[1] Refinement on the Structure of GeO_2 Glass by the Least-Squares Variational Method Coupled with the Anomalous X-Ray Scattering Data

K. Sugiyama and E. Matsubara

The Research Institute of Mineral Dressing and Metallurgy (SENKEN),
Tohoku University, Aoba-ku Sendai 980, Japan

CONTENTS

Page

ABSTRACT 178
1. INTRODUCTION 178
2. EXPERIMENTAL 178
3. RESULTS AND DISCUSSION 180
ACKNOWLEDGEMENTS 186
REFERENCES 186

---

[1] Received December 5, 1990; final form February 2, 1991.

ABSTRACT

The anomalous X-ray scattering (AXS) technique was used to obtain the environmental radial distribution function (RDF) around a germanium in GeO_2 glass. By combining the environmental and ordinary RDFs of GeO_2 glass, germanium was quantitatively shown to be surrounded by four oxygens at a distance of 0.174 nm and to share its corners in order to form a three dimensional tetrahedral network structure. A possible atomic arrangement of GeO_2 glass in near neighbor region is also proposed by refining structural parameters using the least-squares variational method.

1. INTRODUCTION

Investigation of the atomic structure of interesting materials is an essential key to the evolution of our understanding in physics and the chemistry of new materials. The near neighbor atomic correlation of the individual chemical constituents or local chemical environment around a specific element is strongly required for describing the fine structure in multi-component materials. It is well-known that the inter-atomic distances and coordination numbers of disordered systems can be obtained from the radial distribution function (RDF) data using X-ray diffraction and such data provide a convenient picture of their local structure in near neighbor region. The so-called pair function method by Mozzi and Warren /1/ is a useful procedure to estimate the structural parameters of a disordered system containing more than two kinds of atoms, such as silicate glasses. On the other hand, Narten /2/ determined the structural parameters of silicate glass using the least-squares technique by calculating the intensity profiles in order to fit the experimental intensity profile, and the results were similar to those reported by Mozzi and Warren /1/. This least-squares variational method can be one way for refining the structural parameters of disordered system.

Information on atomic correlations and the individual chemical constituents around a specific element is required for describing the fine structure in multi-component systems such as certain arrangements of fundamental local ordering unit. For this requirement, the relatively new method of anomalous X-ray scattering technique (hereafter referred to as AXS) recently received much attention and its usefulness in determining the environmental structure around a specific element in multi-component systems has been well demonstrated /3/. This prompted us to apply the least-squares variational method to the differential intensity profile obtained from the AXS measurements.

The main purpose of this work is to present our recent results for refining the atomic structure of GeO_2 glass at longer atomic distance as well as the structure in the nearest-neighbor region and to discuss the structure of GeO_2 glass.

2. EXPERIMENTAL

The GeO_2 glass sample was prepared by melting regent grade GeO_2 powder (99.999%) in a shallow platinum dish in air at 1773 K, followed by the furnace cooling. The obtained sample was about 30 mm in diameter and a few mm thick. The sample was examined by the ordinary X-ray diffraction using Mo $K\alpha$ radiation. A beam line (7C station) in the Photon Factory, National Laboratory for High Energy Physics, Tsukuba, Japan, where a double Si (111) crystal mono-chromator is provided upstream, was used for the present AXS measurements. The incident beam was monitored by a N_2 gas ion chamber placed in front of the sample, in order to keep the total number of the photon irradiating the sample constant. The pure intrinsic germanium solid state detector was employed in order to separate a fluorescent component from the scattered intensity. Details of the experimental setting were presented by Waseda, Matsubara and Sugiyama /3/.

The intensity profiles were measured at energies of 11.080 and 10.805 keV, which correspond to 25 and 300 eV below the Ge *K* absorption edge (11.103 keV). Then these intensities were corrected for absorption and converted to absolute intensities by the generalized Krogh-Moe-Norman method /4/, including the correction for Compton scattering /5/. The detected energy dependence of intensity results mainly from the variation of the real part of the anomalous dispersion terms of a germanium, f'_{Ge} /6/. Therefore, the resultant intensity difference, $\Delta i(Q)$, may be given by the following equation;

$$\Delta i(Q) = \qquad (1)$$

$$\frac{(I_{300}(Q) - \langle f_{300}^2\rangle) - (I_{25}(Q) - \langle f_{25}^2\rangle)}{c_{Ge}(f'_{Ge\ 300} - f'_{Ge\ 25})} =$$

$$\int_0^{\infty} 4\pi r^2 \sum_{j=1}^{2} \mathrm{Re}[\, f_{j\ 300}(Q) + f_{j\ 25}(Q)\,]$$

$$(\rho_{Gej} - \rho_{oj}) \frac{\sin(Qr)}{Qr} dr$$

where $Q=4\pi\sin\theta/\lambda$ is the wave vector and $I(Q)$ the absolute intensity, c_{Ge} the atomic fraction of germanium, f_j the X-ray atomic form factor of the j-th element /7/, $\langle f^2 \rangle$ the mean square of the atomic scattering factors ; ρ_{Gej} the number density of the j-th atom around a germanium, and ρ_{oj} the average number density for j-th element. "Re" indicates the real part of the value in the parentheses. The subscripts 25 and 300 represent the incident energies corresponding to 25 and 300 eV below the Ge *K* absorption edge; 11.080 and 10.805 keV, respectively. The summation in the above equation indicates the sum over the constituents of the present sample. The environmental RDF for germanium, which represents the local atomic distribution around a germanium can be obtained by the Fourier transformation of the quantity $Q\,\Delta i(Q)/W(Q)$;

$$4\pi r^2 \rho_{Ge}(r) = 4\pi r^2 \rho_0 + \qquad (2)$$

$$\frac{2r}{\pi}\int_0^{\infty} \frac{Q\Delta i(Q)}{W(Q)} \sin(Qr)\, dQ$$

where

$$W(Q) = \sum_{j=1}^{2} c_j \,\mathrm{Re}\,(f_{j\ 300}(Q) + f_{j\ 25}(Q)) \qquad (3)$$

ρ_0 in Eq. (2) is the average number density of atoms in a system.

On the other hand, the so-called reduced interference function $i(Q)$ from the absolute intensity $I(Q)$ is obtained in the following form by applying the common procedures for absorption, polarization and conversion into the absolute units /6/.

$$i(Q) = (\, I(Q) - \langle f^2 \rangle \,) \,/\, \langle f \rangle^2 \qquad (4)$$

where $\langle f \rangle$ is the average atomic scattering factor. By the Fourier transformation of the function $Qi(Q)$, the ordinary RDF can also be estimated:

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + \qquad (5)$$

$$\frac{2r}{\pi}\int_0^{\infty} Qi(Q) \sin(Qr)\, dQ$$

where $\rho(r)$ is the so called average number density distribution function.

3. RESULTS AND DISCUSSION

The two scattering intensity profiles measured at two energies close to the Ge K absorption edge and the corresponding differential intensity profile are presented in Fig. 1 as well as the intensity profile obtained from Mo $K\alpha$ radiation. The environmental interference functions $Qi\Delta(Q)/W(Q)$ of the present sample was estimated and is presented in Fig. 2. The ordinary interference function $Qi(Q)$ calculated from the diffraction experiment using Mo $K\alpha$ radiation is also illustrated in Fig. 2 for comparison. The profiles of these interference functions consist of the first peak at about 15 nm^{-1} followed by a number of peaks, which indicate that a considerable fraction of local ordering unit structures exists in this glass structure although their distribution appears not to be long range ordering. These features stand in contrast to the case of metallic glass, where the rapid damping of interference function is clearly observed.

Environmental and ordinary RDFs were calculated from the interference functions of Fig. 2 using Eqs. (2) and (5), respectively, and they are given in Fig. 3. In this work, the observed intensity data at Q less than 11 nm^{-1} were smoothly extrapolated to zero at Q=0 nm^{-1}. The effect of the extrapolation or the truncation up to Q= 100 nm^{-1} for the environmental analysis (Q=153 nm^{-1} for the ordinary one) in the Fourier transformation is known to make no critical contribution to the RDFs of a glassy sample calculated from the interference functions consisting of the broad peaks /8/. Since the atoms do not approach one another inside the atomic diameter, the calculated RDFs should be zero in the small r region below the nearest-neighbor peak. Therefore, the interference functions given in this work include corrections which take into account experimental uncertainty in order to remove such spurious oscillations of the RDFs in the small r region by the usual method /6,9/.

The ordinary RDF corresponds to the sum of three partial RDFs of Ge-O, Ge-Ge and O-O. From the information on the ionic radii of the constituent elements, one can suggest that the first peak, around 0.17 nm, is a Ge-O pair. It is worth mentioning that in the ordinary RDF the Ge-Ge pair, around 0.32 nm, is well coincident with the atomic pairs characterized by quartz-like GeO_2 structure. Therefore, the fundamental local structures of the present GeO_2 glass sample seems to be rather close to that of quartz-like GeO_2. For convenience, the averaged interatomic distances observed in the structure of quartz-like GeO_2 is shown by arrows in Fig. 3 /10/. On the other hand, the O-O atomic correlations are very difficult to ascribe in the present ordinary RDF, due to its low scattering power for X-rays compared to that of germanium. Structural parameters of Ge-O and Ge-Ge pairs are likely to be obtained. However, definite and precise information on the local atomic arrangements of glassy GeO_2 cannot be determined as a unique solution from the present ordinary RDF data alone. This is particularly true in the higher order correlations because more than two kinds of atomic pairs usually overlap at longer distance.

As shown in Fig. 3, the structural features observed in the environmental RDF for germanium are essentially similar to those of ordinary RDF of GeO_2 glass, although the environmental RDF shows rather poor structural resolution. This is mainly due to the truncation effects which originate in the limit of the Fourier transformation on calculating environmental RDF. When valuable different nature observed in the environmental RDF determined by the AXS measurements is

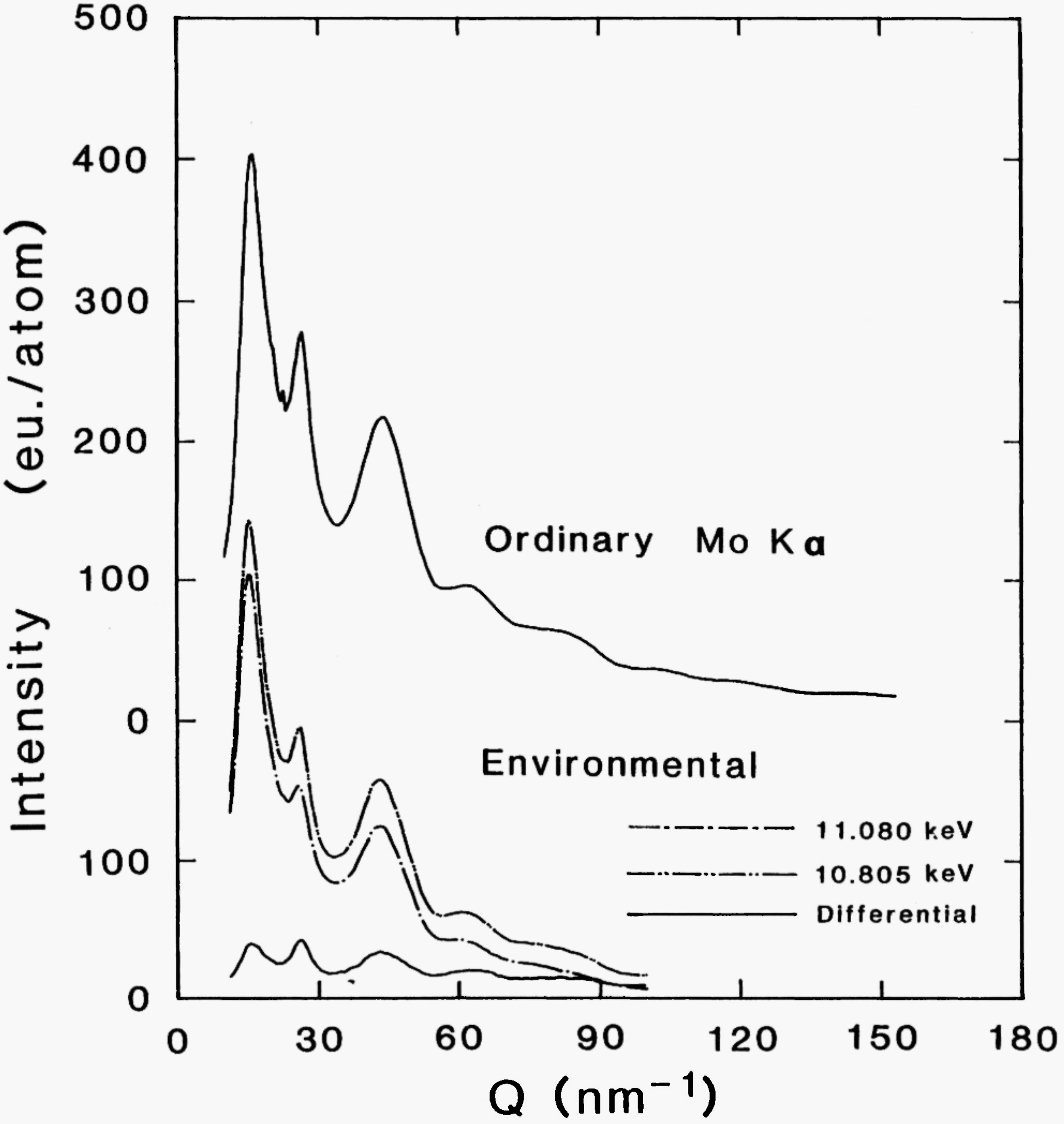

Fig. 1 *(Bottom)* Intensity profiles of GeO_2 glass obtained from the intensity data measured at incidence energies of 11.080 and 10.805 keV and corresponding differential intensity data.

(Top) Intensity profile of GeO_2 glass obtained from the intensity measurement using Mo $K\alpha$ radiation.

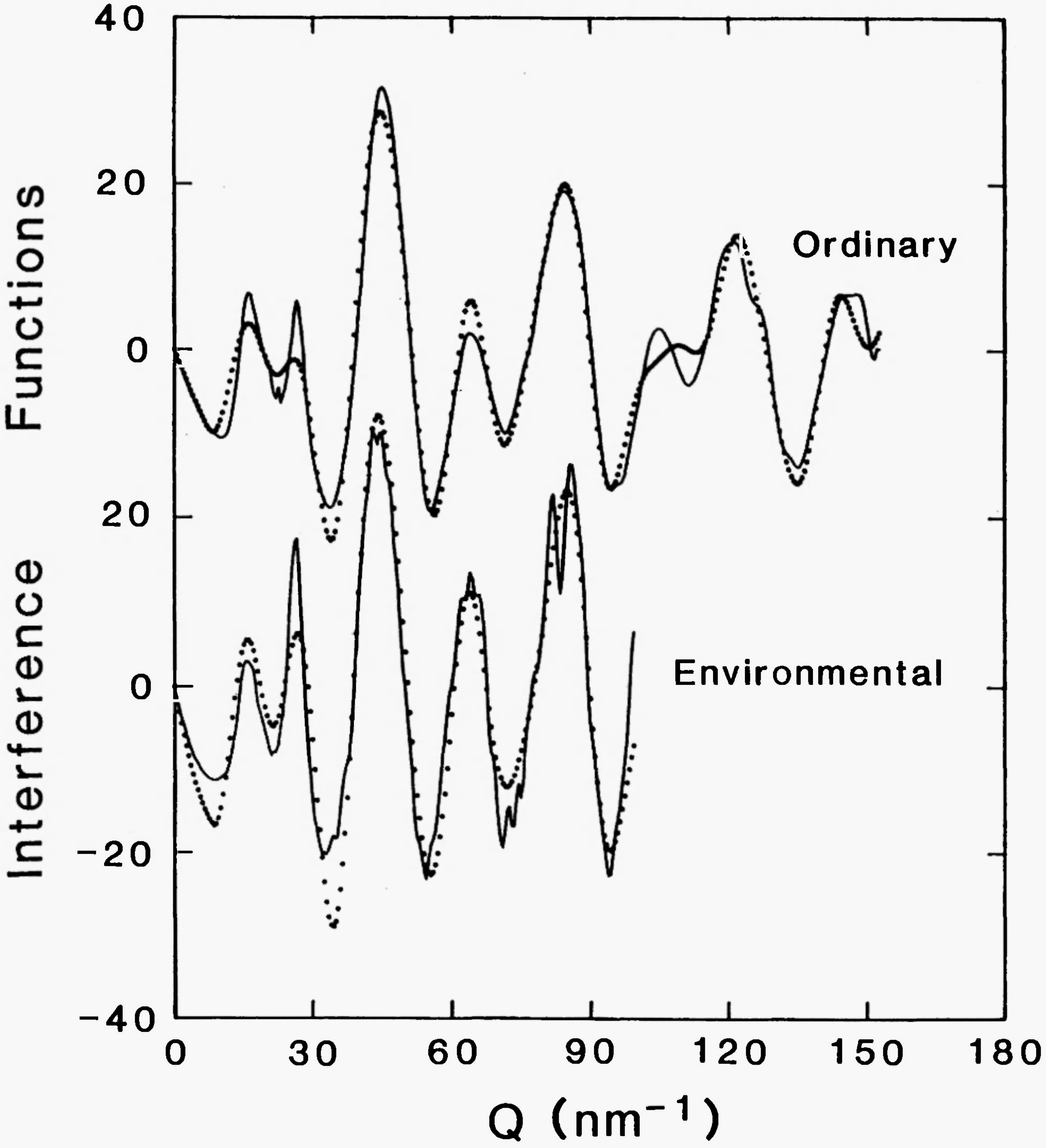

Fig. 2 *(Bottom)* Environmental interference function $Q\,\Delta i(Q)/W(Q)$ for germanium of GeO_2 glass obtained from the intensity data measured at energies close to the Ge K edge. *(Top)* Interference function of GeO_2 glass obtained from the intensity measurement using Mo $K\alpha$ radiation.

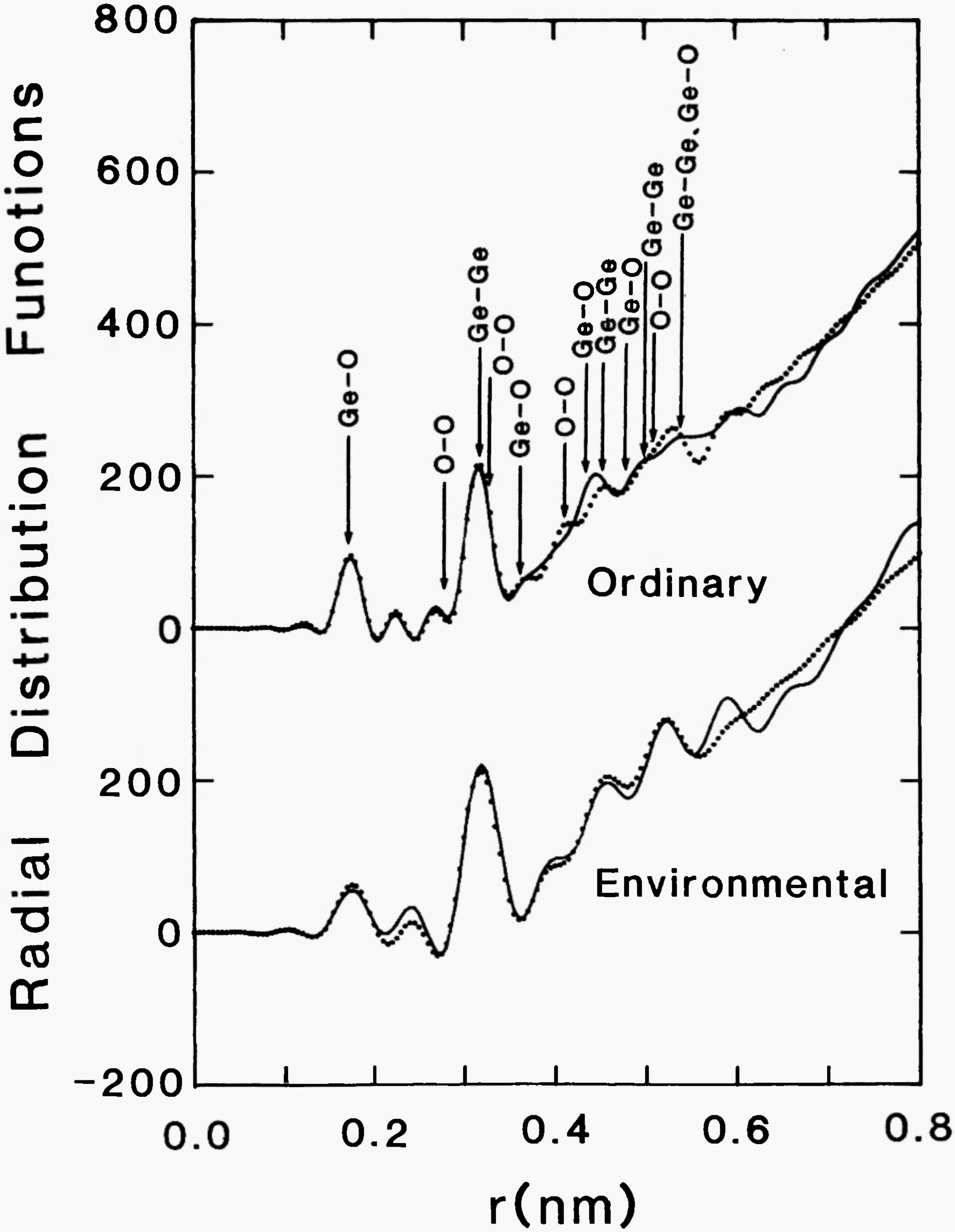

Fig. 3 Environmental radial distribution function $4\pi r^2\rho_{Ge}(r)$ and ordinary radial distribution function $4\pi r^2\rho$ (r), calculated from the interference functions of Fig. 2.

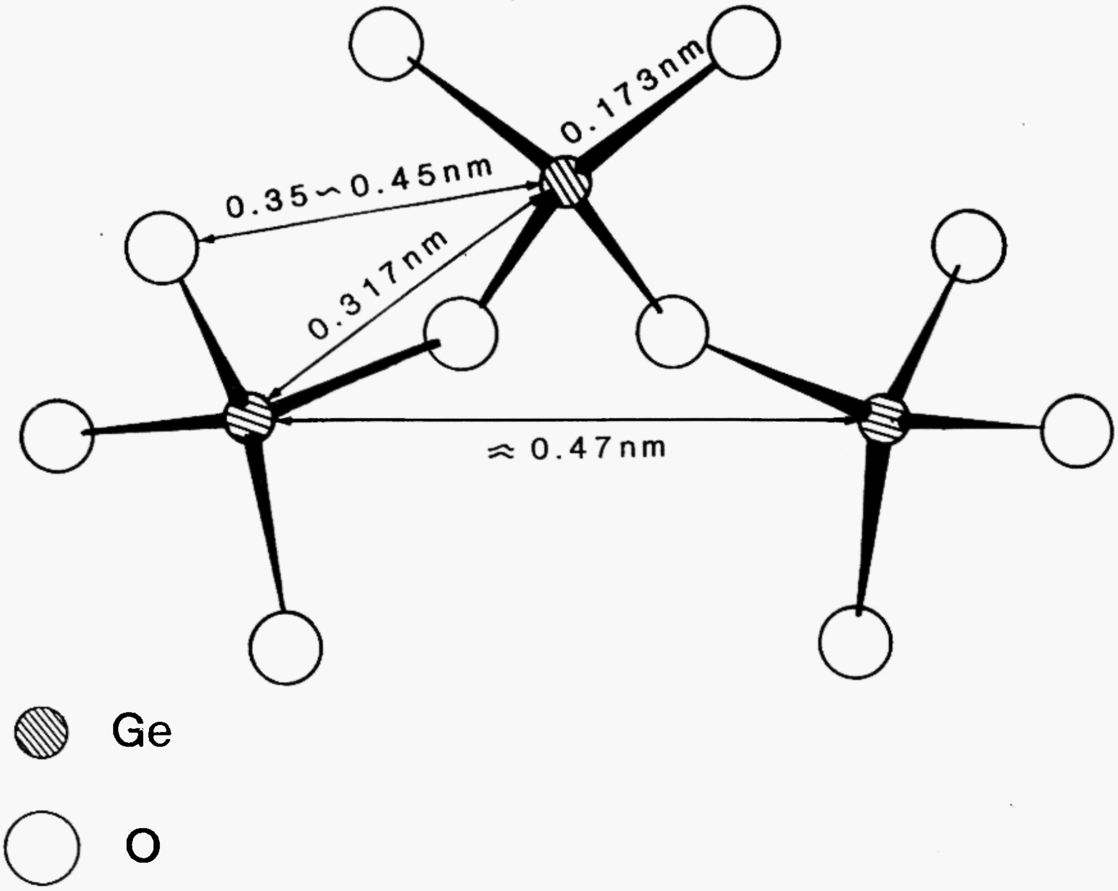

Fig. 4 Schematic diagrams of the arrangements of GeO_2 glass in near neighbor region.

coupled with the ordinary RDF data, resolution of the structural parameters for Ge-O and Ge-Ge pairs can be improved even in higher order correlations. The following data processing was made along these lines. The structural parameters of Ge-O, Ge-Ge and O-O pairs were estimated in this work by applying the least-squares variational technique suggested by Narten /2/ to the interference functions. According to Narten, the reduced interference function *i(Q)* may be given as:

$$i(Q) = \tag{6}$$

$$\Big[\sum_{i=1}^{m} \sum_{k} N_{ik} \exp(-b_{ik}Q^2) f_i f_k \frac{\sin Qr_{ik}}{Qr_{ik}}$$

$$+ \sum_{\alpha=1}^{m} \sum_{\beta=1}^{m} [\exp(-b'_{\alpha\beta}Q^2) f_\alpha f_\beta 4\pi\rho_0$$

$$(Qr'_{\alpha\beta}\cos Qr'_{\alpha\beta} - \sin Qr'_{\alpha\beta})]/Q^3 \Big] \Big/ \langle f \rangle^2$$

where m is the number of elements, N_{ik} is the average number of type-k atoms around any type-i atom at the average distance of r_{ik} and the value of $2b_{ik}$ is the mean square variation. The quantities of $r'_{\alpha\beta}$ and $b'_{\alpha\beta}$ correspond to the mean and the variance of the boundary region which needs not be sharp /2/. It may also be noted that the first and second terms of Eq. (6) represent the discrete Gaussian-like distributions and a continuous distribution with an average number density in the higher order correlations in the disordered system, respectively.

The quantities of N_{ik}, r_{ik} and b_{ik} for the nearest neighbor interactions were obtained by the least-squares calculation of Eq. (6) so as to reproduce the experimental interference function in Fig. 2. The differential interference function $Q\Delta i(Q)/W(Q)$ can be readily calculated by taking the difference of the calculated ordinary coherent intensity similarly estimated at the two energies in the AXS measurements using Eqs. (1), (2) and (3) and compared with the experimental data of $Q\,\Delta i(Q)/W(Q)$ in Fig. 2. Thus, resolution of the structural parameters can be improved at a reasonable level by the least-squares variational technique using the experimental and theoretical interference functions of not only $Qi(Q)$ but also $Q\,\Delta i(Q)/W(Q)$.

At first, the present analysis qualitatively suggests that the structural features of GeO_2 glass are rather close to those of quartz-like GeO_2 /10/. Therefore, the 15% random vacancy model was applied to the quartz-like GeO_2 structure and was used as the initial parameter for the present least-squares calculation. According to the O-O correlations, coordination numbers except for the nearest correlation around 0.28 nm, were fixed as suggested by quartz-like GeO_2 with the 15% random vacancy model because the contribution of the O-O pairs does not critically affect the intensity profile. After several itarations, the interference functions drawn with dotted lines in Fig. 2 were obtained. The RDFs calculated by the Fourier transformation of these interference functions are also drawn with dotted lines in Fig. 3. The resultant structural parameters are summarized in Table 1 together with the crystalline GeO_2 /10/. Since the variations of r and N depend upon the initial structural model, the parameters in Table 1 should be read as not a unique but a possible solution for the GeO_2 glass structure.

The present results quantitatively indicate that the fundamental local ordering unit of GeO_2 glass is tetrahedrally coordinated germanium and its distance is 0.174 nm. Around the first neighboring Ge-Ge pairs, a germanium is surrounded by four germaniums at 0.237 nm, which agrees well with the results of neutron diffraction /11/. With these facts in mind, the atomic arrangements in the near neighbor region as shown in Fig. 4 are quite feasible when considering the simple geometrical factors. This model structure indicates that the germanium tetrahedra link each other and share their corners of coordination polyhedra in order to form a three-dimensional network structure. It may be worth mentioning that the second neighboring Ge-Ge pairs are about eight at a distance of 0.37 nm, which suggests slightly rare structural features compared to the 15% vacancy model as well as the structure of crystalline GeO_2. The structural compensation corresponding to the density difference between the glassy and quartz-like GeO_2 is likely to exist around this region. The present results are not sufficient to build the perfect structural model of GeO_2 glass. Nevertheless, the usefulness of the AXS method coupled with the least-squares variational method has also been demonstrated for the structural characterization of a multi-component disordered system.

Table 1

Summary of the coordination numbers and distances in glassy and quartz-like GeO_2

	Glassy	GeO_2	Quartz-like	GeO_2
Density (Mg/m^3)	3.64		4.21	
Pairs	*r* (nm)	*N* (atom)	*r* (nm)	*N* (atom)
Ge-O	0.173	4.1	0.174	4.0
Ge-O	0.365	4.1	0.348	6.0
Ge-O	0.411	9.8	0.428	14.0
Ge-O	0.488	3.4*	0.479	4.0
Ge-O	0.541	6.0*	0.540	7.0
Ge-Ge	0.317	4.1	0.315	4.0
Ge-Ge	0.453	3.9	0.447	6.0
Ge-Ge	0.497	4.0	0.499	6.0
Ge-Ge	0.535	5.1*	0.539	6.0
O-O	0.277	6.4	0.284	6.0
O-O	0.330	5.1*	0.337	6.0
O-O	0.434	3.4*	0.412	4.0
O-O	0.495	13.6*	0.507	16.0

*) fixed

ACKNOWLEDGEMENTS

The authors are grateful for the support and valuable discussion by Professor Y. Waseda, SENKEN, Tohoku University. The authors also want to thank Professor M. Nomura, Photon Factory, National Laboratory for High Energy Physics, for his kind help on the AXS measurements and Drs. W.R. Busing and A.H. Narten, Oak Ridge National Laboratory, for providing a general FORTRAN least-squares program.

REFERENCES

1. MOZZI, R.L. and WARREN, B.E., *J. Appl. Crystallogr.*, **2**, 164 (1965).
2. NARTEN, A.H., *J. Chem. Phys.*, **56**, 1905 (1972).
3. WASEDA, Y., MATSUBARA, E. and SUGIYAMA, K., *Sci. Rep. Inst.*, Tohoku University, **A34**, 1 (1988).
4. WAGNER, C.N.J., OCKEN, H. and JOSHI, M.L., *Z. Naturforsch.*, **20a**, 325 (1965).
5. CROMER, D.T. and MANN, J.B., *J. Chem. Phys.*, **47**, 1892 (1967).
6. WASEDA, Y., *Novel Application of Anomalous*

X-ray Scattering for Structural Characterization of Disordered Materials, Springer-Verlag, New York (1984).

7. *International Tables for X-ray Crystallography Vol. IV*, The Knoch Press, Birmingham (1974).
8. FURUKAWA, K., *Rep. Progr. Phys.*, **25**, 395 (1962).
9. KAPLOW, R., STRONG, S.L. and AVERBACK, B.L., *Phys. Rev.*, **138**, A1336 (1965).
10. GORDON, S., SMITH, S. and ISAACS, P.B., *Acta Cryst.*, **17**, 847 (1964).
11. LEADBETTER, A.J. and WRIGHT, A.C., *J. Non-Cryst. Solid.*, **7**, 37 (1972).