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**Determination of the Structural Parameters of Local Ordering
in Oxide Melts and Glasses from X-ray Diffraction Data***

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Synopsis

The application of the pair function method coupled with the interference function refining technique is discussed as a procedure for obtaining quantitative estimation of the coordination numbers and interatomic distances in the near neighbor region of oxide melts and glasses. The usefulness of this technique is demonstrated by applying the procedure to the structural analysis of typical rock forming silicate melts.

I. Introduction

Structural studies of oxide melts, particularly silicates, are important from a petrological perspective of magma formation and from a metallurgical view of slag-metal reactions. The recent growth in the technology of advanced ceramics and glasses has necessitated a better understanding of the various properties of oxide melts at the microscopic level. For this purpose, structural information of the melt is essential.

In contrast to crystalline materials, the atomic arrangement in disordered systems such as liquids and glasses is not spatially periodic. As a result, a structural description at the atomic scale of

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such disordered systems usually employs the radial distribution function¹ (hereafter referred to as RDF). The RDF indicates the probability of finding another atom from an origin as a function of radial distance obtained by spherical and time averaging. The RDF is only one dimensional but it gives an almost unique quantitative information describing the atomic arrangements in a disordered system.

X-ray diffraction is well-known as one of the useful methods for determining the RDF from which structural parameters such as interatomic distance and coordination number can be estimated.^{2,3} The coordination number, particularly in the near neighbor region, gives a convenient first order picture of the disordered system. However, at the present time there is no unique method available for estimating the coordination number. Thus, some reservations have been indicated regarding the quantitative accuracy of such structural parameters reported in the earlier x-ray studies on silicate melts and glasses.

The main purpose of this investigation is to present a few important requirements for RDF analysis and to test two methods for estimating the structural parameters of local ordering in oxide melts and glasses from experimental x-ray diffraction data. The proposed methods minimize the difficulties previously encountered, and thus are applied to re-examine the structures of typical rock forming silicate melts of quartz (SiO_2), enstatite (MgSiO_3) and wollastonite (CaSiO_3).

II. Fundamental Requirements for RDF Analysis of Disordered Systems

The apparent profiles of both interference function and RDF of disordered systems are known to be quite similar. This is consistent with the fact that the characteristic structural features of their respective crystal structures become obscure on melting.⁴ The resulting increase in freedom of the atomic configuration contributes to the formation of short-range order. However, in contrast to the structure of metallic melts and glasses, the following point may be noted with respect to the structural features of oxide melts and glasses. There is a distinct local ordering within a narrow region and a complete loss of positional correlation at a few nearest neighbor distance away from any origin. For this reason, the determination of such distinct local ordering unit structure and its distribution is one of the important components in the structural study of oxide melts and glasses. The oxygen coordination number for a metallic ion is also of interest in discussing their structural

aspects.

Figures 1 and 2 show the interference function and its RDF of a quartz glass. Referring to Pauling's,⁵ Ahrens's⁶ and Shannon's⁷ ionic radius for the constituent elements, the well-resolved peaks in the RDF are denoted by Si-O, O-O and Si-Si pairs. The area under each peak in the RDF corresponds to the coordination number which gives rise to local ordering in the melt or glassy structure. The ordinary RDF obtained directly from conventional diffraction experiments cannot be used to describe completely the positions and chemical identities of elements. For this purpose, knowledge of the structure of individual chemical pairs, often called the partial structural functions, is required. However, the determination of partial structural functions is still not an easy task at the present time.⁴ The conventional diffraction experiment provides only a compositionally averaged structural data. In the present case, three partial structural functions are superimposed, so that the area under each peak in the RDF might be affected, more or less, by a few kinds of atomic pairs. The peak observed at about 0.21nm in the RDF of a quartz glass has been considered as a spurious ripple arising mainly from the truncation effect in the Fourier transformation. However, it is now interpreted as a summation of three pair correlation tails and their enhancement.⁸ Therefore, this point should be taken into account in the RDF analysis, particularly in the determination of the coordination number.

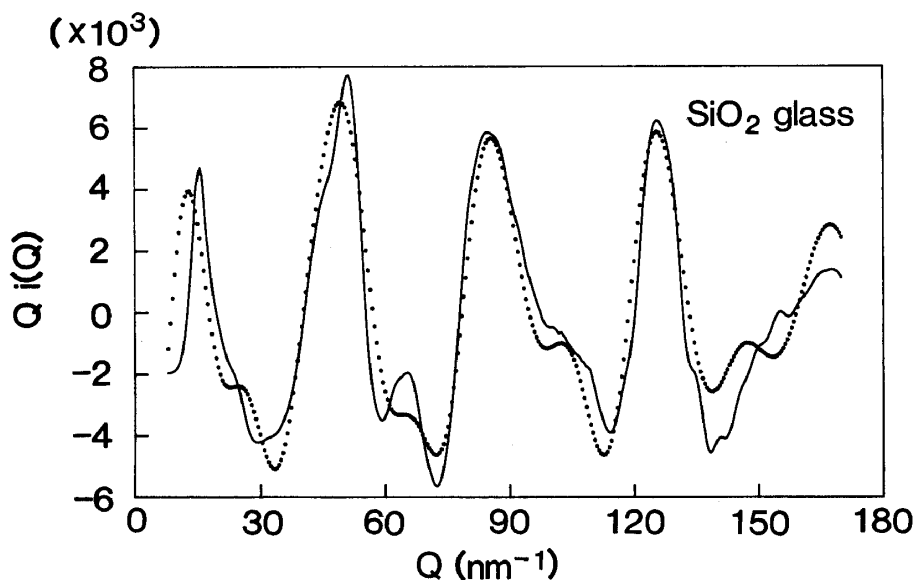


Fig. 1 Interference functions $Q_i(Q)$ of glassy SiO_2 . Solid line: experimental data, Dotted line: calculation by the interference function refining technique.

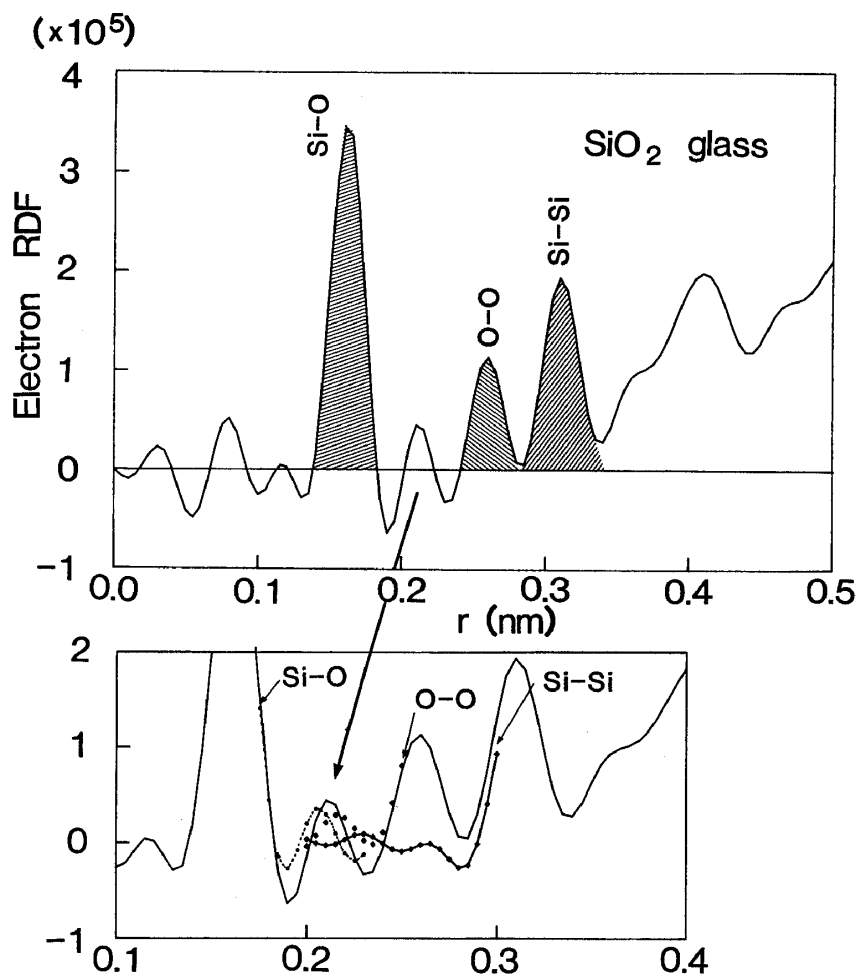


Fig. 2 Electron radial distribution function of glassy SiO_2 .

III. Data Processing by the Pair Function Method

When a compositionally averaged structural function is introduced, an approach similar to the RDF analysis for a simple one-component case can be applied to a disordered system containing more than two kinds of elements. However, the definitions of such structural functions are not unique. As a result, many different equations have been used in the literature. Fortunately these equations are interrelated to each other.⁴ In this work, the definition proposed by Mozzi and Warren⁸ is employed.

The reduced interference function in electron units, $i(Q)$, which is related to the structurally sensitive part of the total scattering intensity, is directly obtained from experiments. This interference function is defined by;

$$i(Q) = [I_{eu}(Q)/N - \sum_{uc} f_j^2] / f_e^2 \quad (1)$$

where $Q=4\pi\sin\theta/\lambda$, θ is half the scattering angle, λ is the wavelength, I_{eu}/N the intensity of unmodified scattering in electron units per unit of composition, f_j and f_e are the atomic scattering factor and the average scattering factor per electron, respectively. The electron RDF can be readily estimated from the interference function data by the following Fourier transformation;

$$RDF_{exp.} = 2\pi^2 r \rho_e \sum_{uc} Z_j + \int_0^{Q_{max}} Qi(Q) \sin Qr \, dQ \quad (2)$$

where ρ_e is the average number density of electrons and Z_j is the atomic number of j -element. The term $\exp[-\alpha^2 Q^2]$ is a convergence factor, introduced to minimize the truncation error and weigh down the uncertainties at the higher wave vector region. This artificial α parameter does not have to be critically selected. However, a zero value of α is assumed in the calculation of the experimental RDF.

On the other hand, the electron RDF can be calculated using the following equation for a particular distance r_{ij} and a coordination number N_{ij} of i - j pairs ;

$$RDF_{cal.} = \sum_{uc} \sum_i \frac{N_{ij}}{r_{ij}} \int_0^{Q_{max}} \frac{f_i f_j}{f_e f_e} e^{-\alpha^2 Q^2} \sin Qr_{ij} \sin Qr \, dQ \quad (3)$$

This theoretical RDF is usually estimated using a value of $\alpha = 0.05$, based on previous studies on various oxide glasses.⁹

These two equations, using the concept of pair functions were employed by Mozzi and Warren⁸ under the name of Pair Function Distribution (PFD). The interatomic distances are easily determined from the positions of the peaks in the experimental RDF data obtained from eq.(2). The number of neighbors can be determined using a least-squares analysis, by finding the quantity of N_{ij} which must be used to bring the calculated RDF using eq.(3) to the best fit with the experimental RDF. Although the present pair function method is effective for only a few near neighbor correlations, the structural parameters in the near neighbor region can be quantified with a much higher reliability compared with those obtained in the previous investigation. Thus, the present method is free from the ambiguity in the procedure for estimating the area under each peak in the experimental RDF.⁴

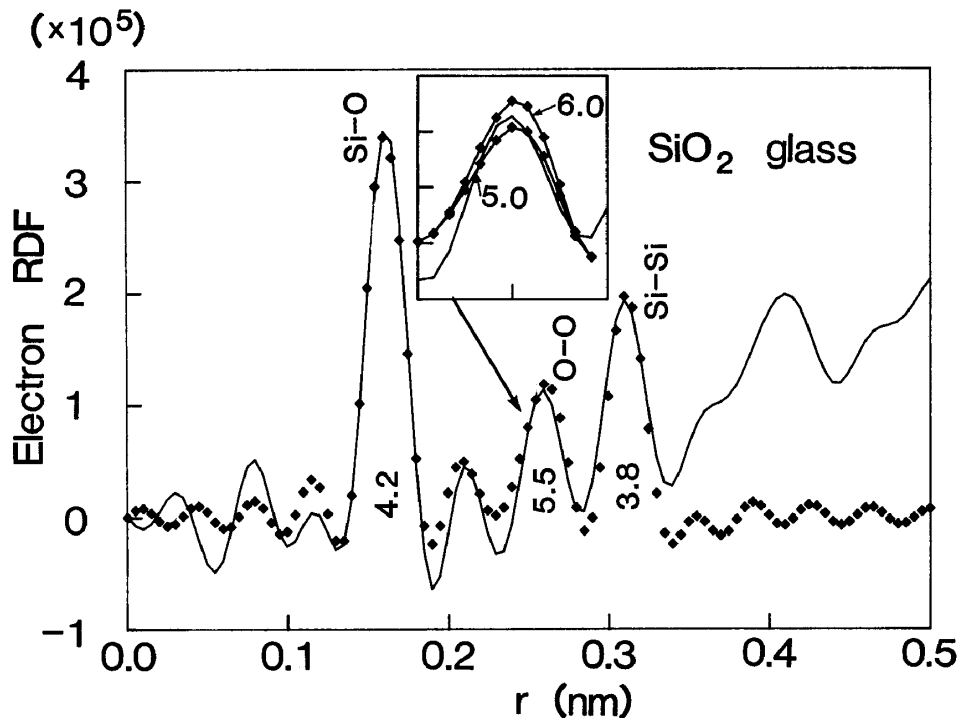


Fig. 3 Comparison of the electron RDF estimated by the pair function method with the experimental data for glassy SiO_2 . Solid line: experimental data, Dotted line: calculation by the pair function method.

Figure 3 indicates a comparison between the RDF_{exp} and the RDF_{cal} in the near neighbor region of a quartz glass. The numerical values in Fig.3 denote the coordination numbers of respective pairs estimated by use of the pair function method. The numerical values for Si-O pairs clearly suggest that each silicon is surrounded by four oxygens. The coordination number for O-O pairs is consistent with the value expected from the geometry of the tetrahedra formed by oxygens whose center is occupied by silicon. The coordination number of Si-Si pairs which corresponds to the correlation of SiO_4 tetrahedral units is estimated to be about four. This shows no significant inconsistencies with the atomic arrangements observed in the beta-quartz type crystal structure.¹⁰ Thus, a quartz glass structure consists mainly of SiO_4 tetrahedral units which distribute randomly to form the random network structure first confirmed from the x-ray diffraction data by Warren and his colleagues.¹¹

The RDFs calculated from the values of $N_{\text{O-O}}$ equal to 5.0 and 6.0 are also given in a small figure inserted into Fig.3. As easily seen from these results, the coordination number can be estimated by this processing method to within a variation of less than $N_{ij} = \pm 0.5$ atom.

IV. Supplemental Data Processing by the Interference Function Refining Technique

The simultaneous use of other methods for estimating the coordination numbers is one way to confirm the structural parameters in disordered systems. For this purpose, the interference function refining technique is employed in this work. This technique is based on the characteristic structural features of silicate melts and glasses; namely the contrast between the narrow distribution of local ordering and a complete loss of positional correlation in the longer distance. In other words, the average number of j elements around i -elements, N_{ij} , is separated by an average distance, r_{ij} . The distribution can be approximated by a discrete Gaussian like distribution with a mean-square variation $2\sigma_{ij}$. The distribution for higher neighbor correlations is approximately expressed by a continuous distribution with an average number density of a system. These features can provide the following expression with respect to the reduced interference function, $i(Q)$;

$$[f_e]^2 i(Q) = \sum_{i=1}^m \sum_k N_{ik} \exp(-\alpha_{ik} Q^2) f_i f_k \frac{\sin Q r_{ik}}{Q r_{ik}} + \sum_{\alpha=k}^m \sum_{\beta=1}^m [\exp(-\sigma'_{\alpha\beta} Q^2) f_{\alpha} f_{\beta} 4\pi\rho_0 (Q r'_{\alpha\beta} \cos Q r'_{\alpha\beta} - \sin Q r'_{\alpha\beta})] / Q^3 \quad (4)$$

The quantities $r'_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ are the parameters of the boundary region which need not be sharp.^{12,13} The structural parameters for near neighbor correlations are determined by a least-squares analysis so as to fit the experimental interference function by iteration. This interference function refining technique has frequently been used for structural investigation of inorganic liquid and glasses. However, it should be kept in mind that this method is not a unique mathematical procedure, but a semiempirical one for the resolution of the peaks in the RDF of disordered systems.

The dotted line in Fig.1 is the resultant interference function calculated from eq.(4) with the initial structural parameters determined by the pair function method. The agreement appears to be satisfactory. Thus, the structural parameters determined by the pair function method can be considered quite realistic. In this analysis, the variation of the coordination number is in the order of ± 0.5 atom.

Various errors in the RDF analysis have already been discussed.¹⁴⁻¹⁶ However, the following point is worthy of note with

respect to the uncertainty of the resultant coordination numbers, mainly arising from counting statistics, estimated by the present pair function method.

The variation in r_{ij} as determined from the experimental RDF data is known to be in the range of ± 0.001 nm. If $F(r)$ is the Fourier transform of the intensity function $i(Q)$, the variance $\pm \sigma^2$ of $F(r)$ is given by the average of the square of the difference between $F(r)$ and the true $\bar{F}(r)$, namely;

$$\sigma^2(F(r)) = E[(F(r) - \bar{F}(r))^2] \quad (5)$$

where E denotes the expectation value of the quantity within the brackets. Substituting eq.(2) into eq.(5) results in;

$$\sigma^2(F(r)) = \int_0^{Q_{\max}} \int_0^{Q_{\max}} Q Q' E[(i(Q) - \bar{i}(Q))(i(Q') - \bar{i}(Q'))] \\ \times \exp(-\alpha^2(Q^2 + Q'^2)) \sin Qr \sin Q'r \, dQ dQ' \quad (6)$$

where $\bar{i}(Q)$ is the true intensity function of $i(Q)$. Because intensities at each point are assumed to be independent, the covariance between any two points in the above equation should be zero. Thus, the above equation can be simplified as follows;

$$\sigma^2(F(r)) = \int_0^{Q_{\max}} Q^2 \sigma^2(i(Q)) \exp(-2\alpha^2 Q^2) \sin^2 Qr \, dQ \quad (7)$$

The variance in $i(Q)$ can be estimated readily from the statistical error in counting of the intensity using the equation of the probable error defined by Cullity.¹⁷ The results given in **Table 1** indicate that the uncertainty in the N_{ij} values arising from the counting statistics is of the order of ± 0.3 atom.

Table 1. Distances and coordination numbers for Si-O, O-O and Si-Si pairs in glassy SiO₂ determined from x-ray diffraction data.

pair	r_{ij} (nm)	N_{ij} (atom)
Si-O	0.162	4.2 \pm 0.23
O-O	0.261	5.5 \pm 0.18
Si-Si	0.312	3.8 \pm 0.20

Figures 4 and 5 show the interference functions and their RDFs for quartz(SiO_2) at 1923 K, enstatite(MgSiO_3) at 1973 K and wollastonite(CaSiO_3) at 1873 K in the liquid state.¹⁸ The solid lines in these figures are the experimental data and the dotted lines correspond to the calculated values along the line similar to the procedure discussed above. The resultant structural parameters concerned with the local ordering in these typical rock forming silicate melts are summarized in Table 2. The agreement is again found to be satisfactory with respect to the structural parameters determined by the pair function method and the interference function refining technique. In addition, these results clearly suggest that the presence of MgO or CaO does not appear to alter significantly the local ordering in the near neighbor region in both enstatite and wollastonite melts. In both these melts, the SiO_4 tetrahedra has been confirmed as the local ordering unit structure, although the distribution of these local ordering units differs from that of quartz. A detailed description concerning the structure of these rock forming silicate melts will not be discussed as it is not the objective of this paper.

Table 2. Structural parameters of local ordering in SiO_2 , MgSiO_3 and CaSiO_3 melts obtained in this work.

pair	Pair function method		Refining technique	
	r_{ij} (nm)	N_{ij} (atom)	r_{ij} (nm)	N_{ij} (atom)
SiO ₂ melt				
Si-O	0.162	3.8	0.162	3.4
O-O	0.265	5.6	0.263	5.5
Si-Si	0.312	3.9	0.312	3.7
MgSiO ₃ melt				
Si-O	0.162	3.9	0.163	4.1
Mg-O	0.212	4.3	0.211	4.0
O-O	0.265	5.4	0.271	6.8
CaSiO ₃ melt				
Si-O	0.161	3.9	0.161	4.6
Ca-O	0.235	5.9	0.235	6.2
O-O	0.267	5.2	0.273	4.9

V. Concluding Remarks

The pair function method coupled with the interference function refining technique has been found to be a useful procedure for determining the structural parameters of local ordering in oxide melts and glasses. It would be of great interest to extend the present method of structural analysis to other silicate melts and glasses in order to evaluate both its usefulness and validity on a wider basis.

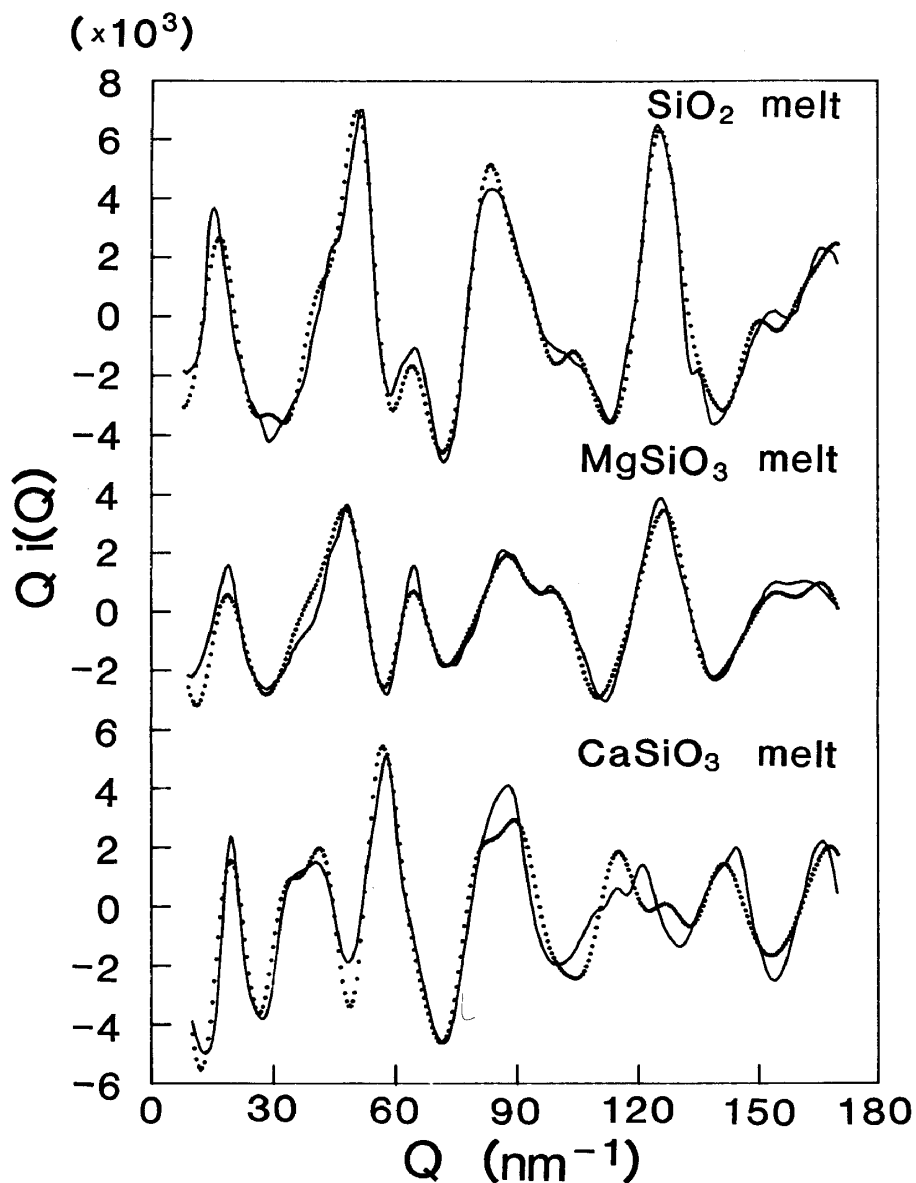


Fig. 4 Interference functions $Q_i(Q)$ of SiO_2 , MgSiO_3 and CaSiO_3 melts. Solid line: experimental data, Dotted line: calculation by the interference function refining technique.

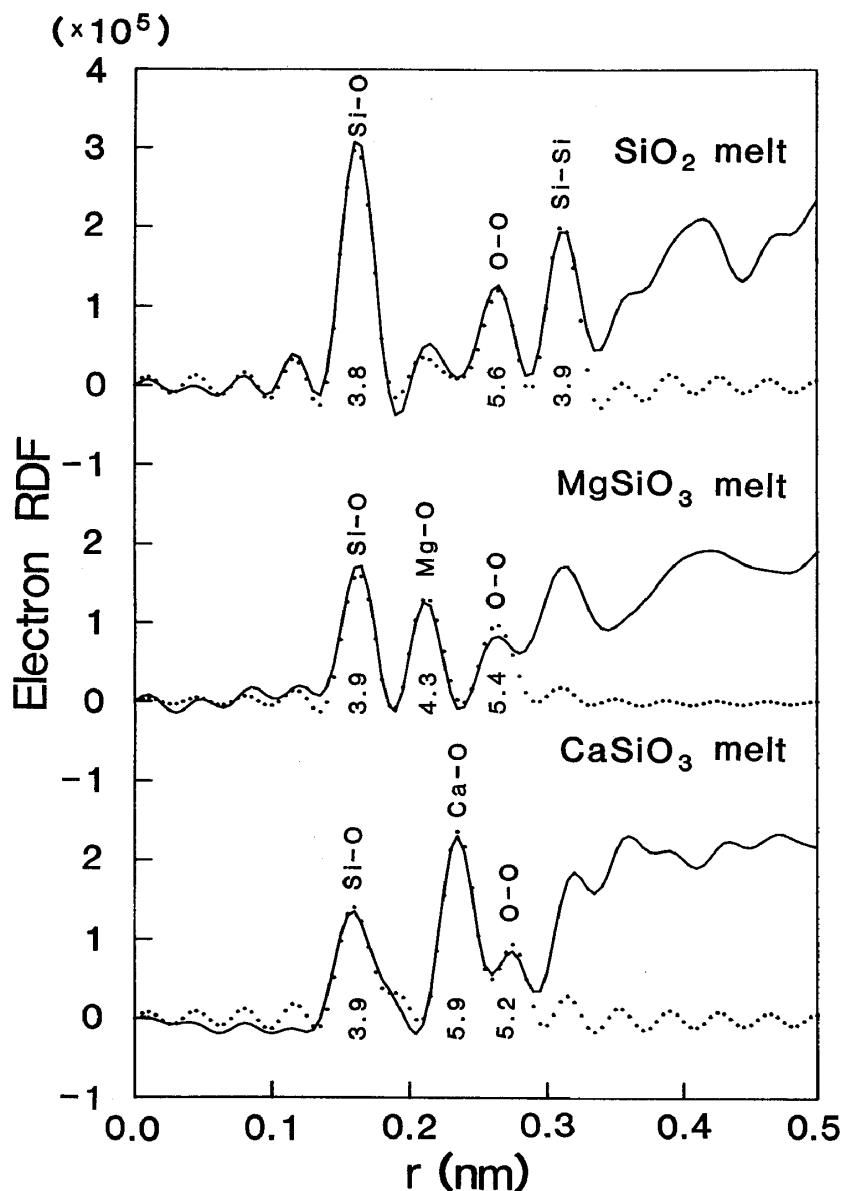


Fig. 5 Comparison of the electron RDF estimated by the pair function method with the experimental data for SiO_2 , MgSiO_3 and CaSiO_3 melts. Solid line: experimental data, Dotted line: calculation by the pair function method.

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