second peak, 2.45 Å, is intermediate between the Si–Si distance of 2.35 Å and the O–O distance of 2.65 Å. YK have shown that, if the material were phase-separated into large clusters of a-Si and a-SiO₂, a well resolved double peak would be expected. The observation of a single peak at 2.45 Å indicates any phase separation must be at the atomic level. The third experimental peak, at 3.11 Å, is the sum of an O–Si–Si contribution, P_4 in fig. 4 with $r_4 = 3.07$ Å, and an Si–O–Si contribution, P_5 in fig. 4 with $r_5 = 3.12$ Å.

An analysis of the SiO_x powder used by YK indicated that $x = 1.08$ and that value will be used in the present analysis rather than $x = 1.00$. For $x = 1.08$, the random model predicts $C_1 = 0.045$, according to eq. (13), while the mixture model predicts $C_1 = 0.46$, according to eq. (15). Using these values of C_1 and x , the expected areas of peaks 1 through 5 can be calculated and compared with experiment. The calculated areas are listed in table 2 for the random and mixture models, together with the peak areas calculated using x but leaving C_1 as a free parameter (labeled general theory in table 2). The sum of peaks two and three in table 1 corresponds to the second RDF peak in table 2 and the sum of peaks four and five in table 1 corresponds to the third RDF peak in table 2. YK do not list an experimental error for their peak areas. Errors of 5%, 10% and 20% have been assigned to the areas of the first three peaks in the RDF, respectively, and these are believed to be conservative error estimates.

The area of the first peak depends only on x and is independent of the C_i , so that all models predict the same area, 1.78 atoms, which is in good agreement with the experimental value, 1.75 ± 0.09 . We may use this agreement to prove some of the original assumptions of the present theory. The first peak is located at 1.64 Å, which is characteristic of an Si–O bond and therefore confirms the assumption of an Si–O bond length of about 1.62 Å. If we divide A_1 by $2\omega_{12}$, we find $N_{12} = 1.96 \pm 0.10$. This proves that each O atom has two Si neighbors, as was originally assumed.

The experimental value of the area of the second peak, (2.65 ± 0.27) atoms, is in good agreement with the prediction of the mixture model, but is almost two standard deviations away from the prediction of the random model, as may be seen

from the values in table 2. The experimental peak area may also be used to solve for C_1 , and the value obtained is $C_1 = 0.50 \pm 0.27$. This may be compared with $C_1 = 0.46$ in the mixture model and 0.045 in the random model. Thus, it is possible to rule out the random model on the basis of the experimental second peak area. However, the experimental value of C_1 obtained, 0.50 ± 0.27 , does have a relatively large experimental error. In fact, this C_1 value falls outside the theoretical limits for C_1 at $x = 1.08$, which are $0.46 \geq C_1 \geq 0$.

The experimental area of the third peak in the RDF is (3.02 ± 0.60) atoms, and this value is in poor agreement with the predictions of both the mixture and random models, as indicated in table 2. The area of the third peak may, like that of the second peak, be analyzed to determine an experimental value for C_1 and the value obtained is $C_1 = 0.31 \pm 0.08$. This value is in very poor agreement with the value $C_1 = 0.045$ predicted in the random model. The experimental value is, however, in agreement, within experimental error, with the independently determined value of $C_1 = 0.50 \pm 0.27$ obtained from the second peak area. This agreement is very important since it tends to confirm both the accuracy of the estimates of the experimental RDF peak areas and the correctness of the assumptions in the present analysis of the RDF of SiO.

The third peak in the experimental RDF is the sum of two peaks, A_4 and A_5 , corresponding to O—Si—Si and Si—O—Si distances. A_5 depends only on x and is therefore the same, namely 1.95 atoms, for both models. A_4 depends on both C_1 and x and is $(3.28 - 7.12 C_1)$ for $x = 1.08$. In the mixture model, there are no Si atoms that are bonded to both Si and O atoms. Consequently, there are no O—Si—Si configurations and A_4 must be zero. This is confirmed by substituting $C_1 = 0.46$ in $A_4 = 3.28 - 7.12 C_1$, yielding $A_4 = 0$. In the random model, almost all Si atoms are type T_2 , T_3 or T_4 for $x = 1.08$. For these types, there are many O—Si—Si configurations, P_4 in fig. 4. Consequently, A_4 is expected to be large for $x = 1.08$ in the random model. This is confirmed by substituting $C_1 = 0.045$ in $A_4 = 3.28 - 7.12 C_1$, yielding $A_4 = 2.96$ atoms in the random model. The random model therefore predicts a much larger third peak in the RDF of a-SiO than does the mixture model. The origin of the different predictions is the number of O—Si—Si configurations, which are favored in the random model. The large difference expected in the third peak of the RDF provides a very accurate experimental method for differentiating between the random and mixture models.

The best estimate of C_1 obtained from the experimental RDF of YK is that found using the third RDF peak, yielding $C_1 = 0.31 \pm 0.08$. This value of C_1 is large and indicates a strong tendency to form Si—Si₄ tetrahedra in SiO powder. The mixture model value of C_1 , 0.46, obtained from eq. (15), is significantly larger than the experimental value. However, as noted earlier, the macroscopic mixture model is already ruled out for SiO powder because it is insoluble in HF. The value of C_1 in the microscopic model, $C_1 \approx \frac{1}{3}$, eq. (16), is in good agreement with the experimental value. Thus, in agreement with YK, we conclude that a microscopic mixture model is an appropriate model for SiO powder. However, the present analysis goes beyond

that of YK in proving that the random model is incorrect for SiO powder. Further, agreement is obtained here between the microscopic mixture model and experiment at all three of the RDF peaks considered.

4. Summary and conclusions

A theory has been presented for the short-range order of amorphous SiO_x alloys with $0 \leq x \leq 2$. Most of the parameters of the theory are fixed and are based on the properties of a-Si and a- SiO_2 . However, the near neighbor environment of the Si atoms is left as a series of free parameters, C_i , for $i = 1$ through 5, eq. (1). The short-range order in the RDF of a- SiO_x is calculated using the present theory. It is shown that, in general, the experimental RDF of a- SiO_x can be used to differentiate between various models of the short-range order, such as the random bonding model and the Si-SiO₂ mixture model. The RDF of commercial SiO powder was shown to be consistent with a microscopic mixture model and inconsistent with the random bonding model or a large scale phase separation model.

From the differences in the infrared absorption spectrum [6] it appears that the structure of SiO powder differs from that of thin SiO films. An RDF of the latter would obviously be helpful in defining these structural differences. Unfortunately, accurate RDF's of thin films of SiO_x are not currently available. Because of the low atomic number of Si and O and because thick films are difficult to prepare, an RDF of an SiO_x film will almost certainly have to be obtained by electron diffraction. A series of RDF's for $x = 0.5$, 1.0 and 1.5 would be very useful, since they would establish the short-range order in the alloy system. These RDF's would also help determine whether the short-range order varies with x .

The present RDF analysis has been confined to the SiO_x alloy system. The same methods could be applied to the GeO_x and SnO_x alloy systems and could provide information about the short-range order in those cases too. It would also be possible, although much more complicated, to extend the present analysis of the RDF to larger r and obtain information about the longer-range order.

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