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The Computation of Radial Distribution Functions for Glassy Materials

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A procedure is described for optimizing the extraction of information from the diffraction data of a glass. A least-squares technique that minimizes the spurious detail in the radial distribution function (RDF) at small and large interatomic distances is employed both to isolate that portion of the total intensity function which contains the interatomic distance information and to remove from this function contributions from the shortest distances, thus eliminating the major source of termination errors. X-ray diffraction data for silica glass is utilized to illustrate the procedure. It is apparent that the procedure would be also applicable to the liquid state.

Introduction

The determination of structural information for a glass is facilitated by an analysis of the distribution of interatomic distances. The distribution is expressed as a radial distribution function (RDF) which is computed from experimental scattering data. In utilizing RDF's for making interpretations, it is important to minimize the uncertainties in these functions, particularly for the larger interatomic distances. Such uncertainties are generated both by the data collection and the data reduction procedures.

Major improvements in data-reduction procedures are effected by the introduction of physical and mathematical criteria which must be satisfied by the distribution of distances. For example, the RDF should indicate zero probability for distances smaller than the shortest bonded distance, and, at sufficiently large distances, the RDF should indicate that all distances are equally probable. The imposition of constraints on RDF's has a long history and may be found in early studies of molecular structure by electron diffraction of gases (Karle & Karle, 1949, 1950).

A number of authors have developed procedures for introducing physical and mathematical criteria into the analytical procedures applied to diffraction data from glasses (Kaplow, Strong & Averbach, 1965; Warren, 1969; Leadbetter & Wright, 1972) with the objective of enhancing the reliability of the resulting RDF's. The procedure to be described here, while concerned with the same criteria, permits very rapid convergence of the data reduction by expressing the RDF explicitly as a function of refinable parameters defining the background intensity and short distances and employs a special method for treating the termination errors. Refinement of these parameters, subject to the aforementioned constraints, produces an RDF free from the errors associated with incorrect scaling of the data, incorrect background intensity, and termination of the data. Applications of the new technique have been made in recent investigations of silica and germania glasses (Konnert & Karle, 1972; Konnert, Karle & Ferguson, 1973). The RDF's of these glasses were found to be consistent with a structure composed nearly entirely of ordered regions similar to tridymite, a crystalline polymorph of silica, having dimensions up to a least 20 Å and bonded efficiently together in configurations analogous to twinned crystals. In such a model the ordered regions have the same bonding topology as the crystalline polymorph and are distorted slightly owing to the junctions between the ordered regions. However, microcrystalline grain boundaries are not implied. The junctions may not vary significantly in energy and density from that in the ordered regions. Illustrative examples will be drawn from the data reduction of the X-ray diffraction data for silica glass.

The general theory relating the RDF to the diffraction pattern will be reviewed briefly at first, in order to facilitate the subsequent discussion. Sources of error in the RDF will then be discussed, followed by a description of the data reduction procedures used to minimize spurious details.

General theory

The total diffracted intensity from a glass, I_t, corrected for systematic effects such as scattering polarization and absorption, is comprised of the interatomic interference scattering, I, the coherent atomic scattering, I_c, and the incoherent atomic scattering, I_i. The pertinent equations are

$$I_t(s) = I(s) + I_c(s) + I_i(s) \tag{1}$$
$$= I(s) + I_b(s)$$
$$i(s) = [I_t(s) - I_b(s)] / \sum f^2(s) \tag{2}$$

where $s = 4\pi \sin\theta/\lambda$, 2θ is the angle between the incident and the diffracted beam, and λ is the wavelength. The sum of the squares of the coherent atomic scattering factors for the unit of composition, uc, *e.g.* SiO_2, is represented by $\sum f^2$. Division of I by $\sum f^2$ produces an intensity function, $i(s)$, that corresponds approximately

to the scattering intensity from vibrating point atoms.

A Fourier sine transform of $si(s)$ produces the radial distribution function $rD(r)$.

$$r^2D(r)=4\pi r^2[\varrho(r)-\varrho_0]=\frac{2r}{\pi}\int_0^\infty si(s)\sin sr\,ds \qquad (3)$$

where $4\pi r^2\varrho(r)$ represents the probability, weighted by the product of the scattering factors of atoms i and j divided by $\sum f^2$, of finding atoms j in the sample separated by the distance interval $(r, r+dr)$ from the atoms i. As will be seen, this relationship holds precisely only when $f_if_j/\sum f^2$ does not vary with scattering angle. The bulk density parameter is ϱ_0. The data reduction procedure isolates $i(s)$ from I_t, and Fourier analysis of $i(s)$ yields $D(r)$.

With the assumption of harmonic motion between pairs of atoms, the Fourier sine transform of $si(s)$ may be represented in terms of the interatomic distances and the bulk density,

$$r^2D(r)=\frac{2r}{\pi}\sum_{i,j}\frac{N_{ij}}{r_{ij}}\int_0^\infty\frac{f_if_j}{\sum f^2}\times\exp(-l_{ij}^2s^2/2)\sin sr_{ij}\sin sr\,ds \qquad (4)$$
$$-4\pi r^2\varrho_0'\frac{(\sum_{uc}f_{(s=0)})^2}{\sum_{uc}f_{(s=0)}^2},$$

where r_{ij} is the distance between the ith and jth atoms, N_{ij} is the coordination number, l_{ij} is the disorder parameter, uc is the unit of composition, (SiO_2) and ϱ_0' is the bulk density in units of composition per Å^3. If there is no other source of disorder, l_{ij} is the root-mean-square amplitude of vibration. The first term on the right-hand side of equation (4) represents $4\pi r^2\varrho(r)$, and the second term represents $4\pi r^2\varrho_0$. This second term is present in the Fourier sine transform of $si(s)$ since the extremely low-angle scattering, where all atoms in the sample are scattering in phase, is not contained in the experimentally measured $i(s)$. If the $f_if_j/\sum f^2$ are not a function of s, the integral in equation (4) may be evaluated.

$$4\pi r^2\varrho(r)=\frac{2r}{\pi}\sum_{ij}\frac{N_{ij}}{r_{ij}}\frac{f_if_j}{\sum f^2}\times\left[\exp\left(-\frac{(r_{ij}-r)^2}{2l_{ij}^2}\right)-\exp\left(-\frac{(r_{ij}+r)^2}{2l_{ij}^2}\right)\right]. \qquad (5)$$

The second exponential in the brackets is negligible for the values of r_{ij} present in glasses. Readers wishing more details on the general theory may refer to the early work in the field (Debye, 1915; Zernicke & Prins, 1927) or a textbook (Guinier, 1956; Warren, 1969).

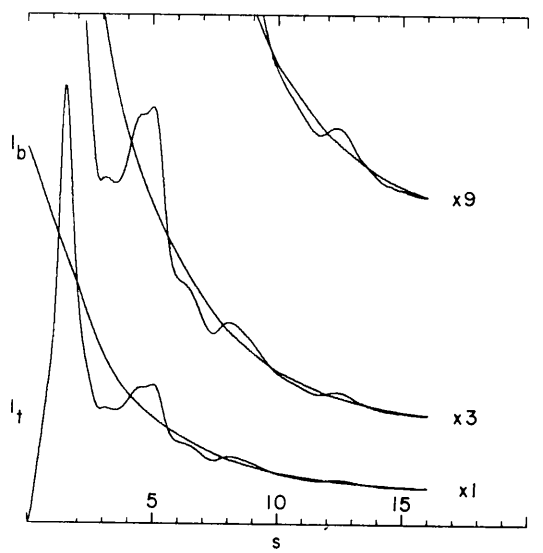

Fig. 1. The total X-ray diffraction pattern for silica glass, I_t, corrected for absorption and polarization, and the final representation for the background intensity, I_b.

Sources of error in RDF

The most troublesome errors aside from systematic ones, causing spurious detail in the RDF, are random errors in the experimental data, the limited scattering angle over which diffraction data may be collected, and the inaccurate separation of the interatomic scattering component from the total intensity. The limited scattering angle results in termination errors from the calculation of the integral in equation (3). In addition, the scattering factors for X-rays do not all have the same shape; *i.e.*, they do not differ from one another by only a scale factor. Therefore $f_if_j/\sum f^2$ will vary somewhat as a function of s. Certain systematic errors may be present in experimental data owing to, for example, inadequate source collimation, extraneous instrumental background and incorrect absorption correction.

Data collection

The X-ray diffraction data for silica glass were collected in the range $0{\cdot}3\le s\le 16{\cdot}0$ in intervals of 0·05 s with Mo $K\alpha$ radiation filtered with Zr so that the intensity ratio for $K\beta/K\alpha$ was 0·006. The cylindrical samples were 0·6–1·0 mm in diameter and the divergence of the beam was such that the intensity profile had a half-width at half-height of 0·08 s units at all scattering angles. Absorption corrections were made.

A pulse-height analyzer with window settings of 11·10 and 23·79 keV was also employed to eliminate spurious signals. The values for the data points at $s<0{\cdot}3$ were obtained by extrapolation to zero intensity at $s=0$. The extrapolation is not arbitrary, but rather is subject to constraints imposed on the analysis.

The statistical accuracy of the data was monitored in order that the contribution of the random errors to the RDF could be assessed and reduced to the desired level. As equation (3) illustrates, an error of $\varepsilon(s)$ in $si(s)$

Table 1. *The parameters representing the scale factor, bulk density, short distances, and background intensity for each cycle of the refinement*

The standard deviations given in parenthesis for the short distance and density parameters were estimated from the parameter values obtained using different starting points for the refinement. These error estimates are approximately three times those indicated by the variance–covariance matrix. The parameters are defined in the text and were varied only in the cycles listed in the first column. The results in this table are based on the use of idealized coordination numbers. A refinement in which the coordination numbers were varied is described in the text.

Cycle	r_{Si-O}	l_{Si-O}	r_{O-O}	l_{O-O}	r_{Si-Si}	l_{Si-Si}
0	1·600 Å	0·0300 Å	2·630 Å	0·0800 Å	3·080 Å	0·1000 Å
1	1·595	0·0510	2·642	0·0994	3·077	0·0949
3	1·595 (0·010)	0·0551 (0·010)	2·640 (0·010)	0·1049 (0·010)	3·080 (0·010)	0·1058 (0·010)

	K	A	ϱ_0'
0	1·000	1·0	0·02286 uc Å^{-3}
1	0·883	0·969	0·02184
3	0·884 (0·010)	0·969	0·02183 (0·0002)

	$0 \le s \le 4$, $c = 1·131$		$2 \le s \le 6$, $c = 0·2600$		$4 \le s \le 8$, $c = 0·2260$		$6 \le s \le 10$, $c = -0·3030$	
	a	b	a	b	a	b	a	b
0	5·785	−0·2305	8·325	−2·543	8·905	−3·089	0·5464	6·415
2	5·844	−0·2235	8·169	−2·378	8·855	−2·986	0·5001	6·683
4	5·842	−0·2229	8·145	−2·362	8·808	−2·956	0·5198	6·642

	$8 \le s \le 12$, $c = -1·376$		$10 \le s \le 14$, $c = -2·378$		$12 \le s \le 16$, $c = -3·012$	
	a	b	a	b	a	b
0	3·118	14·77	3·347	93·6	3·391	373·9
2	3·111	16·80	3·324	123·0	3·349	555·6
4	3·113	16·72	3·325	122·7	3·348	557·5

Table 2. *The total intensity, I_t, and the interference function $si(s)$*

The columns represent $s \times 100$, $I_t \times 100$, $si(s) \times 1000$ and $\sigma[(si)s)] \times 1000$.

5	377	-57	0	275	11579	-1286	3	545	10802	1052	14	815	6553	901	15	1085	4507	-900	38	1355	3889	75	104
10	881	-112	0	280	11329	-1326	3	550	10256	664	13	820	6538	986	15	1090	4483	-951	39	1360	3872	-32	105
15	1494	-164	0	285	11219	-1338	3	555	9807	345	13	825	6520	1065	16	1095	4459	-1003	40	1365	3852	-179	127
20	2301	-212	0	290	11166	-1337	3	560	9393	42	15	830	6496	1131	16	1100	4437	-1038	41	1370	3841	-210	106
25	3216	-256	0	295	11179	-1321	3	565	9056	-201	14	835	6470	1189	17	1105	4415	-1061	41	1375	3823	-340	107
30	4037	-298	0	300	11245	-1291	3	570	8770	-407	14	840	6437	1231	17	1110	4393	-1127	42	1380	3810	-388	108
35	4905	-336	0	305	11258	-1270	3	575	8539	-567	15	845	6400	1259	17	1115	4374	-1155	43	1385	3799	-419	87
40	5785	-370	0	310	11276	-1247	4	580	8367	-676	15	850	6359	1273	18	1120	4352	-1206	44	1390	3785	-495	110
45	6703	-401	0	315	11271	-1227	4	585	8223	-761	15	855	6319	1291	18	1125	4330	-1236	45	1395	3768	-637	111
50	7552	-429	0	320	11249	-1210	4	590	8113	-813	16	860	6276	1297	19	1130	4309	-1303	45	1400	3756	-680	89
55	8422	-453	0	325	11243	-1187	4	595	8053	-814	7	865	6236	1312	19	1135	4294	-1305	46	1405	3744	-769	90
60	9353	-473	0	330	11185	-1177	4	600	7995	-814	6	870	6194	1319	19	1140	4279	-1309	47	1410	3730	-873	91
65	10280	-490	0	335	11162	-1157	4	605	7950	-801	7	875	6155	1336	20	1145	4264	-1315	48	1415	3718	-954	91
70	11195	-503	0	340	11135	-1136	4	610	7914	-777	7	880	6109	1328	20	1150	4252	-1293	48	1420	3709	-989	92
75	12048	-513	0	345	11106	-1115	5	615	7886	-742	7	885	6067	1330	21	1155	4241	-1265	49	1425	3699	-1051	92
80	13063	-516	0	350	11105	-1085	5	620	7857	-707	7	890	6021	1318	21	1160	4232	-1230	50	1430	3693	-1037	93
85	14026	-515	0	355	11102	-1054	5	625	7830	-670	7	895	5972	1292	22	1165	4226	-1159	51	1435	3687	-1026	94
90	14972	-510	1	360	11113	-1016	5	630	7799	-636	7	900	5919	1245	22	1170	4228	-1018	52	1440	3682	-993	94
95	16052	-497	1	365	11158	-966	5	635	7765	-604	8	905	5864	1189	23	1175	4226	-908	53	1445	3679	-938	95
100	17379	-468	1	370	11197	-915	5	640	7719	-587	8	910	5807	1125	23	1180	4231	-737	53	1450	3677	-861	95
105	18961	-423	1	375	11280	-846	5	645	7671	-573	8	915	5751	1053	24	1185	4235	-568	54	1455	3671	-856	96
110	20906	-354	1	380	11364	-775	6	650	7612	-574	8	920	5695	982	24	1190	4243	-357	55	1460	3663	-890	96
115	23351	-252	1	385	11497	-681	6	655	7545	-588	8	925	5639	904	25	1195	4249	-164	56	1465	3659	-850	96
120	26135	-141	1	390	11617	-588	6	660	7467	-618	9	930	5585	830	25	1200	4262	102	57	1470	3650	-903	97
125	29482	56	1	395	11785	-471	6	665	7387	-653	9	935	5524	720	26	1205	4274	357	58	1475	3643	-923	97
130	32986	262	1	400	11945	-354	6	670	7298	-704	9	940	5464	610	27	1210	4285	605	59	1480	3639	-896	98
135	36796	485	2	405	12126	-224	7	675	7205	-763	9	945	5408	512	27	1215	4288	782	60	1485	3637	-817	98
140	39472	713	2	410	12335	-76	8	680	7108	-832	9	950	5353	412	28	1220	4296	1009	60	1490	3633	-790	99
145	41616	906	2	415	12518	68	8	685	7004	-917	10	955	5300	315	28	1225	4298	1176	61	1495	3632	-696	99
150	42766	1052	2	420	12680	208	8	690	6896	-1011	10	960	5249	220	29	1230	4301	1369	62	1500	3629	-642	74
155	42683	1164	2	425	12858	363	8	695	6789	-1109	10	965	5199	124	29	1235	4303	1549	63	1505	3624	-621	75
160	41522	1226	2	430	12999	506	9	700	6685	-1206	10	970	5152	36	29	1240	4304	1721	64	1510	3621	-574	75
165	39476	1255	2	435	13090	630	9	705	6590	-1293	11	975	5105	-53	29	1245	4300	1843	65	1515	3615	-594	75
170	36915	1252	2	440	13216	777	9	710	6501	-1373	11	980	5061	-138	29	1250	4297	1973	66	1520	3608	-622	75
175	34111	1213	2	445	13248	879	9	715	6418	-1445	11	985	5019	-211	29	1255	4286	2018	66	1525	3602	-649	76
180	31411	1144	2	450	13302	997	10	720	6351	-1494	10	990	4983	-269	26	1260	4275	2056	67	1530	3599	-609	76
185	28908	1054	2	455	13325	1102	10	725	6294	-1524	10	995	4945	-331	27	1265	4264	2100	68	1535	3592	-651	76
190	26545	960	2	460	13326	1197	10	730	6247	-1538	10	1000	4910	-386	27	1270	4247	2068	69	1540	3590	-586	76
195	24593	869	2	465	13334	1299	10	735	6214	-1524	12	1005	4883	-423	28	1275	4229	2025	70	1545	3584	-603	76
200	22797	-780	2	470	13341	1403	11	740	6202	-1470	11	1010	4856	-464	29	1280	4208	1942	71	1550	3581	-551	76
205	21284	-678	2	475	13351	1513	11	745	6199	-1395	11	1015	4827	-512	29	1285	4186	1844	72	1555	3575	-582	77
210	19991	-587	2	480	13380	1638	11	750	6208	-1294	11	1020	4799	-558	30	1290	4163	1721	72	1560	3573	-524	77
215	18883	-491	2	485	13420	1773	12	755	6230	-1163	11	1025	4774	-595	30	1295	4139	1590	73	1565	3569	-501	77
220	17931	-484	2	490	13479	1927	12	760	6265	-998	12	1030	4746	-646	31	1300	4111	1402	74	1570	3568	-417	77
225	17105	-569	2	495	13536	2083	12	765	6306	-815	12	1035	4720	-683	32	1305	4087	1244	75	1575	3563	-434	77
230	16361	-647	2	500	13554	2217	13	770	6354	-610	12	1040	4698	-707	32	1310	4059	1047	76	1580	3562	-351	77
235	15710	-718	2	505	13575	2358	13	775	6401	-400	12	1045	4676	-723	33	1315	4032	852	77	1585	3559	-314	77
240	15136	-784	3	510	13511	2438	13	780	6447	-186	13	1050	4655	-741	34	1320	4010	708	78	1590	3560	-171	77
245	14549	-855	3	515	13373	2464	14	785	6485	18	14	1055	4635	-753	34	1325	3988	560	78	1595	3560	-81	77
250	13961	-932	3	520	13118	2396	14	790	6517	211	13	1060	4613	-776	35	1330	3971	484	79	1600	3561	72	77
255	13411	-1007	3	525	12787	2262	15	795	6540	388	14	1065	4591	-800	36	1335	3954	401	80				
260	12861	-1063	3	530	12393	2067	13	800	6552	544	17	1070	4570	-827	36	1340	3940	359	81				
265	12363	-1102	3	535	11896	1774	14	805	6560	678	17	1075	4547	-861	37	1345	3923	268	102				
270	11905	-1205	3	540	11366	1457	14	810	6561	801	18	1080	4526	-884	38	1350	3909	214	83				

introduces into $r^2D(r)$ an error of $2r/\pi\ \varepsilon(s)\ (\sin sr)\ \exp(-\alpha s^2)$. Thus, the random error contribution, $E(r)$, to $r^2D(r)$ is

$$E(r) = \frac{2r}{\pi} \sum_s \varepsilon(s)\ (\sin sr)\ \exp(-\alpha s^2) \qquad (6)$$

where α is an artificial damping factor to be discussed later.

The standard deviations, $\sigma(s)$, of the errors represented by $\varepsilon(s)$ in the experimental $si(s)$ may be estimated from the standard deviations of the total intensity, $\sigma_I(s)$, that are computed from the counting statistics,

$$\sigma(s) = \sum^{s} f^2 \cdot \sigma_I(s)\,. \qquad (7)$$

These σ's may be used to calculate the variance in the RDF produced by the random errors,

$$\sigma^2[r^2D(r)] \simeq \sum_s \left(\frac{2r}{\pi} \sin sr \exp(-\alpha s^2)\sigma(s)\right)^2 . \qquad (8)$$

The effect of a specific random error $\varepsilon(s)$ on an RDF can be computed from equation (6) and can be compared with the probabilistic measure given in equation (8). In order to make this comparison we have employed a Gaussian-distribution random-error generator to construct $E(r)$ functions consistent with the statistics of the experiments. Good agreement was found. An additional check on the accuracy of the procedure can be obtained by collecting many sets of data and computing RDF's from different subsets of the data.

Data reduction

A data reduction procedure is employed in which the termination error is removed and I_b, the background intensity, is scaled and shaped, by requiring the resultant RDF and I_b to satisfy a variety of physical and mathematical constraints.

A. Mathematical and physical criteria employed

The criteria employed are:

1. The inner region of the RDF should be featureless where distances are known not to exist. It will be seen that the correction for the termination error involves removal of the first few distances from the RDF. The requirement for a featureless RDF in its inner region is

Table 3. *The radial distribution function*, $r^3D(r)$

The columns represent $r \times 100$, $r^3D(r) \times 10$ and $\sigma[r^3D(r)] \times 10$.

4	-0	0	228	-90	1	452	-89	3	676	+136	4	900	60	4	1124	-17	3	1348	20	3	1572	-3	3	1796	7	3
8	-0	0	232	-95	1	456	-63	3	680	+153	4	904	48	4	1128	+17	3	1352	20	3	1576	-3	3	1800	6	3
12	-0	0	236	+100	1	460	-31	3	684	+162	4	908	36	4	1132	+18	3	1356	20	3	1580	-4	3	1804	5	3
16	-0	0	240	-105	1	464	1	3	688	+165	4	912	24	4	1136	+21	3	1360	20	3	1584	-5	3	1808	4	3
20	-0	0	244	+111	1	468	27	3	692	+162	4	916	14	4	1140	+25	3	1364	18	3	1588	-6	3	1812	3	3
24	-0	0	248	+116	1	472	45	3	696	+155	4	920	5	4	1144	+31	3	1368	17	3	1592	-7	3	1816	2	3
28	-0	0	252	+122	1	476	56	3	700	+145	4	924	+1	4	1148	+38	3	1372	14	3	1596	-8	3	1820	1	3
32	-0	0	256	+128	1	480	62	3	704	+135	4	928	+5	4	1152	+43	3	1376	12	3	1600	-8	3	1824	-0	3
36	-0	0	260	-134	1	484	68	3	708	+124	4	932	+7	4	1156	+48	3	1380	9	3	1604	-9	3	1828	+1	3
40	-0	0	264	-140	1	488	77	3	712	+113	4	936	+6	4	1160	+50	3	1384	6	3	1608	+10	3	1832	-2	3
44	-1	0	268	-147	1	492	92	3	716	+101	4	940	+4	4	1164	+51	3	1388	3	3	1612	+10	3	1836	-3	3
48	-1	0	272	-153	1	496	111	3	720	+88	4	944	0	4	1168	+50	3	1392	1	3	1616	+10	3	1840	-4	3
52	-1	0	276	-160	1	500	132	3	724	+72	4	948	5	4	1172	+47	3	1396	-1	3	1620	+10	3	1844	-4	3
56	-1	0	280	-167	1	504	150	3	728	+54	4	952	10	4	1176	+45	3	1400	-3	3	1624	+10	3	1848	-5	3
60	-2	0	284	-174	1	508	161	3	732	+34	4	956	14	4	1180	+42	3	1404	-3	3	1628	+9	3	1852	-5	3
64	-2	0	288	+182	1	512	160	3	736	+14	4	960	19	4	1184	+39	3	1408	+4	3	1632	+8	3	1856	+4	3
68	-2	0	292	-190	1	516	148	3	740	3	4	964	23	4	1188	+36	3	1412	+3	3	1636	+7	3	1860	+4	3
72	-3	0	296	+198	1	520	125	3	744	16	4	968	26	4	1192	+33	3	1416	+3	3	1640	+6	3	1864	+4	3
76	-3	0	300	+206	1	524	95	3	748	24	4	972	29	4	1196	+28	3	1420	+2	3	1644	+5	3	1868	+3	3
80	-4	0	304	+213	1	528	63	3	752	25	4	976	33	4	1200	+23	3	1424	+2	3	1648	+4	3	1872	+2	3
84	-5	0	308	+218	2	532	34	3	756	20	4	980	36	4	1204	+17	3	1428	+1	3	1652	+2	3	1876	+2	3
88	-5	0	312	+219	2	536	11	3	760	12	4	984	39	4	1208	+10	3	1432	+0	3	1656	+1	3	1880	+1	3
92	-6	0	316	+216	1	540	-4	3	764	1	4	988	42	4	1212	+3	3	1436	0	3	1660	0	3	1884	+1	3
96	-7	0	320	+210	1	544	-11	3	768	+8	4	992	43	4	1216	2	3	1440	1	3	1664	1	3	1888	+0	3
100	-8	0	324	+199	2	548	-12	3	772	+16	4	996	43	4	1220	7	3	1444	1	3	1668	3	3	1892	0	3
104	-9	0	328	+186	2	552	-10	3	776	+21	4	1000	40	4	1224	9	3	1448	1	3	1672	4	3	1896	0	3
108	-10	0	332	+170	2	556	-8	3	780	+24	4	1004	35	4	1228	9	3	1452	1	3	1676	5	3	1900	1	3
112	-11	0	336	+154	2	560	-9	3	784	+26	4	1008	28	4	1232	8	3	1456	1	3	1680	5	3	1904	1	3
116	-12	0	340	+137	2	564	-12	3	788	+27	4	1012	19	4	1236	6	3	1460	0	3	1684	6	3	1908	0	3
120	-13	0	344	+120	2	568	-17	3	792	+30	4	1016	9	4	1240	5	3	1464	+0	3	1688	6	3	1912	0	3
124	-15	0	348	+103	2	572	-24	3	796	+34	4	1020	+0	4	1244	4	3	1468	-1	3	1692	6	3	1916	-0	3
128	-16	0	352	-86	2	576	-31	3	800	+39	4	1024	-8	4	1248	4	3	1472	-2	3	1696	6	3	1920	-1	3
132	-18	0	356	-70	2	580	-36	3	804	+44	4	1028	-15	4	1252	4	3	1476	-3	3	1700	6	3	1924	-1	3
136	-19	0	360	-53	2	584	-37	3	808	+47	4	1032	+19	4	1256	6	3	1480	-4	3	1704	5	3	1928	-2	3
140	-21	0	364	-38	2	588	-35	3	812	+47	4	1036	+21	4	1260	7	3	1484	-4	3	1708	4	3	1932	-3	3
144	-23	0	368	-23	2	592	-29	3	816	+43	4	1040	+23	4	1264	9	3	1488	-5	3	1712	4	3	1936	-3	3
148	-25	0	372	-10	2	596	-21	3	820	+35	4	1044	+23	4	1268	10	3	1492	-5	3	1716	3	3	1940	-4	3
152	-27	0	376	1	2	600	-11	3	824	+23	4	1048	+23	4	1272	10	3	1496	-5	3	1720	3	3	1944	-4	3
156	-29	0	380	12	2	604	1	4	828	+8	4	1052	+24	4	1276	9	3	1500	-5	3	1724	2	3	1948	-5	3
160	-31	0	384	24	2	608	12	4	832	8	4	1056	+25	4	1280	9	3	1504	-5	3	1728	2	3	1952	-5	3
164	-34	0	388	39	2	612	22	4	836	24	4	1060	+26	4	1284	9	3	1508	-6	3	1732	1	3	1956	-5	3
168	-36	1	392	58	2	616	32	4	840	37	4	1064	+26	4	1288	10	3	1512	-6	3	1736	1	3	1960	-5	3
172	-39	1	396	81	2	620	40	4	844	49	4	1068	+26	4	1292	11	3	1516	-7	3	1740	2	3	1964	-5	3
176	-41	1	400	108	2	624	46	4	848	59	4	1072	+24	4	1296	13	3	1520	-8	3	1744	2	3	1968	-4	3
180	-44	1	404	134	2	628	50	4	852	67	4	1076	+21	4	1300	16	3	1524	-9	3	1748	2	3	1972	-4	3
184	-47	1	408	156	2	632	53	4	856	73	4	1080	+17	4	1304	19	3	1528	-9	3	1752	3	3	1976	-3	3
188	-51	1	412	167	2	636	52	4	860	79	4	1084	+14	4	1308	21	3	1532	-9	3	1756	4	3	1980	-2	3
192	-54	1	416	164	2	640	48	4	864	84	4	1088	+11	4	1312	23	3	1536	-9	3	1760	5	3	1984	-2	3
196	-57	1	420	145	2	644	41	4	868	89	4	1092	+10	4	1316	24	3	1540	-9	3	1764	6	3	1988	-1	3
200	-61	1	424	110	2	648	29	4	872	92	4	1096	+10	4	1320	24	3	1544	-8	3	1768	7	3	1992	-1	3
204	-65	1	428	63	2	652	13	4	876	95	4	1100	+11	3	1324	23	3	1548	-7	3	1772	7	3	1996	-0	3
208	-69	1	432	11	2	656	-8	4	880	95	4	1104	+13	3	1328	22	3	1552	-6	3	1776	8	3	2000	0	3
212	-73	1	436	-39	2	660	-33	4	884	93	4	1108	+15	3	1332	21	3	1556	-5	3	1780	8	3	2004	1	3
216	-77	1	440	-77	2	664	-60	4	888	88	4	1112	+17	3	1336	20	3	1560	-4	3	1784	8	3	2008	1	3
220	-81	1	444	-100	3	668	-88	4	892	81	4	1116	+18	3	1340	20	3	1564	-3	3	1788	8	3	2012	2	3
224	-86	1	448	-103	3	672	-114	4	896	71	4	1120	+17	3	1344	20	3	1568	-3	3	1792	8	3	2016	2	3

extended to the region involving the distances that are removed.

2. The outer region of the RDF should show a uniform distribution of distances. In this context, termination effects and errors in the experimental data cause the outer region to have the appearance of a nonuniform distribution of distances and require correctional procedures.

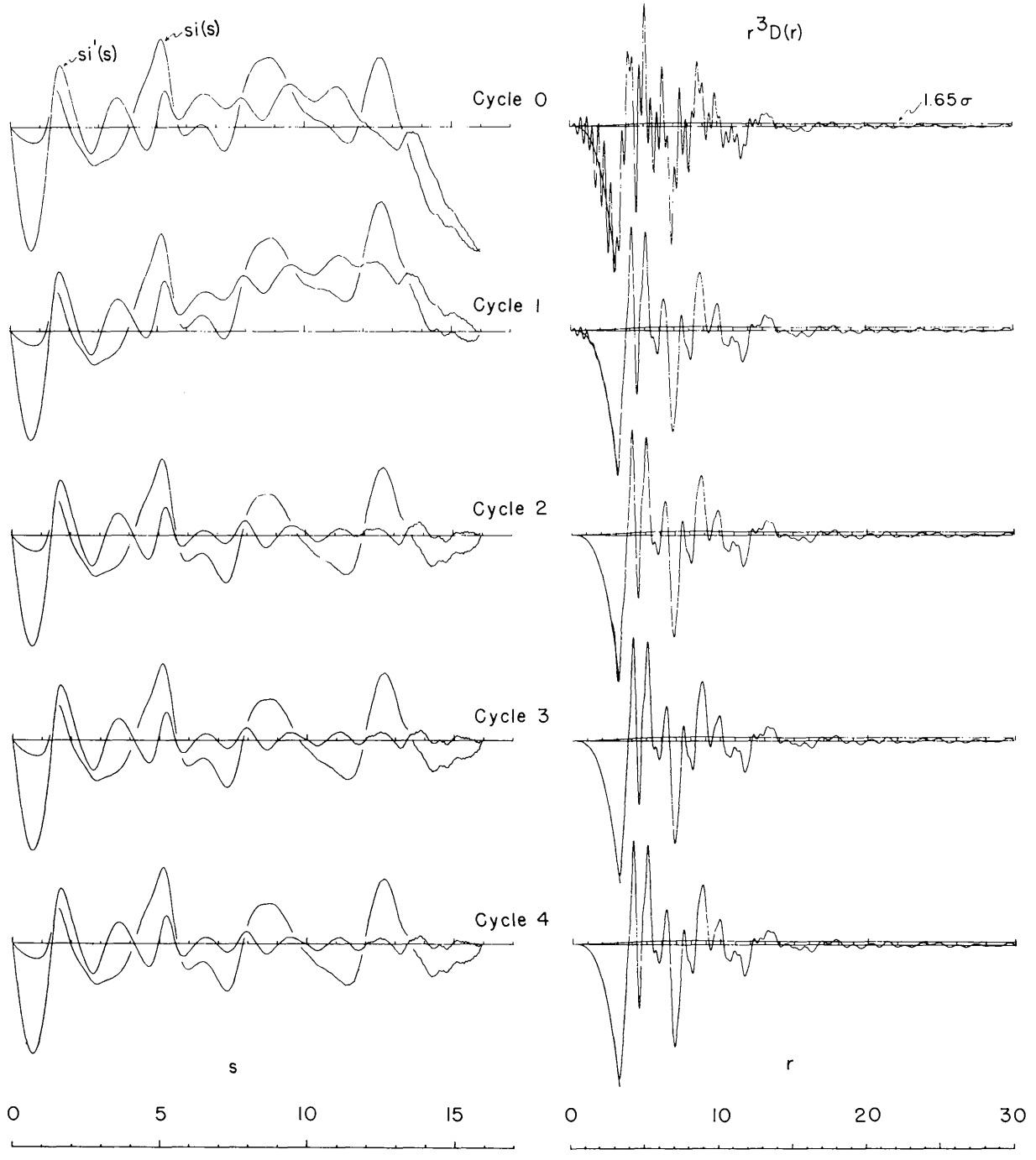

Fig. 2. The sharpened intensity functions $si(s)$, the corresponding functions minus the short distance contributions, $si'(s)$, and the RDF associated with $si'(s)$ for each cycle of the refinement. There is a 10% chance that the absolute value of an error in the RDF from random errors in the data will exceed the $1{\cdot}65\sigma$ curve. The smooth curve accompanying $r^3D(r)$ at small r represents $-4\pi r^3\varrho_0$. The quantity r^3 is employed in order to scale the outer region with respect to the inner region of the RDF in a fashion which readily displays the features.

3. The scaling of the intensity data (and, thus, the RDF) should be consistent with the bulk-density measurement, known coordination number s or both.

4. The background scattering, I_b, should be a smoothly changing function whose shape is compatible with that expected from theory.

B. Initial representation of background intensity

The initial step in the data reduction procedure is to fit with exponential functions an approximate background intensity, I_b, obtained for example, from theoretical values for the scattering factors (Cromer & Mann, 1968) scaled to the total-intensity data. Use is made of overlapping functions of the form $\exp(a+bs^c)$ to represent I_b,

$$I_b(s)=\sum_n W_n(s)\exp(a_n+b_n s^{c_n})+d\cdot s\,, \qquad (9)$$

a technique developed in the field of electron diffraction of gases (D'Antonio, George, Lowrey & Karle, 1971). Each exponential function overlaps to the midpoint of the adjacent exponential function and is assigned a weight, W_n, that varies linearly in the region of overlap from one at its midpoint to zero at the midpoint of the function with which it overlaps, with the exception of the terminal functions which have a weight of unity from their midpoints to the limits of the data. In the analysis of X-ray diffraction data d is set equal to zero. In treating neutron diffraction data, d is set to a non-zero value such that I_b is amenable to fitting with the exponential functions. The background intensity, as composed of its components, is smooth and sufficiently featureless so as not to affect the real distance contributions. This is accomplished by utilizing a limited number of exponential functions, especially in the initial stages of refinement, such that each function spans about 4–6 s units. This choice is particularly relevant to the shortest interatomic distance in the sample being studied. For silica the shortest distances are at approximately $\pi/2$ A. Reference to equation (4), which is discussed later, demonstrates that the intensity contribution for this distance is a sine function with a periodicity of about 4 s units. It is important to avoid the possibility of introducing an incorrect background function having an error with this periodicity or less.

C. Representation of RDF as a function of parameters defining I_b and short distances

The treatment of the termination error is based on the recognition that generally only the two or three shortest distances make a significant contribution to the experimental intensity function, $i(s)$, beyond the measured range of scattering angle, owing to their low thermal or disorder factors. The intensity functions corresponding to the larger distances are essentially damped out at the upper limit of the experimental data range, s_{max}. The contributions from the shortest distances may be removed from $i(s)$ so that s_{max} can accurately replace infinity as the upper limit of the integral (3). Such an intensity function may also be written as a function of parameters defining I_b. The Fourier transform of such an intensity function, $i'(s)$, may be expressed by

$$r^2D'(r)=4\pi r^2[\varrho'(r)-\varrho_0]$$
$$=\frac{2r}{\pi}\int_0^{s_{max}} si'(s)\exp(-\alpha s^2)\sin sr\,ds \qquad (10)$$

$$i'(s)=i(s)-\sum_{sd} N_{ij}f_if_j\exp(-l_{ij}^2s^2/2)\times\sin sr_{ij}/(sr_{ij}\sum f^2) \qquad (11)$$

$$i(s)=\{I(s)-A[\sum_n W_n(s)\exp(a_n+b_ns^{c_n})+d\cdot s]\}/\sum f^2(s) \qquad (12)$$

$$\varrho_0=\varrho_0'(\sum_{uc} f_{(s=0)})^2/\sum_{nc} f_{(s=0)}^2 \qquad (13)$$

$$I(s)=I(s)\text{ measured}/K \qquad (14)$$

where K places the intensity on an absolute scale, sd refers to the shortest distances, α is an artificial damping factor that may be given a small value, if necessary to remove residual termination effects. $\varrho'(r)$ corresponds to $\varrho(r)$ minus the contributions from the shortest distances which have been removed from $i(s)$, and A scales I_b without altering its shape.

D. Least-squares refinement of RDF

The formulation of the least-squares calculation is:

$$\text{minimize}\{\sum_{p<r<q}[rD'(r)+\varrho_0]^2+w\sum_{u<r<v}[rD'(r)]^2\}\,, \qquad (15)$$

where p and q delineate the inner region, u and v delineate the outer region of the RDF and w fixes the relative weights of the two regions. It is seen from equations (10)–(14) that $D'(r)$ is defined in terms of the parameters which are to be optimized by the use of equation (15). The first sum expresses the condition that the inner region of the RDF, including that portion from which the first few distances are removed, should equal $-\varrho_0$; *i.e.*, $\varrho'(r)=0$. The second sum expresses the condition that the outer region display a uniform distribution of distances; $\varrho'(r)=\varrho_0$. The parameters obtained from minimizing the first sum alone have been found to correspond quite closely to the parameters obtained from simultaneously varying both sums. For this reason, it is generally more economical to minimize only the first sum, *i.e.* $w=0$, while monitoring both regions of the RDF to ensure correct behavior. Such a procedure for at least the first cycle of refinement facilitates the estimate of the lower limit of u. Optimal values for the a, b, c and A defining I_b and for K, r_{ij}, l_{ij}, ϱ_0 and N_{ij} are obtained. It was found for SiO_2 that it was necessary to remove the first three peaks, which are comprised of Si–O, O–O, and Si–Si distances, in order to rid the integral in equation (4) of

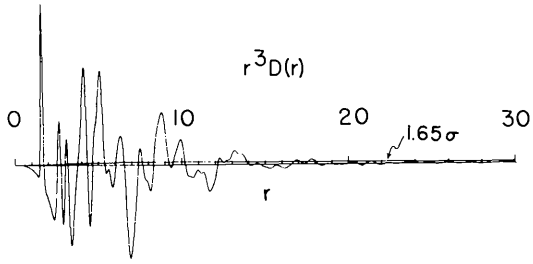

Fig. 3. The final $r^3D(r)$ function with the first three peaks reintroduced without associated termination effects.

termination errors. It is apparent that if the N_{ij} is known for a peak that is isolated in the RDF, then fixing this value in the refinement is a sufficient constraint to obtain K and ϱ_0. Since ϱ_0 is generally a known quantity, an independent check is provided for the scale factor. Alternatively, it is possible to fix ϱ_0 at its known value to obtain K and the N_{ij}. For the refinement of the silica-glass data, the values of the N_{ij} for three shortest distances, the Si–O, the O–O, and the Si–Si, were held constant at 8, 12, and 4 respectively.

The sequence of the refinement of the silica-glass data is outlined below. Fig. 1 shows the X-ray intensities. Table 1 indicates the parameter values and Fig. 2 illustrates the RDF at each stage of refinement. The value of α was taken as zero in the refinement; however, $\alpha = 0{\cdot}0001 \cdot r^2$ for computing the RDF's in Fig. 2. Table 2 gives the total and interference intensities and Table 3 gives the radial distribution function.

The variation of α with respect to r was introduced in order to diminish the effect of the random errors at larger s on the small features of the RDF at large r.

Cycle 1.

The parameters refined were K, A, and the r_{ij}'s and l_{ij}'s for the first three distances. Detail in the inner region of the RDF was minimized from $r = 1{\cdot}4$ to $r = 3{\cdot}0$ Å in increments of 0·1 Å. In this region detail is due primarily to real-distance contributions and termination-error contributions. The termination error arises from a discontinuity in $si(s)$ at the experimental limit of data collection. This discontinuity is the result of real-distance contributions and, or, error in I_b at the termination point, s_{max}. The latter possibility is the reason A is varied in this cycle. Variation of A allows errors in I_b to be limited primarily to broad features, the transform of which introduces errors into the RDF that are concentrated at $r < 1{\cdot}4$ Å.

Cycle 2.

Parameters a and b were refined for each exponential function. The values for the constants c are obtained from a three-point fit of the background line in each Δs range represented by end points and the midpoint. The RDF was sampled at increments of 0·02 in the range $r = 0{\cdot}02$–$3{\cdot}00$. The relatively small sampling increment is necessary since the primary effects of the incorrect background are concentrated at very small r values.

Cycle 3.

The same parameters are varied as in Cycle 1.

Cycle 4.

The same parameters are varied as in Cycle 2.

The fact that $si(s) \simeq 0$ at s_{max} is a coincidence for this data set and is not a necessary condition for the refinement. The refinement proceeds in an essentially identical fashion when $s = 15$ or 15·5 is set as the limit of data instead of the true experimental value of $s = 16$.

Assessment of errors in RDF

As stated, the effect of random errors in the intensity data on the RDF may be readily estimated. Fig. 2 displays the curve representing the $1{\cdot}65\sigma$ values as calculated from equation (6). There is a 10% chance that an error generated from the random errors in the intensity function will exceed the value of this curve. Since the data for silica glass are the average of 15 data sets, it is possible to calculate RDF's from different subsets of data. Reference to these RDF's and the $1{\cdot}65\sigma$ error curve indicated that the main features in the final RDF out to about 20 Å are significant with

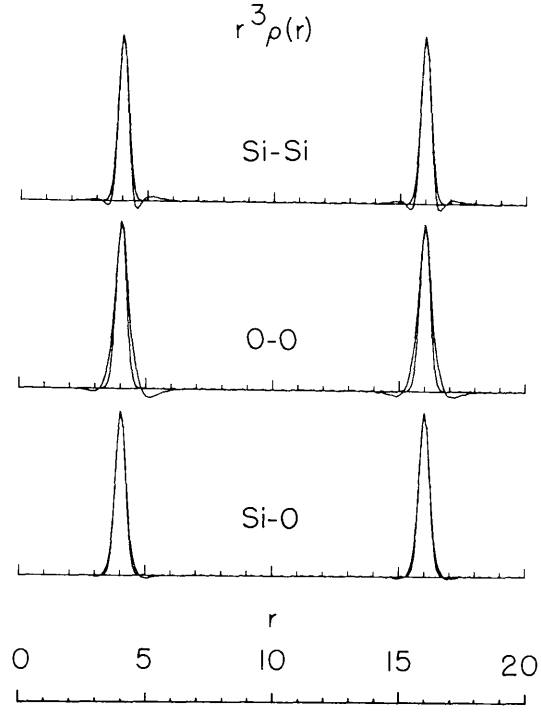

Fig. 4. RDF curves calculated with both constant and variable, neutral atom, scattering factors, $f_i f_j / \sum f^2$, for the three different types of distances. The curves are calculated with $0 \le s \le 16$ and $l_{ij} = 0{\cdot}2$ Å.

respect to the random error of these data in agreement with the implications of Fig. 2.

The appearance of the RDF at small r, where no detail should be present may be used to evaluate the effectiveness of the termination correction (Fig. 3). It is evident from Fig. 2 that the detail disappears in successive cycles. The termination correction is further evidenced by the behavior of $si'(s)$ as illustrated in Fig 2; the function approaches zero in a smoothly oscillating fashion as s_{max} is approached. The absence of detail with long-range periodicity at large r indicates the adequacy of the extrapolation from zero scattering angle to $s=0{\cdot}3$.

The corrections for the silica glass were carried out using the ideal coordination numbers for the first three distances, as mentioned above. Alternatively, we may fix the density parameter at its measured value, 2·20 g cm^{-3}, and proceed with the data reduction treating the coordination numbers as unknown. When this is done, the radial distribution function again ultimately satisfies the imposed mathematical and physical constraints. The coordination numbers are found to be 7·99 (0·01), 11·87 (0·05), 4·13 (0·11), the distance parameters, 1·595, 2·629, 3·077 Å, and the disorder parameters, 0·0512, 0·0989, 0·1113 Å, for the smallest Si–O, O–O and Si–Si distances respectively. The numbers in the parentheses represent least-squares standard deviations and do not include contributions from systematic errors. The resulting RDF is essentially indistinguishable from the one obtained from the refinement using the ideal coordination numbers.

The function, $f_i f_j / \sum f^2$ varies slightly as a function of s. The magnitude of the errors introduced in this way may be estimated by comparing an RDF calculated with the variable scattering factors with an RDF calculated from constant scattering factors obtained as average values over the range of data collection. Representative calculations are presented in Fig. 4. The relative magnitudes of the spurious 'wings' will vary somewhat with the α value employed. The main feature to be pointed out for the purposes of this paper is that variable scattering factors may result in small errors associated with and adjacent to the main peaks in the RDF. Such spurious details related to the identifiable short distances are removed in the analysis. In regions of the RDF where a complete analysis of the peaks is not possible, though, one must exercise care in evaluating the significance of small features adjacent to the large ones. As illustrated by Fig. 4, though, the main features of the RDF are very little in error owing to the slightly variable scattering factors.

Errors in the RDF arising from scattering factors for isolated atoms that ignore bonding effects are quite small. This may be shown approximately by employing different types of scattering factors in the data reduction and observing the effects on the RDF. The RDF calculated assuming Si^{2+} and O^- is essentially the same as that obtained from neutral atoms, and the ϱ_0 is found to be 0·02180 uc/Å^3 instead of 0·02192 uc/Å^3 which is obtained from neutral-atom scattering factors. The measured value is 0·02205 uc/Å^3.

The possibility of systematic errors in the data introducing spurious details into the RDF was investigated in several ways. Tests were made with different systems for collimation and with different data collection intervals to ensure that the resolution of the intensity curve was sufficient to prevent loss of detail in the RDF. Samples of varying size were used to check for incorrect absorption corrections or detector response. A variety of samples from different sources were also used. Different diffractometers were used to further check for systematic errors. No significant effects were found.

Concluding remarks

It has been demonstrated that, by expressing the RDF explicitly as a function of parameters defining the short highly ordered distances and parameters determining the background intensity, it is possible to obtain, with a rapidly converging least-squares technique, an RDF free from termination and background errors. As illustrated in Fig. 2, the RDF changes very little after the first cycle of refinement, the cycle that removes the majority of the termination error. The second cycle shapes the background intensity quite accurately. The final two cycles are carried out to improve the values obtained for the scale factor and the parameters representing the short distances and background intensity.

It is worth noting that, if one is primarily interested in an estimate of the type and degree of long-range ordering present, but not in precise values for a scale factor and short distances, it is necessary only to collect accurate data, introduce a smooth approximate I_b, and employ a large value for α in taking the Fourier sine transform. The simpler procedure yields essentially the same RDF at large r, but with an increased breadth of the peaks which is quite evident at small r and with detail at very small r due to an incorrect I_b.

It appears that diffraction data from glasses contain structural information that has not yet been fully utilized in testing hypothesized models for glass structures. Efficient methods for obtaining this structural information should contribute much towards elucidating the atomic arrangements in glassy material.

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Periodicity in Thickness of Electron-Microscope Crystal-Lattice Images

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High-resolution electron micrographs of crystal lattices showing a recognizable correlation of intensity with atom positions are normally obtained only for very thin crystals (less than about 100 Å thick). For some crystals of niobium and titanium–niobium oxides, it has been observed that this thin-crystal contrast is repeated for thicknesses of the order of 1000 Å. This is regarded as evidence that under conditions of high symmetry of excitation, the wave field in the crystal is essentially periodic with distance in the beam direction if a particular relationship exists between the structure amplitudes and the excitation errors for the diffraction process. This is confirmed by calculations made for f.c.c. lattices with Cu, $CuAu_3$, or Au atoms and for a range of wavelengths.

Introduction

It has been shown recently (Iijima, 1971) that, when a thin crystal is aligned so that the incident electron beam is parallel to a principal axis, high-resolution electron micrographs can be obtained which show a direct correlation between image intensity and the projection of the crystal structure. In this way the distribution of metal atoms in a number of oxide phases has been determined both for perfect crystal regions and for linear or planar faults in the structures (Iijima, 1972, 1973; Iijima & Allpress, 1973). The nature of the contrast observed can be understood semi-quantitatively by application of the phase-object approximation (Cowley & Iijima, 1972). It is observed that when the crystal thickness exceeds that for which the phase-object approximation is expected to be valid, namely about 100 Å for 100 keV electrons, the image contrast no longer shows any obvious relationship to the crystal structure. This may be associated with the onset of three-dimensional dynamical diffraction conditions under which the variations of the relative phases and amplitudes of the many diffracted waves are very complicated and, in general, show no apparent periodicity with increasing thickness. However, for a few special cases an almost exact repetition of the thin-crystal contrast has been observed for relatively large thicknesses suggesting a recurrence of very nearly the same relative amplitudes and phases of the diffracted beams.

Observations

Fig. 1 is part of an electron micrograph of a crystal of the high-temperature phase, H-Nb_2O_5. The incident beam is parallel (within 3×10^{-3} radians) to the short b axis ($b=3{\cdot}8$ Å) of the monoclinic unit cell ($a=21{\cdot}2$, $c=19{\cdot}4$ Å, $\beta=120°$) and the image is obtained with approximately the 'optimum defocus' for phase contrast, $\Delta f=-900$ Å, using a modified JEM-100B electron microscope with a goniometer stage. Thickness determinations of the crystal were made by the observation of the images of planar faults for various tilts of the crystal. The crystal is wedge-shaped with an almost linear increase in thickness.

In the thin part of the crystal, near the edge of the wedge, the lattice image clearly shows the configuration of metal atoms within the unit cell which includes 4×3 and 5×3 blocks of ReO_3-type corner-sharing octahedra, plus atoms in tetrahedral positions which generate the darkest spots. A detailed study of the lattice images of H-Nb_2O_5 in both ordered and disordered forms has been reported by Iijima (1973) (see also Anderson, Browne & Hutchinson, 1972). With increasing crystal thickness this readily interpreted form of the image is lost for thicknesses of 100–150 Å and is replaced by a variety of image forms, none of which has any obvious relationship to the structure. Then for thicknesses of about 500 to 800 Å the thin-crystal image reappears with much the same contrast as for